INITIAL PERFORMANCE TEST PLAN

CONDENSATE COLLECTION AND TREATMENT

REVISED JUNE 2021

Submitted by:

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Submitted to:

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1. INTRODUCTION

The New-Indy Catawba LLC (New-Indy) operates a pulp and paper mill located in Catawba, South Carolina (Mill). In the Fall of 2020, the Mill was taken down for an extensive outage to convert the Mill from manufacturing bleached paper grades (lightweight coated paper and market pulp) to manufacturing unbleached or brown paper (linerboard and market pulp). New-Indy refers to this investment as Project Columbia. Concurrent with this conversion, the Mill installed a hard pipe from the foul condensate collection tank directly to the Mill's aerated stabilization basin (ASB), for the purpose of using the ASB to treat the foul condensates to comply with 40 CFR Part 63, Subpart S. No other physical changes were made to the ASB, with the exception of completion of planned dredging activities. The new hard pipe discharges the foul condensates below the liquid surface of the existing ASB per 40 CFR §63.446(e)(2) to allow for biological treatment of the hazardous air pollutants (HAPs) present in the condensates, primarily methanol (MeOH). Subpart S provides options for condensate collection and treatment; the Mill has chosen to comply with the following requirements, using both the existing Steam Stripper and the ASB for treatment:

- The Mill will collect 7.2 pounds of hazardous air pollutants (HAP) per oven-dried ton of pulp (lb HAP/ODTP) per 40 CFR §63.446(c)(3); and
- The Mill will treat 6.6 lb HAP/ton ODTP through treatment in the Steam Stripper and ASB (combined) per 40 CFR §63.446(e)(4).

40 CFR §63.7(a)(2) requires that an initial performance test (IPT) be conducted within 180 days of start-up to demonstrate compliance with the collection and treatment requirements of Subpart S. The Mill commenced post-project operations on February 1, 2021, so the Mill is required to conduct the performance test prior to July 31, 2021. The Mill plans to begin the IPT on June 21, 2021.

The Mill originally submitted an IPT plan on April 14, 2021, at least 60 days prior to the planned start date of the IPT in accordance with 40 CFR §63.7(b)(1) and (c). The initial IPT plan reflected that the ASB would be the sole control device used for treatment of foul condensates.

The Mill submitted an update to the initially submitted IPT plan on May 14, 2021 that included the ASB and the Steam Stripper historically used for treatment of foul condensates and hydrogen sulfide (H_2S) and methyl mercaptan (MMC) liquid testing requested by Item #2 of the Order to Correct Undesirable Level of Air Contaminants (Order) issued by the South Carolina Department of Health and Environmental Control (SCDHEC) on May 7, 2021. Note that this testing is not required by Subpart S but was included in the IPT plan in response to the Order. At the time that the May 14 update was submitted, the Mill was evaluating different test methods for the H_2S and MMC testing requested by SCDHEC, and the IPT plan discussed several methods being evaluated.

The Mill is submitting this IPT plan as an update to the two plans previously submitted. The updates to the plan are as follows:

- The start date of the IPT is being shifted from June 14, 2021 to June 21, 2021 due to a maintenance outage scheduled for June 16-18, 2021. The IPT is scheduled to conclude on July 11, 2021.
- The Mill has selected test methods for the H_2S and MMC testing requested by SCDHEC.
- The IPT plan has been updated per the June 2, 2021 Information Request issued by U.S. Environmental Protection Agency (U.S. EPA) pursuant to Section 114(a)(1) of the Clean Air Act (CAA) (U.S. EPA Information Request) and per questions from SCDHEC provided via email on June 8 and 9, 2021. Note that the U.S. EPA Information Request included sampling the inlet, outlet, and surface of the Post-Aeration Tank for purposes of calculating Fbio for TRS compounds across the Post-Aeration Tank. Since the U.S. EPA Information Request was issued, a cover has been installed over the Post-Aeration Tank with a carbon filter, as approved by SCDHEC on June 8, 2021. Conducting the surface sampling required for calculating Fbio around the Post-Aeration Tank would require removing the cover over the Post-Aeration Tank. The Mill has included the required sampling in this IPT plan but will only conduct the sampling if the U.S. EPA and/or SCDHEC provide approval for the Mill to remove the cover for the period of testing (July 7-11, 2021). In order to plan for the required sample collection and testing, the Mill would need this approval no later than June 30, 2021.

Regarding treatment of foul condensates in the ASB, this performance test plan was developed using guidance from the “Appendix C of Part 63 – Determination of the Fraction Biodegraded (Fbio) in a Biological Treatment Unit” and the “Technical Support Document for the Evaluation of Aerobic Biological Treatment Units with Multiple Mixing Zones," hereafter referred to as Appendix C of Part 63 and Guidance Document, respectively.

1.1 DOCUMENT ORGANIZATION

This document is organized as follows:

- **Section 1 – Introduction:** provides an introduction, test plan objectives, program contacts, responsibilities, required elements of the test plan, and the test schedule.
- **Section 2 – Facility and Source Description:** provides a process description of Mill operations and summarizes the foul condensate streams collected.
- **Section 3 – Performance Test Plan:** presents the test procedures to be used in the IPT, including the sampling locations and test matrix, sample collection methodology, sample shipping and storage requirements, a summary of the sample analysis methodologies, test run criteria, and process data collection.
- **Section 4 – Internal Quality Assurance (QA)/Quality Control (QC):** presents internal QA/QC procedures for the test program.
- **Section 5 – Data Analysis and Calculations:** presents proposed calculation methods to be used to demonstrate compliance following the IPT.
- **Appendix A – Sampling Matrices:** presents detailed sampling matrices describing the test program.
- **Appendix B – Liquid Sampling Test Methods:** provides the test method procedures for analyses to be conducted during the test program.
- **Appendix C – CMS Matrices:** presents detailed continuous monitoring system (CMS) matrices for continuous monitoring parameters included in the test program.
- **Appendix D – NCASI TB No. 933, Development and Application of a Method for Measuring Reduced Sulfur Compounds in Pulp and Paper Mill Wastewaters.**
- **Appendix E – NCASI TB No. 949, Summary of Industry Experience with Odor Minimization at Wastewater Treatment Plants.**
- **Appendix F – NCASI TB No. 956, Emissions of Reduced Sulfur Compounds and Methane from Kraft Mill Wastewater Treatment Plants.**

- **Appendix G – NCASI TB No. 957, Spatial Ambient Air Sampling and Analysis Methods for Quantifying Reduced Sulfur Compound and Methane Emissions from Kraft Mill Wastewater Treatment Plants.**
- **Appendix H – NCASI TB No. 1000, Mechanistic Approach for Estimating Hydrogen Sulfide Emissions from Wastewater Treatment Plants.**

1.2 PLAN OBJECTIVES

The objectives of this site-specific IPT plan are to provide the sampling and analytical methods used to ensure that representative emissions test results are obtained and to define and collect appropriate data to be used to demonstrate continuous compliance with the condensate collection and treatment requirements of Subpart S and to satisfy the requests of the May 7, 2021 Order issued by SCDHEC and the June 2, 2021 U.S. EPA Information Request. Additional clarification has also been added to the IPT per questions received from SCDHEC via email on June 8 and 9, 2021.

1.3 PROGRAM CONTACTS

New-Indy plans to contract with ALS Global's Kelso, WA lab to perform the liquid methanol and HAP and testing required for the IPT and with ALL4 to assist with the calculations required to determine the quantity of HAP collected and treated during the IPT. New-Indy has also contracted with Arcadis and TRC to assist with sample collection and with Pace Analytical for testing including chemical oxygen demand (COD). Liquid testing for TRS compounds [H_2S, MMC, dimethyl disulfide (DMDS), and dimethyl sulfide (DMS)] conducted per SCHDEC's Order and the U.S. EPA Information Request will be conducted by ALS Global's Simi Valley, CA lab. ALL4 will assist the Mill in calculating Fbio for the TRS compounds consistent with the 40 CFR Part 63 Appendix C procedure 5 as requested in the U.S. EPA Information Request, with the exception of H_2S, which will utilize the Sulfide Emissions Simulator, or "H2SSIM" model, rather than the Appendix C calculations. In addition, MMC and DMDS results from the Appendix C calculations will be adjusted based on the field study results published in the National Council for Air and Stream Improvement (NCASI) Technical Bulletin (TB) No. 956.

Contact information for the source owner/operator, sampling, testing and consulting contractors are provided in Table 1-1.

Table 1-1
Test Program Contact Information

Owner/Operator	**New-Indy Containerboard – Catawba Mill** 5300 Cureton Ferry Road Catawba, SC 29704	**Point of Contact:** Dan Mallett Environmental Manager (803) 981-8010 Dan.Mallett@new-indycb.com
Liquid Sampling Contractor	**TRC** 50 International Drive, Suite 150 Greenville, SC 29615	**Point of Contact:** Jim Kirlin Senior Engineer (864) 421-3890 jkirlin@trcsolutions.com
	Arcadis 3109 West Dr. Martin Luther King Jr. Boulevard, Suite 350 Tampa, FL 33607	**Point of Contact:** Jason Diamond Licensed Remote Pilot (813) 353-5763 Jason.Diamond@arcadis.com
Analytical Testing Contractor	**ALS Kelso** 1317 South 13th Avenue Kelso, WA 98626	**Point of Contact:** Sydney A. Wolf Project Manager Sydney.Wolf@alsglobal.com
	Pace Analytical 106 Vantage Point Drive West Columbia, SC 29172	**Point of Contact:** Blaire Gagne Project Manager Blaire.Gagne@pacelabs.com
	ALS Simi Valley 2655 Park Center Drive, Suite A Simi Valley, CA 93065	**Point of Contact:** Sue Anderson Project Manager (805) 577-2086 Sue.Anderson@alsglobal.com
Consulting Firm	**ALL4 LLC** 300 Chastain Center Blvd, Suite 395 Kennesaw, GA 30144	**Point of Contact:** Sheryl Watkins Sr. Technical Manager (678) 293-9428 swatkins@all4inc.com

1.4 RESPONSIBILITIES

In order to ensure that all of the necessary information is collected and quality assured during the performance test, various key responsibilities will be assigned to the Mill and the contracted firms. These responsibilities include, but are not limited to the following, organized by responsible party:

New-Indy Containerboard will be responsible for:

- Assuring the Mill is in a suitable operating condition for conducting the IPT per 40 CFR §63.7(e)(1).
- Collecting all Foul Condensate, Stripper Outlet, ASB Inlet, ASB Effluent, and Post-Aeration Tank Inlet, Surface, and Outlet samples (if approved) required for methanol, HAP, TRS compounds, or COD analysis and shipping to the testing contractor, on ice, such that they arrive within temperature and hold time constraints of applicable test methods.
- Conducting sample analysis for parameters including temperature, pH, mixed liquor volatile suspended solids (MLVSS), and biochemical oxygen demand (BOD_5) (Note: COD analysis will be performed by the testing contractor, Pace Analytical).
- Conducting onsite analysis for H_2S using the U.S. Environmental Protection Agency (U.S. EPA) Methylene Blue Method (Method 10254) with a Hach 6000 analyzer.
- Completing chain-of-custody forms for test program samples.
- Retaining all necessary operational data (i.e. pulp production rates, foul condensate flow rates, stripper steam feed flow rates, stripped condensate temperature, inlet flow to the ASB and Post-Aeration Tank, temperatures and pH within the ASB and Post-Aeration Tank). Note, as discussed in Section 1.2, sampling at the Post-Aeration Tank will only be conducted if the Mill is approved to remove the cover over the Post-Aeration Tank during the IPT.
- Submitting the final test report to SCDHEC and the U.S. EPA per 40 CFR §63.7(g)(1).

The liquid sampling contractors will be responsible for:

- Collecting all samples within the ASB (center and/or outlet of each treatment zone) using a boat or drone and baler and taking initial measurement of temperature.

The testing contractors will be responsible for:

- Compositing samples prior to analysis as described in this IPT plan.
- Analyzing samples according to and within the hold time requirements of the applicable test methods, including all QA/QC procedures.
- Providing test results to the Mill and to the consulting firm.

The consulting firm will be responsible for:

- Conducting the required calculations to demonstrate compliance with the condensate collection and treatment requirements of Subpart S.
- Calculating Fbio and fraction emitted to air (Fair) for the four individual TRS compounds in the ASB and the Post-Aeration Tank (if approved), as summarized above in Sections 1.3 and 5.3 and as documented in the New-Indy response to the June 2, 2021 U.S. EPA Information Request.
- Preparing the IPT report and providing to the Mill for submittal to SCDHEC and U.S. EPA.

1.5 SITE-SPECIFIC TEST PLAN ELEMENTS

Table 1-2 and Table 1-3 list each of the required elements of a performance test plan pursuant to 40 CFR Part 63, Subparts S and A, respectively, and identify where that information is presented within this document.

Table 1-4 lists the requirements of the SCDHEC Order and U.S. EPA Information Requests pertaining to this IPT and identify where the information to fulfill those requirements is presented within this document.

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
63.457(a)	*Performance tests.* Initial and repeat performance tests are required for the emissions sources specified in paragraphs (a)(1) and (a)(2) of this section, except for emissions sources controlled by a combustion device that is designed and operated as specified in §63.443(d)(3) or (4).	Section 1
63.457(a)(1)	Conduct an initial performance test for all emission sources subject to the limitations in §§63.443, 63.444, 63.445, 63.446, and 63.447.	Section 1
63.457(c), (c)(1)	*Liquid sampling locations and properties.* For purposes of selecting liquid sampling locations and for determining properties of liquid streams such as wastewaters, process waters, and condensates required in §§63.444, 63.446, and 63.447, the owner or operator shall comply with the following procedures: (1) Samples shall be collected using the sampling procedures of the test method listed in paragraph (c)(3) of this section selected to determine liquid stream HAP concentrations; (i) Where feasible, samples shall be taken from an enclosed pipe prior to the liquid stream being exposed to the atmosphere; and (ii) When sampling from an enclosed pipe is not feasible, samples shall be collected in a manner to minimize exposure of the sample to the atmosphere and loss of HAP compounds prior to sampling.	Sections 2 and 3
63.457(c)(2)	The volumetric flow rate of the entering and exiting liquid streams shall be determined using the inlet and outlet flow meters or other methods demonstrated to the Administrator's satisfaction. The volumetric flow rate measurements to determine actual mass removal shall be taken at the same time as the concentration measurements.	Section 3
63.457(c)(3)	The owner or operator shall conduct a minimum of three test runs that are representative of normal conditions and average the resulting pollutant concentrations. The minimum sampling time for each test run shall be 1 hour and the grab or composite samples shall be taken at approximately equally spaced intervals over the 1-hour test run period. The owner or operator shall use one of the following procedures to determine total HAP or methanol concentration… (ii) For determining methanol concentrations, NCASI Method DI/MeOH-94.03. This test method is incorporated by reference in §63.14(f)(1) of Subpart A of this part (iii) Any other method that measures total HAP concentration that has been demonstrated to the Administrator's satisfaction [Note: The Mill will utilize NCASI Method DI/HAPS-99.01, incorporated by reference under §63.14(p)(3)].	Sections 1 and 3
63.457(c)(4)	To determine soluble BOD_5 in the effluent stream from an open biological treatment unit used to comply with §§63.446(e)(2) and 63.453(j), the owner or operator shall use Method 405.1 of part 136 of this chapter with	Section 3

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	the following modifications [Note: The Mill will utilize Standard Method 5210, which is an approved method for BOD_5 under 40 CFR Part 136, Table B]: (i) Filter the sample through the filter paper, into an Erlenmeyer flask by applying a vacuum to the flask sidearm. Minimize the time for which vacuum is applied to prevent stripping of volatile organics from the sample. Replace filter paper as often as needed to in order to maintain filter times of less than approximately 30 seconds per filter paper. No rinsing of sample container or filter bowl into the Erlenmeyer flask is allowed. (ii) Perform Method 405.1 on the filtrate obtained in paragraph (c)(4) of this section. Dilution water shall be seeded with 1 milliliter of final effluent per liter of dilution water. Dilution ratios may require adjustment to reflect lower oxygen demand of the filtered sample in comparison to the total BOD_5. Three BOD_5 bottles and different dilutions shall be used for each sample.	
63.457(c)(5)	If the test method used to determine HAP concentration indicates that a specific HAP is not detectable, the value determined as the minimum measurement level (MML) of the selected test method for the specific HAP shall be used in the compliance demonstration calculations. To determine the MML for a specific HAP using one of the test methods specified in paragraph (c)(3) of this section, one of the procedures specified in paragraphs (c)(5)(i) and (ii) of this section shall be performed. The MML for a particular HAP must be determined only if the HAP is not detected in the normal working range of the method. (i) To determine the MML for a specific HAP, the following procedures shall be performed each time the method is setup. Set up is defined as the first time the analytical apparatus is placed in operation, after any shut down of 6 months or more, or any time a major component of the analytical apparatus is replaced. (A) Select a concentration value for the specific HAP in question to represent the MML. The value of the MML selected shall not be below the calibration standard of the selected test method. (B) Measure the concentration of the specific HAP in a minimum of three replicate samples using the selected test method. All replicate samples shall be run through the entire analytical procedure. The samples must contain the specific HAP at the selected MML concentration and should be representative of the liquid	Section 3, Appendix B

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	streams to be analyzed in the compliance demonstration. Spiking of the liquid samples with a known concentration of the target HAP may be necessary to ensure that the HAP concentration in the three replicate samples is at the selected MML. The concentration of the HAP in the spiked sample must be within 50 percent of the proposed MML for the demonstration to be valid. As an alternative to spiking, a field sample above the MML may be diluted to produce a HAP concentration at the MML. To be a valid demonstration, the diluted sample must have a HAP concentration within 20 percent of the proposed MML, and the field sample must not be diluted by more than a factor of five. (C) Calculate the relative standard deviation (RSD) and the upper confidence limit at the 95 percent confidence level using the measured HAP concentrations determined in paragraph (c)(5)(i)(B) of this section. If the upper confidence limit of the RSD is less than 30 percent, then the selected MML is acceptable. If the upper confidence limit of the RSD is greater than or equal to 30 percent, then the selected MML is too low, and the procedures specified in paragraphs (c)(5)(i)(A) through (C) of this section must be repeated. (ii) Provide for the Administrator's approval the selected value of the MML for a specific HAP and the rationale for selecting the MML including all data and calculations used to determine the MML. The approved MML must be used in all applicable compliance demonstration calculations.	
63.457(c)(6)	When using the MML determined using the procedures in paragraph (c)(5)(ii) of this section or when using the MML determined using the procedures in paragraph (c)(5)(i), except during set up, the analytical laboratory conducting the analysis must perform and meet the following quality assurance procedures each time a set of samples is analyzed to determine compliance. (i) Using the selected test method, analyze in triplicate the concentration of the specific HAP in a representative sample. The sample must contain the specific HAP at a concentration that is within a factor of two of the MML. If there are no samples in the set being analyzed that contain the specific HAP at an appropriate concentration, then a sample below the MML may be spiked to produce the appropriate concentration, or a sample at a higher level may be diluted. After spiking, the sample must contain the specific HAP	Appendix B

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	within 50 percent of the MML. If dilution is used instead, the diluted sample must contain the specific HAP within 20 percent of the MML and must not be diluted by more than a factor of five. (ii) Calculate the RSD using the measured HAP concentrations determined in paragraph (c)(6)(i) of this section. If the RSD is less than 20 percent, then the laboratory is performing acceptably.	
63.457(f)	*HAP concentration measurements.* For the purposes of complying with the requirements in §§63.443, 63.444, and 63.447, the owner or operator shall measure the total HAP concentration as one of the following: (1) As the sum of all individual HAPs; or (2) As methanol.	Section 3
63.457(g)	*Condensate HAP concentration measurement.* For purposes of complying with the kraft pulping condensate requirements in §63.446, the owner or operator shall measure the total HAP concentration as methanol. For biological treatment systems complying with §63.446(e)(2), the owner or operator shall measure total HAP as acetaldehyde, methanol, methyl ethyl ketone, and propionaldehyde and follow the procedures in §63.457(l)(1) or (2).	Section 3, Appendix B
63.457(j)	*Liquid stream calculations.* To demonstrate compliance with the mass flow rate, mass per megagram of ODP, and percent reduction requirements for liquid streams specified in §63.446, the owner or operator shall use the following: (1) The mass flow rates of total HAP or methanol entering and exiting the treatment process shall be calculated using the following equations: $E_b = \frac{K}{n \times 10^6} \left(\sum_{i=1}^{n} V_{bi} C_{bi} \right)$ $E_a = \frac{K}{n \times 10^6} \left(\sum_{i=1}^{n} V_{ai} C_{ai} \right)$ Where: E_b = Mass flow rate of total HAP or methanol in the liquid stream entering the treatment process, kilograms per hour. E_a = Mass flow rate of total HAP or methanol in the liquid exiting the treatment process, kilograms per hour.	Section 5

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	K = Density of the liquid stream, kilograms per cubic meter. V_{bi} = Volumetric flow rate of liquid stream entering the treatment process during each run i, cubic meters per hour, determined as specified in paragraph (c) of this section. V_{ai} = Volumetric flow rate of liquid stream exiting the treatment process during each run i, cubic meters per hour, determined as specified in paragraph (c) of this section. C_{bi} = Concentration of total HAP or methanol in the stream entering the treatment process during each run i, parts per million by weight, determined as specified in paragraph (c) of this section. C_{ai} = Concentration of total HAP or methanol in the stream exiting the treatment process during each run i, parts per million by weight, determined as specified in paragraph (c) of this section. n = Number of runs. (2) The mass of total HAP or methanol per megagram ODP shall be calculated using the following equation: $F = \frac{E_a}{P}$ Where: F = Mass loading of total HAP or methanol in the sample, in kilograms per megagram of ODP. E_a = Mass flow rate of total HAP or methanol in the wastewater stream in kilograms per hour as determined using the procedures in paragraph (j)(1) of this section. P = The production rate of pulp during the sampling period in megagrams of ODP per hour. (3) The percent reduction of total HAP across the applicable treatment process shall be calculated using the following equation:	

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	$R = \frac{E_b - E_a}{E_b} \times 100$ Where: R = Control efficiency of the treatment process, percent. E_b = Mass flow rate of total HAP in the stream entering the treatment process, kilograms per hour, as determined in paragraph (j)(1) of this section. E_a = Mass flow rate of total HAP in the stream exiting the treatment process, kilograms per hour, as determined in paragraph (j)(1) of this section. (4) Compounds that meet the requirements specified in paragraphs (j)(4)(i) or (4)(ii) of this section are not required to be included in the mass flow rate, mass per megagram of ODP, or the mass percent reduction determinations. (i) Compounds with concentrations at the point of determination that are below 1 part per million by weight; or (ii) Compounds with concentrations at the point of determination that are below the lower detection limit where the lower detection limit is greater than 1 part per million by weight.	
63.457(l)	*Biological treatment system percent reduction and mass removal calculations.* To demonstrate compliance with the condensate treatment standards specified in §63.446(e)(2) and the monitoring requirements specified in §63.453(j)(3) using a biological treatment system, the owner or operator shall use one of the procedures specified in paragraphs (1)(1) and (2) of this section. Owners or operators using a nonthoroughly mixed open biological treatment system shall also comply with paragraph (1)(3) of this section. (1) Percent reduction methanol procedure. For the purposes of complying with the condensate treatment requirements specified in §63.446(e)(2) and (3), the methanol percent reduction shall be calculated using the following equations:	Section 5

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	$R = \frac{f_{bio}\left(\mathrm{MeOH}\right)}{\left(1+1.087\left(r\right)\right)} * 100$ $r = \frac{F_{(nonmethanol)}}{F_{(methanol)}}$ Where: R = Percent destruction. fbio(MeOH) = The fraction of methanol removed in the biological treatment system. The site-specific biorate constants shall be determined using the appropriate procedures specified in appendix C of this part. r = Ratio of the sum of acetaldehyde, methyl ethyl ketone, and propionaldehyde mass to methanol mass. F(nonmethanol) = The sum of acetaldehyde, methyl ethyl ketone, and propionaldehyde mass flow rates (kg/Mg ODP) entering the biological treatment system determined using the procedures in paragraph (j)(2) of this section. F(methanol) = The mass flow rate (kg/Mg ODP) of methanol entering the system determined using the procedures in paragraph (j)(2) of this section. (2) Mass removal methanol procedure. For the purposes of complying with the condensate treatment requirements specified in §63.446(e)(2) and (4), or §63.446(e)(2) and (5), the methanol mass removal shall be calculated using the following equation: $F = F_b * \left(f_{bio}\left(MeOH\right)/\left(1+1.087\left(r\right)\right)\right)$ Where: F = Methanol mass removal (kg/Mg ODP). F_b = Inlet mass flow rate of methanol (kg/Mg ODP) determined using the procedures in paragraph (j)(2) of this section. f_{bio}(MeOH) = The fraction of methanol removed in the biological treatment system. The site-specific biorate constants shall be determined using the appropriate procedures specified in appendix C of this part.	

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	r = Ratio of the sum of acetaldehyde, methyl ethyl ketone, and propionaldehyde mass to methanol mass determined using the procedures in paragraph (1) of this section. (3) The owner or operator of a nonthoroughly mixed open biological treatment system using the monitoring requirements specified in §63.453(p)(3) shall follow the procedures specified in Section III.B.1 of Appendix E of this part to determine the biorate constant, Ks, and characterize the open biological treatment system during the initial and any subsequent performance tests.	
63.457(n)	*Open biological treatment system monitoring sampling storage.* The inlet and outlet grab samples required to be collected in §63.453(j)(1)(ii) shall be stored at 4°C (40°F) to minimize the biodegradation of the organic compounds in the samples.	Section 3, Appendix B
63.457(o)	Performance tests shall be conducted under such conditions as the Administrator specifies to the owner or operator based on representative performance of the affected source for the period being tested. Upon request, the owner or operator shall make available to the Administrator such records as may be necessary to determine the conditions of performance tests.	Section 3

Table 1-3
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart A

40 CFR §63.7 Reference	Requirement	Document Section Number(s)
(b)(1); (c)(2)(iv)	*Notification of performance test*. The owner or operator of an affected source must notify the Administrator in writing of his or her intention to conduct a performance test at least 60 calendar days before the performance test is initially scheduled to begin to allow the Administrator, upon request, to review and approve the site-specific test plan required under paragraph (c) of this section and to have an observer present during the test. The owner or operator of an affected source shall submit the site-specific test plan to the Administrator upon the Administrator's request at least 60 calendar days before the performance test is scheduled to take place, that is, simultaneously with the notification of intention to conduct a performance test required under paragraph (b) of this section, or on a mutually agreed upon date.	Intent to Test Notification Submitted with this IPT Plan
(c)(2)(i)	*Submission of site-specific test plan*. Before conducting a required performance test, the owner or operator of an affected source shall develop and, if requested by the Administrator, shall submit a site-specific test plan to the Administrator for approval. The test plan shall include a test program summary, the test schedule, data quality objectives, and both an internal and external quality assurance (QA) program. Data quality objectives are the pretest expectations of precision, accuracy, and completeness of data.	Section 3
(c)(2)(ii)	The internal QA program shall include, at a minimum, the activities planned by routine operators and analysts to provide an assessment of test data precision; an example of internal QA is the sampling and analysis of replicate samples.	Section 4
(c)(2)(iii)	The external QA program shall include, at a minimum, application of plans for a test method performance audit (PA) during the performance test. The PA's consist of blind audit samples provided by the Administrator and analyzed during the performance test in order to provide a measure of test data bias. The external QA program may also include systems audits that include the opportunity for on-site evaluation by the Administrator of instrument calibration, data validation, sample logging, and documentation of quality control data and field maintenance activities.	Section 4
(c)(2)(iv)	The owner or operator of an affected source shall submit the site-specific test plan to the Administrator upon the Administrator's request at least 60 calendar days before the performance test is scheduled to take place, that is, simultaneously with the notification of intention to conduct a performance test required under paragraph (b) of this section, or on a mutually agreed upon date.	Document will be submitted to EPA upon request
(d)	*Performance testing facilities*. The owner or operator shall provide	Section 3

Table 1-3
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart A

40 CFR §63.7 Reference	Requirement	Document Section Number(s)
	performance testing facilities as follows: (1) Sampling ports adequate for test methods applicable to such source. This includes: (i) Constructing the air pollution control system such that volumetric flow rates and pollutant emissions rates can be accurately determined by applicable test methods and procedures; and (ii) Providing a stack or duct free of cyclonic flow during performance tests, as demonstrated by applicable test methods and procedures; (2) Safe sampling platform(s); (3) Safe access to sampling platform(s); (4) Utilities for sampling and testing equipment; and (5) Any other facilities that the Administrator deems necessary for safe and adequate testing of a source.	
(e)	*Conduct of performance test.* (2) Performance tests shall be conducted and data shall be reduced in accordance with the test methods and procedures set forth in this section, in each relevant standard, and, if required, in applicable appendices of parts 51, 60, 61, and 63 of this chapter. (3) Unless otherwise specified in a relevant standard or test method, each performance test shall consist of three (3) separate runs using the applicable test method. Each run shall be conducted for the time and under the conditions specified in the relevant standard. For the purpose of determining compliance with a relevant standard, the arithmetic mean of the results of the three (3) runs shall apply.	Section 5

Table 1-4
IPT Plan Requirements of SCDHEC Order and U.S. EPA Information Request

Reference	Requirement	Document Section Number(s)
SCDHEC Order, Condition 2	On or before May 17, 2021, update and submit to [SCDHEC] for approval the Notification of Intent to Conduct Performance Testing and Test Protocol to comply with 40 CFR 63, Subpart S, dated April 14, 2021, for the condensate collection and treatment system to reflect the restart of the steam stripper and to modify the sampling methods to include methanol, H_2S, and MMC. The updated notification, test protocol, and test report must be submitted to Michael Shroup at shroupmd@dhec.sc.gov. This	Sections 1, 3

Table 1-4
IPT Plan Requirements of SCDHEC Order and U.S. EPA Information Request

Reference	Requirement	Document Section Number(s)
	test must be completed no later than July 31, 2021, to comply with 40 CFR 63, Subpart S.	
U.S. EPA Information Request, Condition 1	The proposed foul condensate test protocol appears to be using 40 CFR Part 63 Appendix C procedure 5 calculate Fbio for methanol. Fbio is an estimate of the fraction of a compound consumed or converted in the Aeration Stabilization Basin (ASB) and can also be used to estimate the fraction of methanol emitted to the air. The protocol does not appear to address calculation of Fbio for hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. In order to calculate Fbio, samples need to be taken in the three zones of the ASB and analyzed for each compound for which we want Fbio calculated in accordance with method 5 of Appendix C. New Indy shall take samples in each of the three ASB zones, conduct analyses of the concentrations of all four TRS compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) in the wastewater samples using the methodology required by request 4 below, and submit the results to EPA. New Indy shall use 40 CFR Part 63 Appendix C procedure 5 for each of the four TRS compounds to calculate and submit to EPA Fbio separately for all four TRS compounds for the ASB.	Sections 1, 3, and 5
U.S. EPA Information Request, Condition 2	New Indy shall take samples on the inlet and outlet, and from the surface of the Post-Aeration Tank and conduct analyses of the concentrations and submit the results to EPA for all four TRS compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) in the wastewater samples using the methodology required by request 4 below. New Indy shall use 40 CFR Part 63 Appendix C procedure 5 for each of the four TRS compounds to calculate and submit to EPA Fbio separately for all four TRS compounds for the Post-Aeration Tank.	Note that monitoring of the Post-Aeration Tank will only be conducted if the Mill receives approval to remove the cover that has been installed over the Post-Aeration Tank since issuance of the U.S. EPA Information Request. Sections 1, 3, and 5
U.S. EPA Information Request, Condition 3	The proposed foul condensate test protocol only requires measurement of hydrogen sulfide and methyl mercaptan both in and out of the steam stripper and both in and out of the ASB. New Indy shall take the required samples for all four TRS compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide), conduct analyses of the concentrations of these compounds in the wastewater samples using	Sections 1, 3, and 5

Table 1-4
IPT Plan Requirements of SCDHEC Order and U.S. EPA Information Request

Reference	Requirement	Document Section Number(s)
	the methodology required by request 4 below, and submit the results to EPA.	
U.S. EPA Information Request, Condition 4	The proposed foul condensate test protocol allows the use of one of three methods for analysis of hydrogen sulfide and methyl mercaptan for samples in and out of the steam stripper and the ASB. Only one of the three methods is acceptable. For the analyses required in requests 1 through 3 above, New Indy shall use NCASI Method RSC 02.02 to sample and measure the concentration of all four TRS compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) at each sampling point.	NCASI Method RSC 02.02 will not be available at the time of this IPT, as discussed in Section 3
U.S. EPA Information Request, Condition 5	The proposed foul condensate test protocol does not provide a sufficient explanation for the selection of the three zones of the ASB for sampling to calculate Fbio. Provide a detailed discussion of how New Indy made the determination of the number of zones in the biological treatment system. Specifically, New Indy should include information for the zones as outlined in the technical document discussed in 40 CFR Part 63 Appendix C, Section III (procedures for determination of Fbio), E (multiple zone concentration measurements).	The tracer study to confirm or revise the selection of the zones of the ASB is currently underway at the time of this IPT revision submittal. See Section 3.
U.S. EPA Information Request, Condition 6	The foul condensate test protocol proposes to "establish a concentration factor to be used to determine continuous compliance with the condensate collection requirements of Subpart S and to be confirmed or re-established during quarterly performance testing." Because of the sparse historical data available for this facility and the potential for significant variability in the methanol concentration, this method of using a methanol correction factor to demonstrate continuous compliance with Subpart S is not acceptable and is not approved and the foul condensate test protocol shall be revised to reflect that.	Section 5
U.S. EPA Information Request, Condition 7	New Indy shall revise the proposed foul condensate test protocol as specified in requests 1-6 above and resubmit it to the EPA and SC DHEC within 14 days of receipt of this letter. Because of the accelerated test schedule and brief period of time between the issuance of this letter and the planned commencement of testing, no further approval by the EPA of the revised test plan is required prior to conducting the test provided the revisions comply with this information request.	All

Table 1-4
IPT Plan Requirements of SCDHEC Order and U.S. EPA Information Request

Reference	Requirement	Document Section Number(s)
U.S. EPA Information Request, Condition 8	New Indy shall complete the required testing by no later than July 16, 2021, and, submit the results of the required testing and all calculations of Fbio within 14 days of completion of the testing but no later than July 30, 2021.	40 CFR §63.7(g)(1) states that the results of the IPT must be submitted before the close of business on the 60th day following the completion of the performance test. New-Indy will submit the IPT report as soon as practicable to ensure accuracy and completeness of the analyses and conclusions, but no later than 60 days following completion of the IPT. See Section 1.

1.6 TEST PROGRAM SCHEDULE

The emissions test program will begin on June 21, 2021. The total length of the sampling effort for condensate collection is expected to be 21 days, and the total length of the sampling effort for condensate treatment is expected to be a minimum of 5 days (July 7 – 11, 2021). In the event of a Mill upset or shutdown during the IPT, the IPT will be extended to include minimum of 15 days for condensate collection and 5 days for condensate treatment. Any changes in the tentative schedule will be communicated via letter or email to SCDHEC and U.S. EPA. Please note the Mill may deviate from this schedule as appropriate. Samples will be taken during daylight hours due to personnel scheduling and, for condensate treatment testing, safety concerns with sampling from the ASB at night. Per 40 CFR §63.457(c)(3), a minimum of three sample runs under normal operating conditions is required, with each run having a minimum sampling time of one hour. To meet this requirement, samples will be obtained at least once per day for the duration of the performance test. Foul Condensate samples will be collected three times per day throughout the 21 days of the performance test; for the first 16 days (collection only), samples collected each day will be composited at the laboratory prior to analysis. During the collection and treatment portion of the test (last five days), Foul Condensate and Stripped Condensate samples will be collected three times per day for individual analysis, and ASB and Post-Aeration Tank samples (if approved) will be collected once per day.

2. GENERAL FACILITY AND SOURCE DESCRIPTION

Project Columbia converted the Mill from manufacturing bleached paper grades (lightweight coated paper and market pulp) to manufacturing unbleached or brown paper (linerboard and market pulp). The original Kraft continuous digester system was modified to produce a higher virgin pulp yield. Kappa number has been increased from less than 30 for bleached pulp to over 90 for unbleached pulp and the cook time in the continuous digester has been shortened. The higher Kappa produces more tons of virgin pulp using the same amount of raw materials (wood and cooking liquor).

The pulp slurry from the continuous digester is sent to the blow tank and through the diffusion washer system, then to one of two parallel pulping lines, each consisting of an enclosed deshive refiner and a 3-stage vacuum drum washer system and associated filtrate tanks. Weak black liquor from the washer filtrate tanks is stored before being recycled to chemical recovery. Rejects from the refiners are sent to the screw presses, with the filtrate being screened and stored before being recycled to chemical recovery. Washed pulp is stored and then sent to the Pulp Dryer Area to produce unbleached market pulp or to the No. 3 Paper Machine Area to produce linerboard. Note: The No. 2 Paper Machine may be used to produce an uncoated lightweight brown sheet but is currently idle.

The No. 1 Evaporator Set was modified to increase the evaporation rate needed to account for the reduction in the solids content of the weak black liquor from the repurposed washers following the conversion to unbleached pulp. No modifications were made to the No. 2 and No. 3 Evaporator Sets, No. 2 and No. 3 Recovery Furnaces, No. 2 and No. 3 Smelt Dissolving Tanks, No. 2 Lime Kiln or Causticizing Area as part of the conversion to unbleached.

As part of compliance with the pulping condensates collection and treatment under 40 CFR Part 63, Subpart S, the following streams are collected in the Foul Condensate Collection Tank and treated in the ASB or Steam Stripper:

- No. 1 Evaporator 5th and 6th effect, Surface Condenser, and Auxiliary Surface Condenser Foul Condensates [40 CFR §63.446(b)(3)(i and ii)];
- No. 2 Evaporator 5th and 6th Effects Foul Condensates [40 CFR §63.446(b)(3)(i and ii)];
- No. 3 Evaporator 5th and 6th Effects and Surface Condenser/Flash Tank Condensates [40 CFR §63.446(b)(3)(i)];
- HVLC Collection System Condensates [40 CFR §63.446(b)(4)]; and
- LVHC Collection System Condensates (including condensates from the precondensers, intercondensers, and aftercondensers) [40 CFR §63.446(b)(5)].

The sampling location for the foul condensates collected and routed to treatment in either the ASB or the Steam Stripper is on the outlet of the Foul Condensate tank, before the line splits between the ASB hardpipe and the Steam Stripper. This sample point is representative of condensates sent to the ASB and the Steam Stripper. The Mill has the following objectives under 40 CFR Part 63 Subpart S for the IPT:

- Demonstrate compliance with the condensate collection and treatment requirements of Subpart S; and
- Establish an operating parameter and limit to be used to determine continuous compliance with the condensate treatment requirements of Subpart S.

In addition, the Mill will collect samples to be analyzed for individual TRS compounds to satisfy Item #2 of the May, 7, 2021 SCDHEC Order and the U.S. EPA Information Request. Pursuant to the U.S. EPA Information Request, the TRS compound data will be used to calculate Fbio for the ASB and the Post-Aeration Tank (if approved) utilizing the approach summarized in Sections 1.3 and 5.3 of this Plan and as documented in the New-Indy response to the U.S. EPA Information Request.

3. PERFORMANCE TEST PLAN

This section addresses the key components of the IPT plan and describes the Mill operating conditions that will be maintained and monitored during the test program, the compliance demonstration parameters that will be monitored during the testing, the applicable test methods, and proposed QA and QC activities. This section also discusses the TRS compound testing to be conducted during the IPT per the Order issued by SCDHEC and the U.S. EPA Information Request.

3.1 TEST RUN CRITERIA

Sampling for the IPT will be conducted under stable Mill operations and normal operating conditions. The Mill is still in start-up mode following the extended outage for the conversion project and has not yet achieved the maximum anticipated pulp production rate. The Mill anticipates operating in the range of approximately 1,400-1,600 ODTP/day during the IPT. In the event of upset conditions resulting in process downtime or excess loading to the ASB, IPT sampling will be paused until the Mill is returned to stable operations. In the event of unplanned Steam Stripper downtime during the treatment portion of the IPT, sampling will be paused until the Steam Stripper is returned to stable operation. In addition, in the event of an unplanned outage of the Post-Aeration Tank aerators, sampling will be paused until the Post-Aeration Tank aerators are returned to service (if Post-Aeration Tank sampling is approved).

3.2 SOURCE OPERATION AND PARAMETER MONITORING

To all extent practicable, all sources will be maintained at a normal operating rate during the IPT. During the condensate treatment performance test, the Mill proposes to limit aeration capacity within the designated zones to the proposed operating limit of aeration horsepower (such as 90% of the available aeration horsepower) to demonstrate the capability of the ASB to comply with the condensate treatment requirements at that level. The Mill will select a target aeration horsepower operating limit prior to the IPT based on ASB performance. The Mill plans to operate the ASB at the proposed operating limit of aeration horsepower for three days prior to the condensate treatment performance test. The Mill plans to operate the Steam Stripper at a range of effective steam to feed ratios (ESFR) during the IPT in order to establish a correlation between ESFR and methanol removal in the Steam Stripper. This correlation will be used following the IPT to monitor compliance with the methanol treatment requirements of Subpart S. The method of calculating ESFR is discussed in Section 5.2.2.

Figure 3-1 below provides a simplified diagram of the Mill's foul condensate collection and treatment system and the Post-Aeration Tank, including flow meters and sample points applicable to this IPT plan.

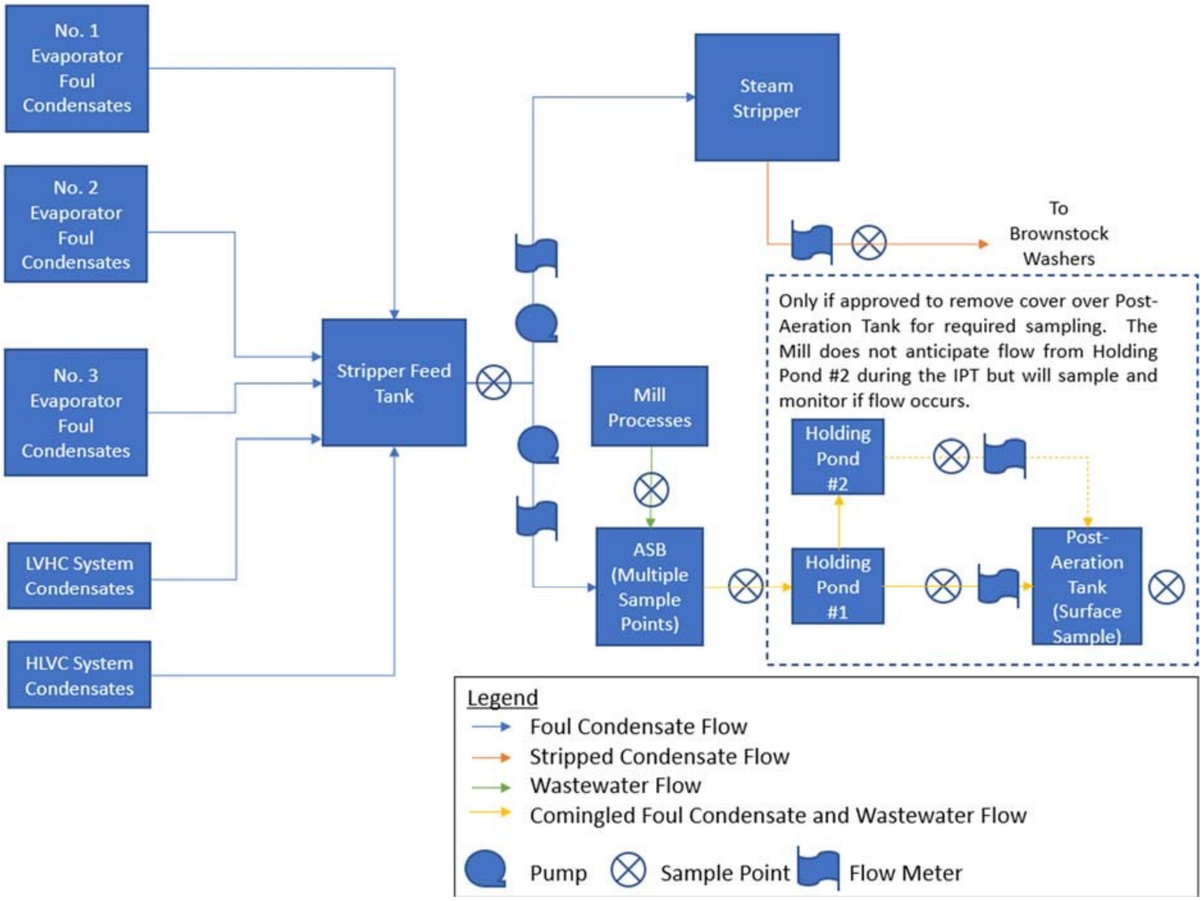


Figure 3-1
Foul Condensate Collection and Treatment System Diagram

Table 3-1 summarizes the parameters that the Mill proposes to monitor during the IPT and associated proposed calculation methods, which will be validated prior to or during the IPT. All of the instruments used for the monitoring parameters listed in Table 3-1 will undergo a continuous monitoring system (CMS) performance evaluation/calibration prior to the IPT. Documentation of the performance evaluations will be included in the IPT report.

Table 3-1
Proposed Monitoring Parameters

Measurement Taken	Measurement Device	Calculation Method	Monitoring Period
Foul Condensate Hardpipe Flow	Continuous Flow Meter	Gallons per day (gpd) = Average gallons per minute (gpm) x Operating minutes per day	24-hour total
Steam Stripper Inlet Condensate Feed Flow	Continuous Flow Meter	Gallons per hour (gph) = Average gallons per minute (gpm) x Operating minutes per hour	1-hour average for each sampling event
Steam Stripper Steam Flow	Continuous Flow Meter	Average rate in pounds per hour (lb/hr)	1-hour average for each sampling event
Foul Condensate to Steam Stripper Feed Temperature	Continuous Temperature Probe	Average temperature in degrees Fahrenheit (°F)	1-hour average for each sampling event
Stripped Condensate Temperature	Continuous Temperature Probe	Average temperature in °F	1-hour average for each sampling event
Stripped Condensate Flow	Continuous Flow Meter	Gallons per hour (gph) = Average gallons per minute (gpm) x Operating minutes per hour	1-hour average for each sampling event

Table 3-1
Proposed Monitoring Parameters

Measurement Taken	Measurement Device	Calculation Method	Monitoring Period
Digester production oven dried tons of pulp (ton ODTP)	Pulp Flow and Consistency Meters	ODTP = ADTUBP/d [Daily Average Flow, gpm x Daily Average Consistency, %/100 x (8.17 + 0.0333 x Daily Average Consistency, %) x 1440 minutes/day /1800] x 0.9	24-hour total
ASB Wastewater Inlet Flow (based on Fresh Water Intake Flow)	Continuous Flow Meter, Evaporation Factor	Wastewater inlet flow rate to ASB, gpd = Average gpm Fresh Water Intake flow x [1 – Evaporation Rate] x Flow Meter Operational Minutes per Day	24-hour total
ASB Outlet Flow (based on ASB Inlet Flow + Foul Condensate Hardpipe Flow)	Continuous Flow Meter	ASB Outlet Flow = ASB Wastewater Inlet Flow + Foul Condensate Hardpipe Flow	24-hour total
Number of Aerators Operating per Zone	Readout in Pi and calculated total	Sum of aerators running in each zone during each day of the condensate treatment performance test	24-hour average
ASB Total Aerator hp-hrs	Readout in Pi or calculated value	Total daily hp-hrs = Sum for all aerators (hp x daily runtime, hrs)	24-hour total
Post-Aeration Tank sampling, if approved to remove cover over Post-Aeration Tank for required sampling			
Post-Aeration Tank Flow	Continuous Flow Meter, Holding Pond Outlet (Flow meters on the outlet of Holding Ponds #1 and #2; no flow from Holding Pond #2 during IPT, but will be monitored if flow occurs)	Flow rate to Post-Aeration Tank, gpd = Average gpm Post-Aeration Tank inlet flow x Flow meter Operational Minutes per Day	24-hour total

Table 3-1
Proposed Monitoring Parameters

Measurement Taken	Measurement Device	Calculation Method	Monitoring Period
Post-Aeration Tank Number of Aerators Operating	Count	Sum of aerators in operation	Instantaneous (during sample collection)
Post-Aeration Tank Total Aerator hp-hrs	Hp-hrs	Total daily hp-hrs = Count of aerators running x hp/aerator x 24 hrs/day	Instantaneous (during sample collection)

3.3 SAMPLE COLLECTION AND TESTING

The following subsections describe sampling conducted for purposes of demonstrating compliance with the foul condensate collection and treatment requirements of Subpart S and the TRS compound testing conducted in accordance with SCDHEC's Order and the U.S. EPA Information Request. Table 3-2 contains an overall sampling matrix for the liquid sampling proposed for the IPT, and Appendix A contains detailed sampling matrices.

Table 3-2
Proposed Condensate Collection and Treatment IPT Sampling Matrix
New-Indy Catawba, SC Mill

Green shading indicates monitoring to be conducted per DHEC order that is not required by Subpart S

Sample Location	Sampling Start Date	Sampling End Date	Number of Daily Samples	Analytes Tested	Who Will Collect Samples?	Who Will Analyze Samples?
Foul Condensate Collection Tank to Hardpipe (also representative of Foul Condensate to Steam Stripper)	21-Jun-2021	6-Jul-2021	(3) per day	Methanol, NCASI MeOH-94.03	Catawba Mill Lab Technicians	ALS Kelso
	7-Jul-2021	11-Jul-2021	(1) per day	Total HAPs; NCASI HAPS-99.01	Catawba Mill Lab Technicians	ALS Kelso
	7-Jul-2021	11-Jul-2021	(2) per day	Methanol, NCASI MeOH-94.03	Catawba Mill Lab Technicians	ALS Kelso
	7-Jul-2021	11-Jul-2021	(3) per day	COD	Catawba Mill Lab Technicians	Pace Analytical
	7-Jul-2021	11-Jul-2021	(3) per day	Hydrogen sulfite (H_2S)	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians (Hach 6000 Analyzer)
	7-Jul-2021	11-Jul-2021	(3) per day	TRS Compounds (H_2S, MMC, DMS, DMDS)	Catawba Mill Lab Technicians	ALS Simi Valley
Steam Stripper Outlet	7-Jul-2021	11-Jul-2021	(3) per day	Methanol, NCASI MeOH-94.03	Catawba Mill Lab Technicians	ALS Kelso
	7-Jul-2021	11-Jul-2021	(3) per day	H_2S	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians (Hach 6000 Analyzer)
	7-Jul-2021	11-Jul-2021	(3) per day	TRS Compounds (H_2S, MMC, DMS, DMDS)	Catawba Mill Lab Technicians	ALS Simi Valley
ASB Inlet Wastewater Stream	7-Jul-2021	11-Jul-2021	(1) per day	Total HAPs; NCASI HAPS-99.01	Catawba Mill Lab Technicians	ALS Kelso
	7-Jul-2021	11-Jul-2021	(1) per day	Liquid Temperature	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians
	7-Jul-2021	11-Jul-2021	(1) per day	COD	Catawba Mill Lab Technicians	Pace Analytical
	7-Jul-2021	11-Jul-2021	(1) per day	H_2S	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians (Hach 6000 Analyzer)
	7-Jul-2021	11-Jul-2021	(1) per day	TRS Compounds (H_2S, MMC, DMS, DMDS)	Catawba Mill Lab Technicians	ALS Simi Valley
ASB Samples: Zone 1 Center and Outlet; Zone 2 Center and Outlet; Zone 3 Center[a]	7-Jul-2021	11-Jul-2021	(1) per day	Methanol, NCASI MeOH-94.03	Arcadis/TRC	NCASI
	7-Jul-2021	11-Jul-2021	(1) per day	Liquid Temperature	Arcadis/TRC	Catawba Mill Lab Technicians
	7-Jul-2021	11-Jul-2021	(1) per day	MLVSS	Arcadis/TRC	Catawba Mill Lab Technicians
	7-Jul-2021	11-Jul-2021	(1) per day	TRS Compounds (H_2S, MMC, DMS, DMDS)	Arcadis/TRC	ALS Simi Valley
ASB Effluent (Zone 3 Outlet)	7-Jul-2021	11-Jul-2021	(1) per day	Methanol, NCASI MeOH-94.03	Catawba Mill Lab Technicians	NCASI
	7-Jul-2021	11-Jul-2021	(1) per day	Liquid Temperature	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians
	7-Jul-2021	11-Jul-2021	(1) per day	Soluble BOD_5	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians
	7-Jul-2021	11-Jul-2021	(1) per day	H_2S	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians (Hach 6000 Analyzer)
	7-Jul-2021	11-Jul-2021	(1) per day	TRS Compounds (H_2S, MMC, DMS, DMDS)	Catawba Mill Lab Technicians	ALS Simi Valley
Post-Aeration Tank sampling, if approved to remove cover over Post-Aeration Tank for required sampling						
Post-Aeration Tank Inlet	7-Jul-2021	11-Jul-2021	(1) per day	H_2S	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians (Hach 6000 Analyzer)
	7-Jul-2021	11-Jul-2021	(1) per day	TRS Compounds (H_2S, MMC, DMS, DMDS)	TRC/Catawba Mill Lab Technicians	ALS Simi Valley
Post-Aeration Tank Surface	7-Jul-2021	11-Jul-2021	(1) per day	H_2S	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians (Hach 6000 Analyzer)
	7-Jul-2021	11-Jul-2021	(1) per day	TRS Compounds (H_2S, MMC, DMS, DMDS)	TRC/Catawba Mill Lab Technicians	ALS Simi Valley
Post-Aeration Tank Outlet	7-Jul-2021	11-Jul-2021	(1) per day	H_2S	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians (Hach 6000 Analyzer)
	7-Jul-2021	11-Jul-2021	(1) per day	TRS Compounds (H_2S, MMC, DMS, DMDS)	TRC/Catawba Mill Lab Technicians	ALS Simi Valley

[a] Pending results of grid sampling and the tracer study anticipated prior to the IPT, there may be more or less than the anticipated three zones. The Mill will provide an update to SCDHEC prior to the IPT, as necessary. Additionally, if the results of the grid study show that there is no significant variation between samples collected at the center and outlet of the treatment zones, only the outlet of the zones will be monitored during the IPT and subsequent quarterly sampling events for performance testing due to the relative increased safety and ease of access of obtaining samples from these points.

3.3.1 Condensate Collection Sampling

During the IPT, the Catawba Mill lab technicians will collect grab samples from the outlet of the Foul Condensate Collection tank three times a day for the full duration of the performance test (21 days). For the first 16 days of the performance test, samples will be composited at the lab prior to analysis, and each day will be considered a test run. For the remaining 5 days, each of the three daily samples will be analyzed individually and sample results will be averaged for the purposes of condensate collection calculations. Samples will be shipped to the laboratories at least once every seven days for analysis, and results will be provided to the Mill and ALL4.

3.3.1.1 Methanol – NCASI MeOH-94.03

Samples will be collected three times daily from the sampling locations identified in Table 3-2 in accordance with the requirements of NCASI MeOH 94.03 test method, which is included in Appendix B. Samples must be collected in 40 milliliter (mL) glass vials, with zero headspace. ALS will provide sample vials to the Mill to use for sample collection. Two vials will be filled for every sample that is collected; one to be sent to the lab for analysis, and one to be retained by the Mill as a back-up in case the original sample is lost or damaged. The pH and temperature for each sample will be measured upon collection and recorded on the chain of custody (COC) form provided by ALS. For the samples taken at the ASB, drops of acid will need to be added upon sample collection until the sample reaches a pH of 2-3. The sampler will then fill the vial to zero headspace (Note: If there is headspace greater than the size of a pea, additional sample will be added). Samples will be stored in a refrigerator between 0 and 4ºC until they are shipped for analysis. Samples must be shipped overnight, in a cooler on ice and must arrive at the lab within 0-4ºC. Sample shipment will be coordinated with ALS to ensure someone will be present to receive the samples on the day they arrive.

3.3.1.2 Acetaldehyde, Methanol, Methyl Ethyl Ketone, Propionaldehyde – NCASI-HAPS-99.01

During the last five days of the IPT, samples will be collected at the sampling locations and frequencies identified in Table 3-2 in accordance with the requirements of NCASI MeOH 99.01

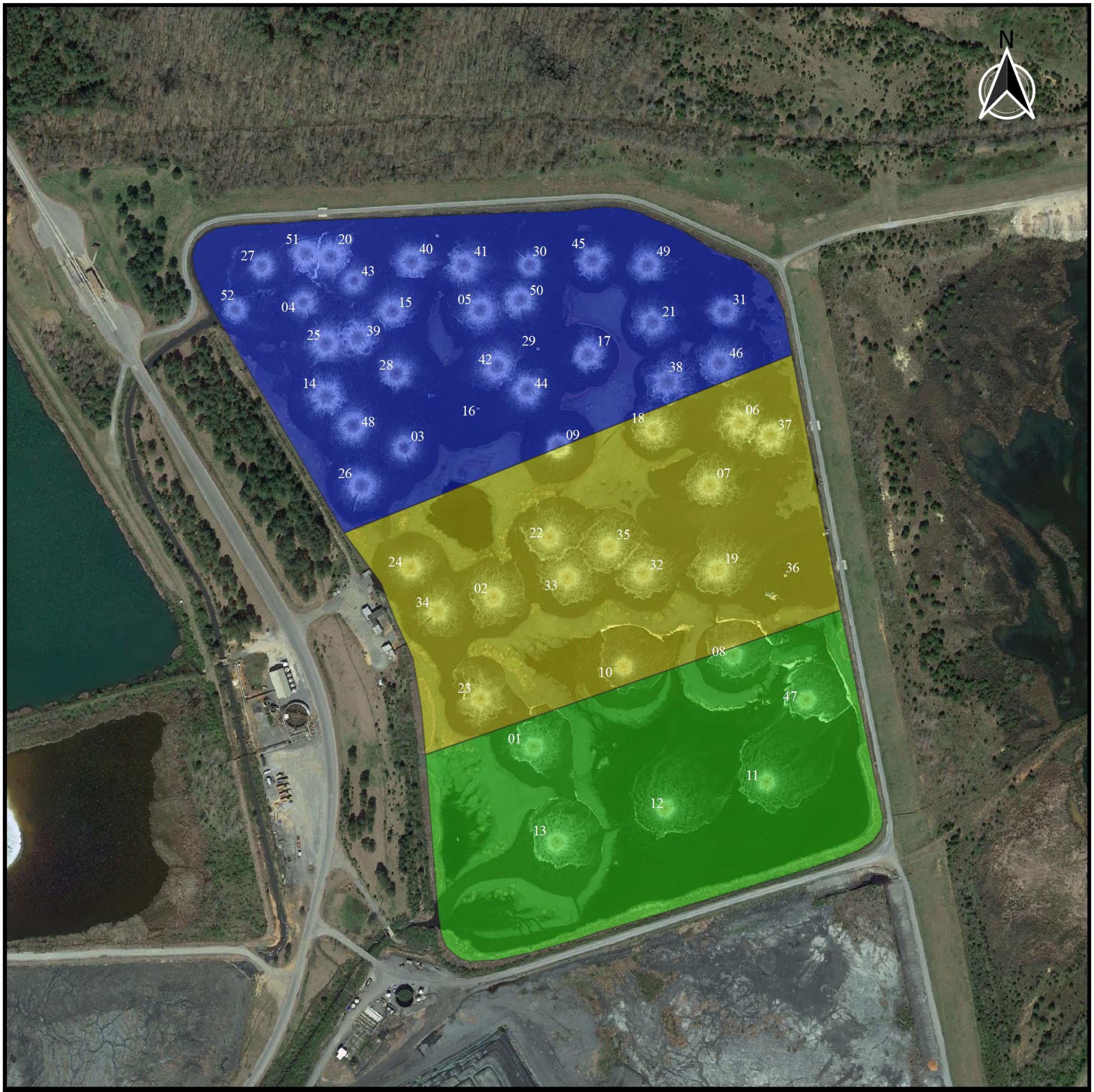
test method, which is included in Appendix B. Samples must be collected in 40 milliliter (mL) glass vials, with zero headspace. ALS will provide sample vials to the Mill to use for sample collection. Two vials will be filled for every sample that is collected; one to be sent to the lab for analysis, and one to be retained by the Mill as a back-up in case the original sample is lost or damaged. The pH and temperature for each sample will be measured upon collection and recorded on the chain of custody (COC) form provided by ALS. (Note: If there is headspace greater than the size of a pea, additional sample will be added). Samples will be stored in a refrigerator between 0 and 4ºC until they are shipped for analysis. Samples must be shipped overnight, in a cooler on ice and must arrive at the lab within 0-4ºC. Sample shipment will be coordinated with ALS to ensure someone will be present to receive the samples on the day they arrive. Note that only the methanol results from this analysis will be used for purposes of determining compliance with condensate collection requirements of Subpart S. The remaining data will be used in the calculations for condensate treatment, as discussed in Section 5.2.

3.3.2 Condensate Treatment Sampling

3.3.2.1 ASB Sampling

Based on observation of flow patterns within the ASB, the Mill believes the ASB to be a non-thoroughly mixed basin. As a result, the ASB will likely be mathematically subdivided into a series of zones for the purposes of the IPT and subsequent performance testing. The Mill plans to conduct a grid study and a tracer study of the ASB prior to the IPT to confirm that the ASB is non-thoroughly mixed and, if so, to mathematically subdivide the ASB into zones for the purposes of the condensate treatment calculations. The Mill has assumed that the ASB will be subdivided into three zones, approximately as shown in Figure 3-2. The Mill will submit updated information to SCDHEC following the tracer study, as needed.

Sampling locations within the ASB were determined using guidance from the Guidance Document and with respect to where future quarterly performance test samples would be obtained. For samples collected from the ASB, the Mill will use a boat or a drone. One set of samples will be collected each day during the treatment portion of the IPT, and each day will be



🟦 Zone 1

🟨 Zone 2

🟩 Zone 3

Figure 3-2
Anticipated ASB
Zones

New-Indy Catawba
Catawba, SC

Aerial Imagery courtesy of Google Satellite © Maxar Technologies, Orbis Inc, USDA Farm Service Agency, York County Government, SC considered a test run. If the identified ASB sample points cannot be safely accessed by a boat, a drone with a sample baler will be used to collect the samples. The drone will be operated by Arcadis. Once the drone has collected a sample from a given sample location, the drone will return to shore where the TRC technician will measure temperature of the sample and fill sample vials and containers for the analyses to be conducted. The Guidance Document suggests the following sampling locations in order to accurately characterize the concentration of the target compound (methanol):

- ASB Inlet;
- ASB Effluent;
- Approximate center of each of the three zones; and/or
- Outlet of each of the three zones.

The Guidance Document advises to avoid sampling edge, bottom, or surface effects. During grid and tracer studies conducted prior to the IPT, the Mill will determine whether there is significant variation between the center and outlet of the mixing zones. If no significant variation is observed, the locations at the outlet of the mixing zones will be used for the IPT and subsequent quarterly sampling events for performance testing due to the relative increased safety and ease of access of obtaining samples from these points.

3.3.2.2 Steam Stripper Sampling

Samples will be collected at the inlet and outlet of the Steam Stripper three times a day during the last five days of the IPT and will be analyzed individually for methanol via NCASI MeOH 94.03. Each sampling event will be considered a test run.

3.3.3 TRS Compounds Sampling

Per the Order issued by SCDHEC and the U.S. EPA Information Request, samples will be collected at the locations and frequencies described in Table 3-2 and analyzed for TRS compounds (H_2S, MMC, DMDS, and DMS). The Mill plans to analyze for H_2S onsite using the Methylene Blue Method with a Hach 6000 analyzer and plans to ship samples to ALS Simi

Valley for analysis for TRS compounds per ALS's sulfur liquid method. Sampling procedures for both methods are summarized in the following subsections.

3.3.3.1 H_2S Only – Methylene Blue Hach 6000 Onsite Analyzer

Hach documentation describing the procedures for sampling and analysis for the Methylene Blue Method using a Hach 6000 analyzer are provided in Appendix B. Sample pH and temperature will be determined and recorded for each sample collected. The ASB influent, effluent, and zone samples and Post-Aeration Tank samples (if approved) may be filtered prior to analysis if the solids content appears too high for the analyzer. A color blank will be needed for each sample taken.

Samples will be collected in clean glass or plastic bottles with tight-fitting caps. The bottle will be completely filled and the cap will be tightened immediately. 10 mL of sample will be transferred to a 10-mL sample cell for analysis. Samples will be analyzed within two hours of collection if possible but will be analyzed during the same day as collection.

3.3.3.2 ALS Sulfur Liquid Method (Derived from ASTM D 5504)

ALS has developed an in-house method derived from ASTM D 5504 using a gas chromatograph equipped with a sulfur chemiluminescence detector (SCD). Four 40 mL glass vials with zero headspace will be collected at the sample locations and frequencies specified in Table 3-2; two vials will be shipped to the ALS Simi Valley, CA lab for analysis, and the remaining two vials will be held at the Mill as back-up. Samples collected from the ASB influent, effluent, and within the ASB and from the inlet, outlet, and surface of the Post-Aeration Tank (if approved) will be filtered to remove sediment.

3.3.4 Sample Collection Methodology

This section summarizes sample container size requirements, sample preparation (i.e. required preservatives), sample storage temperature, sample hold times, and additional details on sample collection procedures.

3.3.4.1 MLVSS – U.S. EPA Method 1684

Samples collected from within the ASB will be analyzed for MLVSS content via U.S. EPA Method 1684 by the Catawba Mill Lab Technicians. Sufficient sample volume for conducting the test will be collected via the drone. Samples will be stored in a refrigerator at 4°C until they are analyzed, and all samples will be analyzed within seven days of collection.

3.3.4.2 Acetaldehyde, Methanol, Methyl Ethyl Ketone, Propionaldehyde – NCASI-HAPS-99.01

Samples will be collected from the sampling locations and frequencies identified in Table 3-2 in accordance with the requirements of NCASI MeOH 99.01 test method, which is included in Appendix B. Samples must be collected in 40 milliliter (mL) glass vials, with zero headspace. ALS will provide sample vials to the Mill to use for sample collection. Two vials will be filled for every sample that is collected; one to be sent to the lab for analysis, and one to be retained by the Mill as a back-up in case the original sample is lost or damaged. The pH and temperature for each sample will be measured upon collection and recorded on the chain of custody (COC) form provided by ALS. The sampler will then fill the vial to zero headspace (Note: If there is headspace greater than the size of a pea, additional sample will be added). Samples will be stored in a refrigerator between 0 and 4ºC until they are shipped for analysis. Samples must be shipped overnight, in a cooler on ice and must arrive at the lab within 0-4ºC. Sample shipment will be coordinated with ALS to ensure someone will be present to receive the samples on the day they arrive.

3.3.4.3 Methanol – NCASI MeOH-94.03

Samples will be collected from the sampling locations and frequencies identified in Table 3-2 in accordance with the requirements of NCASI MeOH 94.03 test method, which is included in Appendix B. Samples must be collected in 40 milliliter (mL) glass vials, with zero headspace. ALS will provide sample vials to the Mill to use for sample collection. Two vials will be filled for every sample that is collected; one to be sent to the lab for analysis, and one to be retained by the Mill as a back-up in case the original sample is lost or damaged. The pH and temperature for each sample will be measured upon collection and recorded on the chain of custody (COC) form provided by ALS. All samples collected from the ASB, including ASB inlet wastewater samples, will need to be preserved with 1N hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) that will be provided by ALS. Drops of acid will need to be added upon sample collection until the sample reaches a pH of 2-3. (Note: If there is headspace greater than the size of a pea, additional sample will be added). Samples will be stored in a refrigerator between 0 and 4ºC until they are shipped for analysis. Samples must be shipped overnight, in a cooler on ice and must arrive at the lab within 0-4ºC. Sample shipment will be coordinated with ALS to ensure someone will be present to receive the samples on the day they arrive.

3.3.4.4 BOD$_5$ – Standard Methods 5210

Soluble (filtered) BOD$_5$ will be monitored at the ASB effluent every day during the condensate treatment performance test by Standard Methods 5210. A composite sampler will be used at the ASB effluent to collect samples. Ice will be applied at the composite sampler to chill samples upon collection. Catawba Lab Technicians will collect sufficient sample for the necessary dilutions and will set up the samples within the required 48-hour hold time. Note that for composite samples, the 48-hour hold time begins when the composite sampler begins sampling such that once a 24-hour composite sample is collected, 24 hours of the hold time is remaining. Samples will be pH-adjusted in the laboratory as needed prior to analysis.

3.3.4.5 COD – Standard Methods 5220

Soluble (filtered) COD of the ASB influent and the Foul Condensate will be monitored every day during the condensate treatment performance test by Standard Methods 5220. A composite sample will be taken of the ASB influent, and a grab sample will be taken of the Foul Condensate stream. Catawba Lab Technicians will collect sufficient sample volume for the test. Samples will be provided to Pace Analytical for testing.

3.3.4.6 TRS Compounds

Per the Order issued by SCDHEC and the U.S. EPA Information Request, samples will be collected for analysis for TRS compounds during the condensate treatment performance test. All samples collected for TRS compound analysis will be grab samples. Proper sample collection methods will be followed for the two test methods to be used: Methylene Blue by Hach 6000 and ALS sulfur liquid method.

3.3.5 Sample Shipping and Storage

The MeOH and HAP samples will be stored on ice or in a controlled temperature refrigerator prior to shipping at the temperatures indicated in Section 3.3. Vial samples should be carefully packaged in foam sleeves when shipping. Samples will ship via overnight delivery under chain of custody to the laboratory for analysis (ALS – Kelso, WA). Sample holding time is 14 days for NCASI HAPS-99.01 and 30 days for NCASI MeOH-94.03. Sample shipment and receipt times should be coordinated with ALS. Samples will not be shipped on Fridays or days prior to holidays unless ALS has confirmed that someone will be able to receive the samples upon arrival.

Samples collected for TRS compound analysis per the Order issued by SCDHEC and the U.S. EPA Information Request to be shipped to the ALS Simi Valley, CA lab will be stored on ice or in a controlled temperature refrigerator at ≤4°C. Vials will be carefully packaged in foam sleeves when shipping. Samples will ship via overnight delivery under chain of custody to the laboratory for analysis. There is not a specified hold time for the ALS sulfur liquid test method.

3.3.6 Sample Analysis Methodology

The following sections present a summary of the test methods to be utilized for the liquid samples to be collected as part of this liquid sampling effort.

3.3.6.1 Methanol – NCASI MeOH-94.03

Methanol will be measured using the NCASI Method DI/MEOH 94.03 - Methanol in Process Liquids by gas chromatography/flame ionization detection (GC/FID), May 2000 in accordance with 40 CFR §63.457(c)(3)(ii). This method was validated on February 24, 1998 to meet the U.S. Environmental Protection Agency (U.S. EPA) Method 301 criteria for measuring methanol in process liquids from the sources specified in the method. The NCASI MeOH-94.03 test method is provided in Appendix B.

3.3.6.2 Acetaldehyde, Methanol, Methyl Ethyl Ketone, Propionaldehyde – NCASI HAPS-99.01

Total HAP will be measured using the NCASI HAPS-99.01 Method, February 2000, by GC/FID. The method has been validated in two laboratories using U.S. EPA Method 301, Field Validation of Emission Concentrations from Stationary Sources (Appendix A to 40 CFR 63) and is a validated method. The NCASI HAP-99.01 test method is provided in Appendix B. Foul Condensate samples will be analyzed by this method during the last week of the IPT for purposes of calculating the "r" factor for the foul condensate treatment calculations, as discussed in Section 5.2. Additionally, the methanol results from this test method will be used for purposes of calculating methanol collection, as discussed in Section 5.1.

3.3.6.3 TRS Compounds

The TRS compounds (H_2S, MMC, DMDS, and DMS) will be measured using the ALS sulfur liquid method, and H_2S will be analyzed onsite using the Methylene Blue Method with a Hach 6000 analyzer. As stated previously, this analysis is not required by Subpart S but is included in this IPT plan per the Order issued by SCDHEC and the U.S. EPA Information Request.

3.3.6.4 BOD_5 – Standard Method 5210

Soluble (filtered) BOD_5 will be measured using Standard Method 5210. This method has been approved by U.S. EPA.

3.3.6.5 COD – Standard Method 5220

Soluble (filtered) COD will be measured using Standard Method 5220. This method has been approved by U.S. EPA.

3.3.6.6 MLVSS – U.S. EPA Method 1684

MLVSS will be measured using U.S. EPA Method 1684.

4. QA/QC PROGRAM

4.1 QA/QC PROCEDURES

The test program shall incorporate the appropriate QA/QC procedures specified in respective test methods (NCASI Method DI/MEOH 94.03, NCASI Method HAPS-99.01, Standard Methods 5210, and Standards Methods 5220). The complete NCASI test methods are provided in Appendix B. The following sections summarize the overall data quality objectives and internal and external QA for the condensate program.

4.2 DATA QUALITY OBJECTIVES

Quality assurance procedures are designed to assess and document data accuracy, precision, and completeness. Accuracy is the percent difference between a measurement and a reference or standard value. Precision is a measure of mutual agreement of replicate measurements. Completeness is a measure of the amount of valid data compared to the amount that was expected to be obtained under correct operating conditions.

4.3 INTERNAL QA PROGRAM

Test data precision will be measured using replicate sample runs and analysis. For each week of foul condensate collection and treatment testing for methanol, one duplicate sample will be analyzed for each sample point. The Catawba Mill Laboratory Technicians will follow Mill procedures regarding QA for BOD_5 samples in accordance with Standard Methods 5210, such as running blanks, standards, and duplicate samples at specified frequencies.

4.4 EXTERNAL QA PROGRAM

Test data accuracy for methanol and HAP testing will be determined through preparation of field matrix spikes. The matrix spike is a separate aliquot of the sample spiked with known concentrations of the analytes of interest. It is analyzed to determine, including the matrix interferences, if the procedure is working within established control limits. It is carried through the complete preparation and analytical procedure. The recoveries of the spiked analytes are evaluated to determine accuracy in a given matrix. ALS will prepare matrix spikes as per their operating protocol and the selected analytical method. The lab will provide the appropriate number of trip blanks with the shipped bottles and the Mill will return those with the collected liquid samples.

Test data accuracy for COD testing will be determined using replicate sample runs and analysis. Pace will follow laboratory procedures regarding QA for COD samples in accordance with Standard Methods 5220, such as running blanks, standards, and duplicate samples at specified frequencies.

Test data accuracy for TRS compounds and sulfides testing will be determined using replicate sample runs and analysis. ALS will follow laboratory procedures regarding QA for TRS compound samples in accordance with the test method.

4.5 SAMPLE IDENTIFICATION AND CHAIN OF CUSTODY

The Mill technician(s) and TRC are responsible for collecting the samples and ensuring that the samples are accounted for and that proper custody procedures are followed. ALS Kelso will supply sample bottles and labels for all samples collected for methanol and HAP analysis. ALS Simi Valley will supply sample bottles and labels for all samples collected for TRS compound analysis.

4.6 PROCESS DATA QUALITY ASSURANCE

The Mill will establish continuous monitoring systems (CMS) for the process data parameters discussed in Section 3.2. CMS matrices, including thresholds for CMS downtime and the definition of good data quality, are provided in Appendix C.

5. DATA ANALYSIS AND CALCULATIONS

All data will be reviewed for validity and accuracy. This section describes the proposed calculations that will be performed to determine compliance with the methanol collection and treatment requirements of Subpart S.

5.1 HAP COLLECTION CALCULATIONS

The Mill pulp production rate, condensate flow rate to the ASB and Steam Stripper in million gallons per day (MGD), and foul condensate methanol concentration will be used to calculate methanol collection in terms of lb HAP/ODTP, with HAP measured as methanol. Daily pulp production will be calculated as presented in Table 3-1. The 15-day average methanol collection will be calculated using the equation below, in accordance with 40 CFR §63.457(j).

$$15\ day\ average\ lb\ \frac{HAP}{ODTP} = lb\ \frac{HAP}{ODTP}\ to\ ASB + lb\ \frac{HAP}{ODTP}\ to\ Steam\ Stripper$$

Where:

$$15\ day\ average\ \ lb\frac{HAP}{ODTP}\ to\ ASB$$

$$= \frac{\sum_{i=1}^{15}[Methanol\ Concentration\ (ppm) \times Flow\ to\ ASB\ (MGD)\ \times 8.34\ \frac{lb}{gal}]}{\sum_{i=1}^{15} ODTP}$$

$$15\ day\ average\ \ lb\frac{HAP}{ODTP}\ to\ Steam\ Stripper$$

$$= \frac{\sum_{i=1}^{15}[Methanol\ Concentration\ (ppm) \times Flow\ to\ Steam\ Stripper\ (MGD)\ \times 8.34\ \frac{lb}{gal}]}{\sum_{i=1}^{15} ODTP}$$

The 15-day rolling average lb HAP/ODTP will be calculated for days 15-21 of the IPT. Following the IPT, the Mill will continue to collect daily foul condensate samples to be tested for methanol and will calculate the 15-day rolling average lb HAP/ODTP collection on a daily basis.

5.2 HAP TREATMENT CALCULATIONS

The total HAP treatment will be calculated daily as the sum of the lb HAP/ODTP treated in the ASB and the lb HAP/ODTP (measured as methanol) treated by the Steam Stripper, as discussed in the following subsections. The lb HAP/ODTP treated results for the five days of the treatment IPT will be averaged to determine compliance with the condensate treatment requirements of Subpart S. The IPT report submitted to DHEC following the IPT will include a detailed description of the calculation methods used. This section also describes calculations to be used for monitoring ongoing compliance with the treatment requirements of Subpart S.

5.2.1 ASB Treatment Calculations

HAP treatment in the ASB on a lb HAP/ODTP basis will be determined using the calculations provided in Appendix C to Part 63 and 40 CFR §63.457(l). The fraction of methanol biodegraded (Fbio) in the ASB will be calculated per Appendix C, as well as the ratio of the sum of acetaldehyde, methyl ethyl ketone, and propionaldehyde mass to the ratio of methanol mass in the foul condensate stream, and then applied to the 15-day rolling average methanol collection in lb HAP/ODTP to determine the HAP treated, per the equations below:

$$r = \frac{F(nonmethanol), \frac{lb}{ODTP}}{F(methanol), \frac{lb}{ODTP}}$$

$$lb \frac{HAP}{ODTP} Treated\ in\ ASB = lb \frac{HAP}{ODTP} to\ ASB\ (15\ day\ average) \times \left[\frac{Fbio(Methanol)}{(1 + 1.087 \times r)}\right]$$

The daily lb HAP/ODTP treated will be calculated for the five days of the condensate treatment performance test. The Mill plans to use published meteorological data from the same month of the previous year for the Fbio calculations or June 2021 meteorological data if it is published in time to be used in the report.

Following the IPT, the Mill plans to establish a site-specific operating parameter for monitoring continuous compliance with the ASB condensate treatment portion of the requirements of Subpart S. The Mill anticipates that the proposed operating parameter will either be aerator horsepower or COD to aerator horsepower ratio (COD/HP). In the IPT report submitted to DHEC following the IPT, the Mill will provide the rationale for the selected monitoring parameter, the operating parameter value, monitoring frequency, averaging time, all data and calculations used to develop the value and a description of why the value, monitoring frequency, and averaging time demonstrate continuous compliance with the condensate treatment standard. The Mill will continue to operate according to the proposed parameter(s) following the IPT while awaiting approval from SCDHEC.

5.2.2 Steam Stripper Treatment Calculations

The methanol removed in the Steam Stripper will be calculated according to the equation below for each set of samples collected:

$$lb\,\frac{HAP}{ODTP}\ Treated\ in\ Steam\ Stripper = \frac{Steam\ Stripper\ Inlet, lbs\ MeOH - Steam\ Stripper\ Outlet, lbs\ MeOH}{ODTP}$$

Following the IPT, the Mill plans to establish a correlation between ESFR and methanol removal efficiency for purposes of demonstrating continuous compliance with the treatment requirements of Subpart S. The mass percent HAP reduction across the Steam Stripper for each set of samples collected (three samples per day during the five days of the treatment test) will be calculated as follows:

$$Ri = \{[E(bi) - E(ai)] \div E(bi)\ \times 100\}$$

Where:

Ri = Methanol removal efficiency of the Steam Stripper, percent

E(bi) = Mass flow rate of total methanol in the liquid stream entering the Steam Stripper for each hour “i" (lb/hr), where:

$$E(bi) = Steam\ Stripper\ Inlet\ Flow\ (gpm)_i \times 60\ \frac{minutes}{hr} \times \frac{Foul\ Condensate\ Methanol\ Concentration\ (ppm)_i}{1{,}000{,}000} \times 8.34\ \frac{lb}{gal}$$

E(ai) = Mass flow rate of total methanol in liquid stream exiting the Steam Stripper for each hour “i" (lb/hr), where:

$$E(ai) = Stripped\ Condensate\ Flow\ (gpm)_i \times 60\ \frac{minutes}{hr} \times \frac{Stripped\ Condensate\ Methanol\ Concentration\ (ppm)_i}{1{,}000{,}000} \times 8.34\ \frac{lb}{gal}$$

ESFR will be calculated during each hour of sampling according to the equation below:

$$ESFRi = \ [Msi - Mf(STi)] \ \times \frac{(Tsc - Tcf)/100}{Vb(SFTi)}$$

Where:

MSi = Mass steam rate entering the Steam Stripper for each hour “i" (lbs/hr)

Mf(SFTi) = Mass rate of the condensate liquid stream entering the Steam Stripper for each hour “i" (lbs/hr)

Tsc = Temperature of stripped condensate (°F)

Tcf = Temperature of condensate feed to the stripper (°F)

Vb(STFi) = Volumetric flow rate of the liquid stream entering the Steam Stripper for each hour “i" (gph)

In the IPT report submitted to DHEC following the IPT, the Mill will provide the calculated ESFR values and their correlation to methanol removal in the Steam Stripper, as well as the Mill’s proposal for using this correlation to demonstrate continuous compliance with the methanol treatment requirements of Subpart S.

5.3 TRS COMPOUND FBIO CALCULATIONS

Items 1 and 2 of the U.S. EPA Information Request require that the Mill calculate Fbio of the four individual TRS compounds (H_2S, MMC, DMS, DMDS) in the ASB and the Post-Aeration Tank (if approved) in accordance with Method 5 of Appendix C to 40 CFR Part 63. Note that analysis of TRS concentrations and calculation of Fbio for TRS compounds is not required by 40 CFR Part 63, Subpart S but is included in this IPT plan per the U.S. EPA Information Request. Per New-Indy's response to U.S. EPA Information Request, the Hydrogen Sulfide Emissions Simulator, or "H2SSIM" model, developed by NCASI will be used for estimating the fraction of hydrogen sulfide destroyed, rather than the Appendix C calculations. The H2SSIM model uses the direct emissions measurement data presented in NCASI Technical Bulletin (TB) No. 956 and the H2SSIM software tool described in NCASI TB No. 1000 to generate H_2S emissions estimates. H_2S emissions estimates from H2SSIM are built upon the field and laboratory work reported in the following documents:

- NCASI TB No. 933, Development and Application of a Method for Measuring Reduced Sulfur Compounds in Pulp and Paper Mill Wastewaters (provided in Appendix D);
- NCASI TB No. 949, Summary of Industry Experience with Odor Minimization at Wastewater Treatment Plants (provided in Appendix E);
- NCASI TB No. 956, Emissions of Reduced Sulfur Compounds and Methane from Kraft Mill Wastewater Treatment Plants (provided in Appendix F);
- NCASI TB No. 957, Spatial Ambient Air Sampling and Analysis Methods for Quantifying Reduced Sulfur Compound and Methane Emissions from Kraft Mill Wastewater Treatment Plants (provided in Appendix G); and
- NCASI TB No. 1000, Mechanistic Approach for Estimating Hydrogen Sulfide Emissions from Wastewater Treatment Plants (provided in Appendix H).

H2SSIM is an Excel-based Visual Basic for Applications (VBA) tool that builds upon EPA's Water9 approach. This tool applies a series of mass-balances and industry specific data to simulate the fate of sulfide along several different pathways. For ASBs, the estimates were most sensitive to pH, redox condition (i.e. aerobic vs. anaerobic vs. anoxic conditions), sulfide load, and aeration horsepower.

Similar to H_2S, the situation is also more complicated for MMC and DMDS, as MMC is easily oxidized to DMDS. Liquid material balance data in conjunction with emissions data from the field study results published in NCASI TB No. 956 indicate that a significant fraction of the MMC entering the ASBs with the influent is oxidized to DMDS. Therefore, MMC and DMDS results from the Appendix C calculations will be adjusted based on the field study results published in NCASI TB No. 956. Note that calculating Fbio for any individual TRS compound may be difficult or impossible in the event of non-detect results from the liquid sampling.

APPENDIX A – SAMPLING MATRIX

Table A-1
Condensate Collection and Treatment IPT Sampling Matrix
New-Indy Catawba, SC Mill

Green shading indicates monitoring to be conducted per SCDHEC Order and/or U.S. EPA Information Request that is not required by Subpart S

Description of Source/ Location of Sample	Analyte/ Pollutant	Test/Sampling Method	Sampling Start Date	Sampling End Date	Type of Sample (Grab/ Composite Sampler)	No. of Days Sampled	Samples Collected per Day	Field Back-Up Samples	Weekly Duplicate Analysis	Sample Bottles Per Sample Needed[a]	Total No. of Bottles Needed[b]	Composite Daily Samples at Lab Before Analysis (Y/N)?	Total No. of Analyses Needed[c]	Method Reporting Limit (MRL)	Container Size	Preservative Added	Hold Time	Sample Storage Requirements	Quality Assurance/ Quality Control	Data to Collect with Sample/Comments
Foul Condensate to Hardpipe (also representative of Foul Condensate to Steam Stripper)	Methanol[d]	NCASI MeOH-94.03	21-Jun-21	6-Jul-21	Grab	16	3	1	1	2	98	Y	18	0.5 mg/L	40 mL glass vials, zero headspace required	None	30 days	<4ºC	In accordance with test method	Liquid Temperature, pH; Samples to be composited by ALS Kelso each day
	Methanol, Acetaldehyde, Methyl Ethyl Ketone, Propionaldehyde	NCASI HAPS-99.01	7-Jul-21	11-Jul-21	Grab	5	1	1	1	2	11	N	6	1 mg/L	40 mL glass vials, zero headspace required	None	15 days	<4ºC	In accordance with test method	Liquid Temperature, pH
	Methanol	NCASI MeOH-94.03	7-Jul-21	11-Jul-21	Grab	5	2	1	1	2	21	N	11	0.5 mg/L	40 mL glass vials, zero headspace required	None	30 days	<4ºC	In accordance with test method	
	COD	Standard Methods 5220	7-Jul-21	11-Jul-21	Grab	5	1	0	1	1	6	N	6	Depends on dilutions used	Sufficient volume for dilutions	None	28 days	<4ºC	In accordance with test method	
	TRS Compounds (H_2S, MMC, DMS, DMDS)	ALS Sulfur Liquid	7-Jul-21	11-Jul-21	Grab	5	3	1	1	4	61	N	16	Varies by Compound[e]	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
	Hydrogen Sulfide	Methylene Blue (Method 10254 utilizing a Hach 6000 Analyzer)	7-Jul-21	11-Jul-21	Grab	5	3	0	1	1	16	N	16	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	
Steam Stripper Outlet	Methanol	NCASI MeOH-94.03	7-Jul-21	11-Jul-21	Grab	5	3	1	1	2	31	N	16	0.5 mg/L	40 mL glass vials, zero headspace required	None	30 days	<4ºC	In accordance with test method	Liquid Temperature, pH
	TRS Compounds (H_2S, MMC, DMS, DMDS)	ALS Sulfur Liquid	7-Jul-21	11-Jul-21	Grab	5	3	1	1	4	61	N	16	Varies by Compound[e]	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
	H_2S	Methylene Blue (Method 10254 utilizing a Hach 6000 Analyzer)	7-Jul-21	11-Jul-21	Grab	5	3	0	1	1	16	N	16	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	
ASB Influent	COD	Standard Methods 5220	7-Jul-21	11-Jul-21	Composite	5	1	0	1	1	6	Automatic Sampler	6	Depends on dilutions used	Sufficient volume for dilutions	N/A	28 days	<4ºC	In accordance with test method	Liquid Temperature, pH
	Methanol, Acetaldehyde, Methyl Ethyl Ketone, Propionaldehyde	NCASI HAPS-99.01	7-Jul-21	11-Jul-21	Grab	5	1	1	1	2	11	N	6	1 mg/L	40 mL glass vials, zero headspace required	1 N HCl or H_2SO_4	15 days	<4ºC	In accordance with test method	
	TRS Compounds (H_2S, MMC, DMS, DMDS)	ALS Sulfur Liquid	7-Jul-21	11-Jul-21	Grab	5	1	1	1	4	23	N	6	Varies by Compound[e]	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
	H_2S	Methylene Blue (Method 10254 utilizing a Hach 6000 Analyzer)	7-Jul-21	11-Jul-21	Grab	5	1	0	1	1	6	N	6	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	
Zone 1 Center and/or Outlet	Methanol	NCASI MEOH-94.03	7-Jul-21	11-Jul-21	Grab	5	1	1	1	2	11	N	6	0.5 mg/L	40 mL glass vials, zero headspace required	1 N HCl or H_2SO_4	30 days	<6ºC	In accordance with test method	Liquid Temperature, pH
	MLVSS	U.S. EPA Method 1684	7-Jul-21	11-Jul-21	Grab	5	1	0	1	1	6	N	6	Depends on dilutions used	Sufficient volume for dilutions	N/A	7 days	<4ºC	In accordance with test method	
	TRS Compounds (H_2S, MMC, DMS, DMDS)	ALS Sulfur Liquid	7-Jul-21	11-Jul-21	Grab	5	1	1	1	4	23	N	6	Varies by Compound[e]	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
Zone 2 Center and/or Outlet	Methanol	NCASI MEOH-94.03	7-Jul-21	11-Jul-21	Grab	5	1	1	1	2	11	N	6	0.5 mg/L	40 mL glass vials, zero headspace required	1 N HCl or H_2SO_4	30 days	<4ºC	In accordance with test method	
	MLVSS	U.S. EPA Method 1684	7-Jul-21	11-Jul-21	Grab	5	1	0	1	1	6	N	6	Depends on dilutions used	Sufficient volume for dilutions	N/A	7 days	<4ºC	In accordance with test method	
	TRS Compounds (H_2S, MMC, DMS, DMDS)	ALS Sulfur Liquid	7-Jul-21	11-Jul-21	Grab	5	1	1	1	4	23	N	6	Varies by Compound[e]	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	

Table A-1
Condensate Collection and Treatment IPT Sampling Matrix
New-Indy Catawba, SC Mill

Green shading indicates monitoring to be conducted per SCDHEC Order and/or U.S. EPA Information Request that is not required by Subpart S

Description of Source/ Location of Sample	Analyte/ Pollutant	Test/Sampling Method	Sampling Start Date	Sampling End Date	Type of Sample (Grab/ Composite Sampler)	No. of Days Sampled	Samples Collected per Day	Field Back-Up Samples	Weekly Duplicate Analysis	Sample Bottles Per Sample Needed[a]	Total No. of Bottles Needed[b]	Composite Daily Samples at Lab Before Analysis (Y/N)?	Total No. of Analyses Needed[c]	Method Reporting Limit (MRL)	Container Size	Preservative Added	Hold Time	Sample Storage Requirements	Quality Assurance/ Quality Control	Data to Collect with Sample/Comments
Zone 3 Center and/or Outlet	Methanol	NCASI MEOH-94.03	7-Jul-21	11-Jul-21	Grab	5	1	1	1	2	11	N	6	0.5 mg/L	40 mL glass vials, zero headspace required	1 N HCl or H_2SO_4	30 days	<4ºC	In accordance with test method	
	MLVSS	U.S. EPA Method 1684	7-Jul-21	11-Jul-21	Grab	5	1	0	1	1	6	N	6	Depends on dilutions used	Sufficient volume for dilutions	N/A	7 days	<4ºC	In accordance with test method	
	TRS Compounds (H_2S, MMC, DMS, DMDS)	ALS Sulfur Liquid	7-Jul-21	11-Jul-21	Grab	5	1	1	1	4	23	N	6	Varies by Compound[e]	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
ASB Effluent	Methanol	NCASI MEOH-94.03	7-Jul-21	11-Jul-21	Grab	5	1	1	1	2	11	N	6	0.5 mg/L	40 mL glass vials, zero headspace required	1 N HCl or H_2SO_4	30 days	<6ºC	In accordance with test method	Liquid Temperature, pH
	Soluble BOD_5	Standard Methods 5210	7-Jul-21	11-Jul-21	Composite	5	1	0	1	1	6	Automatic Sampler	6	Depends on dilutions used	Sufficient volume for dilutions	N/A	48 hours	<4ºC	In accordance with test method	Liquid Temperature, pH
	TRS Compounds (H_2S, MMC, DMS, DMDS)	ALS Sulfur Liquid	7-Jul-21	11-Jul-21	Grab	5	1	1	1	4	21	N	6	Varies by Compound[e]	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
	H_2S	Methylene Blue (Method 10254 utilizing a Hach 6000 Analyzer)	7-Jul-21	11-Jul-21	Grab	5	1	0	1	1	6	N	6	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	
Post-Aeration Tank sampling, if approved to remove cover over Post-Aeration Tank for required sampling																				
Post-Aeration Tank Inlet	TRS Compounds (H_2S, MMC, DMS, DMDS)	ALS Sulfur Liquid	7-Jul-21	11-Jul-21	Grab	5	1	1	1	4	23	N	6	Varies by Compound[e]	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	Liquid Temperature, pH
	H_2S	Methylene Blue (Method 10254 utilizing a Hach 6000 Analyzer)	7-Jul-21	11-Jul-21	Grab	5	1	0	1	1	6	N	6	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	
Post-Aeration Tank Surface	TRS Compounds (H_2S, MMC, DMS, DMDS)	ALS Sulfur Liquid	7-Jul-21	11-Jul-21	Grab	5	1	1	1	4	23	N	6	Varies by Compound[e]	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	Liquid Temperature, pH
	H_2S	Methylene Blue (Method 10254 utilizing a Hach 6000 Analyzer)	7-Jul-21	11-Jul-21	Grab	5	1	0	1	1	6	N	6	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	
Post-Aeration Tank Oulet	TRS Compounds (H_2S, MMC, DMS, DMDS)	ALS Sulfur Liquid	7-Jul-21	11-Jul-21	Grab	5	1	1	1	4	23	N	6	Varies by Compound[e]	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	Liquid Temperature, pH
	H_2S	Methylene Blue (Method 10254 utilizing a Hach 6000 Analyzer)	7-Jul-21	11-Jul-21	Grab	5	1	0	1	1	6	N	6	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	

[a] Two sample bottles will be collected at each sampling event for methanol and HAPs samples; an original and a duplicate as back-up in the event of sample damage or loss. No back-up samples will be collected for BOD_5, COD, or MLVSS.

[b] For methanol and HAPs, total number of bottles needed = [(Number of days sampled) * (Samples collected per day) * (Sample bottles per sample)] + [(Number of weekly duplicate analysis samples) x (Number of weeks of study)]

[c] For methanol and HAPs, number of analyses needed = [(Number of days sampled) * (Samples collected per day)] + [Weekly duplicate analysis x Number of weeks of study)]. Back-ups will only be analyzed in the event of damage to the original sample. Back-ups can be discarded upon receipt of valid laboratory results.

[d] The three daily samples collected will be composited at the lab for one analysis per day.

[e] MRL is 0.84 µg/L for H_2S , 1.2 µg/L for MMC, 1.5 µg/L for DMS, and 1.2 µg/L for DMDS.

APPENDIX B – LIQUID SAMPLING TEST METHODS

NCASI METHOD DI/HAPS-99.01

SELECTED HAPS IN CONDENSATES BY GC/FID

NCASI
Southern Regional Center
February 2000

Acknowledgements

This method was prepared by Dr. MaryAnn Gunshefski, Senior Research Scientist at the NCASI Southern Regional Center. Other assistance was provided by Alex Gholson, Senior Research Scientist, Dean Hoy, Research Associate, and Larry LaFleur, NCASI Fellow, at the NCASI West Coast Regional Center.

NCASI would like to acknowledge the following laboratories and individuals for their voluntary participation in the interlaboratory validation of this method:

- Columbia Analytical Services, Jacksonville FL, Ward Dickens and Josh Apple
- Columbia Analytical Services, Kelso WA, Ed Wallace and Loren Portwood
- Data Analysis Technologies, Inc. Dublin OH, Ron Mitchum
- Performance Analytical Inc. (a division of Columbia Analytical Services), Simi Valley CA, Michael Tuday and John Yokoyama
- STL-Savannah Labs, Savannah GA, Craig Ratkey and Myron Young
- Weyerhaeuser Co., Federal Way WA, Rick Bogar and Mike Grove

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National Council for Air and Stream Improvement, Inc. (NCASI). 2000. *Methods Manual - Selected HAPS in Condensates by GC/FID*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Disclaimer

NCASI METHOD DI/HAPS-99.01

SELECTED HAPS IN CONDENSATES BY GC/FID

1.0 Scope and Application

1.1 This method is used for the analysis of methanol (CAS # 67-56-1), acetaldehyde (CAS # 75-07-7), methyl ethyl ketone (CAS # 78-93-3), and propionaldehyde (CAS # 123-38-6) in condensate samples from pulp and paper mills by gas chromatography/flame ionization detection (GC/FID). A version of this method was published as Appendix I of NCASI Technical Bulletin No. 684, *Method for Analysis of Methanol, Acetone, Acetaldehyde and Methyl Ethyl Ketone in Liquid Samples*, and has been rewritten to conform with the contents and format established by the EMMC for EPA wastewater methods.

1.2 Types of condensates for which this method can be used include condensate to be piped to a biological treatment system and condensate entering the stripper system.

1.3 The method has been validated in two laboratories using United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63), and is a validated method.

1.4 This method is applicable for detecting methanol, acetaldehyde, MEK, and propionaldehyde in condensates at the parts per million (ppm) level. A correction factor may be needed. All correction factors are given in Section 17.0.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of chromatograms. Each analyst must demonstrate an ability to generate acceptable results with this method.

2.0 Summary of the Method

2.1 Samples are collected directly from the condensate stream using an appropriate collection vessel. For sample streams which are extremely hot, a cooling coil is used to lower the temperature of the sample to below 160°F. The samples are kept refrigerated until analysis.

2.2 In the laboratory, an aliquot of the sample is transferred to an autosampler vial. An aliquot of an internal standard solution is added to each of the autosampler vials. The internal standard is also used as a time reference peak. An aliquot of a surrogate solution can also be added. The aqueous samples are then introduced directly into the gas chromatograph equipped with a capillary column. The GC column is temperature programmed to separate the analytes from other compounds which may be present in the sample. The analytes are detected with a flame ionization detector which is interfaced to the gas chromatograph.

2.3 Identification of the analytes is determined by comparison of their relative retention times with the relative retention times of a known standard. If the results are questionable, confirmation may be performed by using a mass spectrometer as the detector.

2.4 The sensitivity of the method is defined as the minimum measurement level (MML) and for undiluted samples is set at 1 mg/L for this method.

2.5 Quality is assured through frequent testing of the analytical systems. This is accomplished by using a second source reference material, a resolution test mixture, calibration check samples and spike recovery samples. Method blanks , duplicates, and matrix spikes must also be analyzed with each analytical batch to ensure data quality.

3.0 Definitions

3.1 The definitions below are specific to this method, but conform to common usage as much as possible.

3.1.1 Batch - grouping of samples, not more than 20

3.1.2 mg/L - milligrams per liter

3.1.3 May - This action, activity, or procedural step is neither required nor prohibited.

3.1.4 Must not - This action, activity, or procedural step is prohibited.

3.1.5 Must - This action, activity, or procedural step is required.

3.1.6 Should - This action, activity, or procedural step is suggested, but not required.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analyses by running laboratory blanks as described in Section 9.2.6.

4.2 Glassware must be scrupulously cleaned. Clean all glassware by detergent washing with hot water and rinsing with tap water. The glassware should then be drained dry and baked at over 100°C for several hours.

4.3 Injections into the GC must be made with a clean syringe. Carryover of analytes from previously injected high level standards or samples can have a large influence on the measured values of subsequent samples or standards. After injection of the sample, the syringe should be cleaned immediately by rinsing the syringe ten times with VOC-free DI water.

4.4 Several compounds which are not HAPs can interfere with the chromatography if the separation is not efficient. These compounds include methyl mercaptan, ethanol, acetone, and dimethyl sulfide. When performed properly, this method does sufficiently separate these compounds from the analytes of interest at concentrations found in condensates.

4.5 Compounds may interfere with the internal standard. Two internal standards are specified by the method so that one free of interference can be selected. When initially analyzing samples of unknown composition, an injection without internal standard can be performed to determine if an interference exists.

5.0 Safety

5.1 All chemicals should be treated as potential health hazards. It is recommended that prudent practices for handling chemicals in the laboratory (EPA Good Laboratory Practice) be employed.

5.2 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness of OSHA regulations regarding safe handling of chemicals used in this method. Material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.3 Methanol, MEK, propionaldehyde, and acetaldehyde are flammable liquids which may be harmful if inhaled or ingested. Use in a laboratory fume hood and wear appropriate gloves, eye protection, and other protective clothing.

6.0 Equipment and Supplies

6.1 Brand names and suppliers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and material other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.2 Sampling equipment

6.2.1 Samples are to be collected in glass bottles to zero headspace. It is recommended that 40 mL glass vials with Teflon™ faced silicone backed lids (VOA vials) be used.

6.2.2 Figure 1 gives a schematic showing the configuration of a VOA sample cooling train. Valve sizes should be small enough to yield controllable low flow rates (i.e., <1000 mL per minute). The diameter of the tubing should be small (i.e., around 0.25 inch inside diameter).

6.3 Laboratory glassware and supplies

6.3.1 Autosampler vials capable of holding 2 mL[1]

6.3.2 Volumetric flasks

6.3.3 Volumetric pipets

6.3.4 Syringes (including gas-tight syringes)

6.4 Analytical equipment

6.4.1 Gas chromatography system - gas chromatography analytical system complete with a cryogenically cooled temperature-programmable gas chromatograph with either a purge-packed or split/splitless injection port

6.4.2 Guard column - 10 m x 0.53 mm deactivated fused silica capillary column

6.4.3 Column - 75 m x 0.53 mm x 3 µm, 6% cyanopropylphenyl 94% dimethylpolysiloxane bonded phase (624 phase) fused silica capillary column (for example: J&W Scientific DB-624, Hewlett Packard HP-624)

6.4.4 GC detector - flame ionization with appropriate data system; a large-bore jet tip is recommended, capillary jet tips were found to result in frequent flame-outs

7.0 Reagents and Standards

7.1 **Deionized water** - Deionized water should be tested immediately before use to verify the absence of any target analytes. If it is found to be contaminated, it may be necessary to prepare fresh deionized water, purge the water with nitrogen or helium, or boil the water to remove the contaminant(s).

7.2 **Analytical standards** - Reagent grade or the highest purity methanol, acetaldehyde, propionaldehyde, methyl ethyl ketone, cyclohexanol, and 2,2,2-trifluoroethanol must be used. Each neat material should be analyzed for purity and to verify the absence of other target analytes or contaminants prior to being used for the preparation of

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[1] It was found that a small bubble in the vial allowed rapid mixing of the sample to disperse the internal standard.

standards. The minimum acceptable purity is 95%. Some suppliers of propionaldehyde report 97% purity and upon inquiry indicate there may be from 1 to 2% water.

7.3 **Internal standard primary spiking solution** - Cyclohexanol or 2,2,2-trifluoroethanol can be used as the internal standard.

7.3.1 Prepare primary stock solution by adding 1.56 mL cyclohexanol to a tared 50 mL ground glass stoppered volumetric flask. Weigh the flask after the addition of the internal standard and record the weight to the nearest 0.1 mg. Fill the flask to 50 mL with DI water. This will result in a nominal 30,000 mg/L primary stock solution. Compute the exact concentration (mg/L) using the weight gain. The solution can be stored at room temperature for over 6 months.

7.3.2 Prepare primary stock solution by adding 1.36 mL of 2,2,2-trifluoroethanol to a tared 50 mL ground glass stoppered volumetric flask partially filled with DI water. Weight the flask after the addition of the standard and record the weight to the nearest 0.1 mg. This should result in a nominal 40,000 mg/L primary stock solution. Compute the exact concentration (mg/L) using the weight gain. This solution must be stored in a refrigerator.

7.4 **Calibration primary stock solution** - Fill a 50 mL ground glass stoppered volumetric flask with approximately 45 mL DI water. Tare the flask after the addition of the water. After each addition of analyte, weigh and record the weight gain to the nearest 0.1 mg. Using a syringe, add 3.15 mL of methanol, taking care to drop the methanol directly into the water without wetting the sides of the flask. In a like manner, add 64 µL of acetaldehyde, 62 µL of propionaldehyde, and 62 µL of methyl ethyl ketone. Once all the analytes have been added, fill the flask to the mark. This will result in a nominal 50,000 mg/L methanol, 1000 mg/L acetaldehyde, 1,000 mg/L propionaldehyde, and 1000 mg/L methyl ethyl ketone primary stock solution. Use this weight gain to compute the exact analyte concentrations. Note that acetaldehyde and propionaldehyde are extremely volatile and degrade in the neat solutions over time. A chilled gas-tight syringe must be used to deliver the neat compounds to the volumetric flask. New neat standards for acetaldehyde and propionaldehyde should be obtained when the second source standard requirement is not met using freshly prepared standards. An alternative would be to purchase a primary stock solution from a chemical reference supply company. The primary stock must be stored in the refrigerator and must be re-prepared monthly. The storage time of sealed or nitrogen blanketed standard solutions has not been evaluated at this time. Longer storage time may be allowed in cases where data are provided that supports it.

7.5 **Calibration and matrix spike solutions** - Prepare standard solutions by dilutions of the stock solution using gas-tight syringes to measure the required aliquots of primary standard. The required dilutions are shown below. Prepare matrix spike solutions by calculating the concentration of analytes desired and diluting the primary stock solution.

µL of stock solution to add to 10 mL volumetric flask	Resulting acetaldehyde, MEK, and propionaldehyde concentration (mg/L)	Resulting methanol concentration (mg/L)
2,000	200	10,000
500	50	2,500
200	20	1,000
50	5	250
10	1	50

7.6 **Second source standard or certified reference standard** - A second source standard or certified reference standard containing the analytes in an aqueous solution must be prepared or obtained and analyzed after every recalibration of the instrument. The standard must be stored in a refrigerator and must be re-prepared monthly. The storage time of sealed or nitrogen blanketed standard solutions has not been evaluated at this time. Longer storage time may be allowed in cases where data are provided that supports it.

7.7 **Resolution test mixture** - Prepare a resolution test mixture containing the analytes of interest along with the possible interferences described in Section 4.3. This mixture can be prepared by first preparing a resolution stock solution by adding 2.5 mL of dimethyl sulfide, 1.0 mL of acetone, and 0.5 mL of ethanol to a 25 mL volumetric flask and diluting with methanol. Then add 10µL of the primary stock solution and 50 µL of resolution stock solution to 10 mL of DI water. Analyze 2.0 mL of this mixture as if it were a sample.

8.0 Sample Collection, Preservation, and Storage

8.1 **Collection** - Grab samples are collected directly from the process liquid stream using an appropriate collection vessel, typically a 40 mL VOA vial. For sample streams which are greater than 160°C, a cooling coil is used to lower the temperature of the sample to below 160°F. The cooling coil tubing should be flushed for two to three minutes with the condensate to be sampled prior to collecting a sample. This is done by opening both valves and allowing the sample to run through the tubing. After the line is flushed, valves are throttled back to slow the flow rate. The temperature of the liquid to be sampled should be checked to be sure it is cool prior to collecting the sample. Use caution when sampling even moderately hot streams into glass vials, since the heat may cause the glass to break. Fill the vial to zero headspace with the sample.

8.2 **Preservation** - No preservation is necessary for condensate samples.

8.3 **Storage** - All samples must be stored in a refrigerator (4°C) until analysis. Samples may be stored for 14 days, at which time the recovery of acetaldehyde may fall to less than 80%.

9.0 Quality Control

9.1 Each field sampling program or laboratory that uses this method is required to operate a formal quality assurance program. Laboratory or field performance is compared to established criteria to determine if the results of the analyses meet the performance criteria of the method.

9.2 GC Maintenance

9.2.1 Injector maintenance - The septum and injection liner should be replaced when necessary. If this is not done, retention time shifts and peak broadening can occur.

9.2.2 Bakeouts - Water can build up in the GC, causing peak broadening and FID flame out. Frequent bakeouts of the system help to purge the system of excess water. Keeping the injection port purge flowing throughout the chromatographic run will help to remove water from the system (e.g., disable “gas saver” on HP 6890 systems).

9.3 Initial GC/FID performance

9.3.1 Second source or certified reference material - A second source or certified reference material must be evaluated after each recalibration of the instrument. Recoveries between 85 and 115% are required for methanol, and between 80 and 120% for the other three analytes.

9.3.2 Resolution test mixture - The resolution test mixture described in Section 7.6 must be analyzed after each recalibration, and weekly thereafter. This is to assure that the chromatography system is working appropriately. Baseline resolution between acetaldehyde/methanol and ethanol/propionaldehyde/acetone is required. The dimethyl sulfide and acetone need not be baseline resolved. Figures 2 and 3 contain sample chromatograms.

9.3.3 Reproducibility check - When the instrument is set up to perform this method a reproducibility/sensitivity check must be performed. Seven aliquots of the resolution test mix must be analyzed. The %RSD of the seven analyses must be less that 14% for acetaldehyde and less than 10% for propionaldehyde and MEK.

9.4 Continuing GC/FID performance

9.4.1 Blanks - One method blank must be prepared per analytical batch to demonstrate that all materials are interference free. The concentration of the analytes in the blank must be below 0.5 mg/L.

9.4.2 Calibration verification - Before each set of samples is analyzed, a calibration check is done to determine that the GC/FID system is operating within acceptable parameters. The calibration check must involve the analysis of a calibration standard in the mid-range of the calibration curve. The concentrations of the analytes must be within ±15% of the expected concentration for acetaldehyde, propionaldehyde, and MEK, and ±10% for methanol. If the calibration fails to meet these expected criteria, the GC/FID system may require maintenance. If routine maintenance does not correct the problem, a new standard prepared from a fresh calibration stock solution should be run. If this still fails, the instrument will need to be recalibrated.

9.4.3 Replicates - Replicates consist of running two or more separate aliquots of the sample through the entire analytical procedure. A duplicate must be performed for each batch of samples. The relative percent difference and the mean should be tabulated in a method precision log.

9.4.4 Matrix spike recovery - A matrix spike may be prepared for each batch of samples. Using the mean concentration determined by the replicate analyses or the level determined from a single measurement, determine the spiking level which will give at least three times the sample concentration. If the sample does not have detectable levels of analytes, spike the sample at approximately five times the lowest calibration level of the instrument. Spike the sample with the determined amount of the calibration standard/matrix spike solution (Section 7.4) and analyze the sample in the normal manner. Calculate the percent recovery using Equation 1.

Equation 1

$$R = \left(\frac{C_S - C_N}{C_T} \right) \times 100$$

Where:

R = percent recovery of matrix spike
C_S = measured concentration of spiked sample
C_N = measured concentration of native sample
C_T = theoretical concentration of spike

10.0 Calibration and Standardization

10.1 FID operating conditions

Assemble the GC/FID and establish the operating conditions outlined in Table 1 or 2. Once the GC/FID system is optimized for analytical separation and sensitivity, the same operating conditions must be used to analyze all samples, blanks, calibration standards, and quality assurance samples. Note that constant injections of aqueous samples can cause water to build up in the system. This will cause the retention times to shift and the peaks to broaden. It is recommended that a bakeout of the system be performed after approximately 50 injections. This should consist of heating the injector to 250°C, the oven to over 200°C but less than 260°C, and the detector to 350°C for several hours.

10.3 GC/FID analysis of calibration standards

10.3.1 Determine the retention times of the analytes by taking 2.0 mL of the mid-range calibration solution and adding 10 µL of the internal standard solution. This will result in concentrations of 150 mg/L or 200 mg/L of cyclohexanol or 2,2,2-trifluoroethanol, respectively, in the autosampler vial. Inject 1 µL of this solution and determine the relative retention times of the analytes to the internal standard using Equation 2.

10.3.2 Prepare a five-point calibration curve for the four analytes by taking 2.0 mL of each calibration solution and adding the internal standard solution as described above. The calibration range is defined in Section 7.4. Use of an internal standard for calibration is required.

10.3.3 Calculate the relative response factor (RRF_M) for each analyte using Equation 3. If the relative standard deviation (RSD) of the average RRF_M is less than 10% for methanol and 15% for acetaldehyde, propionaldehyde, and MEK, the calibration is acceptable. The average RRF_M can be used in all subsequent calculations. If the calibration does not pass the criteria the calibration curve solutions must be reanalyzed and reevaluated. It may be necessary to perform instrument maintenance prior to reanalysis. If reanalysis also fails to produce a linear curve, new calibration standards must be prepared and analyzed.

10.3.4 Analyze and calculate the concentration of the mid-range calibration standard daily, prior to each sample set, using Equation 4. Calculate the percent recovery of the standard using Equation 5 to verify the calibration. In-house percent recovery control limits must be determined, and are not to exceed ±10% for methanol and ±15% for the other three analytes. If the limits are exceeded, either prepare a new standard or perform instrument maintenance. If necessary, recalibrate the instrument.

Equation 2

$$RRT_A = \left[\frac{Rt_A}{Rt_{IS}}\right]$$

Where:

RRT_A = relative retention time of compound A
Rt_A = retention time of compound A
Rt_{IS} = retention time of internal standard (cyclohexanol or 2,2,2-triflouroethanol)

Equation 3

$$RRF_M = \left[\frac{A_M}{A_{IS}} \times \frac{C_{IS}}{C_M}\right]$$

Where:

A_M = area of methanol peak
A_{IS} = area of internal standard peak
C_M = concentration of methanol injected
C_{IS} = concentration of internal standard injected

Equation 4

$$C_A = \left[\frac{A_A \times C_{IS}}{A_{IS} \times RRF_A}\right]$$

Where:

C_A = concentration of compound A in sample (mg/L)
A_A = area of the compound A peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_M = relative response factor of compound A (Section 10.3)

Equation 5

$$\text{Percent Recovery} = \left[\frac{C_M}{C_E} \times 100\right]$$

Where:

C_M = concentration of analyte measured
C_E = concentration of analyte expected

10.4 Analytical range and minimum calibration level

10.4.1 Demonstrate that the calibration curve is linear (relative response factors exhibit a RSD less than 10% for methanol or 15% for the other three analytes) throughout the range of the calibration curve described in Section 7.4.

10.4.2 Demonstrate that acetaldehyde, propionaldehyde and MEK are detectable at 1.0 mg/L with an RSD of less than 14% for acetaldehyde and less than 10% for the other two analytes as described in Section 9.3.3.

11.0 Procedure

11.1 Transfer an aliquot (2.0 mL) of the sample to an autosampler vial by gas-tight syringe. Add 10 µL of the internal standard primary spike solution (30,000 mg/L cyclohexanol or 40,000 mg/L 2,2,2-trifluoroethanol) to each of the autosampler vials. Perform the analysis by direct aqueous injection into the GC/FID. If the concentration of an analyte is more that 10% above the calibrated range, the sample should be diluted and reanalyzed to measure the analyte concentration.

11.2 If dilution is necessary, inject some fractional volume less than 2.0 mL using a gas-tight syringe into an autosample vial which is then brought to 2 mL with DI water and analyzed as described in Section 11.1. Calculate the dilution factor using Equation 6.

Equation 6

$$DF = \frac{2}{V}$$

Where:

DF = the dilution factor
V = the volume of sample (mL) injected into the autosample vial

12.0 Data Analysis and Calculations

12.1 GC/FID data analysis

12.1.1 The analytes are identified by comparison of the retention times relative to the internal standard established in the calibration to the relative retention times in the samples. The sample component relative retention time (RRT) should fall within ±0.01 RRT units of the RRT of the standard component.

12.1.2 Calculate the sample concentration, using the internal standard response factors established in Section 10.3.3, according to Equation 7. Use a dilution factor of 1 if no dilution is made and choose the proper correction factor based on the internal standard and hardware configuration used. Use a correction factor of 1 if no significant correction factor is found.

Equation 7

$$C_A = \left[\frac{A_A \times C_{IS} \times CF \times DF}{A_{IS} \times RRF_A} \right]$$

Where:

C_A = concentration of compound A in sample (mg/L)
A_A = area of the compound A peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_M = relative response factor of compound A (Section 10.3)
CF = correction factor from Method 301 validation (Table 3)
DF = dilution factor

12.1.3 If samples cannot be analyzed without dilution, the MML must be adjusted to reflect the lowest dilution factor used by multiplying the MML (1 mg/L) by the dilution factor calculated in Equation 6.

12.2 Data review requirements

12.2.1 The data are reviewed for accuracy of the identification, GC problems, interferences, and bias. Any problems should be corrected prior to reporting analytical results.

12.2.2 All the chromatograms are manually reviewed to confirm internal standard and analyte identification as well as the integration areas. As part of this review, the analyst assesses whether or not the concentration is within the calibration range of the instrument. The analyst should determine whether dilution of the samples is required. Another tool that can be utilized to identify the analyte peaks is to overlay the sample chromatogram with the standard chromatogram.

12.2.3 The internal standard area counts must be reviewed and added to a control chart. The in-house determined control limits must not exceed ±20% of the mean.

12.2.3 Any inconsistencies between replicate analyses must be resolved (i.e., if an analyte is detected in one replicate and not the other), and attempts made to determine the reason for the inconsistencies.

12.2.4 Generate a report that includes the retention time, the area, and the calculated concentrations of the analytes, internal standard recovery (based on area counts), and surrogate recovery in percent.

12.2.5 Report the results for the least dilute sample where the concentration measured was within the acceptable calibration range.

12.2.6 Where analytes are not detected or are detected below the lowest calibration standard, report the Minimum Measurement Level. Report a revised Minimum Measurement Level in accordance with Section 12.1.3 for any dilute analyses where less dilute samples were not run and for any analyte that was not detected.

12.3 Data reporting requirements

12.3.1 Report results in mg/L to three significant figures.

12.3.2 Report all corresponding blanks, replicates, and matrix spike recoveries for each analytical batch of samples.

13.0 Method Performance

13.1 Single laboratory method validation studies were performed during the development of the method, and included evaluation based on the United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63). A summary of the method performance data is presented in Section 17, Table 3.

14.0 Pollution Prevention

14.1 The laboratory should check state and local requirements to determine if pollution prevention equipmentis required or recommended in its area.

15.0 Waste Management

15.1 It is the responsibility of the laboratory to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and lands by minimizing releases into the environment. Compliance with all sewage discharge permits and regulations is also required.

16.0 References

16.1 National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). 1994. *Volatile organic emissions from pulp and paper mill sources, Part X - Test methods, quality assurance/quality control procedures, and data analysis protocols*. Technical Bulletin No. 684. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

16.2 United States Environmental Protection Agency (EPA). Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63).

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 Through the use of the EPA Method 301 validation procedure, this method has been shown to be a valid method for measurement of methanol, acetaldehyde, methyl ethyl ketone, and propionaldehyde in condensates from kraft mill sources. A summary of these validation data is presented in Table 3.

Table 1. GC/FID Operating Conditions for Selected HAPs Analysis
Purged-Packed Injector

Injection:	Direct (Splitless)
Injector Temperature:	170°C
Injection Volume:	1 µL
Injection Liner Size:	2 mm id (no packing)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 75 m x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	5°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	40°C/min to 150°C for 7 minutes
Ramp 3:	70°C/min to 250°C for 4 minutes
Retention Time Order:	Acetaldehyde, Methanol, Propionaldehyde, 2,2,2-Trifluoroethanol, Methyl Ethyl Ketone, Cyclohexanol
Cyclohexanol Retention Time:	22.081 min
Relative Retention Time:	Acetaldehyde - 0.336 Methyl Mercaptan - 0.356 Methanol - 0.367 Ethanol - 0.458 Propionaldehyde - 0.487 Acetone - 0.499 Dimethyl sulfide - 0.503 2,2,2-Trifluoroethanol - 0.608 MEK - 0.672

Table 2. GC/FID Operating Conditions for Selected HAPs Analysis
Split/Splitless Injector

Injection:	Direct (Splitless)
Purge Flow Rate:	approx. 40 mL/min
Purge Time:	0.25 min
Injector Temperature:	110°C
Injection Volume:	1 µL
Injection Liner Size:	2 mm id with fused silica packing in the bottom (Restex #20713-200.5)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 75 m x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	5°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	40°C/min to 150°C for 7 minutes
Ramp 3:	70°C/min to 250°C for 4 minutes
Retention Time Order:	Acetaldehyde, Methanol, Propionaldehyde, 2,2,2-Trifluoroethanol, Methyl Ethyl Ketone, Cyclohexanol
Cyclohexanol Retention Time:	22.081 min
Relative Retention Time:	Acetaldehyde - 0.336 Methyl Mercaptan - 0.356 Methanol - 0.367 Ethanol - 0.458 Propionaldehyde - 0.487 Acetone - 0.499 Dimethyl sulfide - 0.503 2,2,2-Trifluoroethanol - 0.608 MEK - 0.672

Table 3. Method 301 Validation Results

	Correction Factor (CF)			
Internal standard Injector	Acetaldehyde	Methanol	Propionaldehyde	Methyl ethyl ketone
Cyclohexanol Packed purge	1.12	NA[a]	1.12	0.97
Cyclohexanol Split/splitless	1.09	1.04	1.09	1.03
2,2,2-Trifluoroethanol Packed purge	1.14	NA[a]	1.14	1.07
2,2,2-Trifluoroethanol Split/splitless	1.06	NA[a]	1.06	NA[a]

[a] not applicable due to insignificant bias

Figure 1. VOA Sample Cooling Train

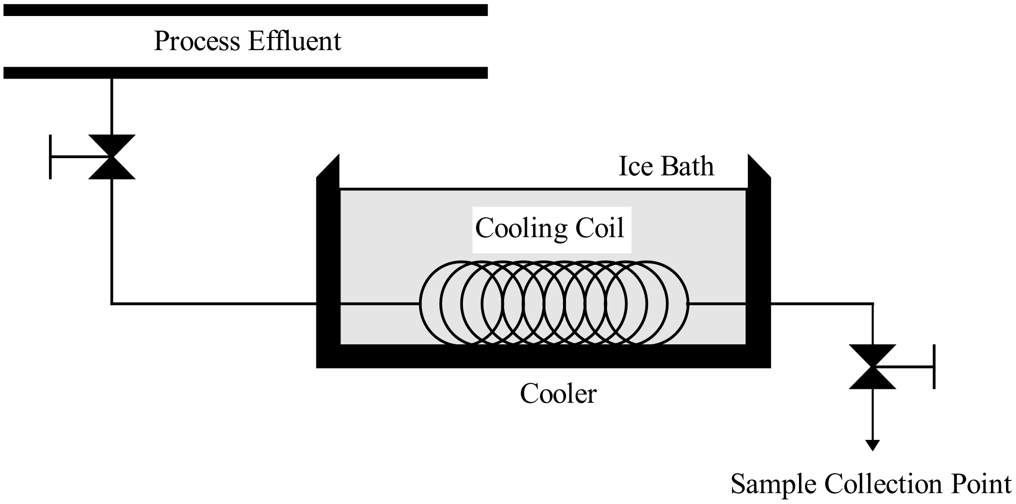


Figure 2: Entire Sample Chromatogram of Resolution Test Mixture

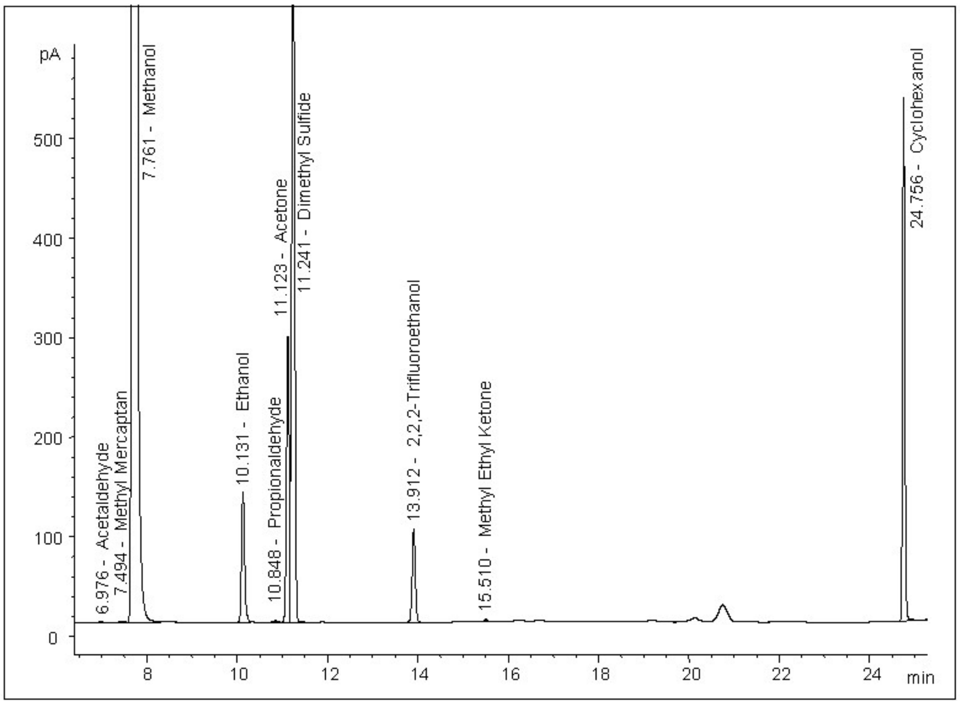


Figure 3: Partial Sample Chromatogram of Resolution Test Mixture

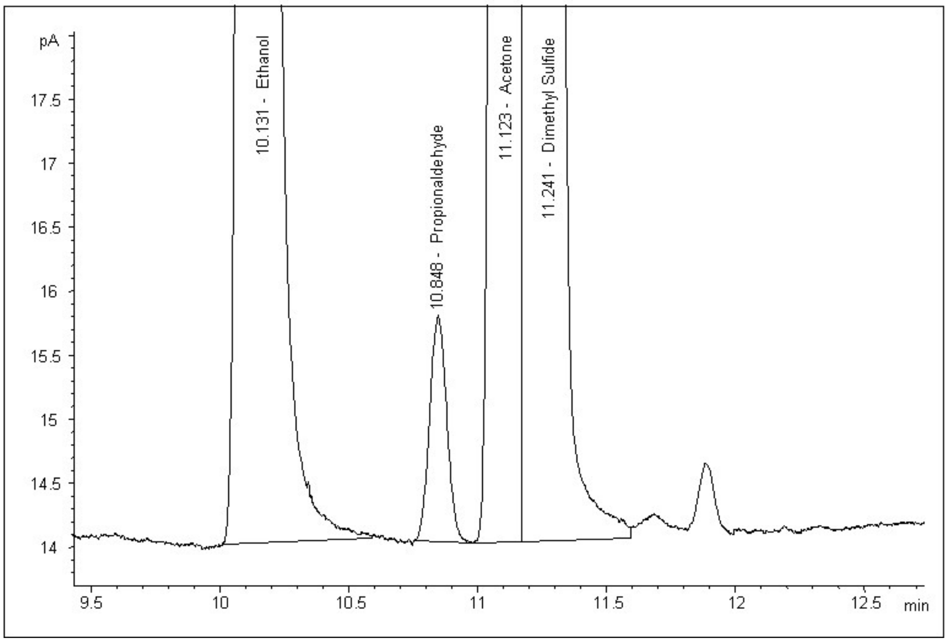
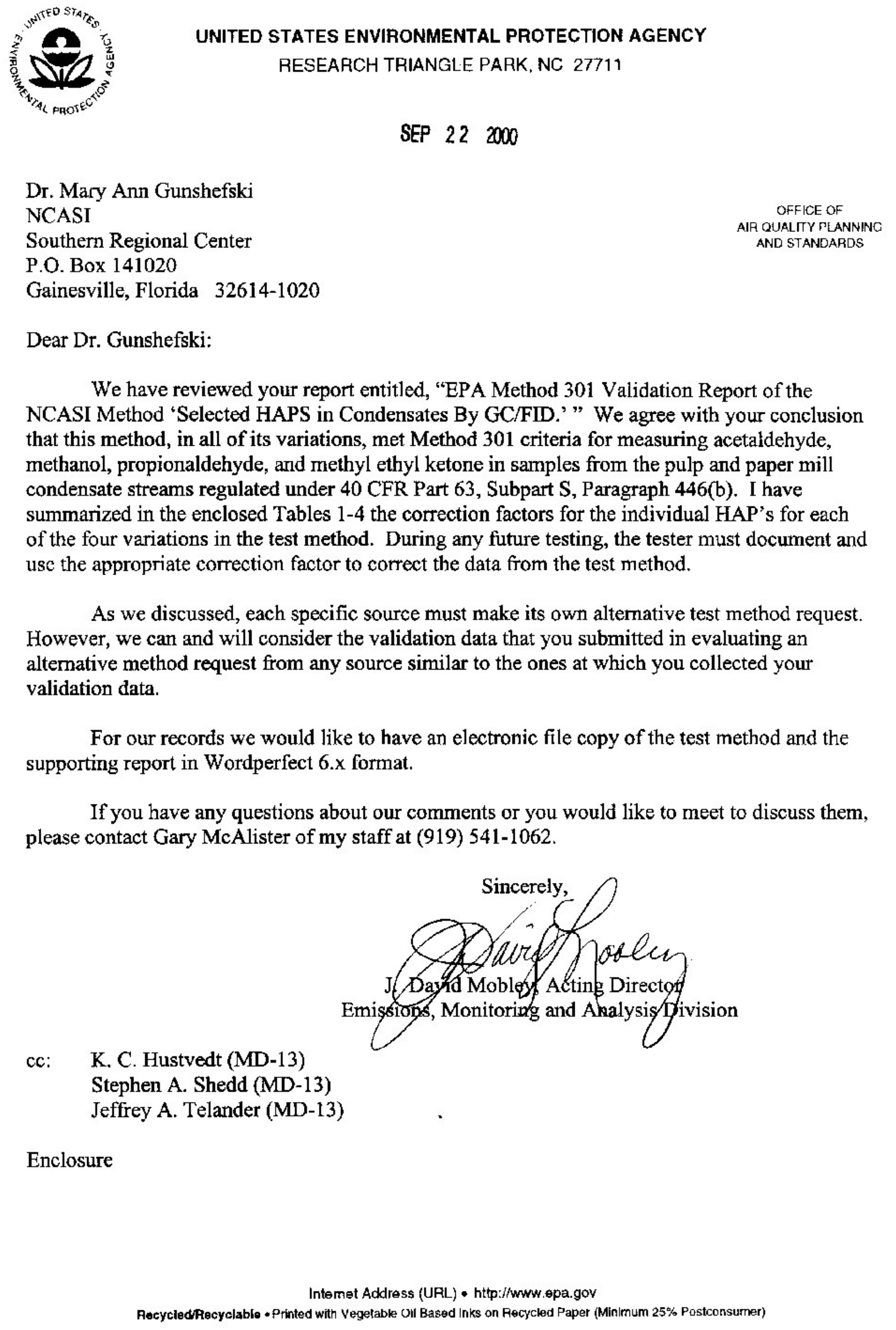


Figure 4. EPA Method 301 Validation Approval Letter – page 1



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

SEP 22 2000

Dr. Mary Ann Gunshefski
NCASI
Southern Regional Center
P.O. Box 141020
Gainesville, Florida 32614-1020

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Dear Dr. Gunshefski:

We have reviewed your report entitled, "EPA Method 301 Validation Report of the NCASI Method 'Selected HAPS in Condensates By GC/FID.' " We agree with your conclusion that this method, in all of its variations, met Method 301 criteria for measuring acetaldehyde, methanol, propionaldehyde, and methyl ethyl ketone in samples from the pulp and paper mill condensate streams regulated under 40 CFR Part 63, Subpart S, Paragraph 446(b). I have summarized in the enclosed Tables 1-4 the correction factors for the individual HAP's for each of the four variations in the test method. During any future testing, the tester must document and use the appropriate correction factor to correct the data from the test method.

As we discussed, each specific source must make its own alternative test method request. However, we can and will consider the validation data that you submitted in evaluating an alternative method request from any source similar to the ones at which you collected your validation data.

For our records we would like to have an electronic file copy of the test method and the supporting report in Wordperfect 6.x format.

If you have any questions about our comments or you would like to meet to discuss them, please contact Gary McAlister of my staff at (919) 541-1062.

Sincerely,

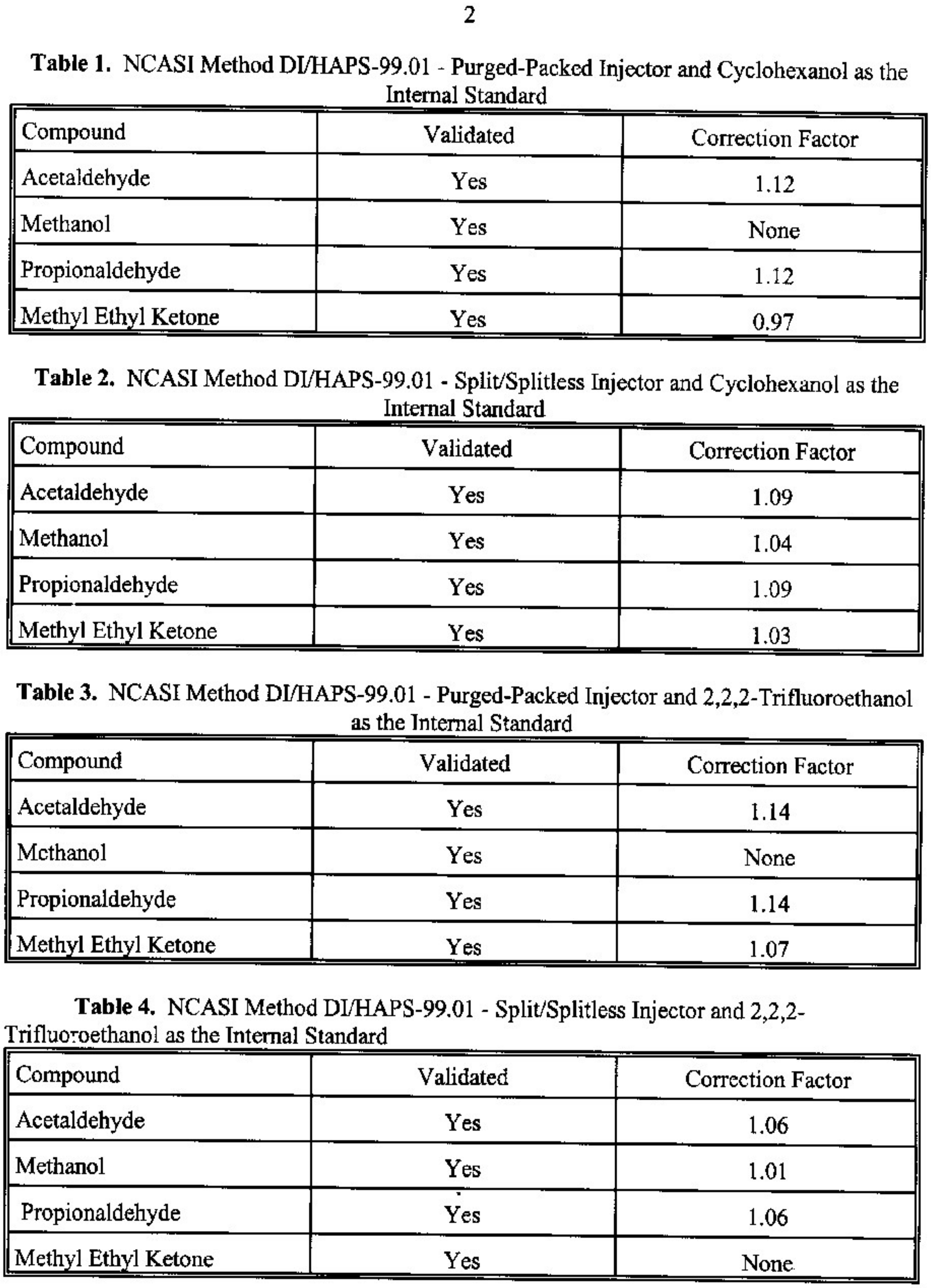
David Mobley

J. David Mobley, Acting Director
Emissions, Monitoring and Analysis Division

cc: K. C. Hustvedt (MD-13)
Stephen A. Shedd (MD-13)
Jeffrey A. Telander (MD-13)

Enclosure

Figure 4. (cont.) EPA Method 301 Validation Approval Letter – page 2



2

Table 1. NCASI Method DI/HAPS-99.01 - Purged-Packed Injector and Cyclohexanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.12
Methanol	Yes	None
Propionaldehyde	Yes	1.12
Methyl Ethyl Ketone	Yes	0.97

Table 2. NCASI Method DI/HAPS-99.01 - Split/Splitless Injector and Cyclohexanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.09
Methanol	Yes	1.04
Propionaldehyde	Yes	1.09
Methyl Ethyl Ketone	Yes	1.03

Table 3. NCASI Method DI/HAPS-99.01 - Purged-Packed Injector and 2,2,2-Trifluoroethanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.14
Methanol	Yes	None
Propionaldehyde	Yes	1.14
Methyl Ethyl Ketone	Yes	1.07

Table 4. NCASI Method DI/HAPS-99.01 - Split/Splitless Injector and 2,2,2-Trifluoroethanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.06
Methanol	Yes	1.01
Propionaldehyde	Yes	1.06
Methyl Ethyl Ketone	Yes	None

NCASI METHOD DI/MEOH-94.03

METHANOL IN PROCESS LIQUIDS AND WASTEWATERS BY GC/FID

NCASI
Southern Regional Center
May 2000

Acknowledgements

This method was prepared by Dr. MaryAnn Gunshefski, Senior Research Scientist, and Jim Stainfield, Research Associate at the NCASI Southern Regional Center. Other assistance was provided by Terry Bousquet, Senior Research Scientist, with the NCASI West Coast Regional Center.

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(919) 558-1999
publications@ncasi.org

National Council for Air and Stream Improvement, Inc. (NCASI). 2000. *Methods Manual - Methanol in process liquids and wastewaters by GC/FID*. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.

NCASI METHOD DI/MEOH-94.03

METHANOL IN PROCESS LIQUIDS AND WASTEWATERS BY GC/FID

1.0 Scope and Application

1.1 This method is used for the analysis of methanol (CAS # 67-56-1) in process liquid samples from pulp and paper mills by gas chromatography/flame ionization detection (GC/FID). This is an update of the NCASI Method DI/MEOH-94.02. An older version of this method was published in Appendix I of NCASI Technical Bulletin 684 as *Method for Methanol, Acetone, Acetaldehyde, and Methyl Ethyl Ketone in Liquid Samples*, and has been rewritten to conform with the contents and format established by the EMMC for EPA wastewater methods. This version includes only methanol, since methanol is the only compound for which the method has been validated at this time.

1.2 Types of process liquids for which this method can be used include samples from both kraft pulping mills and sulfite pulping mills. Liquid types include condensate, dirty hot water plant liquid, evaporator condensate, foul condensate, influent to sludge ponds, stripped condensate, treated effluent, untreated effluent and weak wash.

1.3 The method has been single laboratory validated using the United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63), and is a validated method.

1.4 This method is applicable for detecting methanol in process liquids at the part per million (ppm) level.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of the Method

2.1 Samples are collected directly from the process liquid stream using an appropriate collection vessel. For sample streams which are extremely hot, a cooling coil is used to lower the temperature of the sample to below 160°F. Effluent samples must be preserved with acid to pH 2-3 upon collection. The samples are kept refrigerated until analysis.

2.2 In the laboratory, an aliquot of the sample is transferred to an autosampler vial. To each of the autosampler vials, an aliquot of an appropriate internal standard solution must be added. The internal standard is also used as a time reference peak. The aqueous samples are then directly introduced into the gas chromatograph equipped with a capillary column. The GC column is temperature programmed to separate the methanol from other compounds which may be present in the sample. The methanol is detected with a flame ionization detector which is interfaced to the gas chromatograph.

2.3 Identification of methanol is determined by comparison of its retention time with the retention time of a known standard. If the results are questionable, confirmation can be performed by using a different GC column.

2.4 The sensitivity of the method is defined as the minimum measurement level (MML) and for undiluted samples is set at 0.5 mg/L for this method.

2.5 Quality is assured through testing of the analytical systems. This is accomplished by using a second source reference material, calibration check samples and spike recovery samples. Method blanks, duplicates and matrix spikes should also be analyzed with each analytical batch to ensure data quality.

3.0 Definitions

3.1 The definitions below are specific to this method, but conform to common usage as much as possible.

3.1.1 Batch - grouping of samples, not more than 20

3.1.2 mg/L - milligrams per liter

3.1.3 May - This action, activity, or procedural step is neither required nor prohibited.

3.1.4 Must not - This action, activity, or procedural step is prohibited.

3.1.5 Must - This action, activity, or procedural step is required.

3.1.6 Should - This action, activity, or procedural step is suggested, but not required.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analyses by running laboratory blanks as described in Section 9.4.1.

4.2 Glassware must be scrupulously cleaned. Clean all glassware by detergent washing with hot water and rinsing with tap water. The glassware should then be drained dry and baked at over 100°C for several hours.

4.3 Injections into the GC must be made with a clean syringe. Carryover of analytes from previously injected high level standards or samples can have a large influence on the measured values of subsequent samples or standards. After injection of the sample, the syringe should be cleaned immediately by rinsing the syringe ten times with VOC-free DI water.

4.4 Several compounds can interfere with the chromatography if the separation is not efficient. These compounds include methyl mercaptan, ethanol, acetone, and dimethyl sulfide. When the cryogenic GC method is performed properly, this method does sufficiently separate these compounds from methanol at concentrations found in condensates. When the non-cryogenic GC method is performed properly, the method used dilution to remove these interferences. This can be achieved because the methanol concentration in these types of samples is much larger than the concentration of these other compounds.

4.5 Compounds may interfere with the internal standard. When initially analyzing samples of unknown composition, an injection without internal standard can be performed to determine if an interference exists.

5.0 Safety

5.1 All chemicals should be treated as a potential health hazard. It is recommended that prudent practices for handling chemicals in the laboratory be employed.

5.2 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness of OSHA regulations regarding safe handling of chemicals used in this method. Material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.3 Methanol is a flammable liquid which may be harmful if inhaled or ingested. Use in a laboratory fume hood and wear appropriate gloves, eye protection and other protective clothing.

6.0 Equipment and Supplies

6.1 Brand names and suppliers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and material other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.2 Sampling equipment

6.2.1 Samples are to be collected in glass or plastic bottles to zero headspace. It is recommended that 40 mL glass vials with Teflon™ faced silicone backed lids (VOA vials) be used.

6.2.2 Figure 1 shows the configuration of a VOA sample cooling train. Valve sizes should be small enough to yield controllable low flow rates (i.e., <1000 mL per minute). The diameter of the tubing should be small (i.e., around 0.25 inch inside diameter).

6.3 Laboratory glassware and supplies

6.3.1 Autosampler vials capable of holding 2 mL

6.3.2 Volumetric flasks

6.3.3 Volumetric pipets

6.3.4 Syringes

6.4 Analytical equipment

6.4.1 Gas chromatography system - gas chromatography analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns and gases.

6.4.2 Guard column - 10 m x 0.53 mm deactivated fused silica capillary column

6.4.3 Column - 30 m x 0.53 mm x 3 µm bonded phase DB-624 fused silica capillary column (J&W Scientific or equivalent), 30 m x 0.32 mm x 025 µm bonded phase DB-WAX fused silica capillary column (J&W Scientific or equivalent), 75 m x 0.53 mm x 3 µm bonded phase DB-624 fused silica capillary column (J&W Scientific or equivalent) [non-cryogenic method], or other column shown to be capable of separating methanol from typical components found in process liquids.

6.4.4 GC detector - Flame ionization with appropriate data system ; a large-bore jet tip is recommended, capillary jet tips were found to result in frequent flame-outs.

7.0 Reagents and Standards

7.1 **Deionized water -** Deionized water should be tested immediately before use to verify the absence of any target analytes. If it is found to be contaminated, it may be necessary to prepare fresh deionized water, purge the water with nitrogen or helium, or boil the water to remove the contaminant(s).

7.2 **Analytical standards** - Reagent grade or the highest purity methanol and cyclohexanol must be used.

7.3 **Internal standard primary spiking solution**- Prepare primary stock solution by adding 0.312 mL cyclohexanol to a tared 100 mL ground glass stoppered volumetric flask. Weigh the flask after the addition of the internal standard and record the weight to the nearest 0.1 mg. Fill the flask to 100 mL with DI water. This will result in a nominal 3,000 mg/L primary stock solution. Compute the exact concentration (mg/L) using the weight gain. The solution can be stored at room temperature for over 6 months. A higher concentration of internal standard should be prepared and used if the upper limit of the calibration curve being used is above 100 mg/L. Additionally, another internal standard material could be used if it is demonstrated that it does not interfere with any other peaks in the chromatogram.

7.4 **Calibration primary stock solution** - Fill a 100 mL ground glass stoppered volumetric flask with approximately 90 mL DI water. Tare the flask after the addition of the water. Using a syringe, add 0.126 mL of methanol, taking care to inject the methanol directly into the water. This will result in a nominal 1,000 mg/L methanol primary stock solution. Use this weight gain to compute the exact methanol concentration.

7.5 **Calibration solutions** - Prepare five standard solutions by serial dilutions of the stock solution. For the cryogenic GC methods, the calibration range is 0.5 to 1000 mg/L. It has been found that the linear range can be extended up to 10,000 mg/L, but the accuracy at the lower concentrations is compromised, and the possibility for interferences increases. For the non-cryogenic GC method, the required calibration range is 0.5 to 100 mg/L.

7.6 **Second source standard or certified reference material** - A second source standard or certified reference standard containing methanol in an aqueous solution must be prepared or obtained and analyzed after every calibration of the instrument. A second source standard is a standard that is made from methanol purchased from a different vendor than that which was used to prepare the calibration primary stock solution.

8.0 Sample Collection, Preservation and Storage

8.1 **Collection** - Grab samples are collected directly from the process liquid stream using an appropriate collection vessel, typically a 40 mL VOA vial. For sample streams which are greater than 160^{o}F, a cooling coil is used to lower the temperature of the sample to below 160°F. The cooling coil tubing should be flushed for two to three minutes with the wastewater to be sampled prior to collecting a sample. This is done by opening both valves and allowing the sample to run through the tubing. After the line is flushed, valves are restricted to slow the flow rate. The temperature of the liquid to be sampled should be checked to be sure it is cool prior to collecting the sample. Use caution when sampling even moderately hot streams into glass vials, since the heat may cause the glass to break. Fill the vial to zero headspace with the sample.

8.2 **Preservation** - Effluent samples must be preserved with acid upon collection. This can be accomplished by adding several drops of dilute (1N) acid (i.e., HCl, H_2SO_4) to the sample vial before sample collection to bring the pH down to 2-3, then fill to zero headspace as described above. Do not acidify to below pH 2. No preservation is necessary for other types of process liquids.

8.3 **Storage** - All samples must be stored in the refrigerator (4°C) until analysis. Samples may be stored for at least 30 days.

9.0 Quality Control

9.1 Each field sampling program or laboratory that uses this method is required to operate a formal quality assurance program. Laboratory or field performance is compared to established criteria to determine if the results of the analyses meet the performance criteria of the method.

9.2 GC Maintenance

9.2.1 Injector maintenance - The septum and injection liner should be replaced when necessary. If this is not done, retention time shifts, peak broadening and low continuing calibration verification recoveries can occur.

9.2.2 Bakeouts - Water can build up in the GC, causing peak broadening and FID flame out. Frequent bakeouts of the system help to purge the system of excess water.

9.3 Initial GC/FID performance

9.3.1 Second source or certified reference material - A second source or certified reference material must be evaluated after each recalibration of the instrument. Recoveries between 85 and 115% are required for methanol.

9.3.2 Reproducibility check - When the instrument is set up to perform this method a reproducibility/sensitivity check must be performed. Seven aliquots of the 0.5 mg/L calibration standard must be analyzed. The %RSD of the seven analyses for methanol must be less that 15%.

9.4 Continuing GC/FID performance

9.4.1 Blanks - One method blank must be prepared per analytical batch to demonstrate that all materials are interference free. The concentration of methanol in the blank must be below 0.5 mg/L.

9.4.2 Calibration verification - Before each set of samples is analyzed, a calibration check is done to determine that the GC/FID system is operating within acceptable parameters. The calibration check must involve the analysis of a calibration standard in the mid-range of the calibration curve. The concentration of methanol must be within ±10% of the expected concentration. If the calibration fails to meet these expected criteria, the

GC/FID system may require maintenance. If routine maintenance does not correct the problem, a new standard prepared from a fresh calibration stock solution should be run. If this still fails, the instrument will need to be recalibrated.

9.4.3 Replicates - Replicates consist of running two or more separate aliquots of the sample through the entire analytical procedure. A duplicate must be performed for each batch of samples. The relative percent difference and the mean should be tabulated in a method precision log.

9.4.4 Matrix spike recovery - A matrix spike may be prepared for each batch of samples. Using the mean concentration determined by the replicate analyses or the level determined from a single measurement, determine the spiking level which will give at least three times the sample concentration. If the sample does not have detectable levels of analytes, spike the sample at approximately five times the lowest calibration level of the instrument. Spike the sample with the determined amount of the calibration standard or matrix spike solution and analyze the sample in the normal manner. Calculate the percent recovery using Equation 1.

Equation 1

$$R = \left(\frac{C_S - C_N}{C_T} \right) \times 100$$

Where:

R = percent recovery of matrix spike
C_S = measured concentration of spiked sample
C_N = measured concentration of native sample
C_T = theoretical concentration of spike

10.0 Calibration and Standardization

10.1 FID operating conditions

Assemble the GC/FID and establish the operating conditions outlined in Table 1, 2, or 3. Other chromatographic columns and conditions may be used if it has been established that methanol is separated from compounds which may cause interference, and quality control parameters are met. Once the GC/FID system is optimized for analytical separation and sensitivity, the sample operating conditions must be used to analyze all samples, blanks, calibration standards and quality assurance samples. Note that constant injections of aqueous samples can cause water to build up in the system. This will cause the retention times to shift and the peaks to broaden. It is recommended that after approximately 50 injections a bakeout of the system be performed. This should consist of heating the injector to 250°C, the oven to over 200°C and the detector to 350°C for at least several hours.

10.2 GC/ FID analysis of calibration standards

10.2.1 Determine the retention time of methanol by taking 2.0 mL of the mid-range calibration solution and adding 10 µL of the internal standard solution. If a 3,000 mg/L internal standard primary stock solution was prepared, this will result in a concentration of 15 mg/L of cyclohexanol in the autosampler vial. If a different concentration was used, calculate the correct concentration resulting in the autosampler vial. Inject 1 µL of this solution and determine the relative retention time of methanol to the internal standard using Equation 2.

10.2.2 Prepare a five-point calibration curve for methanol by taking 2.0 mL of each calibration solution and adding the internal standard solution as described above. The calibration range is defined in Section 7.5. Use of an internal standard for calibration is required.

10.2.3 Calculate the relative response factor (RRF_M) for methanol using Equation 3. If the relative standard deviation (RSD) of the average RRF_M is less than 10% for methanol, the calibration is acceptable. The average RRF_M can be used in all subsequent calculations. If the calibration does not pass the criteria the calibration curve solutions must be reanalyzed and reevaluated. It may be necessary to perform instrument maintenance prior to reanalysis. If reanalysis also fails to produce a linear curve, new calibration standards must be prepared and analyzed.

10.2.4 Analyze and calculate the concentration of the mid-range calibration standard daily, prior to each sample set, using Equation 4. Calculate the percent recovery of the standard using Equation 5 to verify the calibration. In-house percent recovery control limits must be determined, and are not to exceed

±10% for methanol. If the limits are exceeded, either prepare a new standard or perform instrument maintenance. If necessary, recalibrate the instrument.

Equation 2

$$RRT_M = \left[\frac{Rt_M}{Rt_{IS}} \right]$$

Where:

RRT_M = relative retention time of methanol
Rt_A = retention time of methanol
Rt_{IS} = retention time of internal standard (cyclohexanol)

Equation 3

$$RRF_M = \left[\frac{A_M}{A_{IS}} \times \frac{C_{IS}}{C_M} \right]$$

Where:

A_M = area of methanol peak
A_{IS} = area of internal standard peak
C_M = concentration of methanol injected
C_{IS} = concentration of internal standard injected

Equation 4

$$C_M = \left[\frac{A_M \times C_{IS}}{A_{IS} \times RRF_M} \right]$$

Where:

C_M = concentration of methanol in sample (mg/L)
A_M = area of methanol peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_M = relative response factor of methanol (Section 10.2.3)

Equation 5

$$\text{Percent Recovery} = \left[\frac{C_M}{C_E} \times 100\right]$$

Where:

C_M = concentration of methanol measured
C_E = concentration of methanol expected

10.3 Analytical range and minimum calibration level

10.3.1 Demonstrate that the calibration curve is linear (relative response factors exhibit a RSD less than 10% for methanol) throughout the range of the calibration curve described in Section 7.5.

10.3.2 Demonstrate that methanol is detectable at 0.5 mg/L with an RSD of less than 15% for methanol as described in Section 9.3.2.

11.0 Procedure

11.1 Transfer an aliquot (2.0 mL) of the sample to an autosampler vial. Add 10 µL of the internal standard primary spike solution to each of the autosampler vials. Perform the analysis by direct aqueous injection into the GC/FID. If the concentration of an analyte is more that 10% above the calibrated range, the sample should be diluted and reanalyzed to measure the analyte concentration.

11.2 If dilution is necessary, volumetric flasks can be utilized to achieve the desired concentrations. An aliquot of the diluted sample is then analyzed as described in Section 11.1. Calculate the dilution factor using Equation 6.

Equation 6

$$DF = \frac{V_T}{V_S}$$

Where:

DF = dilution factor
V_S = volume of sample (mL) used
V_T = total volume of dilution (mL)

12.0 Data Analysis and Calculations

12.1 GC/FID data analysis

12.1.1 The analytes are identified by comparison of the relative retention times established in the calibration to the retention times in the samples. The sample component relative retention time (RRT) should fall within ±0.01 RRT units of the RRT of the standard component.

12.1.2 Calculate the sample concentration, using the internal standard response factors established in Section 10.2.3, according to Equation 7.

Equation 7

$$C_A = \left[\frac{A_A \times C_{IS} \times CF \times DF}{A_{IS} \times RRF_A} \right]$$

Where:

C_A = concentration of compound A in sample (mg/L)
A_A = area of the compound A peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_M = relative response factor of compound A (Section 10.3)
CF = correction factor from Method 301 validation (Table 3)
DF = dilution factor

12.2 Data review requirements

12.2.1 The data are reviewed for accuracy of the identification, GC problems, interferences and bias. Any problems should be corrected prior to reporting of analytical results.

12.2.2 All chromatograms must be manually reviewed to confirm internal standard and analyte identification and area integrations. As part of this review, the analyst assesses whether or not the concentration is within the calibration range of the instrument. The analyst should determine if the level of interferences and baseline noise can be corrected with dilution of the samples. Another tool that can be utilized to identify the analyte peaks is to overlay the sample chromatogram with the standard chromatogram.

12.2.3 The internal standard area counts must be reviewed and added to a control chart. The in-house determined control limits must not exceed ±20% of the mean.

12.2.4 Any inconsistencies between replicate analyses are resolved (i.e., if methanol is detected in one replicate and not the other), and attempts are made to determine the reason.

12.2.5 Generate a report that includes the retention time, the area, and the calculated concentrations of the analytes, and internal standard recovery (based on area counts).

12.2.6 Report the results for the least dilute sample where the concentration measured was within the acceptable calibration range.

12.2.7 Where analytes are not detected or are detected below the lowest calibration standard, report the Minimum Measurement Level. Report a revised Minimum Measurement Level in accordance with Section 12.1.3 for any dilute analyses where less dilute samples were not run and for any analyte that was not detected.

12.3 Data reporting requirements

12.3.1 Report results in mg/L to appropriate number of significant figures for individual situations.

12.3.2 Report all corresponding blanks, replicates and matrix spikes recoveries for each analytical batch of samples.

13.0 Method Performance

13.1 Single laboratory method validation studies were performed during the development of the method, and included evaluation based on the United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63). The method performance data are presented in Section 17, Table 4.

14.0 Pollution Prevention

14.1 The laboratory should check with state and local requirements to determine if pollution prevention equipment, such as solvent recovery devices, are required or recommended in their area. Use of these devices to reclaim solvents can be part of a pollution prevention program to reduce air emissions.

15.0 Waste Management

15.1 It is the responsibility of the laboratory to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and lands by minimizing releases into the environment. Compliance with all sewage discharge permits and regulations is also required.

16.0 References

16.1 National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). 1994. *Volatile Organic Emissions from Pulp and Paper Mill Sources, Part X - Test Methods, Quality Assurance/Quality Control Procedures, and Data Analysis Protocols*. Technical Bulletin No. 684. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

16.2 United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63).

17.0 Tables, Diagrams, Flowcharts And Validation Data

17.1 Through the use of the EPA Method 301 validation procedure, this method has been shown to be a valid method for measurement of methanol in treated effluent, untreated effluent, stripped condensate, foul condensate and weak wash from kraft mill sources; and condensate, evaporator condensate, influent to sludge and dirty hot water plants from sulfite mill sources. A summary of these validation data are presented in Table 4.

Table 1. GC/FID Operating Conditions for Methanol Analysis
DB-624 Column with Cryogenics

Injection:	Direct (Splitless)
Injector Temperature:	110°C
Injection Volume:	1 µL
Injection Liner Size:	2 mm id (no packing)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 30 m x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	0°C for 3 min
Ramp 1:	5°C/min to 50°C for 0 minutes
Ramp 2:	70°C/min to 105°C for 17 minutes
Ramp 3:	70°C/min to 220°C for 3 minutes
Retention Time Order:	Acetaldehyde, Methyl Mercaptan, Methanol, Ethanol, Propionaldehyde, Methyl Ethyl Ketone, Cyclohexanol
Relative Retention Time:	Methanol - 0.260

Table 2. GC/FID Operating Conditions for Methanol Analysis
DB-WAX Column with Cryogenics

Injection:	Direct (Splitless)
Injector Temperature:	110°C
Injection Volume:	1 μL
Injection Liner Size:	2 mm id (no packing)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-WAX, 30 m x 0.32 mm id x 025 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	0°C for 3 min
Ramp 1:	5°C/min to 50°C for 4 minutes
Ramp 2:	70°C/min to 100°C for 10 minutes
Ramp 3:	70°C/min to 200°C for 4 minutes
Retention Time Order:	Acetaldehyde, Acetone, Methyl Ethyl Ketone, Methanol, Cyclohexanol
Relative Retention Time:	Methanol - 0.235

Table 3. GC/FID Operating Conditions for Methanol Analysis
DB-624 Column without Cryogenics

Injection:	Direct (Splitless)
Injector Temperature:	110°C
Injection Volume:	1 µL
Injection Liner Size:	2 mm id (no packing)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 75 m x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	Off
Temperature Program °C:	
Initial:	35°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	70°C/min to 150°C for 10 minutes
Ramp 3:	70°C/min to 220°C for 3 minutes
Retention Time Order:	Acetaldehyde, Methyl Mercaptan, Methanol, Ethanol, Propionaldehyde, Methyl Ethyl Ketone, Cyclohexanol
Relative Retention Time:	Methanol - 0.260

Table 4. Method 301 Validation Results for Methanol

Source	Statistical Parameters			Interpretation Information		
	RSD (S) %	RSD (U/L) %	CF	High Spiked Sample Conc. (mg/L)	Low/Unspiked Sample Conc. (mg/L)	Average Sample Conc. (mg/L)
Condensate [a]	10	9	NA	957	567	578
Dirty Hot Water Plant [a]	18	36	NA	5891	2688	2450
Evaporator Condensate [a]	14	17	NA	1467	782	757
Foul Condensate	21	9	NA	6735	3006	3382
Influent to Sludge [a]	16	36	NA	585	274	246
Stripped Condensate	7	2	NA	447	70	63
Untreated Effluent	2	16	NA	12	53	51
Weak Wash	34	8	NA	3690	24	-98 [c]
Treated Effluent [b]	15	13	NA	133	30	10

[a] from a sulfite mill

[b] used double spiking procedure, and treated with nitric acid for preservation

[c] This value is negative due to less than 100% recovery of the spike, and the small concentration of methanol present as compared to the spike concentration

RSD(S) - Relative standard deviation of spiked samples

RSD(U/L) - Relative standard deviation of unspiked or low level spiked samples

CF - Correction factor as calculated in the Method 301 validation procedure. A correction factor is calculated only if there is a high bias present

NA - Not applicable

Figure 1. VOA Sample Cooling Train

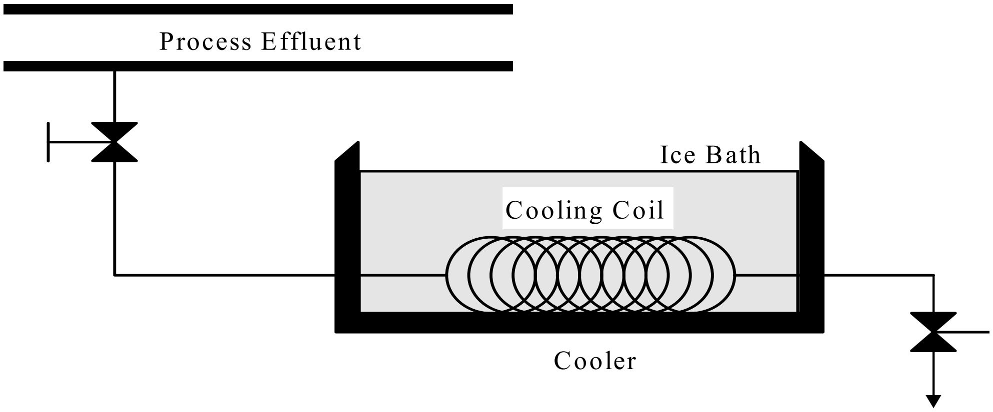
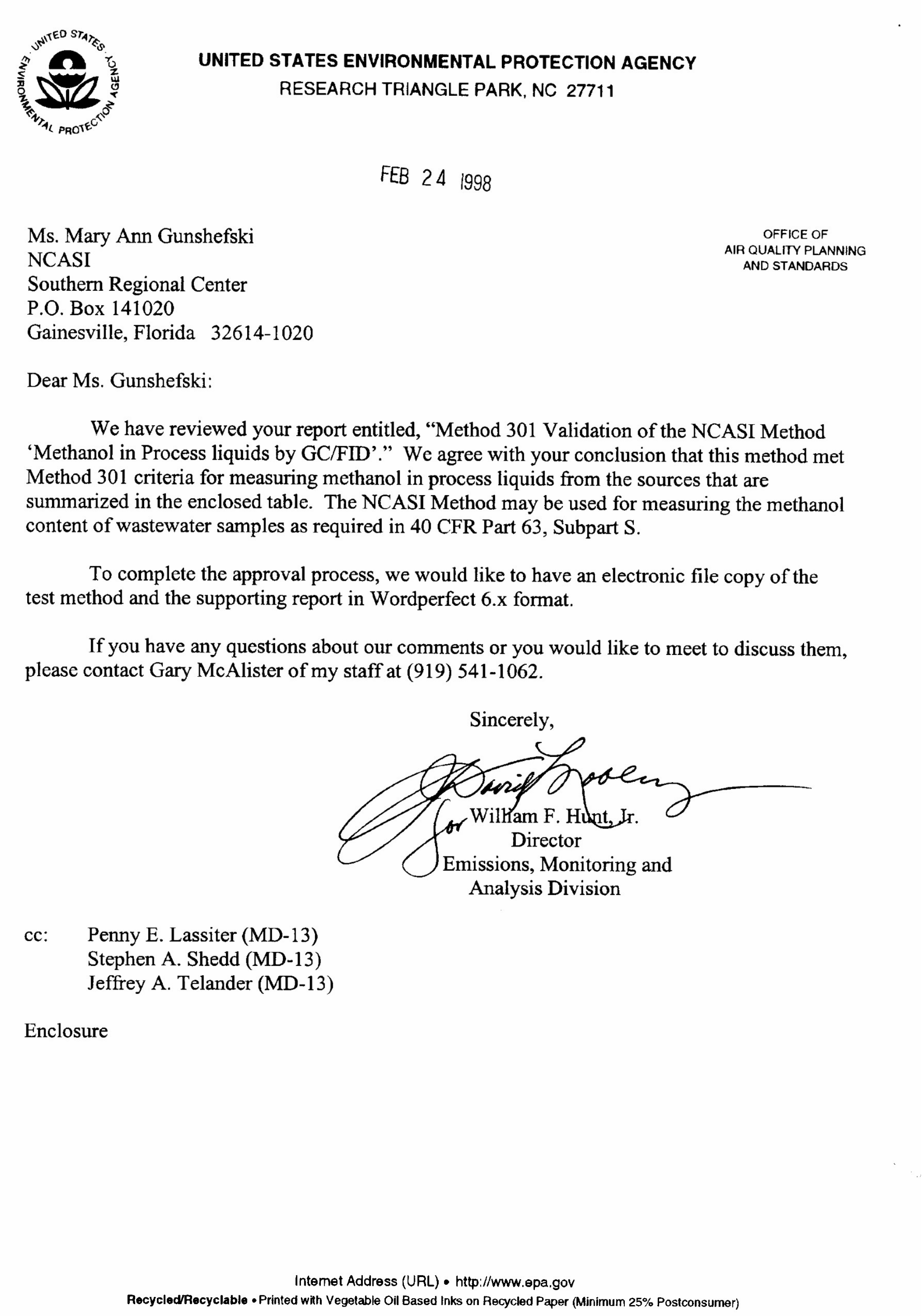


Figure 2: Approval Letter from EPA - Page 1



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

FEB 24 1998

Ms. Mary Ann Gunshefski
NCASI
Southern Regional Center
P.O. Box 141020
Gainesville, Florida 32614-1020

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Dear Ms. Gunshefski:

We have reviewed your report entitled, "Method 301 Validation of the NCASI Method 'Methanol in Process liquids by GC/FID'." We agree with your conclusion that this method met Method 301 criteria for measuring methanol in process liquids from the sources that are summarized in the enclosed table. The NCASI Method may be used for measuring the methanol content of wastewater samples as required in 40 CFR Part 63, Subpart S.

To complete the approval process, we would like to have an electronic file copy of the test method and the supporting report in Wordperfect 6.x format.

If you have any questions about our comments or you would like to meet to discuss them, please contact Gary McAlister of my staff at (919) 541-1062.

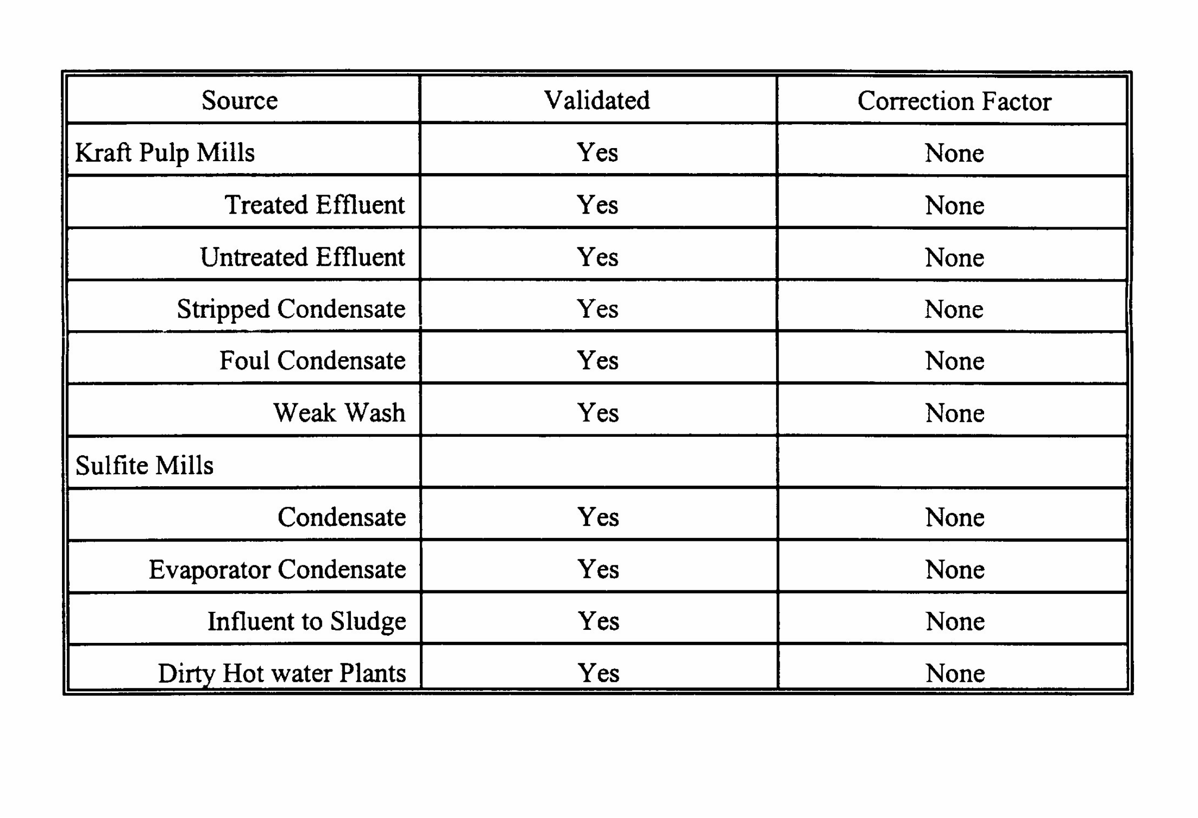
Sincerely,

for William F. Hunt, Jr.
Director
Emissions, Monitoring and
Analysis Division

cc: Penny E. Lassiter (MD-13)
Stephen A. Shedd (MD-13)
Jeffrey A. Telander (MD-13)

Enclosure

Figure 3: Approval Letter form EPA - Page 2



Source	Validated	Correction Factor
Kraft Pulp Mills	Yes	None
Treated Effluent	Yes	None
Untreated Effluent	Yes	None
Stripped Condensate	Yes	None
Foul Condensate	Yes	None
Weak Wash	Yes	None
Sulfite Mills		
Condensate	Yes	None
Evaporator Condensate	Yes	None
Influent to Sludge	Yes	None
Dirty Hot water Plants	Yes	None

Sulfide

DOC316.53.01136

USEPA[1] Methylene Blue Method[2]

Method 8131

5 to 800 µg/L S^{2-} (spectrophotometers)

Reagent Solution

0.01 to 0.70 mg/L S^{2-} (colorimeters)

Scope and application: For testing total sulfides, H_2S, HS^-, and certain metal sulfides in groundwater, wastewater, brines and seawater.

[1] USEPA accepted for reporting wastewater analysis. Procedure is equivalent to Standard Method 4500-S^{2-} D.

[2] Adapted from Standards Methods for the Examination of Water and Wastewater.

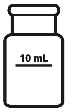
Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2495402 
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906 

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
Some sulfide loss can occur if dilution is necessary.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

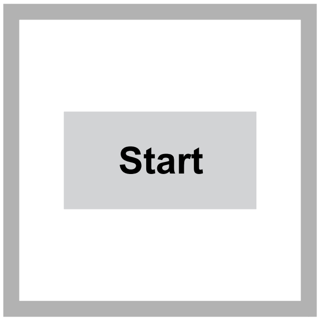
Description	Quantity
Sulfide 1 Reagent	1–2 mL
Sulfide 2 Reagent	1–2 mL
Water, deionized	10–25 mL
Pipet, serological, 10-mL	1
Pipet Filler, safety bulb	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2
Stoppers	2

Refer to Consumables and replacement items on page 5 for order information.

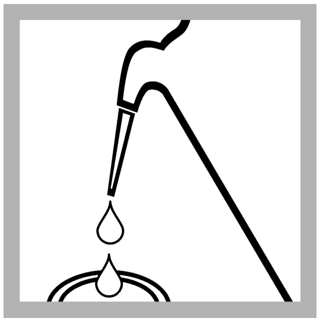
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Prevent agitation of the sample and exposure to air.

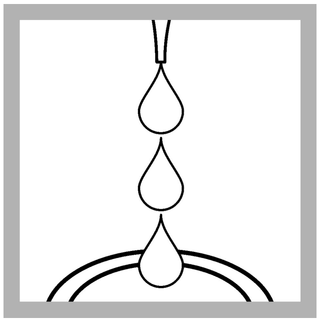
Reagent solution procedure



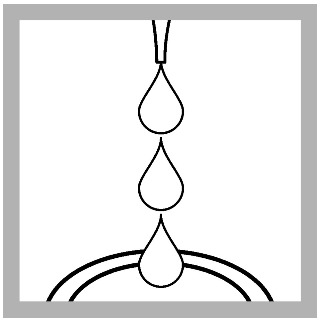
1. Start program **690 Sulfide**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



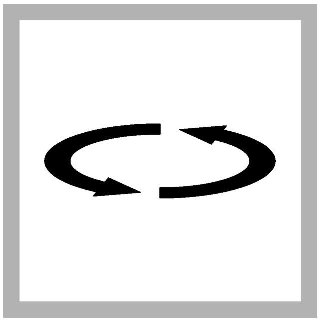
2. Prepare the blank: Fill a sample cell with deionized water. Use 10 mL for spectrophotometers and 25 mL for colorimeters.



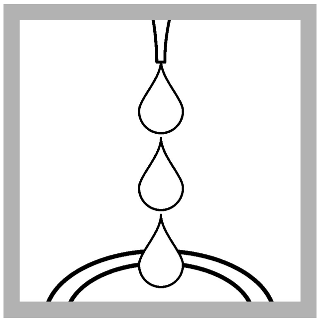
3. Prepare the sample: Use a pipet to add sample to a second sample cell. Use 10 mL for spectrophotometers and 25 mL for colorimeters. Do not mix the sample more than necessary to prevent sulfide loss.



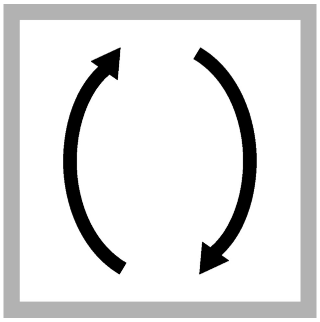
4. Add Sulfide 1 Reagent to each sample cell. Use 0.5 mL for spectrophotometers and 1.0 mL for colorimeters.



5. Swirl to mix.

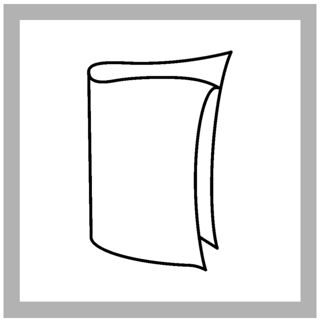


6. Add Sulfide 2 Reagent to each sample cell. Use 0.5 mL for spectrophotometers and 1.0 mL for colorimeters.

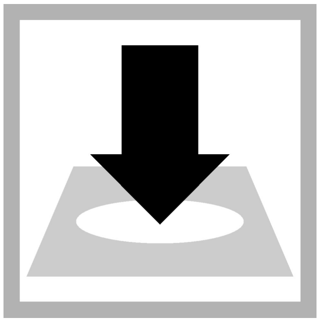


7. Close the sample cell. Invert the sample cell to mix. A pink color will develop initially. If sulfide is present, the solution becomes blue.

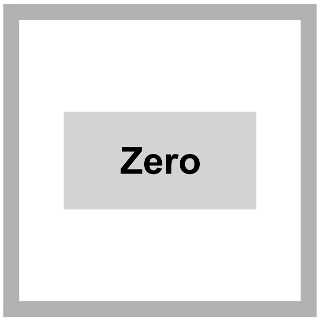
8. Start the instrument timer. A five-minute reaction time starts.



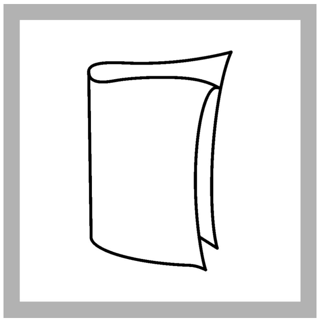
9. When the timer expires, clean the blank sample cell.



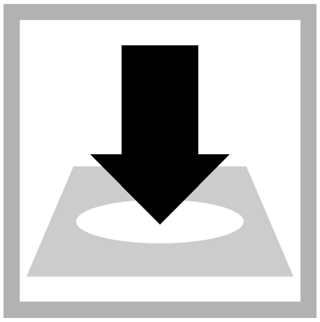
10. Insert the blank into the cell holder.



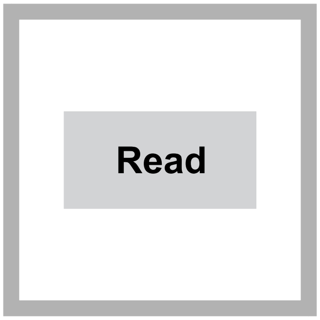
11. Push **ZERO**. The display shows 0 µg/L or 0.00 mg/L S^{2-}.



12. Clean the prepared sample cell.



13. Insert the prepared sample into the cell holder.



14. Push **READ**. Results show in µg/L or mg/L S^{2-}.

Soluble sulfides

To measure soluble sulfides, use a centrifuge to separate the solids. To make an estimate of the amount of insoluble sulfides in the sample, subtract the soluble sulfide concentration from the total (with solids) sulfide concentration.

1. Fill a centrifuge tube completely with sample and immediately cap the tube.
2. Put the tube in a centrifuge and run the centrifuge to separate the solids.
3. Use the supernatant as the sample in the test procedure.

Interferences

Interfering substance	Interference level
Barium	Concentrations more than 20 mg/L barium react with the sulfuric acid in Sulfide 1 Reagent and form a $BaSO_4$ (barite) precipitate. To correct for this interference: **1.** Dilute the sample in the test procedure as follows: • Spectrophotometers: use a 0.1-mL or 1.0-mL sample volume and add deionized water to the 10-mL mark. • Colorimeters: use a 0.25-mL or 2.5-mL sample volume and add deionized water to the 25-mL mark. **2.** Add both Sulfide 1 and Sulfide 2 reagents per the procedure steps. **3.** After the 5-minute reaction period, pour the sample into a 50-mL beaker. **4.** Pull the sample into a Luer-Lock syringe (10 cc for spectrophotometers or 60 cc for colorimeters). **5.** Put a 0.45-µm filter disc on the Luer-Lock tip and filter the sample into a clean sample cell for measurement. Use deionized water to prepare the blank. **6.** Set the instrument zero and read the result, per the procedure steps. **7.** Multiply by the appropriate dilution factor for the dilution used (10 or 100).
Strong reducing substances such as sulfite, thiosulfate and hydrosulfite	Prevent the full color development or reduce the blue color
Sulfide, high levels	High concentrations of sulfide can inhibit the full color development. Use a diluted sample in the test procedure. Some sulfide loss can occur when the sample is diluted.
Turbidity	Pre-treat the sample to remove sulfide, then use the pre-treated sample as the blank in the test procedure. Prepare a sulfide-free blank as follows: **1.** Measure 25 mL of sample into a 50-mL Erlenmeyer flask. **2.** Add 30-g/L Bromine Water by drops with constant swirling until a yellow color remains. **3.** Add 30-g/L Phenol Solution by drops with constant swirling until the yellow color is removed. **4.** Use this solution to replace the deionized water blank in the test procedure.

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
690	520 µg/L S^{2-}	504–536 µg/L S^{2-}	5 µg/L S^{2-}

Summary of method

Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. High sulfide levels in oil field waters may be determined after proper dilution. The measurement wavelength is 665 nm for spectrophotometers or 610 nm for colorimeters.

Pollution prevention and waste management

Reacted samples contain hexavalent chromium and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Water, deionized	varies	4 L	27256
Sulfide Reagent Set	—	—	2244500
Includes:			
Sulfide 1 Reagent	1–2 mL	100 mL MDB	181632
Sulfide 2 Reagent	1–2 mL	100 mL MDB	181732

Required apparatus

Description	Quantity/test	Unit	Item no.
Pipet, serological, graduated, 10 mL	1	each	53238
Pipet filler, safety bulb	1	each	1465100
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Optional reagents and apparatus

Description	Unit	Item no.
Bromine Water, 30-g/L	29 mL	221120
Phenol Solution, 30-g/L	29 mL	211220
Stoppers for 18-mm tube	25/pkg	173125
Flask, Erlenmeyer, 50 mL	each	50541

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
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FAX: (970) 669-2932

09/2018, Edition 11

APPENDIX C – CMS MATRIX

Table C-1
Proposed Condensate Collection and Treatment CMS
New-Indy Catawba, SC Mill

Location of Measurement	Measurement Taken	Measurement Device	Calculation Method	Monitoring Period	CMS Downtime	Definition of Good Data Quality	CMS Verification/Calibration
Foul Condensate Hardpipe	Flow	Continuous flow meter	Gallons per day (gpd) = Average gallons per minute (gpm) x Operating minutes per day	24 hour total	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of flow meter and transmitter
Foul Condensate to Steam Stripper	Flow	Continuous flow meter	Gallons per hour (gph) = Average gallons per minute (gpm) x Operating minutes per hour	1-hour average	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of flow meter and transmitter
Steam Stripper Steam Feed Rate	Flow	Continuous flow meter	Average steam feed rate in pounds per hour (lb/hr)	1-hour average	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of meter and transmitter
Foul Condensate Steam Stripper Feed Temperature	Temperature	Continuous temperature probe	Average temperature in degrees Farenheit (°F)	1-hour average	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of meter and transmitter
Stripped Condensate Temperature	Temperature	Continuous temperature probe	Average temperature in degrees Farenheit (°F)	1-hour average	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of meter and transmitter
Stripped Condensate Flow	Flow	Continuous flow meter	Gallons per hour (gph) = Average gallons per minute (gpm) x Operating minutes per hour	1-hour average	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of meter and transmitter
Pulp Flow and Consistency meter	Digester production oven dried tons of pulp (ODTP)	Continuous pulp flow and consistency meters	ODTP = ADTUBP/d [(Daily average pulp slurry flow, gpm) x Daily average pulp consistency, %)/100 * gpm)*(pulp consistency, %/100)[8.17 + (0.0333 * pulp consistency, %)] * 1440 / 1800] * 0.9 ODTUBP/ADTUBP	24 hour total	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of pulp slurry flow meter and calibration of pulp consistency measurement devices per TAPPI method
Fresh Water Intake Flow (used for calculation of ASB Wastewater Inlet Flow)	Flow	Continuous flow meter	Wastewater inlet flow rate to ASB, gpd = Average gpm Fresh Water Intake flow x (1 - Evaporation Rate) x Flow Meter Operational Minutes per Day	24 hour total	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of flow meter and transmitter
Number of Aerators Operating per ASB Zone	Count	Readout in Pi	Sum of aerators operating per zone	Instantaneous	Failure to obtain data for an operating day	Measurement is consistent with regular in-field verification	Per manufacturer recommendations for instrumentation, as applicable
ASB Total Aerator hp-hrs	Hp-hrs	Readout in Pi or calculated value	Total daily hp-hrs = Sum for all aerators (75 hp x daily runtime, hrs)	24 hour total	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Measurement is consistent with regular in-field verification	Per manufacturer recommendations for instrumentation, as applicable
Post-Aeration Tank monitoring, if approved to remove cover over Post-Aeration Tank for required sampling							
Post-Aeration Tank Flow[1]	Flow	Continuous flow meter	Flow rate to Post-Aeration Tank, gpd = Average gpm Post-Aeration Tank inlet flow x Flow meter Operational Minutes per Day	24 hour total	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of flow meter and transmitter
Post-Aeration Tank Number of Aerators Operating	Count	Manual Count	Sum of aerators operating	Instantaneous (during sample collection)	Failure to obtain data for an operating day	N/A	N/A
Post-Aeration Tank Total Aerator hp-hrs	Hp-hrs	Calculated value	Total daily hp-hrs = Count of aerators running x hp/aerator x 24 hrs/day	Instantaneous (during sample collection)	Failure to obtain data for an operating day	N/A	N/A

[1] As noted in Figure 3-1, the Post-Aeration Tank can receive flow from Holding Ponds #1 and #2. The Mill does not anticipate any flow from Holding Pond #2 during the IPT, but there is a flow meter to measure flow from Holding Pond #2. In the event of flow from Holding Pond #2 during the IPT, the flow from Holding Ponds #1 and #2 will be summed to calculate flow to the Post-Aeration Tank. It will be assumed that flow out of the Post-Aeration Tank is equivalent to flow entering the Post-Aeration Tank.

APPENDIX D – NCASI TB NO. 933, DEVELOPMENT AND APPLICATION OF A METHOD FOR MEASURING REDUCED SULFUR COMPOUNDS IN PULP AND PAPER MILL WASTEWATERS

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NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

DEVELOPMENT AND APPLICATION OF A METHOD FOR MEASURING REDUCED SULFUR COMPOUNDS IN PULP AND PAPER MILL WASTEWATERS

TECHNICAL BULLETIN NO. 933
JUNE 2007

by
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Acknowledgments

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National Council for Air and Stream Improvement, Inc. (NCASI). 2007. *Development and application of a method for measuring reduced sulfur compounds in pulp and paper mill wastewaters.* Technical Bulletin No. 933. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

PRESIDENT'S NOTE

In recent years, NCASI's technical program has addressed the identification of odorous compounds in wastewaters and their emission from wastewater treatment plants (WWTPs). To facilitate this, staff evaluated existing analytical methods and, where necessary, developed new methods aimed at identifying and quantifying wastewater constituents that may contribute to odors in and around treatment systems. As part of this effort, NCASI developed and applied NCASI Method RSC-02.02 for the determination of total (inorganic) sulfide, methyl mercaptan (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS) in pulp and paper mill wastewaters. These reduced sulfur compounds have been associated with odors in WWTPs and are often tracked as part of odor reduction programs. This report presents the results of a single laboratory evaluation of the method to assess precision and accuracy, method blanks, linearity, and reproducibility. Concentrations of total sulfide, MeSH, DMS, DMDS, and DMTS measured in samples collected throughout the WWTPs of over twenty mills are also included. Information in this report will be of use to mill personnel who might wish to coordinate analyses of these compounds and to those tasked with reducing emissions or odors related to reduced sulfur compounds.

Ron Yeske

Ronald A. Yeske

June 2007

MOT DU PRÉSIDENT

Depuis les dernières années, le programme technique de NCASI a examiné l'identification des composés odorants dans les eaux usées et leur émission par les systèmes de traitement des eaux usées (STEU). Pour ce faire, le personnel de NCASI a évalué les méthodes analytiques existantes et, lorsque cela s'avérait nécessaire, a développé de nouvelles méthodes visant à identifier et quantifier les composants des eaux usées susceptibles de contribuer aux odeurs à l'intérieur et autour des systèmes de traitement. Dans la même foulée, NCASI a développé et appliqué sa méthode RSC-02.02 pour déterminer les sulfures totaux (inorganiques), le méthyle mercaptan (MeSH), le sulfure de diméthyle (SDM), le disulfure de diméthyle (DSDM) et le trisulfure de diméthyle (TSDM) dans les eaux usées des fabriques de pâtes et papiers. Ces composés de soufre réduit sont associés aux odeurs dans les STEU et sont souvent surveillés dans le cadre des programmes de réduction des odeurs. Le présent rapport montre les résultats d'une évaluation en laboratoire de cette méthode afin d'en déterminer la précision et l'exactitude, les blancs de méthode, la linéarité et la reproductibilité. Le rapport contient également les concentrations de sulfures totaux, MeSH, SMD, DSDM et TSDM mesurées dans des échantillons collectés dans les STEU de plus de vingt fabriques. Le personnel des fabriques qui souhaite coordonner les analyses de ces composés et celui en charge de la réduction des émissions ou des odeurs reliées aux composés de soufre réduit trouveront utile l'information contenue dans ce rapport.

Ron Yeske

Ronald A. Yeske

Juin 2007

DEVELOPMENT AND APPLICATION OF A METHOD FOR MEASURING REDUCED SULFUR COMPOUNDS IN PULP AND PAPER MILL WASTEWATERS

TECHNICAL BULLETIN NO. 933
JUNE 2007

ABSTRACT

This research was initiated to develop and apply a method for determination of total (inorganic) sulfide, methyl mercaptan (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS) in pulp and paper mill wastewater samples. NCASI Method RSC-02.02 utilizes separate preservations and injections for determination of total sulfide (zinc acetate at pH 10) and organic reduced sulfur compounds (ORSCs) (ascorbic acid at pH 2.5). All samples are acidified (pH <2.5) prior to direct injection on a gas chromatogram equipped with a pulsed flame photometric detector (PFPD). Daily calibration verifications yielded average recoveries of 106% for total sulfide (n=94) and average recoveries ranging from 95 to 102% for the ORSCs (n=42). Method blanks were free of the target analytes. Precision and accuracy were assessed using surrogate and matrix spike recovery experiments and replicate analyses. Surrogate recoveries for total sulfide, MeSH, DMS, DMDS, and DMTS in over 1077 samples ranged from 73 to 131%, with an average recovery of 106%. Matrix spike recoveries averaged 93, 106, 102, 112, and 96% for total sulfide, MeSH, DMS, DMDS, and DMTS, respectively. Precision results as reflected by pooled relative percent differences (RPDs) for duplicate analyses ranged from 2.1 to 5.3%. Storage stability studies indicated stability of the samples for up to 14 days. Injection pH significantly impacted recovery of total sulfide, with pH 2.5 yielding the highest recovery (96%). Studies to assess matrix and sampling variability yielded average relative standard deviations of 38.9% for total sulfide, 29.8% for MeSH, 20.6% for DMS, 34.2% for DMDS, and 41.0% for DMTS, well above the variability of ~5% observed for the analytical method.

Investigations conducted in conjunction with odor reduction studies at these mills yielded a wide range of results for reduced sulfur compound concentrations from similar locations within wastewater treatment plants (WWTPs). Median concentrations at primary clarifier outlets were 3.5 mg S/L for total sulfide, 38 μg S/L for MeSH, 66 μg S/L for DMS, 22 μg S/L for DMDS, and <20 μg S/L for DMTS. Median concentrations at the fronts of ASBs were 2.9 mg S/L for total sulfide, 60 μg S/L for MeSH, 68 μg S/L for DMS, 68 μg S/L for DMDS, and <20 μg S/L for DMTS. Median concentrations from midpoints of treatment were 0.29 mg S/L for total sulfide and <20 μg S/L for ORSCs. In final effluents, sample medians were <20 μg S/L for all target analytes.

KEYWORDS

analytical methods, dimethyl disulfide, dimethyl sulfide, effluent, methyl mercaptan, reduced sulfur compounds, total sulfide, wastewater

RELATED NCASI PUBLICATIONS

Special Report No. 05-01 (June 2005). *Evaluation of sulfide ion detector tubes for determining sulfide concentrations in pulp and paper mill wastewaters.*

NPRI Handbook 03.A.001 (March 2004). *Hydrogen sulphide – Pulp and paper.*

Methods Manual 02.B.011 (December 2002). *Method RSC-02.01: Reduced sulfur compounds by direct injection GC/PFPD*.

Technical Bulletin No. 849 (August 2002). *Compilation of speciated reduced sulfur compound and total reduced sulfur emissions data for kraft mill sources*.

DÉVELOPPEMENT ET APPLICATION D'UNE MÉTHODE POUR MESURER LES COMPOSÉS DE SOUFRE RÉDUIT DANS LES EAUX USÉES DES FABRIQUES DE PÂTES ET PAPIERS

BULLETIN TECHNIQUE N^{O} 933
JUIN 2007

RÉSUMÉ

Les auteurs du rapport ont initié cette recherche afin de développer et d'appliquer une méthode pour déterminer les sulfures totaux (inorganiques), le méthyle mercaptan (MeSH), le sulfure de diméthyle (SDM), le disulfure de diméthyle (DSDM) et le trisulfure de diméthyle (TSDM) dans les échantillons d'eau usée de fabriques de pâtes et papiers. Dans la méthode RSC-02.02 de NCASI, la préservation des échantillons et l'ajustement du pH préalable aux injections sont séparés pour déterminer les sulfures totaux (acétate de zinc à pH 10) et les composés organiques de soufre réduit (COSR) (acide ascorbique à pH 2,5). Tous les échantillons sont acidifiés (pH <2,5) préalablement à l'injection directe dans un chromatographe en phase gazeuse muni d'un détecteur photométrique à flamme pulsée (pulsed flame *photometric detector, PFPD)*. Les vérifications quotidiennes de calibration ont donné des pourcentages de récupération moyens de 106% pour les sulfures totaux (n=94) et des pourcentages de récupération moyens s'échelonnant de 95 à 102% pour les COSR (n=42). Les blancs de méthode ne contenaient pas les substances ciblées pour analyse. Les auteurs ont évalué la précision et l'exactitude en réalisant des expériences sur la récupération des étalons analogues (*surrogate*) et des matrices enrichies ainsi que des analyses des réplicas. Les pourcentages de récupération des étalons analogues pour les sulfures totaux, le MeSH, SDM, DSDM et TSDM dans plus de 1077 échantillons s'échelonnaient entre 73 et 131%, avec un pourcentage de récupération moyen de 106%. Les moyennes de récupération pour les matrices enrichies étaient de 93, 106, 102, 112 et 96% pour les sulfures totaux, le MeSH, le SDM, le DSDM et le TSDM, respectivement. La précision des résultats, représentée par le regroupement des différences relatives des pourcentages (relative percent differences, RPDs) pour les analyses des duplicatas, s'échelonnait de 2,1 à 5,3%. Les études de stabilité lors de l'entreposage indiquaient que la stabilité des échantillons se prolongeait jusqu'à 14 jours[1]. Le pH d'injection a produit un impact significatif sur la récupération des sulfures totaux. Le pH de 2,5 a produit la récupération la plus élevée (96%). Les études visant à évaluer la variabilité de la matrice et de l'échantillonnage a produit des écarts types relatifs moyens de 38,9% pour les sulfures totaux, 29,8% pour le MeSH, 20,6% pour le SDM, 34,2% pour le DSDM et 41,0% pour le TSDM. Ces valeurs se trouvent bien au dessus de la variabilité de ~5% observée pour la méthode analytique.

Les investigations réalisées en combinaison avec les études de réduction des odeurs dans ces fabriques ont produit un large intervalle de résultats pour les concentrations de composés de soufre réduit et ce, pour des endroits similaires dans les systèmes de traitement des eaux usées (STEU). Les concentrations médianes aux sorties de clarificateurs primaires étaient de 3,5 mg S/L pour les sulfures totaux, 38 μg S/L pour le MeSH, 66 μg S/L pour le SDM, 22 μg S/L pour le DSDM et <20 μg S/L pour le TSDM. Les concentrations médianes à l'avant des BSA (bassins de stabilisation aérés) étaient de 2,9 mg S/L pour les sulfures totaux, 60 μg S/L pour le MeSH, 68 μg S/L pour le SDM, 68 μg S/L pour le DSDM et <20 μg S/L pour le TSDM. Les concentrations médianes d'échantillons prélevés à mi chemin dans les systèmes de traitement étaient de 0,29 mg S/L pour les sulfures totaux et <20 μg S/L pour les COSR. Dans les effluents finaux, les médianes des échantillons étaient de <20 μg S/L pour toutes les substances ciblées pour analyse.

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[1] Il s'agit du délai de conservation (N.d.T.)

MOTS CLÉS

Méthodes analytiques, disulfure de diméthyle, sulfure de diméthyle, effluent, méthyle mercaptan, composés de soufre réduit, sulfures totaux, eau usée

AUTRES PUBLICATIONS DE NCASI DANS CE DOMAINE

Rapport spécial n° 05-01 (juin 2005). *Evaluation of sulfide ion detector tubes for determining sulfide concentrations in pulp and paper mill wastewaters*.

NPRI Handbook 03.A.001 (mars 2004). *Hydrogen sulphide – Pulp and paper*.

Methods Manual 02.B.011 (décembre 2002). *Method RSC-02.01: Reduced sulfur compounds by direct injection GC/PFPD*.

Bulletin technique n° 849 (août 2002). *Compilation of speciated reduced sulfur compound and total reduced sulfur emissions data for kraft mill sources*.

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DEVELOPMENT AND APPLICATION OF A METHOD FOR MEASURING REDUCED SULFUR COMPOUNDS IN PULP AND PAPER MILL WASTEWATERS

1.0 INTRODUCTION

Odor is an ongoing issue for many pulp and paper facilities and an important part of many mill environmental management programs. Anti-nuisance laws and permit requirements that address fugitive odors are becoming more common and pulp and paper mills are often under pressure to control odors. Historically, most of the attention in the pulp and paper industry has been on kraft mills and the reduced sulfur compounds (RSCs) generated during kraft pulping and regulated as total reduced sulfur (TRS). TRS includes hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS). As process emissions of RSCs have been reduced, emissions of RSCs from wastewater treatment plants (WWTPs) have become an issue at many mills. To better understand the factors that influence releases of RSCs to the air, a simple, accurate, and sensitive method to measure RSCs in wastewater samples was developed (Gholson, Hoy, and Chambers 2002). Development of additional methods to assess odorous compounds in air and water (Cook and Hoy 2003) and studies to develop effective models for predicting air emissions are ongoing. NCASI has developed, evaluated, and applied analytical methods for measuring RSCs, volatile fatty acids, and other odorous compounds at WWTPs. These research efforts indicate that RSCs, specifically total sulfide, MeSH, DMS, DMDS, and dimethyl trisulfide (DMTS), frequently cause odors associated with WWTP operations. Accurate, reproducible measurement of sulfide and other reduced sulfur species in pulp and paper mill wastewaters is of considerable importance to the industry.

NCASI developed Method RSC-02.01, a gas chromatography (GC) pulsed flame photometric detector (PFPD) method for the analysis of RSCs in aqueous samples at concentrations of 20 to 1000 µg S/L (Gholson, Hoy, and Chambers 2002). Since its development, the method has been revised and used to measure RSCs in a variety of aqueous phase samples from many WWTPs. This report discusses the development and application of NCASI RSC-02.02, including quality assurance and control data, WWTP sample analysis, sample preservation studies, and efforts to adapt the method for determination of freely available sulfide.

1.1 Analytical Methods for Reduced Sulfur Compounds in Aqueous Samples

The chemical nature of RSCs makes them a challenge to measure. The main difficulties encountered during determination of RSCs have been reviewed (Wardencki 1998) and can be summarized as the need to detect highly reactive compounds at low concentrations. Determination of RSCs is challenging due to their absorptive, adsorptive, photo reactive, volatile, biologically active, and oxidative properties that can lead to losses during sample collection, storage, and analysis. For example, aerobic biological activity can remove sulfide, while anaerobic activity can generate sulfide. The polar nature of these compounds (especially sulfide and MeSH) makes them attractive to active sites common to surfaces (e.g., metal) encountered during sampling and analysis.

Sulfide determinations are, by necessity, method defined because sulfide assumes various forms depending on sample pH, temperature, ionic strength, and the biological constituents present. Table 1.1 presents a glossary of terms that define various forms. Total sulfide is defined here as dissolved hydrogen sulfide plus hydrosulfide ion plus acid soluble metallic sulfide and sulfide weakly associated with organics in the sample. S^{2-} is considered to be present in negligible amounts unless sample pH is above 14. To obtain a measurement of dissolved sulfide, samples undergo either flocculation or filtration prior to analysis. Dissolved sulfide includes H_2S (un-ionized sulfide) and HS^- (ionized sulfide). Some methods, for example Hach Method 1851 (Hach Company 2003), recommend sample centrifugation and analysis of the supernatant for determination of dissolved sulfide. Un-ionized H_2S has been calculated using the dissolved sulfide concentration, sample pH, and practical ionization constant for H_2S. Freely available sulfide varies from dissolved sulfide in that it also includes sulfides which may dissociate from organics readily in the matrix and therefore be freely available as sulfide. The acid soluble metallic sulfides are any of the metal sulfides that are soluble in acid. For example, iron sulfide (FeS) is commonly present in wastewaters. The organic reduced sulfides include any of the various organic compounds that contain sulfide, and the organic reduced sulfur compounds (ORSCs) commonly detected in wastewaters include MeSH, DMS, DMDS, and DMTS. Sulfides in all the forms listed in Table 1.1 may be anticipated in pulp and paper mill wastewaters.

Table 1.1 Glossary of Terms for Sulfide Compounds

Parameter	Description
Total sulfide	Dissolved H_2S and HS^-, acid-soluble metallic sulfides, and sulfide weakly associated with organics
Dissolved sulfide	Sulfide remaining after suspended solids have been removed by flocculation and settling ($HS^- + H_2S$)
HS^-	Water soluble ionized hydrogen sulfide
H_2S	Un-ionized hydrogen sulfide, calculated from dissolved sulfide, sample pH, and practical ionization constant of H_2S
Freely available sulfide	Dissolved sulfide plus sulfide weakly associated with organics
Acid-soluble metallic sulfides	Metal sulfides soluble in acid solution
Organic reduced sulfide compounds	Organic compounds containing sulfur, commonly MeSH, DMS, DMDS, DMTS

The preservation technique recommended in *Standard Methods* and in EPA Method 376.1 for sulfide involves addition of a basic zinc acetate solution (APHA 2005; USEPA 1978). These methods analyze samples after acidification and therefore assess total sulfide. NCASI RSC-02.01 and RSC-02.02 utilize a similar preservation and analysis approach, also providing a measurement of total sulfide concentration.

The majority of methods utilized for the detection of organic sulfur compounds (MeSH, DMS, DMDS, and DMTS) use gas chromatography with a sulfur selective detector. These methods differ mainly in the approach used to isolate and introduce the compounds to the GC. GC methods used to analyze RSCs in aqueous streams include solvent extraction (Andersson and Berfstrom 1969; Prakash and Murry 1976), sparging (Rayner, Murry, and Williams 1967; Caron and Kramer 1989; Saunders and Larson 1996; O'Conner and Genest 1997), headspace (Chai, Liu, and Zhu 2000; NCASI 2000), and direct injection (Bérubé, Parkinson, and Hall 1999). Solvent extraction methods suffer from poor sensitivity because a concentration step cannot be performed due to the volatility of RSCs. Multiple solvents may be needed to effectively extract all the compounds, and the solvents may interfere with GC analysis. Sparging methods are complicated, multi-step, time- and labor-intensive procedures. They require special glassware and gas handling equipment with gas phase calibrations. Headspace methods have been used for analysis of RSCs in black liquor (Chai, Dhasmana, and Zhu 1998) and are currently under investigation by NCASI for application to wastewater samples.

NCASI used the direct aqueous injection approach for determination of total sulfide and ORSCs described by Bérubé, Parkinson, and Hall (1999) as the basis for development of Method RSC-02.01

(Gholson, Hoy, and Chambers 2002). Injection volume was minimized so less potential interferents entered the column, a cool injection port was applied to minimize the amount of water entering the column, and the injection sleeve was packed with glass wool to prevent nonvolatile components from getting onto the column. A sensitive detector, the pulse flame photometric detector (PFPD), was required to achieve the desired detection limits using a small injection volume (Cheskis, Atar, and Amirav 1993). The PFPD eliminated the flame-out problem associated with direct aqueous injections, as the flame is reignited three times per second. Because of the pulsed flame, the sample signal can be delayed to minimize the contribution of carbon to the sulfur signal, resulting in both better selectivity and a higher signal to noise ratio. The PFPD yields a sensitivity of 1 pg S for DMS, an order of magnitude increase in sensitivity over a flame photometric detector. A capillary column was used with the PFPD, increasing sensitivity by decreasing peak width. NCASI has analyzed a variety of samples from WWTPs since the method's initial development and evaluation, and in the process has revised the method to enhance its performance.

2.0 REVISION OF NCASI METHOD RSC-02.01 (RSC-02.02)

This section provides information regarding the revision of NCASI Method RSC-02.01 and a summary of the quality assurance and quality control data acquired during the past several years for the original method (NCASI 2002; Gholson, Hoy, and Chambers 2002) and its recent revision, RSC-02.02 (Appendix A). Major revisions include a section describing the forms of sulfide assessed using the method; sections on precautions required to deactivate metal surfaces and clean the injection port; procedures to address excessive peak broadening; changes to the lower calibration limit of the method (increased from ~10 to ~20 µg S/L); procedures to verify the concentration of the sulfide standard; additional instructions regarding preparation of the zinc acetate preservation solution; surrogate recovery procedures and criteria; and revisions to the quality control criteria for calibration curves, daily calibration verifications, matrix spike recoveries, and duplicate precision.

2.1 Method Summary

Method RSC-02.02 is used to determine concentrations of total sulfide, MeSH, DMS, DMDS, and DMTS in wastewaters from pulp and paper mills. RSCs are measured by direct aqueous injection GC/PFPD. The concentration of sulfide measured using this method represents the total amount of sulfide in the sample that is volatile at pH 2.5. It is believed that this includes all freely dissolved sulfide plus sulfide weakly associated with either dissolved organic matter or certain transition metals. If the native pH of a sample is greater than 2.5, the actual sulfide concentration in solution might be less than the concentration measured by this method.

The method utilizes separate injections for total sulfide and ORSCs. This is required in order to preserve the compounds effectively. Samples collected for total sulfide analyses are preserved by the addition of 39.8 mg of zinc acetate dehydrate and ~0.0005 equivalents of NaOH per 40 mL (VOA vial) of sample (pH >10). Preservation of MeSH, DMS, DMDS, and DMTS involves addition of 120 mg of ascorbic acid and adjustment to pH <2.5 using a 1:3 phosphoric acid solution. Prior to analysis a portion of the sample is transferred to an autosampler vial in the laboratory, acidified to pH <2.5 (total sulfide), and spiked with internal standard (thiophene) and a surrogate recovery standard (thioanisole). Samples are analyzed via GC/PFPD by injecting a 1 µL sample in split mode onto a GC equipped with a Crossbond® 6% cyanopropylphenyl/ 94% dimethyl polysiloxane fused silica capillary column (J&W DB-624, 30 m x 0.25 mm i.d. with 1.4 µm film). The injection port is cleaned and the injection port liner is changed prior to each sample set to avoid problems associated with buildup of contaminants in the system, especially ones that generate a sulfur dioxide artifact peak that can interfere with quantitation of methyl mercaptan. RSCs are identified by comparing their relative retention times with the relative retention times of the internal standard using a multipoint calibration covering the range from ~20 to 1000 µg S/L. Samples with concentrations above the highest calibration point are diluted prior to analysis. The criterion for acceptable linearity is a mean absolute percent error (MAPE) for the curve of ≤20%. The results of the calibration curve for each compound are either fitted to a quadratic equation or described by an average relative response factor, depending on which meets the MAPE criterion.

The quality of the data generated using this method is assured by calibration checks, daily blank assessments, sample duplicate analyses, and matrix spiked samples with each set of samples analyzed on a given day. In addition, surrogate spike recoveries are determined within each matrix tested. The resolution of the separation of DMS and CS_2 is determined periodically to assure that chromatography is consistent.

2.2 Mill Wastewater Treatment Plants Sampled

A variety of samples collected from WWTPs were utilized during validation and application of this method. Table 2.1 shows information regarding mill furnish, process type, condensate management, and WWTP type.

Table 2.1 Mill Wastewater Treatment Plants Sampled

Mill Code	Furnish[a]	Process Type[b]	Condensate Management	WWTP[c]
A	SW	kraft	hard piping	ASB
B	SW, deink	GW, TMP, recycle	NA	AS/ASB
C	SW, OCC	kraft	hard piping	ASB
D	SW	kraft, dissolving kraft	hard piping	ASB
E	SW, OCC	kraft, recycle	steam stripping	ASB
F	SW/HW, OCC	kraft, recycle	steam stripping	ASB
G	SW, HW	kraft	steam stripping	ASB
H	SW, HW, deink	kraft, recycle	steam stripping/hard piping	ASB/AS
I	SW	kraft	steam stripping/hard piping	ASB
J	HW, SW, OCC	kraft, recycle, NSSC	hard piping	ASB
K	HW, SW	kraft	hard piping	ASB
L	SW, deink	TMP, recycle	NA	AS
M	HW, OCC	NSSC, recycle	hard piping	ASB/AS
N	HW/SW	kraft	hard piping	AS
O	SW	kraft	steam stripping	ASB
P	SW	kraft	steam stripping	ASB
Q	SW/HW, OCC	kraft, recycle	steam stripping	ASB
R	SW/HW	kraft	steam stripping	ASB
S	SW/HW	kraft	steam stripping	ASB
T	SW/HW	kraft	hard piping	ASB
U	SW/HW	kraft	NA	ASB
V	SW/HW	kraft	steam stripping	AS/ASB

[a] HW = hardwood; SW = softwood; OCC = old corrugated containers
[b] GW = groundwood; TMP = thermo-mechanical pulping; NSSC = neutral sulfite semi-chemical
[c] AS = activated sludge; ASB = aeration stabilization basin
NA = not applicable

3.0 METHOD VALIDATION

Preparation and preservation of the standards utilized in this method have proven to be critical steps. During initial method development, primary standards of MeSH, DMS, DMDS, and DMTS were gravimetrically prepared from neat compounds to a concentration of approximately 1000 µg S/mL in methanol. The total sulfide standard was prepared from sodium sulfide nonahydrate in purged deionized water. Because the PFPD has an equal molar response for sulfur, standards were prepared to have equal quantities of sulfur. Primary stocks were utilized to prepare a five-point calibration curve at concentrations of ~20, 50, 200, 500, and 1000 µg S/L. An independent check standard containing MeSH, DMS, and DMDS was obtained from Crescent Chemicals. The recoveries of an aliquot of this standard diluted to a concentration of 500 µg/mL and analyzed four times over a six-day period provide an indication of the validity of the calibration stocks. The analyses of the independent check standards yielded average recoveries and RSDs, respectively, of 85.5% and 11.1% for MeSH, 119% and 6.9% for DMS, and 112% and 10.7% for DMDS, verifying that calibration standards and independent check standards were in good agreement for these compounds. Confirmation of the sulfide standard is more complex due to the instability of the standards.

3.1 Sulfide Standard Concentration

Standards of unpreserved sulfide solutions (500 µg S/L) were found to be unstable, losing over 20% after 24 hours, depending on the handling of the stock solution (Figure 3.1).

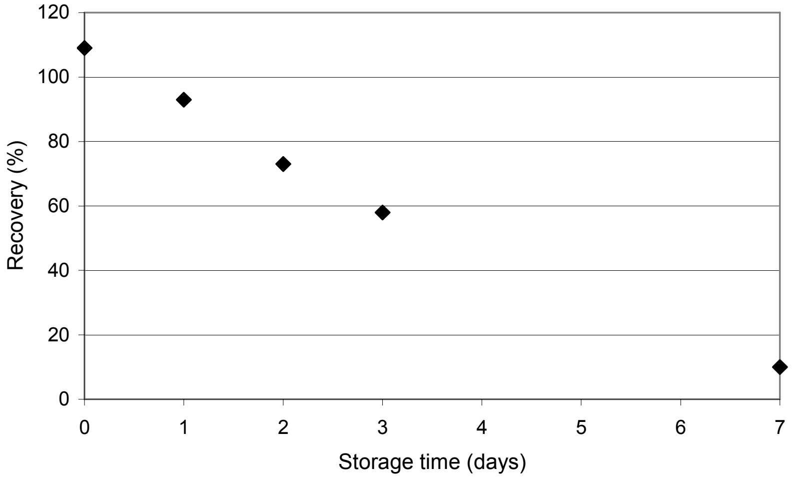


Figure 3.1 Unpreserved Sodium Sulfide Standard Recovery over Storage Time

To increase stability of the sulfide standard, it was prepared at a concentration of 500 µg S/mL in a solution of 0.03 molar zinc acetate adjusted to pH 10 with 1N sodium hydroxide solution. This standard was a dispersed colloid of a zinc bisulfide complex which has been found to be stable to oxidation over a period of several months when stored at 4°C. When using the preserved stock standard, care must be taken to allow it to come to room temperature and to mix it thoroughly prior to removing an aliquot for use. Because this solution is a colloidal suspension, verifications of reproducibility of the standard concentration were performed by analyzing three replicates from the vial. Reproducibility and stability were also verified for each set of samples by conducting a calibration verification and calculating the percent recovery. The sulfide standard utilized in the laboratory was periodically verified for concentration accuracy using an independent laboratory. Verification included confirmation of the standard concentration using three different analytical techniques: EPA Method 376.1, sulfide by titration (USEPA 1978); EPA Method 376.2, sulfide by colorimetry (methylene blue) (USEPA 1997); and peroxide oxidation followed by EPA Method 300 (USEPA 1993). Oxidation converts the sulfide in the standard to sulfate, which is assessed by ion chromatography. Results obtained for the sulfide standard verifications are summarized in Table 3.1. They indicate good agreement with the gravimetrically calculated concentration of the total sulfide standard.

Table 3.1 Confirmation of Total Sulfide Standard Concentration Using Three Independent Methods

Gravimetric (mg S/L)	EPA Method 376.1 (mg S/L)	EPA Method 376.2 (mg S/L)	EPA Method 300 (mg S/L)	Average (mg S/L)
197.9	193	204	188	195
149.1	156	158	136	150

3.2 Instrument Calibration

To establish the calibration function for the method, a multipoint internal standard calibration covering the operating range of the method (~20 to 1000 µg S/L) was performed (Appendix A, Section 10.2). The best quadratic fit was assessed by plotting the response ratio of each compound versus the ratio of the standard concentration versus the internal standard. Curve-fitting software (Agilent Chemstation) was utilized to find the best quadratic fit for the data. Alternatively, the average response factors for each compound were calculated and evaluated to determine which approach best met the calibration criteria based on a MAPE of <20% for each compound. The MAPE calculation is shown in Equation 1. This approach is utilized to evaluate the fit between model predictions and measured values. In this case the prediction determined using a quadratic fit curve was compared to the measured concentrations for the target compounds determined at each concentration level of a five-point calibration curve. The MAPE data for eighteen calibration curves analyzed over a period of five years are summarized in Table 3.2. Outliers were determined using a Grubbs test, and one value for total sulfide was removed.

$$MAPE = \frac{\sum \left| \frac{C_{cal} - C}{C_{cal}} \right| * 100}{n} \qquad \text{(Equation 1)}$$

where: MAPE is the mean absolute percent error
C_{cal} is the concentration in the calibration standard
C is the concentration measured for the calibration level
n is the number of calibration levels

Table 3.2 Mean Absolute Percent Error (MAPE) Calculations for Calibration Curves

Compound	MAPE Average	Standard Deviation	Range of MAPEs	n
Total sulfide	11.4	5.42	3.20 - 25.5	17
MeSH	10.0	5.36	4.02 - 21.0	18
DMS	10.6	4.50	3.30 - 19.2	18
DMDS	9.78	4.35	3.40 - 16.8	18
DMTS	9.85	4.28	2.20 - 16.6	18

These data indicate good agreement between the concentrations determined using a quadratic fit equation for the calibration curve and the gravimetrically determined concentrations of the standards.

3.3 Ongoing Calibration Verification

A calibration verification or ongoing recovery standard was assessed daily with each set of samples analyzed (n <20). This check was conducted at a concentration of ~200 µg S/L by spiking 1.8 mL of purged Barnstead deionized water with the target analytes and calculating the recovery of the spike following acidification of the samples with 1:3 phosphoric acid and direct injection on the GC/PFPD under the conditions described in Appendix A, Section 11.0.

Results of the calibration verifications performed during this study are summarized in Table 3.3. The data were examined for the presence of outliers using a Grubbs test and none were found. Table 3.3 contains the average percent recovery determined for 94 calibration verifications conducted in conjunction with total sulfide analyses and 42 calibration verifications conducted in conjunction with ORSC analyses. The pooled relative standard deviation (RSD) of the recoveries and the range of recoveries observed are provided. Average calibration verification recoveries ranged from 95 to 111% across all target analytes. Pooled RSDs for the recoveries ranged from 8.3 to 11.5%. Calibration verification criteria for the method were established from these data using the standard EPA calculations of warning and action limits (IDQTF 2005). Warning limits are the average recovery ±2 times the SD of recoveries, and action limits are the average recovery ±3 times the SD of recoveries. Warning limits for the target analytes ranged from 74.7 to 129%.

Table 3.3 Daily Calibration Verification Summary for NCASI Method RSC-02.02

Parameter	Total Sulfide	MeSH	DMS	DMDS	DMTS
Average % recovery	106	95	100	111	102
Pooled RSD of recoveries, %	11.2	10.6	10.5	8.3	11.5
Range of % recoveries	81.0 - 130	72.0 - 121	83.0 - 119	94.0 - 131	85.0 - 134
Warning limits	81.0 - 129	74.7 - 115	79.3 - 122	92.5 - 129	78.5 - 126
Action limits	70.1 - 141	64.7 - 125	68.7 - 132	83.3 - 138	66.7 - 137
n	94	42	42	42	42

3.4 Method Detection Limit

The method detection limit (MDL) was calculated using the EPA approach described in 40 CFR Part 136 Appendix B (Federal Register 1984). A sample of final effluent from an unbleached kraft mill was stored without preservation and used as a matrix for the MDL experiment after the sulfide concentration had dropped to less than 50 μg S/L. The sample was fortified with the ORSCs at the concentrations listed in Table 3.4. The sample was analyzed ten times, with the results shown in Table 3.4 (experiment 1). Except for total sulfide, the MDLs obtained were below the calibration range and an analysis of a standard at these levels failed to provide peaks greater than three times the baseline noise. The experiment was repeated to confirm these findings and yielded similar results (experiment 2). This illustrates the potential for the EPA MDL method to underpredict the concentration at which analytes can be detected. Until a better estimate of the MDL can be made, the lower level of the calibration curve is a safe value to use as a detection limit.

Table 3.4 Method Detection Limit Study Findings

Compound	Mean Concentration (μg S/L)[a]	RSD (%)	Experiment 1 MDL (μg S/L)	Experiment 2 MDL (μg S/L)
Total sulfide	52.2	21.8	32.0	34.0
MeSH	23.4	10.0	6.6	9.9
DMS	14.7	12.5	5.2	10.1
DMDS	22.9	12.1	5.9	5.6
DMTS	22.5	5.8	3.8	5.0

[a] results for n = 10 replicates

3.5 Analytical Method Blanks

A blank was analyzed with each sample set to assess background levels of the target analytes in purged Barnstead deionized water, the spiking solutions of internal standard and surrogate, and background concentrations that may be released from the GC system upon acidification. Blanks were prepared by placing a 1.8 mL aliquot of purged Barnstead deionized water in an autosampler vial and spiking it with the appropriate amount of internal standard and surrogate compound. The solution was acidified (pH <2.5) by addition of 15 to 20 μL of 1:3 phosphoric acid and was injected onto the GC/PFPD. None of the target analytes were detected in the analytical method blanks during determination of total sulfide (n=94) or ORSCs (n=42).

3.6 Precision and Accuracy

3.6.1 *Surrogate Recovery*

Each sample was spiked with a surrogate (thioanisole), and its recovery was determined. These data provide an assessment of the method's accuracy in each sample matrix measured. A summary of the surrogate recovery data is provided in Table 3.5.

Table 3.5 Surrogate Recovery Summary

Parameter	Thioanisole Results
Average % recovery	106
Pooled RSD of recoveries	6.8
Range of % recoveries	73.0 - 131
Warning limits	92.0 - 121
Action limits	85.0 - 128
n	1077

To evaluate the impact of sample matrix on surrogate recovery, the data were examined by plotting the recoveries obtained in samples collected from primary clarifiers, the front portions of aerated stabilization basins (ASBs), midpoints of ASBs, final effluents, and hard piped condensates. An additional category called "other" included all samples collected at sites such as process sewers and belt press filtrates. Surrogate recoveries from total sulfide and ORSCs are summarized in Figures 3.2 and 3.3, respectively, in the form of box-and-whisker plots. Each plot provides a central box that covers the middle 50% of the data; the sides of the box are the lower and upper quartiles, and the horizontal line drawn through the box is the median. The whiskers extend to the lower and upper values of the data (range), and the single point (+) is the mean. Values that fall beyond the whiskers but within three interquartile ranges are suspected outliers and are plotted as small boxes. A Grubbs test was utilized to determine any outliers (n=2), and they were removed from the data set prior to graphing.

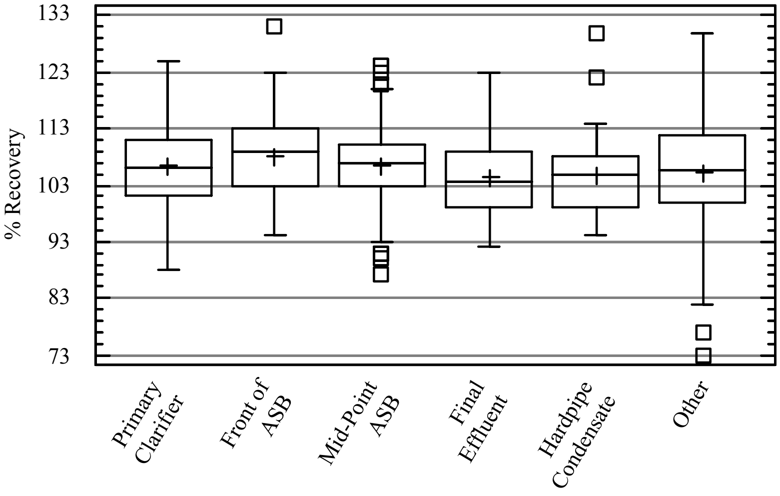


Figure 3.2 Surrogate Recoveries of Total Sulfide in Wastewater Treatment Plant Matrices

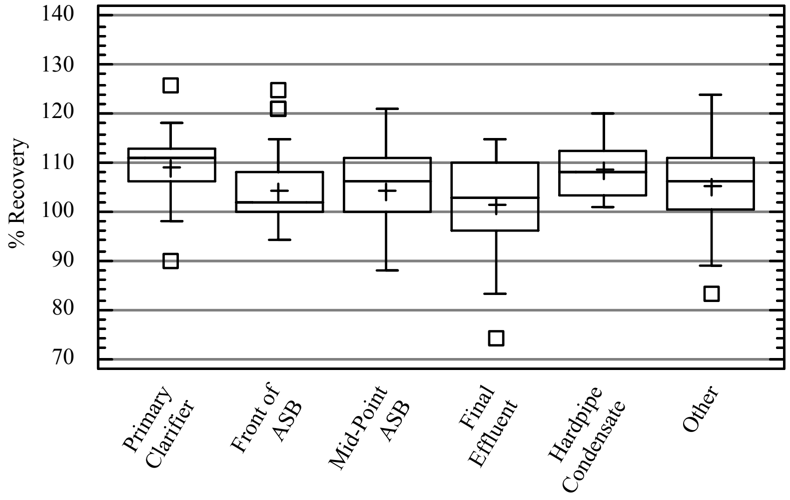


Figure 3.3 Surrogate Recoveries of Organic Reduced Sulfur Compounds in Wastewater Treatment Plant Matrices

3.6.2 *Accuracy in a Matrix: Matrix Spike Recovery*

Accuracy was assessed with each sample set analyzed by fortifying a sample with the target analytes at concentrations one to five times the native concentration. Recoveries of the spiked target compounds were calculated for each experiment and a summary of the data is provided in Table 3.6. A Grubbs test was utilized to determine any outliers (n=1), and they were removed from the data set prior to summarizing the data and performing subsequent calculations. Average matrix spike recoveries ranged from 93 to 112%, with a pooled relative standard deviation ranging from 11.7 to 24.1% depending on the target compound. These data were utilized to calculate matrix spike recovery criteria for Method RSC-02.02 by calculating the warning and action limits listed in the table (IDQTF 2005).

Table 3.6 Matrix Spike Recovery Summary

Parameter	Total Sulfide	MeSH	DMS	DMDS	DMTS
Average % recovery	93	106	102	112	96
Pooled RSD of recoveries	20.7	20.0	11.7	16.5	24.1
Range of % recoveries	43.0 - 124	38.0 - 172	77.9 - 131	75.2 - 158	44.7 - 143
Warning limits, %	54.7 - 132	74.7 - 115	78.3 - 126	75.1 - 149	50.1 - 143
Action limits, %	35.4 - 151	42.1 - 169	66.3 - 138	56.5 - 168	26.8 - 166
n	70	33	34	34	34

3.6.3 *Precision in a Matrix: Duplicate Analyses*

Method precision was evaluated with each sample set by analyzing a sample in duplicate and determining the relative percent difference (RPD) between the sample and duplicate concentrations. Precision data were assessed by pooling the RPDs observed between duplicate sets. Table 3.7 is a summary of these data as well as the calculated upper warning and action limits for method precision. The average pooled RPDs ranged from 2.1 to 5.3%, indicating good precision for the method. The highest variability was observed for total sulfide and methyl mercaptan, as anticipated, as these compounds are the most unstable and reactive of the target compounds.

Table 3.7 Precision in Wastewater Treatment Plant Matrices

Parameter	Total Sulfide	MeSH	DMS	DMDS	DMTS
Average pooled RPD%	5.3	5.2	2.8	2.1	3.9
Range of RPDs%	0.2 - 17	0.6 - 20	0.2 - 6.0	0.1 - 8.0	<0.02 - 11
Warning limits, %	13.1	16.3	6.6	6.3	9.8
Action limits, %	16.9	21.9	8.5	8.4	12.8
n[a]	69	20	17	17	14

[a] n is dependent on compounds detected in native samples utilized during these assessments

3.7 Sample Preservation and Stability

3.7.1 *Initial Experiments to Assess the Stability of Reduced Sulfur Compounds using Various Preservation Techniques*

Due to the reactivity of RSCs, which can react with surfaces, volatilize, oxidize, or be biochemically transformed, sample stability is often one of the major problems encountered. Gholson, Hoy, and Chambers (2002) conducted studies to address surface reactivity by deactivating sampling glassware with acid and trimethylsilozanes, collecting samples using standard volatile organic methods (no-splash sampling, zero headspace storage, and refrigeration), adjusting sample pH to <2.5 or >10 to control bioreactivity, and using antioxidants to control oxidation. Experiments to control oxidation included an investigation of the use of sodium thiosulfate, ascorbic acid, sodium bisulfite, glutathione, and pyrogallol. Results indicated that sodium thiosulfate and sodium bisulfite were incompatible with the analytical method, and chromatographic interferences were encountered with glutathione. Ascorbic acid was found to be more effective than pyrogallol in preserving MeSH and sulfide. These findings indicated that reducing pH using phosphoric acid and ascorbic acid improved stability for MeSH, DMS, DMDS, and DMTS in most matrices, but stability of sulfide was still lacking in several matrices. Additional studies were conducted to improve the stability of total sulfide using a zinc acetate solution to form a stable complex of zinc sulfide.

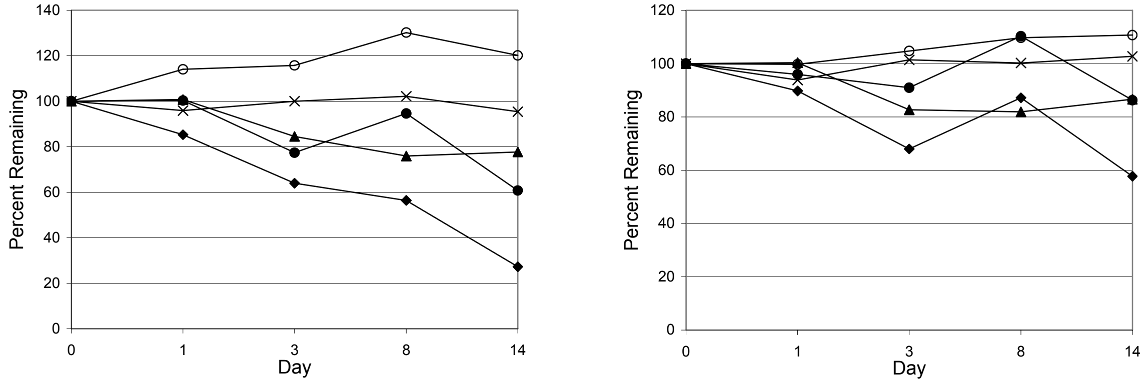
3.7.2 *Sample Storage Stability*

Experiments were conducted to investigate the storage stability of total sulfide in effluent samples from Mills A and E (a bleached and an unbleached kraft mill, respectively) when preserved using a solution of ascorbic acid and zinc acetate at pH 10 and at pH 2.5 over a period of 14 days. Aliquots of the various samples were analyzed in duplicate or triplicate on each day assessed (Appendix A, Section 11, acidification and direct injection on the GC/PFPD). The concentrations remaining in each aliquot on each day of testing were calculated and are shown in Figure 3.4.

These results indicate that ORSCs were stable (>~80% remaining) in solutions of ascorbic acid and zinc acetate at pH 2.5 out to 14 days in Mill E effluent and out to 8 days in Mill A effluent. The concentrations of sulfide remaining in solution dropped off over three days under similar conditions. The findings at pH 10 were more variable for sulfide, but the general trend for the ORSCs was decreasing after Day 3 for all but DMDS. This was probably due to oxidation of MeSH to DMDS in the matrix; thus as MeSH decreased DMDS increased.

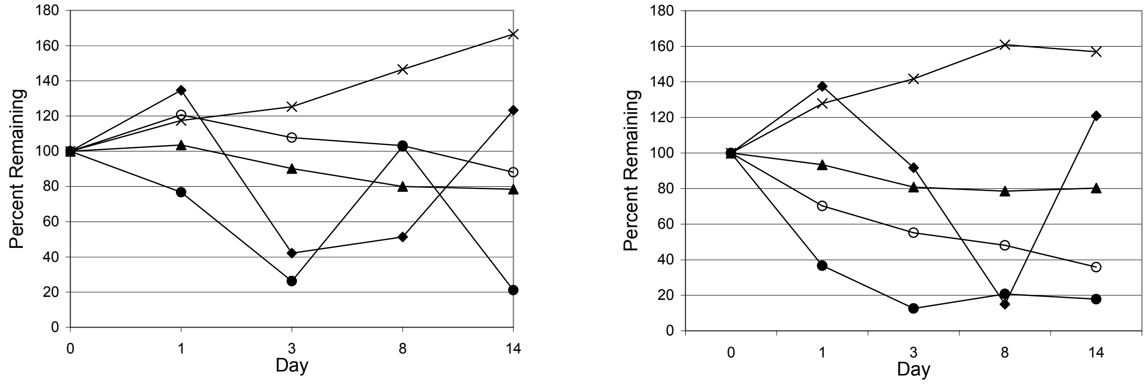
To assess the impact of ascorbic acid versus zinc acetate the experiment was repeated using solutions of zinc acetate at pH 10 and 2.5 without the addition of ascorbic acid. Results are illustrated in Figure 3.5. When the percent of sulfide remaining dropped below 60%, one more experiment was conducted to confirm this trend, and then further analyses were discontinued. At pH 2.5 this occurred between Day 0 and Day 1 in the effluents from Mills A and E, although in Mill E effluent the ORSCs appeared stable so further analyses were conducted out to Day 7. At pH 10 it was apparent after Day 1 that MeSH was not stabilized, but sulfide remained stable out to 16 days.

As illustrated in Figure 3.4, ascorbic acid at pH 2.5 stabilized ORSCs but not sulfide. Figure 3.5 illustrates stabilization of sulfide at pH 10 with zinc acetate, while methyl mercaptan is lost under those conditions. Based on these experiments, two preservation schemes were adopted for the NCASI RSC method: preservation at pH 2.5 with the addition of ascorbic acid to act as an antioxidant for stabilization of the ORSCs, and preservation at pH 10 with zinc acetate for stabilization of total sulfide. The effectiveness of this approach was further substantiated by the stability observed for the sulfide standard in zinc acetate at pH 10, as discussed in Section 3.1.



Mill A effluent, pH 2.5 with ascorbic acid and zinc acetate

Mill E effluent, pH 2.5 with ascorbic acid and zinc acetate

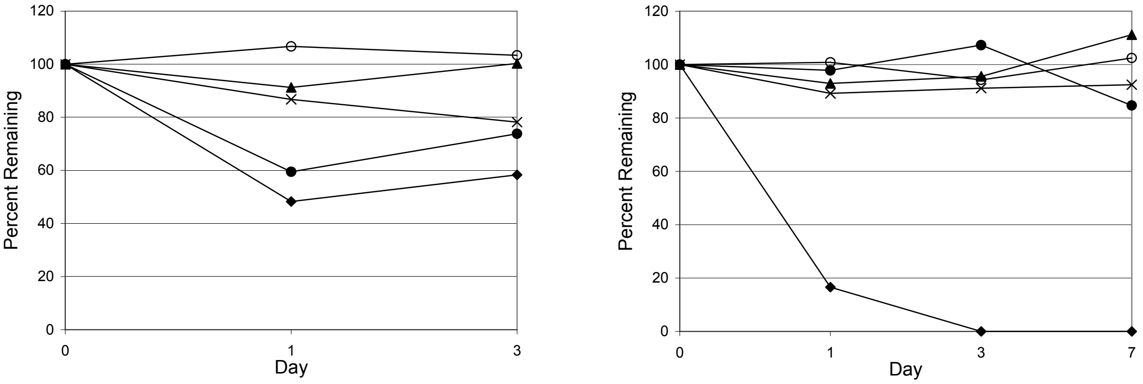


Mill A effluent, pH 10 with ascorbic acid and zinc acetate

Mill E effluent, pH 10 with ascorbic acid and zinc acetate

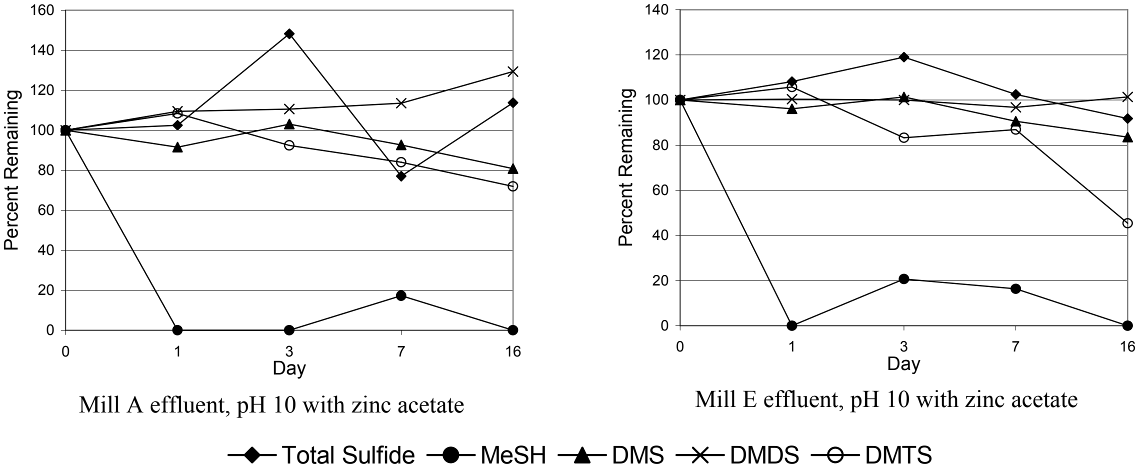
—◆— Total Sulfide —●— MeSH —▲— DMS —×— DMDS —○— DMTS

Figure 3.4 Reduced Sulfur Compound Percent Remaining at pH 2.5 and pH 10 Preservation with Zinc Acetate and Ascorbic Acid



Mill A effluent, pH 2.5 with zinc acetate

Mill E effluent, pH 2.5 with zinc acetate



Mill A effluent, pH 10 with zinc acetate

Mill E effluent, pH 10 with zinc acetate

Figure 3.5 Reduced Sulfur Compound Percent Remaining at pH 2.5 and pH 10 Preservation with Zinc Acetate

3.7.3 *Ongoing Investigations of Sample Preservation and Stability*

While conducting a survey of the aqueous phase in a WWTP, wherein samples were split between the NCASI West Coast Regional Center and another laboratory, questions arose regarding differences in total sulfide concentrations reported using Method RSC-02.01. The method uses ascorbic acid at pH 2.5 for preservation of the ORSCs and zinc acetate at pH 10 for preservation of sulfide. The other laboratory utilized a different preservation for the target analytes that used zinc acetate and ascorbic acid adjusted to a final pH of 12.8 with sodium hydroxide solution. The concentration differences observed were most pronounced in samples from the front portion of the WWTP (settling pond outlet and the front portion of the ASB). Additional experiments were conducted to examine the difference in total sulfide concentrations due to preservation. NCASI staff collected samples at two mills in order to determine total sulfide concentrations in the native samples within 2 hours of collection. Samples were collected and aliquoted for preservation with zinc acetate at pH 10, ascorbic acid at pH 2.5, and zinc acetate plus ascorbic acid at pH >12. Unpreserved samples were also analyzed. Each of the differently preserved aliquots was analyzed on Days 0, 1, 4, or 5, and 14 using RSC-02.01 for total sulfide, yielding the results illustrated in Figures 3.6 and 3.7. As indicated in the figures, samples preserved with zinc acetate and ascorbic acid at pH >12 yielded the highest concentrations of total sulfide in all samples except Day 14 in the samples collected from Mill J. In all cases preservation with zinc acetate at pH 10 or 12 in the sample collected at Mill A yielded higher concentrations than Day 0 unpreserved samples. This might indicate a loss of sulfide due to volatilization or oxidation in the Day 0 unpreserved sample. Alternatively, the high preservation pH may contribute to release of sulfide from other sulfur containing molecules in the matrix, yielding a false positive bias that is indicated by the trend of increasing concentrations over time for the samples preserved at pH 12.8. Samples preserved with ascorbic acid at pH 2.5 and unpreserved samples gave similar results on Days 0 and 1 in Mill A, while the ascorbic acid preserved sample concentrations were slightly lower in the Mill J samples. Concentrations of total sulfide in unpreserved samples dropped to nondetect on Day 4 or 5 in both sample matrices. Sulfide concentrations in samples preserved with ascorbic acid at pH 2 dropped steadily over the 14-day period in both matrices.

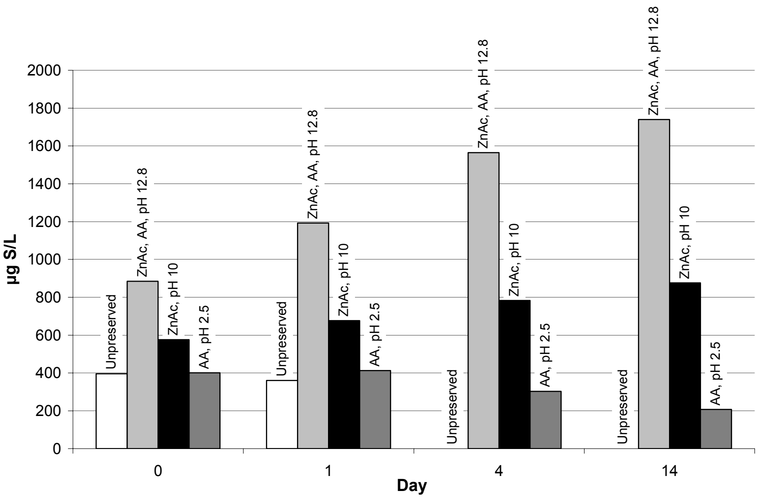


Figure 3.6 Mill A Preservation and Stability Results

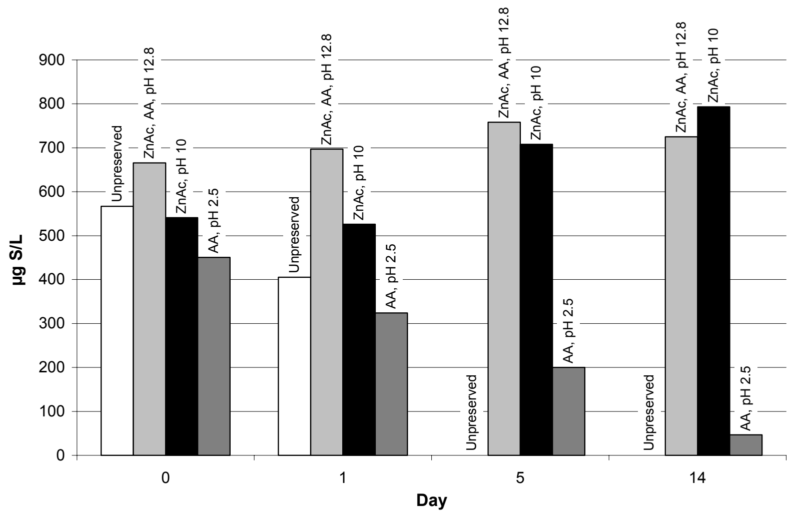
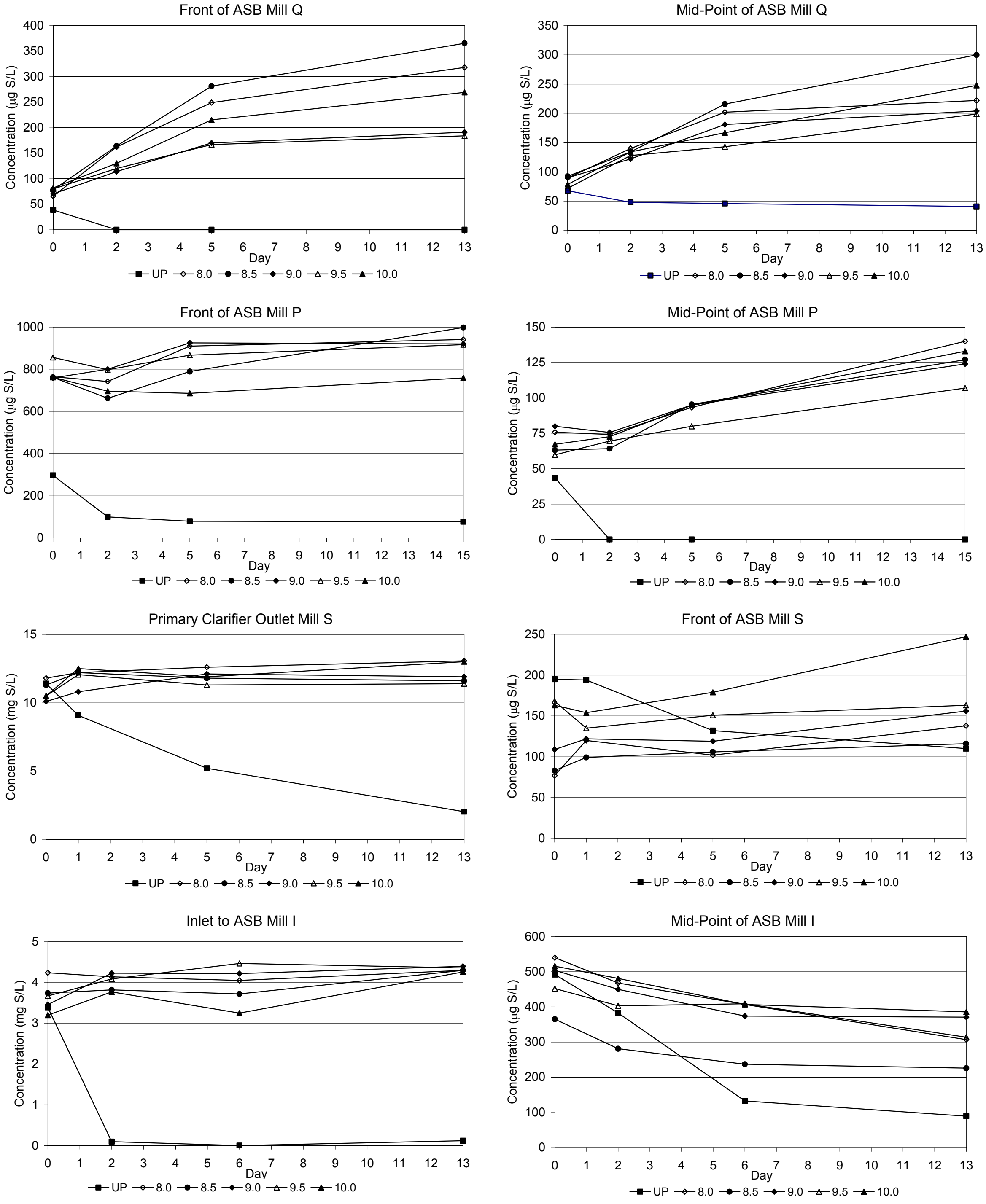


Figure 3.7 Mill J Preservation and Stability Results

Because preliminary experiments indicated that total sulfide concentrations increased with increasing pH (higher concentrations at pH 12 than at pH 10) and over time, further studies were done to address and understand this phenomenon. The objective of these studies was to evaluate the impact of sample preservation using zinc acetate over a pH range of 8 to 10 on total sulfide concentrations over a period of ~14 days. Samples for this work were collected from four mills (Mills I, P, Q, and S). Experimental work focused on samples collected at inlets to ASBs (primary clarifier outlet), front portions of ASBs, and midpoints of ASBs, as these sample matrices yielded the greatest differences in concentrations due to preservation pH observed in previous work. Unpreserved grab samples were collected by mill personnel and shipped to the NCASI West Coast Regional Center (WCRC) via overnight courier. Samples were collected using procedures for volatile organic compounds, were stored at 4°C, and were shipped to NCASI on ice. Comparisons were based on relative concentrations of total sulfide remaining in a sample starting from a designated Day 0 selected by the WCRC laboratory. Upon arrival at the laboratory, samples were screened to assess the amounts of base (1N NaOH) required to adjust a pH 8 zinc acetate stock to a pH that would allow the stock to be added to samples to achieve the desired pH of 8.0, 8.5, 9.0, 9.5, and 10.0 while adding the same amount of zinc acetate and the same volume of preservation stock (5 mL in a 40 mL VOA vial) to each sample, thus keeping the dilution factor constant. Samples were aliquoted in the laboratory in sets of three and adjusted to approximately pH 8, 8.5, 9, 9.5, and 10. An additional aliquot of unpreserved (UP) sample was also prepared. This provided a set of replicate samples to be analyzed on approximately Days 0, 2, 5 to 7, and 14. One replicate was analyzed using RSC-02.01 and the other was used to verify sample pH. This allowed verification that the targeted pH value was maintained while loss of sulfide was minimized. The actual day of analysis shifted slightly for the various sampling sets, depending on sample arrival at the laboratory.

Information regarding the samples utilized in this study are summarized in Table 2.1. Note that the initial pH of the sample from the primary clarifier at Mill S was 9 and that the Mill I samples were received at pH >8. The pHs of the designated aliquots were re-measured on each day of analysis to confirm that the adjusted pH level had been achieved and maintained over the 14 day period. Results of the preservation study are shown in Figure 3.8.

Different patterns were observed depending on the matrix and mill sampled. Unpreserved samples generally yielded the lowest concentrations of total sulfide on Day 0. Exceptions were observed in samples from the primary clarifier (initial pH (pH_i) 9.17, concentration 11.4 mg S/L) and the front of the ASB (pH_i 6.8, concentration 195 μg S/L) from Mill S, as well as from the midpoint of the ASB (pH_i 7.9, concentration 495 μg S/L) from Mill I. In those samples concentrations of total sulfide in unpreserved samples on Day 0 were similar to or higher than those in preserved samples. Stability of total sulfide in the unpreserved samples was poor, with 50% losses observed between Day 0 and Day 2 in a majority of the samples. Exceptions were observed in samples collected at the midpoint of the Mill I ASB and the front of the Mill S ASB. Based on these observations and previous studies, collection and shipment of unpreserved samples for total sulfide analyses using volatile sample collection techniques is not recommended.



Front of ASB Mill Q

Mid-Point of ASB Mill Q

Front of ASB Mill P

Mid-Point of ASB Mill P

Primary Clarifier Outlet Mill S

Front of ASB Mill S

Inlet to ASB Mill I

Mid-Point of ASB Mill I

Figure 3.8 Preservation pH and Total Sulfide Concentrations over a 14-Day Period

Preservation pHs in the range of 8.0 to 10.0 yielded similar results for total sulfide. This suggest that the shift in total sulfide concentrations observed following addition of base and zinc acetate is matrix-specific and may be affected by two phenomena. The first involves a chemical pathway that results in an increased level of total sulfide immediately following addition of basic zinc acetate solution (possibly related to nucleophilic substitution or base catalyzed reactions). Another pathway occurs slowly over time to further increase total sulfide levels in some matrices. Investigations into the nature of these phenomena are still in progress. When biases for pH 9 and 10 results were plotted versus concentrations in the samples it was noted that the major bias occurred in samples with concentrations around 0.1 mg S/L (Figure 3.9). Therefore, samples with concentrations of sulfide below 0.1 mg S/L should be analyzed as soon as possible following collection.

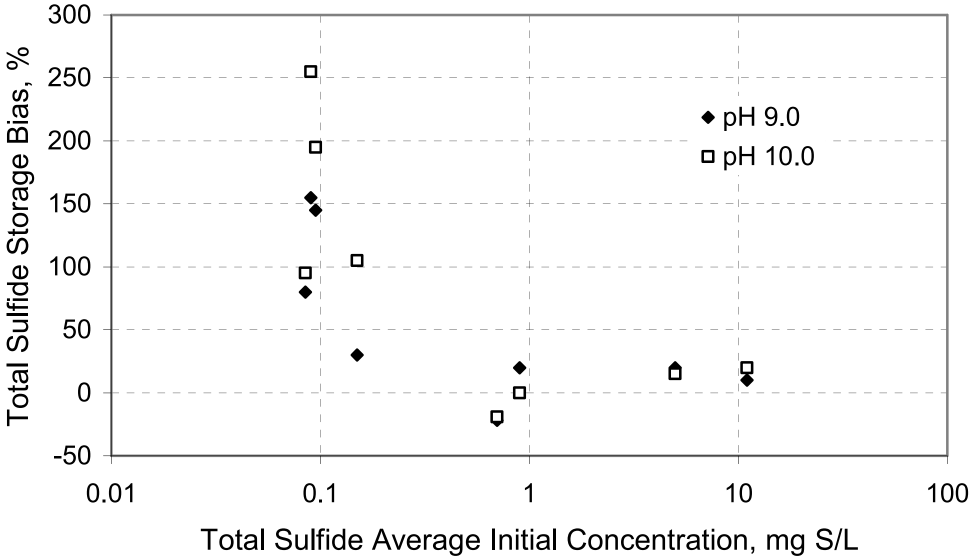


Figure 3.9 Total Sulfide Bias after Fourteen Days of Storage

Results of the preservation pH study indicate that in some matrices a change in native pH by the addition of basic zinc acetate preservation solution used in NCASI Methods RSC-02.01 and RSC-02.02 results in an increase in total sulfide concentrations measured. This increase was observed in samples collected from Mills Q and P at the fronts and midpoints of their ASBs. It was also observed in the sample collected from the midpoint of the ASB at Mill I. In the samples that demonstrated this increase it was observed at all pHs tested within the range of 8 to 10. This trend was observed in five of the ten samples tested.

Seven out of ten samples yielded increased total sulfide concentrations after one or two days of storage. Six out of ten samples yielded increased concentrations after five or six days. After 13 to 14 days, all samples tested to date (Mill I is not included) yielded increased total sulfide levels compared to unpreserved samples on Day 0. The magnitude of these changes appears to be matrix-specific and has not previously been observed in samples collected past the midpoint of the treatment system or prior to the front of the ASB. Therefore, the RSC-02.01 protocol is retained in RSC-02.02 for total sulfide analyses of samples requiring preservation and shipping, as limited benefits regarding alternative pHs of preservation were observed during this study. Investigations of alternative preservation schemes will continue, but based on the findings of this study and the volume of literature available regarding sulfide preservation, the basic zinc acetate approach is the best available procedure at this time for samples requiring preservation or shipment.

Unpreserved samples lost total sulfide rapidly between Day 0 and Day 2 of analysis; therefore, analysis of unpreserved samples is not recommended if storage or shipping is required.

3.8 pH Adjustment Prior to Direct Injection

The objective of this study was to evaluate the impact of sample acidification following preservation with zinc acetate at pH 10 to release total sulfide for analysis. The experiment examined a range of pH adjustments prior to direct injection of total sulfide standards preserved using zinc acetate at pH 10 as specified in RSC-02.01 and RSC-02.02. In order to free sulfide bonds with zinc prior to direct injection onto the GC, samples were acidified to pH 2.0 to 2.5. This adjustment can also free sulfides associated with other metals and organics in the matrix.

Results of injection pH experiments are summarized in Table 3.8. The data indicate that in order to obtain recovery of the zinc preserved sulfide standard the pH of the sample must be adjusted to below pH 4 prior to injection. At pH 6, 0% recovery was observed. The post acidic injections were made in an effort to free any sulfide trapped in the injection port in the form of zinc sulfide. The first acidic injection following the pH 6 injection yielded additional sulfide. The second acidic injection also yielded additional sulfide, but to a smaller degree. Injection at pH 4 resulted in about 63% recovery of the sulfide standard, but further acidic injections did not result in additional detections of sulfide. This may be accounted for by losses expected to occur out of the split vent of the gas chromatograph during injection.

Table 3.8 Effects of Injection pH on Sulfide Standard Recovery

	pH 6 (% recovery)	pH 4 (% recovery)	pH 2.5 (% recovery)
Aliquot injected	0	63	96
First post acidic injection	30	0	0
Second post acidic injection	16	0	0

Experiments to investigate an optimum pH of adjustment prior to direct injection in order to free sulfide from the zinc preservative indicated that the currently used pH <2.5 is optimal for the greatest recovery of total sulfide.

3.9 NCASI Method RSC-02.02 Comments

As the data presented in the previous sections illustrate, NCASI Method RSC-02.02 is a precise (RSDs <12% in standards, RPDs <20% in samples matrices) and accurate (average recoveries >95%in standards, >93% in matrices) method for determination of RSCs in pulp and paper mill matrices. Sample preservation at pH 2.5 with ascorbic acid has proven effective for stabilization of ORSCs. Sample preservation at pH 10 with zinc acetate has proven effective in a majority of matrices assessed, although a high bias is sometimes observed in samples with initial concentrations below approximately 0.1 mg S/L. Preservation and storage stability studies indicated that >80% of the target compounds remained after a 14 day holding period using the preservation scheme in RSC-02.02 (Appendix A, Section 8.2).

Major challenges relate to the volatile and reactive nature of RSCs, which requires special attention to active sites on all syringes and instrumentation that will come in contact with samples. Instrument maintenance is required on a daily basis, as well as careful sample handling to reduce losses following sample acidification (total sulfide).

4.0 METHOD APPLICATION

NCASI has used Methods RSC-02.01 and RSC-02.02 to survey WWTPs for total sulfide and ORSC levels in the aqueous phase. Many of the mills surveyed contacted NCASI for assistance in gathering data to address a variety of information needs; therefore, similar sampling sites were not always included at each mill. These data have been utilized by mills to help direct odor reduction efforts and provide insight regarding areas of the WWTP where increases (generation) and decreases (volatilization, oxidation, precipitation) of sulfide and ORSC concentrations are observed.

Many sulfur conversions can occur in the WWTP. Sulfide may be precipitated by metals as metal sulfides. It can become weakly associated with organics. Oxidation reactions, both chemical and biochemical, such as the conversion of methyl mercaptan to dimethyl disulfide and the oxidation of sulfide to sulfate, may take place. As the pH of the aqueous phase shifts, so does the equilibrium of sulfide. At higher pHs (>7.2) a majority of sulfide is water soluble (HS^-) and at lower pHs (<6.8) the sulfide is in gaseous form ($H_2S(g)$). In anaerobic areas sulfate maybe converted to sulfide by sulfate reducing bacteria. All these reactions contribute to a high level of variability with regard to sulfur forms and concentrations in the WWTP.

4.1 Results for Wastewater Treatment Plant Samples

Data for RSC concentrations in aqueous samples collected at the mills listed in Table 2.1 are summarized in Table 4.1. The data are not necessarily reflective of industry-wide RSC concentrations because the mills from which samples were collected were investigating odor sources and thus might represent a group with generally higher RSC levels. Sampling sites were variable, depending on each mill's WWTP configuration and information needs. Commonly sampled sites included output from the primary clarifier, front portion of the ASB or AS, midpoint of the ASB, and final effluent. Some samples required dilution prior to analysis in order to be within the working range of the method.

Results obtained on highly diluted samples have not been assessed or validated for this method; therefore, these data may be subject to error. The statistics in Table 4.1 (average, median, and SD) were calculated by substituting half the lower calibration limit (0.015 mg S/L for total sulfide, 10 µg S/L for ORSCs) for all target analytes with concentrations below the lower calibration limit of the method. A median value in the table near half the lower calibration limit indicates that the target analyte was not detected in a majority of samples assessed. Table 4.1 contains information from a total of 22 different units of operation. Figures showing concentrations of total sulfide and ORSCs in samples from the outlet of the primary clarifier, front of the ASB, and midpoint of the ASB can be found in Appendix B, Section B1. A majority of final effluent samples yielded concentrations below the lower calibration limit and were not graphed. The complete data set for the sampling sites assessed at each mill is provided in Appendix B, Section B2. These data characterize RSC concentrations encountered in aqueous samples from various locations in pulp and paper mill WWTPs.

Table 4.1 Reduced Sulfur Compound Summary for Mill Wastewater Treatment Plants

Parameter	Total Sulfide[a] (mg S/L)	MeSH[b] (µg S/L)	DMS[b] (µg S/L)	DMDS[b] (µg S/L)	DMTS[b] (µg S/L)
Primary clarifier outlet					
Range	<0.03 - 22.9	<20 - 3960	<20 - 2670	<20 - 2710	<20 - 470
Average	6.5	375	206	218	56
Median	3.5	38	66	22	10
SD[c]	7.1	847	502	489	98
n[d]	33	33	33	33	33
Front of ASB or AS					
Range	<0.03 - 21.6	<20 - 13900	<20 - 4680	<20 - 8410	<20 - 2500
Average	4.89	1795	682	1073	184
Median	2.95	60	68	68	18
SD	5.31	3346	1148	2178	463
n	32	32	32	32	32
Midpoint of ASB					
Range	<0.03 - 24.0	<20 - 2910	<20 - 2260	<20 - 2540	<20 - 353
Average	3.95	345	232	343	32.2
Median	0.29	<20	<20	<20	<20
SD	7.14	661	477	658	67
n	27	27	27	27	27
Final effluent					
Range	<0.03 - 0.46	<20 - 221	<20 - 59.8	<20 - 113	<20 - <20
Average	0.09	23.2	13.0	14.5	NA
Median	0.02	<20	<20	<20	NA
SD	0.12	39.7	10.2	19.1	NA
n	29	30	30	30	30

[a] half the lower calibration limit of 0.030 mg S/L (or 0.015 mg S/L) utilized for non-detects during these calculations

[b] half the lower calibration limit of 20 µg S/L (or 10 µg S/L) utilized for non-detects during these calculations

[c] standard deviation

[d] number of samples assessed

NA = not detected above lower calibration limit of the method

Figure 4.1 shows changes in concentrations of total sulfide observed in WWTPs as the wastewater progressed from primary clarification to final effluent. Some WWTPs were sampled more than once and are listed as the mill code followed by a roman numeral to indicate the different sampling dates. This graph includes different samplings that occurred at Mills C, D, J, K, O, S, and V to illustrate the variability observed at a given mill during distinct sampling episodes.

Figure 4.2 provides an indication of differences observed in ORSCs at various mills. This graph shows changes in methyl mercaptan concentrations through the WWTPs sampled. As indicated, methyl mercaptan concentrations at Mills C, D, and K increased following addition of hard piped condensates after primary clarification near the front portion of the ASB in those WWTPs.

Concentrations of DMS, DMDS, and DMTS yielded median results <68 µg S/L at all sampling locations surveyed at every mill. Trends in concentrations followed those observed for methyl mercaptan and were often linked to input of hard piped condensates to the WWTP.

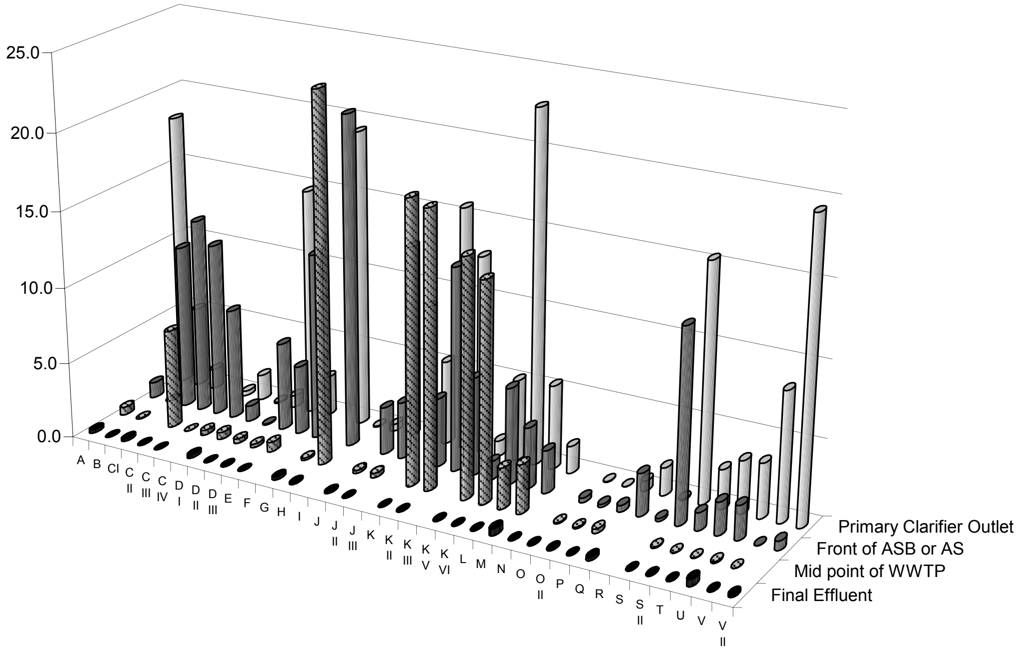


Figure 4.1 Total Sulfide Concentration (mg S/L) Changes in Wastewater Treatment Plants

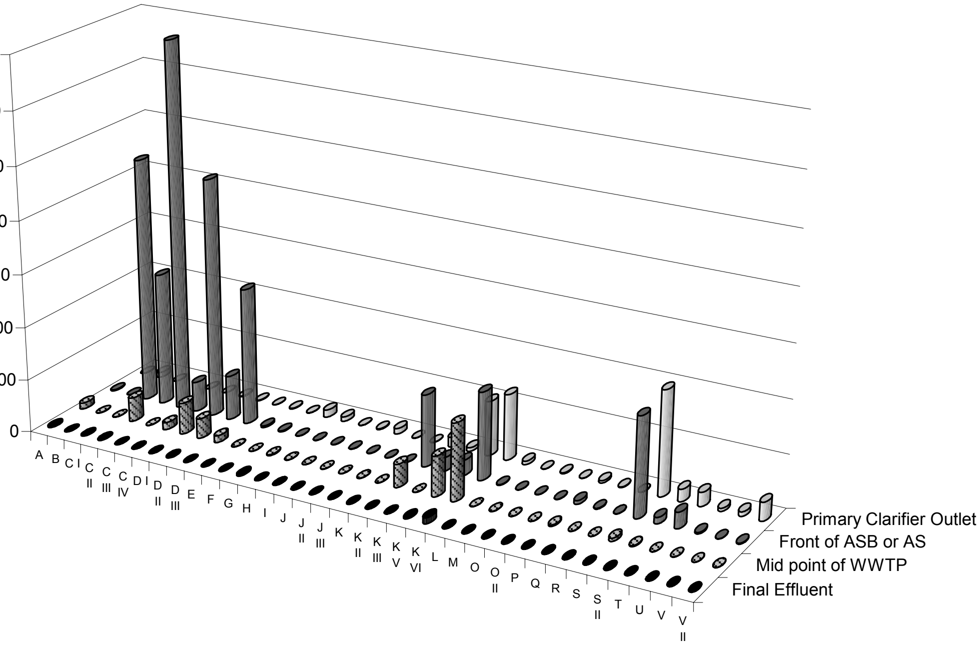


Figure 4.2 Methyl Mercaptan Concentration (μg S/L) Changes in Wastewater Treatment Plants

4.2 Matrix and Sampling Variability

In addition to the variability inherent in the method, pulp and paper mill matrix concentrations are expected to vary spatially (from site to site and sampling point to sampling point) and temporally (over time at the same mill). Temporal variability was assessed during application of the method to WWTP samples and results are presented in this section. Temporal variability would be anticipated to be higher at the front end of the WWTP (e.g., primary clarifier and first portion of the ASB), and decrease as effluent progresses through treatment. Therefore, several of the variability studies focused on samples from these front end locations. Several factors may impact matrix concentrations and variability, including pH, dissolved oxygen, volatilization, generation, and degradation. In addition, process variability occurring at each mill can impact concentrations of the target analytes in the WWTP. Experiments were conducted to assess matrix variability at various mills over the course of these studies. Study designs varied over the fours years during which this work was conducted and are described below with each data set. Results include variability due to the sampling process as a consequence of the reactivity and volatility of RSCs. Matrix-specific variability is represented more directly by results for DMS, which is more stable than the other RSCs.

The first experiment examined the variability of total sulfide concentrations at the ASB inlet of Mill D. Samples were collected every hour for seven hours and analyzed for total sulfide. Concentrations ranged from 2588 to 7729 μg S/L, with an average of 6052 μg S/L and a relative standard deviation of 31.2%. Further experiments at that site explored variability by collecting two to three samples per day for three days at the ASB inlet and one sample per day for three days at the ASB outlet. All target RSCs were evaluated during this experiment, yielding the results shown in Table 4.2.

Table 4.2 Variability in Mill D Aerated Stabilization Basin Sample Concentrations

	Total Sulfide	MeSH	DMS	DMDS	DMTS
ASB inlet					
Range (μg S/L)	312 - 4240	423 - 4030	481 - 1980	309 - 2280	86.3 - 2180
Average (μg S/L)	2568	2744	1117	948	996
RSD%	55	45	43	61	88
ASB outlet					
Range (μg S/L)	47.2 - 50.5	<20 - 28.4	27.1 - 33.8	132 - 170	<20
Average (μg S/L)	48.4	25.9	31.1	153	<20
RSD%	3.1	8.7	9.3	9.3	NA

NA = not applicable, concentration below lower calibration limit

The second study examined variability of the RSCs in an ASB at Mill T during one day. Samples were collected three times per day (AM, midday, PM) at the mix box prior to the ASB, the inlet of the ASB, and the outlet of the ASB. Results are summarized in Table 4.3.

The third experiment involved collection of samples three times per day for four days from the clarifier outlet at Mill J to assess variability in total sulfide concentrations. Concentrations ranged from 1150 to 6180 μg S/L, with an average of 3145 μg S/L and a relative standard deviation of 69.8%.

Table 4.3 Variability in Mill T Aerated Stabilization Basin Sample Concentrations

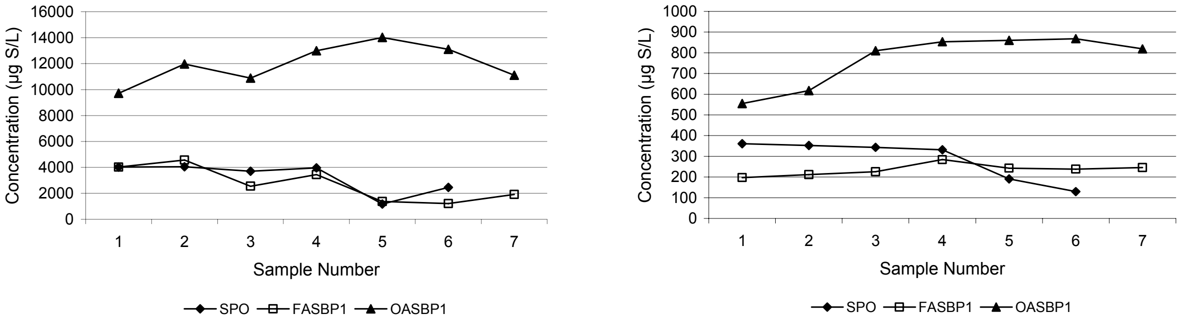
	Total Sulfide	MeSH	DMS	DMDS	DMTS
Mix Box Prior to ASB					
Range (µg S/L)	2600 - 4220	362 - 682	506 - 576	291 - 706	91.1- 183
Average (µg S/L)	3476.7	532	541	511	134
RSD%	23.5	30.3	6.5	40.8	34.4
ASB Inlet					
Range (µg S/L)	1610 - 2540	405 - 745	655 - 950	1120 - 2460	116 - 238
Average (µg S/L)	2160	605	838	1806	177
RSD%	22.6	29.4	19.1	37.1	34.4
ASB Outlet					
Range (µg S/L)			42.8 - 83.6	<20 - 180	
Average (µg S/L)	<30	<20	68.1	110.3	<20
RSD%	NA	NA	32.4	74.3	NA

NA = not applicable, concentration below lower calibration limit

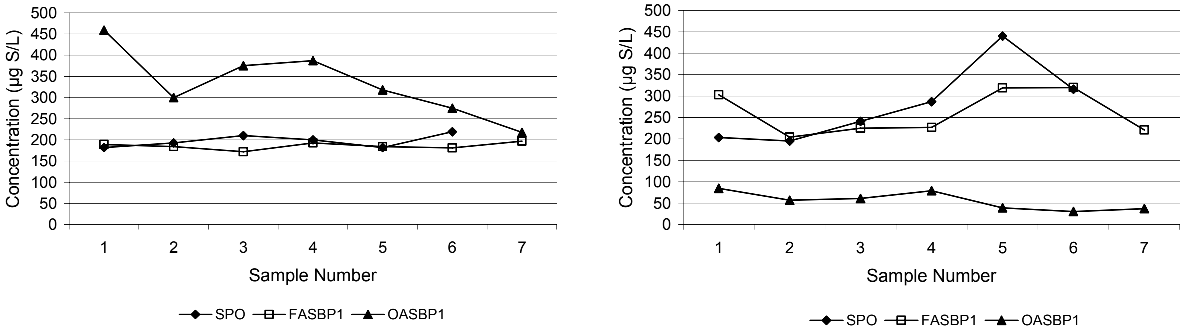
The fourth experiment examined variability over a two day period at Mill K, with samples collected three times per day from the settling pond prior to the ASB (SPO), the front of ASB Pond 1 (FASBP1), and the outlet of ASB Pond 1 (OASBP1). Results are summarized in Table 4.4 and illustrated in Figure 4.3.

Table 4.4 Variability in Mill K Wastewater Treatment Plant Sample Concentrations

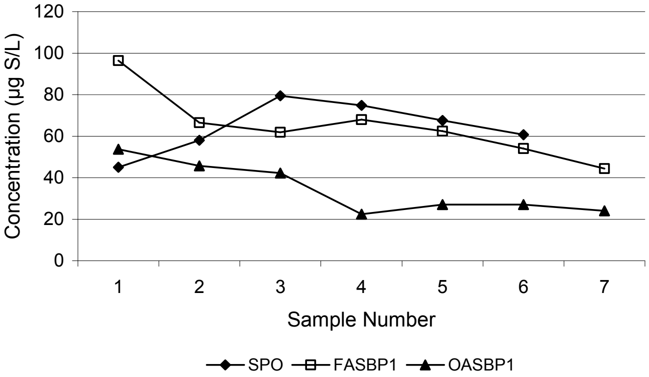
	Total Sulfide	MeSH	DMS	DMDS	DMTS
SPO					
Range (µg S/L)	1174 - 4056	130 - 361	182 - 219	195 - 440	45.0 - 79.5
Average (µg S/L)	3231	285	198	280	64.3
RSD%	33.2	31.7	3.9	29.7	17.7
FASBP1					
Range (µg S/L)	1208 - 4571	197 - 284	172 - 193	204 - 320	44.4 - 96.4
Average (µg S/L)	2727	235	186	260	64.8
RSD%	44.8	11.0	4.1	18.3	23.0
OASBP1					
Range (µg S/L)	9713 - 14022	555 - 868	218 - 459	30.5 - 84.5	22.4 - 53.7
Average (µg S/L)	11970	769	333	55.5	34.6
RSD%	11.6	15.4	22.2	35.1	33.2



Total Sulfide MeSH



DMS DMDS



DMTS

Figure 4.3 Variability in Mill K Wastewater Treatment Plant Samples

Additional studies were conducted at mill P over a four-day period. An average of three samples was collected at each site on each day of the study. The primary clarifier inlet and outlet and the ASB inlet and outlet were sampled, with the results reported in Table 4.5.

The level of variability observed during these samplings illustrates the complexity of assessing changes in RSC concentrations throughout a WWTP over time. Overall variability (RSD%) (Table 4.6) throughout the experiments described herein ranged from 3.1 to 81.4% with an average of 38.9% for total sulfide; from 8.7 to 46.7% with an average of 29.8% for MeSH; from 3.9 to 59.1% with an average of 20.6% for DMS; from 9.3 to 61.0% with an average of 34.2% for DMDS; and from 17.7 to 88.0% with an average of 41.0% for DMTS. This variability may be influenced by matrix, sampling method, and analytical variability, which was determined to be less than 5.3% for all target analytes (Section 3.6.3).

Table 4.5 Variability in Mill P Wastewater Treatment Plant Sample Concentrations

	Total Sulfide	MeSH	DMS	DMDS	DMTS
Primary clarifier inlet					
Range (µg S/L)	213 - 853	31.5 - 93.7	29 - 46.9	751 - 1120	<20 - 44.1
Average (µg S/L)	526	56.0	37.0	840	22.0
RSD%	39.9	34.1	16.1	13.4	43.0
Primary clarifier outlet					
Range (µg S/L)	<30 - 1080	21.8 - 141	24.0 - 44.4	152 - 665	24.7 - 184
Average (µg S/L)	637	86	34	431	94
RSD%	64.7	46.7	22.0	42.5	51.6
ASB inlet					
Range (µg S/L)	<30 - 1020	62.6 - 232	23.1 - 114	73.3 - 465	20.7 - 73.3
Average (µg S/L)	417	134	42	217	43.0
RSD%	81.4	46.0	59.1	57.7	44.0
ASB outlet					
Range (µg S/L)	197 - 466	9.5 - 96.2	22 - 38	<20 - 20.7	<20
Average (µg S/L)	290	49.0	29	20.7	NA
RSD%	32.8	29.5	21.1	31.2	NA

NA = not applicable, concentration below lower calibration limit

Table 4.6 Matrix and Sampling Variability Summary (RSD%)

	Total Sulfide	MeSH	DMS	DMDS	DMTS
Mill D					
ASB inlet	31.2 and 55	45	43	61	88
ASB outlet	3.1	8.7	9.3	9.3	NA
Mill T					
Mix box to ASB	23.5	30.3	6.5	40.8	34.4
ASB inlet	22.6	29.4	19.1	37.1	34.4
ASB outlet	NA	NA	NA	NA	NA
Mill J					
Primary clarifier outlet	69.8				
Mill C					
Setting pond outlet	33.2	31.7	3.9	29.7	17.7
ASB inlet pond 1	44.8	11.0	4.1	18.3	23.0
ASB outlet pond 1	11.6	15.4	22.2	35.1	33.2
Mill P					
Primary clarifier inlet	39.9	34.1	16.1	13.4	43.0
Primary clarifier outlet	64.7	46.7	22.0	42.5	51.6
ASB inlet	81.4	46.0	59.1	57.7	44.0
ASB outlet	32.8	29.5	21.1	31.2	NA
Overall Range	3.1 - 81.4	8.7 - 46.7	3.9 - 59.1	9.3 - 61	17.7 - 88
Overall Average	38.9	29.8	20.6	34.2	41.0

NA = not applicable, concentration below lower calibration limit

5.0 SUMMARY AND CONCLUSIONS

This research indicates that NCASI Method RSC-02.02 is effective for assessing total sulfide, MeSH, DMS, DMDS, and DMTS in pulp and paper mill wastewaters. The method utilizes a separate preservation and injection for determinations of total sulfide and ORSCs. Samples are preserved with zinc acetate at pH 10 for total sulfide and with ascorbic acid at pH 2.5 for ORSCs. All samples are acidified (pH <2.5) prior to direct injection on the GC and are detected using a PFPD. The applicable method range is ~20 to 1000 µg S/L without sample dilution, and can be extended above that range using sample dilution prior to acidification and analysis.

Method validation results indicate good agreement between concentrations determined using a quadratic fit equation for over 17 calibration curves and gravimetrically determined concentrations of standards. Daily calibration verifications yielded average recoveries of 106% for total sulfide (n=94) and average recoveries of 95 to 102% for ORSCs (n=42). Method blanks were free of the target analytes (n=94). Precision and accuracy were assessed using surrogate spikes, matrix spikes, and replicate analyses. Surrogate recoveries for total sulfide, MeSH, DMS, DMDS, and DMTS in over 1077 pulp and paper mill wastewater samples ranged from 73 to 131%, with an average of 106%. Matrix spike recoveries averaged 93, 106, 102, 112, and 96% for total sulfide, MeSH, DMS, DMDS, and DMTS, respectively. Precision results as reflected by pooled RPDs for duplicate analyses ranged from 2.1 to 5.3% for all target analytes. Storage stability using method-specified preservations indicated stability of the samples for up to 14 days. Injection pH significantly impacted recovery of total sulfide, with pH 2.5 yielding the highest recovery (96%).

The method was effectively applied to a variety of samples collected throughout WWTPs and some process sewers from over 20 pulp and paper mills. Results were highly variable. Variability may have been due to changes in matrices over time or to sampling techniques. Throughout several studies to assess variability at selected sampling sites, RSDs were 38.9% for total sulfide, 29.8% for MeSH, 20.6% for DMS, 34.2% for DMDS, and 41.0% for DMTS. This is well above the variability of ~5% observed for the analytical method alone.

Results of investigations conducted in conjunction with odor reduction studies at 20 mills yielded a wide range of RSC concentrations from similar locations within WWTPs. These data are not necessarily reflective of industry-wide concentrations because the participating mills were in the process of investigating odor sources. Median concentrations at primary clarifier outlets were 3.5 mg S/L for total sulfide, 38 µg S/L for MeSH, 66 µg S/L for DMS, 22 µg S/L for DMDS, and <20 µg S/L for DMTS. Median concentrations at the fronts of ASBs were 2.9 mg S/L for total sulfide, 60 µg S/L for MeSH, 68 µg S/L for DMS, 68 µg S/L for DMDS, and <20 µg S/L for DMTS. Median concentrations from midpoints of ASBs were 0.29 mg S/L for total sulfide and <20 µg S/L for ORSCs. Final effluent sample medians were <20 µg S/L for all target analytes.

NCASI Method RSC-02.02 has proven to be an effective tool for investigating odorous compounds in pulp and paper mill wastewater treatment plants.

REFERENCES

American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF). 2005. *Standard methods for the examination of water and wastewater* 20th Ed. Greenberg, A.E., Clesceri, L.S., and Eaton, A.D. (eds.), 4-124, 126. Washington DC: American Public Health Association, American Water Works Association, Water Environment Federation.

Andersson, K., and Berfstrom, J.G.T. 1969. The formation of organic sulfur compounds during kraft pulping: Part 1. Cooking procedure and method of analysis of organic sulfur compounds formed. *Svensk Papperstidning* 72(11):375-379.

Bérubé, P.R., Parkinson, P.D., and Hall, E.R. 1999. Measurement of reduced sulphur compounds contained in aqueous matrices by direct injection into a gas chromatograph with a flame photometric detector. *Journal of Chromatography A* 830:485-489.

Caron, F., and Kramer J.R. 1989. Gas chromatographic determination of volatile sulfides at trace levels in natural freshwaters. *Analytical Chemistry* 61:114-118.

Chai, X.S., Dhasmana, B., and Zhu, J.Y. 1998. Determination of volatile organic compound contents in kraft mill streams using headspace gas chromatography. *Journal of Pulp and Paper Science* 24(2):50-54.

Chai, X.S., Liu, P.H., and Zhu, J.Y. 2000. Analysis of volatile organic sulfur compounds in kraft liquors by full evaporation headspace gas chromatography. In *Proceedings of TAPPI International Environmental Conference and Exhibit*, 157-170, Atlanta, GA: TAPPI Press.

Cheskis, S., Atar, E., and Amirav, A. 1993. Pulsed-flame photometer: A novel gas chromatography detector. *Analytical Chemistry* 65:539-555.

Cook, D., and Hoy, D.R. 2003. Analytical techniques for investigating odors at pulp and paper facilities: preliminary results. In *Proceedings from the 2003 TAPPI Environmental Conference*, Portland, OR, USA. Atlanta, GA: TAPPI Press

Federal Register. 1984. Appendix B to Part 136–Definition and procedure for the determination of the method detection limit, rev. 1.11. *Federal Register* 49(209): October 26.

Gholson, A., Hoy, D.R., and Chambers, L. 2002. A direct aqueous injection gas chromatographic method for measuring reduced sulfur compounds in pulp mill effluents. In *Proceedings from the 2002 TAPPI Environmental Conference*, Montreal, QC, Canada. Atlanta, GA: TAPPI Press.

Hach Company. 2003. Method 8131 sulfide: Methylene blue method. In *Water analysis handbook*, 4th ed., rev. 2, 989-992. Loveland, CO: Hach Company.

Intergovernmental Data Quality Task Force (IDQTF). 2005. *Uniform federal policy for quality assurance project plans: Evaluating, assessing, and documenting environmental data collection and use programs – Part 1: UFP-QAPP manual.* EPA Publication No. EPA-505-B-04-900A; DoD Publication No. DTIC ADA 427785. Washington, DC: United States Environmental Protection Agency, United States Department of Defense; United States Department of Energy.

National Council for Air and Stream Improvement, Inc. (NCASI). 2000. *Laboratory studies of in-digester black liquor oxidation (IDO) for TRS destruction.* NCASI Technical Bulletin No. 804. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

———. 2002. Method RSC-02.01: Reduced sulfur compounds by direct injection. In *NCASI Methods Manual.* Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

O'Conner, B.L., and Genest, S. 1997. *A method for the analysis of total reduced sulphur (TRS) compounds in kraft mill aqueous process streams*. PPR 1300. Pulp and Paper Research Institute of Canada.

Prakash, C.B., and Murry, F.E. 1976. Analysis of malodorous sulphur compounds in kraft mill aqueous solutions. *Svensk Papperstidning* 79(15):501-504

Rayner, H.B., Murry, F.E., and Williams, I.H. 1967. Studies on the gas chromatographic analysis of kraft mill sulfides. Part II. The determination of microgram quantities of methyl mercaptan, methyl sulfide and methyl disulfide in aqueous solution. *Pulp and Paper Magazine of Canada* 68(6):T301-304.

Saunders, F.Y., and Larson, L.J. 1996. A method for the measurement of TRS content of waste streams. In *Proceedings of the 1995 NCASI Southern Regional Meeting*. Special Report No. 96-01, 430-435. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

United State Environmental Protection Agency (USEPA). 1993. Method 300.0: Determination of inorganic anions by ion chromatography. Rev. 2.1. Cincinnati, OH: United State Environmental Protection Agency Office of Research and Development, Environmental Monitoring Systems Laboratory.

———. 1997. Method 376.2. Sulfide (colorimetric, methylene blue). In *Methods and guidance for analysis of water* (on CD). EPA 821-C97-001. Washington, DC: United State Environmental Protection Agency Office of Water.

———. 1978. Methods for the chemical analysis of water and wastes (MCAWW). EPA/600/4-79/020. In *EPA methods and guidance for analysis of water, ver. 2.0.* http://infotrek.er.usgs.gov/pls/apex/f?p=119:38:1416115483171713::::P38_METHOD_ID:5317.

Wardencki, W. 1998. Problems with the determination of environmental sulphur compounds by gas chromatography. *Journal of Chromatography A* 793:1-19.

APPENDIX A

NCASI METHOD RSC-02.02

REDUCED SULFUR COMPOUNDS BY DIRECT INJECTION GC/PFPD

1.0 SCOPE AND APPLICATION

1.1 This method is used for the determination of the reduced sulfur compounds (RSCs) total sulfide as hydrogen sulfide (H_2S) [7783-06-4], methyl mercaptan (MeSH) [74-93-1], dimethyl sulfide (DMS) [75-18-3], dimethyl disulfide (DMDS) [624-92-0], and dimethyl trisulfide (DMTS) [3658-80-8] in wastewaters from pulp and paper mills. The RSCs are measured by direct aqueous injection gas chromatography with pulsed flame photometric detection (GC/PFPD).

1.2 The concentration of sulfide (H_2S) measured using this method represents the total amount of sulfide in the sample volatile at pH 2.5. It is believed that this includes all freely dissolved sulfide plus sulfide weakly associated with either dissolved organic matter or certain transition metals. If native sample pH is greater than 2.5, the actual total sulfide concentration in solution might be less than the concentration measured by this method.

1.3 The method has been applied to influent to wastewater treatment, samples from within the wastewater treatment system, and effluent from wastewater treatment.

1.4 This method has been validated for a single laboratory.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of chromatograms. Each analyst must demonstrate an ability to generate acceptable results with this method.

2.0 SUMMARY OF THE METHOD

2.1 Samples are collected directly from the aqueous process stream or wastewater basin using appropriate collection vessels. Samples require two different preservation techniques to preserve all analytes. Samples are kept refrigerated until analysis.

2.2 In the laboratory, an aliquot of the sample is transferred to a 2-mL sealed vial. An aliquot of an internal standard solution is added to each of the vials. The sample is acidified (total sulfide only) and injected into the GC with a split injection. The GC column is temperature programmed to separate the analytes from other compounds which may be present in the sample. The analytes are selectively detected with a PFPD.

2.3 Identification of the RSCs is determined by comparison of their relative retention times with the relative retention times of an internal standard. If the results are questionable, confirmation using a second column may be necessary.

2.4 The RSCs are quantified by comparison with liquid standards using the internal standard technique. Multiple standards are analyzed to cover a calibration range of 20 to 1000 µg S/L. Calibration to lower concentrations may be possible for some compounds. Dilution is required to analyze samples with concentrations above 1000 µg S/L.

2.5 The method detection limit was calculated using the USEPA procedure in 40 CFR Part 136 Appendix B (Federal Register 1984) in a final effluent collected from an unbleached kraft mill after allowing the sulfide level to drop to less than 50 µg S/L. The method detection limit determined for total sulfide was 32.0 µg S/L. The sensitivity of the method has not been determined for MeSH, DMS, DMDS, and DMTS, and the detection limits have not been established. MeSH, DMS, DMDS, and DMTS have been successfully calibrated down to concentrations of 20 µg S/L.

2.6 Data quality is assured with ongoing recovery assessments, duplicate analyses, surrogate recovery experiments, matrix spike experiments, and blank analyses. MeSH, DMS, and DMDS standards are checked by comparing the results with an independently prepared standard. The sulfide standard is verified by independent analysis using EPA Methods 376.1 and 376.2.

3.0 DEFINITIONS

3.1 The definitions below are specific to this method, but conform to common usage as much as possible.

3.1.1 µg/L – micrograms of compound per liter

3.1.2 µg S/L – micrograms of sulfur per liter

3.1.3 May – this action, activity, or procedural step is neither required nor prohibited

3.1.4 Must not – this action, activity, or procedural step is prohibited

3.1.5 Must – this action, activity, or procedural step is required

3.1.6 Should – this action, activity, or procedural step is suggested, but not required

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, injection port liners, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analyses by running laboratory blanks.

4.2 Glassware must be scrupulously cleaned, and glassware that comes in contact with concentrations less than 50 µg S/L may need to be deactivated. Glassware can be deactivated either by soaking in acid followed by silylation or by Siltek^{TM} coating as described in Section 6.1.1. After use, clean all glassware by washing with mild detergent in hot water and rinsing with tap water. The glassware should then be drained until completely dry.

4.3 It is required that all metal surfaces that come in contact with the sample be deactivated. This includes injection port liners, seals, and syringe needles. Deactivate the metal surfaces as described in Section 6.1.1.3.

4.4 The internal standard, thiophene, may be present in some pulp mill process streams. If the composition on a matrix is unknown, a sample analyzed without internal standard should be examined for the presence of thiophene. The surrogate, thioanisole, can be used as an internal standard if interference with thiophene is identified.

4.5 Some compounds can interfere with the chromatography if the separation is not efficient. Specific interference includes partial coelution of carbon disulfide with dimethyl disulfide. When performed properly, this method separates these compounds sufficiently. During the development of the method, carbon disulfide was not detected in any of the wastewater samples analyzed.

4.6 After a number of injections of samples, a sulfur dioxide artifact peak can interfere with methyl mercaptan. A clean, deactivated injection port liner should be installed after approximately 20 sample injections. The injection port gold seal should also be cleaned with deionized water, methanol, and acetone using a long cotton swab prior to inserting the clean injection port liner during liner changes.

5.0 SAFETY

5.1 All chemicals should be treated as potential health hazards. It is recommended that prudent practices for handling chemicals in the laboratory be employed (NRC 1995).

5.2 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness of OSHA regulations regarding safe handling of chemicals used in this method. Material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.3 The RSCs are either flammable gases or liquids that may be harmful if inhaled or ingested. These compounds can also cause a considerable nuisance odor. Use them in a laboratory fume hood and wear appropriate gloves, eye protection, and other protective clothing.

6.0 EQUIPMENT AND SUPPLIES

***Note**: Brand names and suppliers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and material other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1 Sampling Equipment

6.1.1 Samples are to be collected in amber glass bottles with minimal headspace. It is recommended that 40-mL amber, borosilicate glass vials with Teflon™ faced silicone backed lids (VOA vials) be used. Although passivation of glassware for RSC compounds is common practice, passivation of sample containers during this study has not been found to be necessary in the standard operating range of this method. Some improvement of the lower level calibration response has been found when using passivated autosampler vials. If passivation of glassware is desired, one of the following techniques can be used.

6.1.1.1 Soak clean glassware in a 10% HCl solution for at least one hour. Rinse the glassware thoroughly with water, followed by an acetone rinse, air drying, and treatment with 5% dimethyldichlorosilane in toluene. Rinse the glassware with toluene, methanol, and water, then air dry it.

6.1.1.2 Treat clear VOA vials with the Siltek deactivation process (Restek Corporation, Bellefonte, PA). Caution: strong caustic detergents will remove the Siltek coating.

6.1.1.3 Treat syringe needles by slowly pumping a 15% solution of BSTFA in hexane three times followed by a rinse with acetone, methanol, and water.

6.1.2 The use of automatic sample collection equipment has not been validated for this method and should not be incorporated until its effectiveness has been proven.

6.2 Laboratory Glassware and Supplies

6.2.1 Amber 2-mL autosampler vials deactivated if desired by one of the methods described in Section 6.1.1

6.2.2 Volumetric flasks (10-mL, 50-mL)

6.2.3 Syringes (including gas-tight syringes) deactivated by methods described in Section 6.1.1.3

6.3 Analytical Equipment

6.3.1 Gas chromatography system – gas chromatography analytical system complete with a cryogenically cooled, temperature programmable gas chromatograph with a split/splitless injection port and all required accessories including syringes, analytical columns, and gases

6.3.2 Injection port liner – 4-mm deactivated (silanized or Siltek) straight glass liner lightly packed with a plug of deactivated (silanized) quartz two-thirds the distance from the septum end of the liner (Section 17, Figure 1)

6.3.3 Column – 30 m x 0.25 mm x 1.4 µm, 6% cyanopropylphenyl 94% dimethylpolysiloxane bonded phase (624 phase) fused silica capillary column

6.3.4 GC detector – pulsed flame photometric detector (OI Analytical or equivalent) with appropriate data system

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Deionized (DI) water should be tested immediately before use to verify the absence of any target analytes. If the water is contaminated, it may be necessary to prepare fresh deionized water, purge the water with nitrogen or helium, or boil the water to remove the contaminant(s).

7.1.2 Prepare phosphoric acid solution by combining one part of phosphoric acid (reagent grade) with three parts deionized water.

7.1.3 Prepare acidified DI water by adding phosphoric acid solution (Section 7.1.2) to DI water (Section 7.1.1) until the pH is between 2.3 and 2.7. It takes approximately 0.5 mL of acid in 1 L of water to reach this pH.

7.1.4 L-Ascorbic acid (ACS reagent grade)

7.1.5 Methanol (distilled in glass)

7.1.6 Prepare the zinc acetate solution (40 mmole/L) by adding 1.75 g of zinc acetate dehydrate (reagent grade) to 200 mL of DI water. Slowly adjust the pH drop wise by adding 1N NaOH while stirring the DI water containing the zinc acetate (this takes 20 to 30 minutes). Dropwise addition is important up to pH 8.0 in order to produce small crystals of the resulting salt which will homogenize upon shaking. Once pH 8.0 is achieved dropwise addition is not longer required. Finish adjusting the pH to between 12 and 12.5 using the 1N NaOH solution (total 1N NaOH required is approximately 20 mL). This solution should produce a fine, even suspension which does not settle rapidly. If you shake the container and then let it sit, it will usually remain in suspension for over 20 minutes.

7.1.7 Prepare dimethyldichlorosilane (DMDCS) 5% in toluene by adding 25 mL of DMDCS to 475 mL of toluene. It is also available as a mixture from Supelco as Sylon CT.

7.1.8 Prepare N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) 15% in hexane by adding 1.5 mL of BSTFA to 8.5 mL of hexane.

7.1.9 Toluene (distilled in glass)

7.1.10 Hexane (distilled in glass)

7.1.11 $CaCl_2$ desiccant, 96%+ ACS reagent grade

7.1.12 Prepare NaOH 1 N by dissolving 40 g of pellets (97+%) into 1 L of DI water.

7.2 Analytical Standards

Analytical standards are prepared from pure standards. Reported purity should be greater than 95% for all the neat material used.

7.2.1 Prepare the internal standard primary solution by weighing 26 mg (to the nearest 0.1 mg) of thiophene and diluting to 10 mL in volumetric flasks with methanol. Prepare the primary standard at a concentration of approximately 1 mg S/mL. Calculate the actual concentration using Equation 1.

Equation 1

$$C_S = \frac{(m * FS)}{V_S}$$

where: C_S *is the concentration of sulfur in the standard (mg S/mL)*
m is the mass of the compound added to the standard (mg)
FS is the fraction of sulfur in the compound (Section 17, Table 6 except for $NaS_2 \bullet 9H_2O$*, which is 0.1335)*
V_S *is the total volume of the standard (mL)*

7.2.2 Prepare the surrogate standard primary solution by weighing, to the nearest 0.1 mg, 40 mg of thioanisole and diluting to 10 mL in volumetric flasks with methanol. Prepare the primary standard at a concentration of approximately 1 mg S/mL. Calculate the actual concentration using Equation 1.

7.2.3 Prepare a combined internal standard and surrogate working solution by adding 400 µL of each primary stock (Sections 7.2.1 and 7.2.2) to a 10-mL volumetric flask and diluting to the mark with methanol. The concentration in the solution is approximately 40 µg S/mL for each compound.

7.2.4 Prepare a primary and working standard of sulfide from sodium sulfide nonahydrate (Na_2S). The $Na_2S \cdot 9H_2O$ should be either opaque or white crystals. This material is hydroscopic and will turn into a slurry if not stored in a dry environment such as a desiccator containing anhydrous $CaCl_2$ and wrapped with tape to seal the bottle. It will also turn yellow or green (elemental sulfur) in storage. Prepare the working solution by adding 340 mg of zinc acetate dihydrate to 40 mL of purged DI water. Slowly adjust the pH drop wise by adding 1N NaOH while stirring the water containing the zinc acetate (this takes 10 to 20 minutes). Dropwise addition is important up to pH 8.0 in order to produce small crystals of the resulting salt which will homogenize upon shaking. Once pH 8.0 is achieved dropwise addition is not longer required. Finish adjusting to between 10.5 and 11 using the 1 N NaOH solution. Add 38 mg of $Na_2S \cdot 9H_2O$, weighed to the nearest 0.1 mg, while continuing to stir for 5 minutes. his solution should be a well dispersed suspension with no visible clumping of the solids. Transfer the solution quantitatively into a 50-mL volumetric flask and dilute to the mark with purged DI water. The concentration in the solution will be approximately 100 µg S/mL, with an equivalent total sulfide concentration of 106 µg/mL. Calculate the actual concentration using Equation 1. The fraction of sulfur (FS) in $Na_2S \cdot 9H_2O$ is 0.1335.

7.2.5 Prepare a primary solution of MeSH by slowly bubbling MeSH gas into a tared 10-mL volumetric flask containing methanol. Allow the MeSH to dissolve into the methanol until approximately 15 mg (weighed to the nearest 0.1 mg) has been added. This corresponds to approximately 7.5 mL of pure gas at room temperature. Use a thin (1/16 inch) Teflon line to transfer the MeSH into the methanol and be sure that any methanol clinging to the line is knocked back into the volumetric flask before measuring the final weight. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.6 mg/mL as MeSH. Calculate the actual concentration using Equation 1.

7.2.6 Prepare a primary solution of DMS by weighing 19 mg (to the nearest 0.1 mg) of DMS into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.9 mg/mL as DMS. Calculate the actual concentration using Equation 1.

7.2.7 Prepare a primary solution of DMDS by weighing 15 mg (to the nearest 0.1 mg) of DMDS into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.5 mg/mL as DMDS. Calculate the actual concentration using Equation 1.

7.2.8 Prepare a primary solution of DMTS by weighing 13 mg (to the nearest 0.1 mg) of DMTS into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.3 mg/mL as DMTS. Calculate the actual concentration using Equation 1.

7.2.9 Prepare a working solution of MeSH by adding 1.0 mL of the primary solution (Section 7.2.4) to a 10-mL volumetric flask and diluting with methanol. MeSH is not stable when mixed with the other standards.

7.2.10 Prepare a primary solution of carbon disulfide (CS_2) by weighing 12 mg (to the nearest 0.1 mg) of CS_2 into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.2 mg/mL as CS_2. Calculate the actual concentration using Equation 1.

7.2.11 Prepare a working solution of mixed RSCs and CS_2 by adding 1.0 mL of the primary solutions of DMS (Section 7.2.6), DMDS (Section 7.2.7), DMTS (Section 7.2.8), and CS_2 (Section 7.2.10) to a 10-mL volumetric flask and diluting with methanol.

7.3 Calibration Standards

7.3.1 Prepare a multilevel calibration working solution by adding 500 µL of each of the individual working solutions of sulfide (Section 7.2.4), MeSH (Section 7.2.9), and mixed RSCs (Section 7.2.11) to a 5-mL volumetric flask. Dilute to the mark with purged DI water and adjust the pH to around 2.5 with phosphoric acid solution. The calibration working solution has limited stability and should be prepared the day it is used.

7.3.2 Prepare a nominal 20 µg S/L calibration standard by adding 4.0 µL of the multipoint calibration solution (Section 7.3.1) to 1.8 mL of pH 2.5 adjusted DI water (Section 7.1.3) in a 2-mL autosample vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

Equation 2

$$C_{cal} = \frac{C_{WS} * V_{WS}}{V_{cal}}$$

where: C_{cal} *is the concentration of the analyte/internal standard in the calibration standard (µg S/L)*
C_{WS} *is the concentration of the analyte in the working solution (µg S/mL)*
V_{WS} *is the volume of working solution added to the calibration standard (mL)*
V_{cal} *is the volume of the calibration standard (0.002 L)*

7.3.3 Prepare a nominal 50 µg S/L calibration standard by adding 10 µL of the multipoint calibration solution (Section 7.3.1) to 1.8 mL of pH 2.5 adjusted DI water (Section 7.1.3) in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.4 Prepare a nominal 200 µg S/L calibration standard by adding 40 µL of the multipoint calibration solution (Section 7.3.1) to 1.8 mL of pH 2.5 adjusted DI water in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.5 Prepare a nominal 500 µg S/L calibration standard by adding 100 µL of the multipoint calibration solution (Section 7.3.1) to 1.7 mL of pH 2.5 adjusted DI water in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.6 Prepare a nominal 1000 µg S/L calibration standard by adding 200 µL of the multipoint calibration solution (Section 7.3.1) to 1.6 mL of pH 2.5 adjusted DI water in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.1) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.7 Prepare a daily calibration check standard (200 µg S/L) by adding 4.0 µL of the working standards of sulfide (Section 7.2.4), MeSH (Section 7.2.9), and mixed RSCs (Section 7.2.11) to 1.8 mL of pH 2.5 adjusted DI water (Section 7.1.3) in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.1) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.8 When preparing standards or samples, the autosampler vial has an air bubble after being sealed. This is important so that the analyte and internal standard spikes can be mixed well before analyzing the sample or standard. At least three good inverted shakes should be performed before injecting the standard or sample.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Collection

Collect grab samples directly from the process liquid stream using appropriate collection vessels, typically 40-mL VOA amber vials. Fill each vial with the sample, leaving minimum headspace. Collect a separate sample for analyzing total sulfide because of the preservation technique. A substantial quantity of preservative is required, so a dilution factor is needed to correct for dilution due to preservation. This can be accomplished by measuring the volume of preservative added and the final volume of the sample including preservative.

8.2 Preservation

8.2.1 Preservation for the analysis of MeSH, DMS, DMDS, and DMTS requires the addition of 120 mg of ascorbic acid to a 40-mL VOA vial (3 g/L) and pH adjustment to <2.5 with phosphoric acid solution. To adjust the pH, add a representative sample to an extra vial containing ascorbic acid. Measure the volume of phosphoric acid required to reach the target pH and discard that sample. Use that volume of acid to adjust the samples to be analyzed. If the volume of acid needed is less than 2 mL, no correction for dilution is required.

8.2.2 Preservation for the analysis of total sulfide requires the addition of 5 mL of zinc acetate solution (Section 7.1.6) to a 40-mL VOA vial. The final pH of the sample should be greater than 10. Adjust the pH with 1 N NaOH solution if necessary. A correction for the dilution of the sample by the preservative must be made. For example, if 35 mL of sample is diluted to 40 mL, the measured concentration should be multiplied by a dilution factor of 1.14. Sample volumes can be measured gravimetrically or using calibrated glassware (graduated cylinder).

8.3 Storage

All samples must be stored in a refrigerator (4°C) until analysis. Storage stability has been found to be matrix-dependent. Using the prescribed preservation techniques, greater than 80% recovery was found for all compounds in both a bleached kraft mill effluent and an unbleached kraft mill effluent after 14 days of storage. Storage of zinc acetate preserved samples with native concentrations of <0.1 mg S/L collected in highly aerated portions of WWTP have yielded increasing concentrations of total sulfide over time.

9.0 QUALITY CONTROL

To control the quality of the data generated using this method, an initial calibration check, independent standard check, daily blank checks, daily calibration checks, surrogate recovery experiments, periodic duplicates, and periodic matrix spikes should be performed.

9.1 Initial Calibration Check

A multipoint internal standard calibration should be performed covering the operating range of the method (20 to 1000 µg S/L). A wider or narrower range is acceptable if all sample concentrations fall within that range. The criterion for acceptable linearity is a mean absolute percent error (MAPE) for the curve of less than or equal to 20% (Section 10.2.3).

9.2 Independent Standard Check

When a primary standard is prepared for calibration and matrix spike experiments, it should be compared with an independent standard either prepared from another source of compound or obtained from a certified standard vendor. Only methyl mercaptan, dimethyl sulfide, and dimethyl disulfide are commercially available as solutions in methanol at this time (Crescent Chemicals). The independent standard should match the primary standard used for calibration and matrix spikes within 30%. This check will minimize bias due to errors in standard preparation.

9.3 Daily Blank Checks

A daily blank check should be performed before running samples. A blank check should be performed if carryover is suspected (e.g., after running a sample outside the calibration range). A blank check consists of analyzing 1.8 mL of purged DI water with internal standard and surrogate as described in Section 11.1. The RSC level in the blank should not exceed 20% of the lowest calibration point (4 µg S/L for MeSH, DMS, DMDS, and DMTS; 6 µg S/L for total sulfide).

9.4 Daily Calibration Checks

Prepare and analyze a mid-level calibration point every day that samples are analyzed. The percent recovery of each compound in the standard should be within 20% of the percent recovery of the same calibration level in the multipoint calibration. If the daily calibration check fails, it should be repeated. If it fails a second time, the standards (working, primary, internal standard) should be re-prepared. If it continues to fail, the multipoint calibration should be repeated. A summary of single laboratory daily calibration checks for this method is provided in Section 17, Table 1.

9.5 Surrogate Recovery Check

In this method thioanisole is utilized as a surrogate for the reduced sulfur compounds. All samples are spiked with 9 µL of the thioanisole spiking solution (Section 7.2.1) to monitor surrogate recovery. The percent recovery of the surrogate should be determined and the results charted to document the surrogate recovery of the method. Performance criteria for acceptable surrogate recovery, as determined during a single-laboratory validation of this method, are presented in Section 17, Table 2.

9.6 Duplicate Analyses

A duplicate sample should be analyzed with each set of samples (batch of samples no greater than 20). Duplicate analysis requires the analyses of separate aliquots of the sample. The relative percent difference between the two samples should be calculated and charted to estimate the method's precision. Section 17, Table 3 lists the relative percent differences found during a single laboratory validation of the method.

9.7 Matrix Spike Analyses

A matrix spike analysis should be performed with each set of samples (batch of samples no greater than 20). A known amount of the RSC working solutions should be added to a sample so that the native plus the spike level of each RSC is at least one times the native level. The percent recovery of the matrix spike should be determined and the results charted to document the recovery of the method. Section 17, Table 3 lists the recovery found during single laboratory validation studies.

9.8 Field Replicates and Field Spikes

Depending on specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of sampling and sample transporting techniques.

9.9 Resolution Checks

The resolution of the separation should be checked periodically (ideally on a daily basis) by measuring the valley between the DMS and CS_2 peaks. The valley should be less than 10% of the average peak heights of the two peaks. If the valley is 10% or greater, maintenance of the injection port and/or column is necessary.

10.0 CALIBRATION AND STANDARDIZATION

10.1 GC/PFPD Operating Conditions

Assemble the GC/PFPD and establish the operating conditions outlined in Section 17, Table 4. Use the conditions specified by the PFPD manufacturer to optimize for the detection of sulfur compounds. Once the GC/PFPD system is optimized for analytical separation and sensitivity, the same operating conditions must be used to analyze all samples, blanks, calibration checks, and quality assurance samples.

If excessive peak broadening is observed for sulfide and MeSH, a pressure pulse during the injection might keep the injection focused on the column. This has been necessary when using autoinjectors with a rapid injection stroke. An initial pressure of 30 psi for 0.2 min followed by a rapid drop back to a constant flow of 1.2 mL/min sharpened the early eluting peaks. Keep the pressure pulse time to a minimum because the PFPD loses its sulfur response at high carrier gas flow rates.

10.2 Initial Multipoint Calibration

The square root of the PFPD response for sulfur is approximately linear with respect to concentration over the operating range of the method. To demonstrate this and establish a calibration function for the method, prepare and analyze calibration standards to cover this range. The internal standard calibration approach should be used for this method. Calibrate the RSCs using concentrations normalized to the sulfur content of the standard. The use of sulfur concentrations ensures that the concentrations prepared cover the operating range of the detector. It also allows the relative response factors to be checked, because, theoretically, they should all be 1.

10.2.1 Determine the retention times of the analytes by analyzing a daily calibration solution (Section 7.3.7). A chromatogram similar to that shown in Section 17, Figure 2 should be obtained. Identify the peaks and determine their relative retention times using Equation 3. Section 17, Table 6 lists the relative retention times for the RSCs using this method.

Equation 3

$$RRT_i = \frac{RT_i}{RT_{IS}}$$

where: RRT_i *is the relative retention time for compound i*
RT_i *is the retention time for compound i*
RT_{IS} *is the retention time for the internal standard*

10.2.2 Prepare a five-point calibration curve to determine the relationship between instrument response and concentration over the operating range for each analyte. Analyze each of the calibration standards prepared as described in Sections 7.3.2 through 7.3.7.

10.2.3 The results of the calibration standard analyses for each compound are either fitted to a quadratic equation or described by an average relative response factor using internal standard calibration techniques. To find the best quadratic fit for the data, plot the response ratio of each compound as calculated in Equation 4 versus the ratio of the standard concentration versus the internal standard concentration. Curve-fitting software either in the data system (e.g., Agilent Chemstation) or external to the data system (e.g., Excel) can be used to fit the best quadratic equation in the form of Equation 5.

Equation 4

$$RR = \frac{A_i}{A_{IS}}$$

where: RR is the response ratio
A_i is the area of the peak for compound i
A_{IS} is the area of the internal standard peak

Equation 5

$$RR_i = a + b * C_R + c * C_R^2$$

where: RR is the response ratio
a is the y-intercept from the quadratic regression
b is the linear constant from the quadratic regression
C_R is the ratio of the compound concentration versus the internal standard concentration
c is the quadratic constant from the quadratic regression

If the calibration criteria cannot be met using a quadratic fit, the average response factor can be used. Calculate the average response factor by finding the mean of the relative response factors calculated for each concentration of standard, as shown in Equation 6.

Equation 6

$$RRF_i = \left(\frac{A_i \times C_{IS}}{A_{IS} \times C_{cal}} \right)$$

where: RRF_i is the relative response factor for compound i
A_i is the area of the peak for compound i
A_{IS} is the area of the internal standard peak
C_{cal} is the concentration as sulfur in the calibration standard (µg S/L)
C_{IS} is the concentration of internal standard as sulfur (µg S/L)

To evaluate the closeness of the fit for the calibration, use the calibration model chosen (quadratic curve or average response factor) to calculate the concentration for each calibration level. Use Equation 7 to calculate the concentration using the quadratic model or Equation 8 to calculate the average response factor model. Determine the error for each level and calculate the mean absolute percent error (MAPE) as shown in Equation 9. The MAPE is used by software packages such as SAS and Statgraphics to evaluate the fit between a model prediction and the measured values.

Equation 7

$$C_i = \frac{\left(-b+\sqrt{b^2-4c(a-RR)}\right)}{2c} * C_{IS}$$

where: C_i *is the measured concentration of compound i (µg S/L)*
a is the y-intercept from the quadratic regression
b is the linear constant from the quadratic regression
c is the quadratic constant from the quadratic regression
RR is the response ratio
C_{IS} *is the concentration of internal standard as sulfur (µg S/L)*

Equation 8

$$C_i = \frac{RR}{RRF} * C_{IS}$$

where: C_i *is the measured concentration of compound i (µg S/L)*
RR is the response ratio
RRF is the relative response factor
C_{IS} *is the concentration of internal standard as sulfur (µg S/L)*

Equation 9

$$MAPE = \frac{\sum \left| \frac{C_{cal} - C}{C_{cal}} \right| * 100}{n}$$

where: MAPE is the mean absolute percent error
C_{cal} *is the concentration in the calibration standard*
C is the concentration measured for the calibration level
n is the number of calibration levels

The MAPE should be below 20% for each compound. Section 17, Table 5 lists the MAPE found for several calibrations using both an average and a quadratic calibration model. Section 17, Figure 3 shows a typical calibration curve for the PFPD response with a quadratic fit.

If a 20% MAPE cannot be achieved, one or more of the following actions should be taken.

10.2.3.1 Standards should be reanalyzed if the analysis appears to be suspect due to large variation from predicted response.

10.2.3.2 Standards should be reprepared if they appear to be suspect after reanalysis.

10.2.3.3 System maintenance should be performed, including replacing the injection port liner, replacing the septum, clipping the column, checking the split ratio, and checking the detector parameters.

10.2.3.4 The calibration range may be reduced by eliminating the low level or high level calibration standard. If the calibration range is changed, do not report values that are measured outside this range. This is especially true for the quadratic model, where large errors can occur.

10.3 Daily Calibration Check

Prior to analyzing samples each day, a daily calibration check should be prepared (Section 7.3.7) and analyzed. Calculate the percent recovery of the standard using Equation 10 to verify the calibration. In-house percent recovery control limits should be determined, and should not exceed ±20%. If the calibration check does not pass, the action items in Section 10.2.3 should be repeated. If these fail, the initial multipoint calibration should be repeated. Section 17, Table 1 summarizes the results for daily calibration checks during the method evaluation and subsequent single laboratory analyses.

Equation 10

$$R = \left(\frac{C_i}{C_{IC}} \right) \times 100$$

where: *R is the recovery in percent*
C_i is the measured concentration for compound i (µg S/L)
C_{IC} is the concentration measured during the initial calibration (µg S/L)

10.4 BLANK ANALYSIS

A method blank should be prepared and analyzed with the initial calibration and every day on which samples are analyzed. Prepare the blank the same as the calibration standards, but only add the internal standard solution (Section 7.3). The blank concentration should be less than 20% of the lowest calibration point. High blank levels can be caused by contaminated reagent water/acid, contaminated internal standard, contaminated glassware or syringes, and dirty injection ports. Resolution of sulfur dioxide, a common contaminate, from methyl mercaptan is critical for meeting the blank criteria. Section 17, Figure 4 shows a typical sample with MeSH resolved from the artifact peak.

11.0 PROCEDURE

11.1 Sample Analysis

Transfer a known volume (1.8 mL) of the sample to an autosampler vial using a deactivated gas-tight syringe. If the sample is preserved at pH 2.5, no pH adjustment is required. If the sample is preserved at pH 10, phosphoric acid solution should be added to bring the pH to between 1.5 and 2.5. Determine the amount of acid needed using a trial sample, then add the determined amount to the sample to be analyzed (typically 15 to 20 µL). Add 9 µL (assuming a sample volume of 1.8 mL) of the internal standard solution (40 mg S/L thiophene and thioanisole) to the vial. Be sure that the spike goes into the sample liquid and that it is well mixed (Section 7.3.8). Inject the sample using the exact instrumental conditions used for the analysis of the calibration standards (Section 10.1). Calculate the concentration of each RSC using Equation 7 or 8, depending on the calibration model. If the concentration is above the calibration range, the sample must be diluted and reanalyzed.

11.2 Dilution

If dilution is necessary, inject some fractional volume less than 1.8 mL into the vial using a deactivated gas-tight syringe, bring it to 1.8 mL with DI water pH adjusted to 2.5, and analyze it as described in Section 11.1. Calculate the dilution factor by dividing 1.8 mL by the volume of sample used. For samples preserved for total sulfide analysis, dilution by the preservative must also be accounted for by multiplying the two dilution factors together.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Identification of Compounds

An analyte is identified by comparison of the relative retention time of the sample with the relative retention time of an authentic standard of the target compound analyzed using the same analytical conditions. Section 17, Table 6 lists the relative retention time windows for the RSCs and the absolute retention time windows for the internal standards.

12.2 Quantification of Compounds

Measure the concentration of each analyte as sulfur using Equation 7 or 8, then adjust for dilution and percent sulfur using Equation 11 to report the concentration as mass of compound instead of sulfur. The fraction of sulfur in each compound can be found in Section 17, Table 6.

Equation 11

$$C = \frac{C_i * DF}{FS}$$

where: C *is the concentration of compound in the sample (µg/L)*
C_i *is the measured concentration for compound* i *(µg S/L)*
DF *is the dilution factor*
FS *is the fraction of sulfur in the compound*

12.3 Duplicate Precision Estimate

Duplicate samples should be analyzed with each set of samples. Calculate the relative percent difference (RPD) for each duplicate pair as shown in Equation 12.

Equation 12

$$RPD = \frac{2 * \left| C_1 - C_2 \right|}{\left(C_1 + C_2 \right)} \times 100$$

where: RPD *is the relative percent difference in the two determinations*
C_1 *is the first concentration measured (µg/L)*
C_2 *is the second concentration measured (µg/L)*

12.4 MATRIX SPIKE CALCULATION

A matrix spike experiment should be performed with each set of samples analyzed. Calculate the percent recovery using Equation 13.

Equation 13

$$R = \frac{(C_{MS} - C)}{C_S} \times 100$$

where: R is the percent recovery
C_{MS} *is the concentration measured in the matrix spiked sample (µg/L)*
C is the concentration measured in the unspiked sample (µg/L)
C_S *is the theoretical concentration of the spiked compound (µg/L)*

13.0 METHOD PERFORMANCE

13.1 Single laboratory performance of this method is detailed in Section 17, Tables 2 and 3. Single laboratory precision is estimated to be 12.3% MeSH and 10% or less for the other RSCs. The average matrix spike recoveries ranged from 93 to 112% for all target analytes. The average surrogate spike recovery was 106%.

13.2 Interlaboratory precision estimates have not been determined for this method.

14.0 POLLUTION PREVENTION

14.1 The laboratory should check state and local requirements to determine if pollution prevention equipment is required or recommended in its area.

15.0 WASTE MANAGEMENT

15.1 It is the responsibility of the laboratory to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and lands by minimizing releases into the environment. Compliance with all sewage discharge permits and regulations is also required.

16.0 REFERENCES

16.1 Federal Register. 1984. Appendix B to Part 136–Definition and procedure for the determination of the method detection limit, rev. 1.11. *Federal Register* 49(209): October 26.

16.22 National Research Council (NRC) 1995. *Prudent practices in the laboratory*. Washington, DC: National Academy Press.

16.3 Taylor, J.K. 1987. *Quality assurance of chemical measurements.* Chelsea, MI: Lewis Publishers.

17.0 TABLES AND DIAGRAMS

Table 1. Results of Daily Calibration Checks

Compound	Mean Recovery	RSD (%)	n
Total sulfide	106	11.2	94
Methyl mercaptan	95.0	10.6	42
Dimethyl sulfide	100	10.5	42
Dimethyl disulfide	111	8.3	42
Dimethyl trisulfide	102	11.5	42

Table 2. Surrogate Recovery

Compound	Mean Recovery	RSD (%)	n
Thioanisole	106	6.7	1077

Table 3. Duplicate Results and Matrix Spike Recovery

	Duplicate Precision		Matrix Spike Recovery		
Compound	Pooled RSD[a] (%)	n	Mean Recovery (%)	RSD (%)	n
Total sulfide	9.4	87	93	20.7	70
Methyl mercaptan	12.3	33	106	20.0	33
Dimethyl sulfide	5.6	34	102	11.7	34
Dimethyl disulfide	7.0	33	112	16.5	34
Dimethyl trisulfide	4.7	25	96	24.1	34

[a] equation for pooled relative standard deviation can be found in Taylor 1987

Table 4. GC/PFPD Operating Conditions for Measuring Reduced Sulfur Compounds

Injection port	split (15:1 ratio)
Injection volume	2 µL
Split vent flow rate	16 mL/min helium
Injector temperature	110°C
Injection liner	4 mm id with fused silica wool packing (deactivated, either Siltek or Silanized)
Carrier gas	helium
Carrier gas flow rate	constant flow mode at 1.2 mL/min (pressure pulse at injection might be necessary see Section 10.1)
Column	J&W DB-624, 30 m x 0.25 mm id with 1.4 µm film fused silica capillary column or equivalent
Oven temperature program	
Initial	10°C
Ramp 1	6°C/min to 35°C for 2 minutes
Ramp 2	8°C/min to 170°C
Ramp 3	40°C/min to 250°C for 3 minutes
Detector	PFPD (OI model 5380 or equivalent)
Temperature	250°C
Combustion tube	2 mm
Optical filter	BG-12 (purple)
Hydrogen flow	11 mL/min
Air flows	optimized as described by manufacturer
Pulse rate	3.1 Hz
Signal	square root of PMT signal

Table 5. Summary of Initial Calibration Results

	Average Response Factor		Quadratic Fit			
Compound	Mean RRF[a]	Mean MAPE[b]	Mean a[c]	Mean b[d]	Mean c[e]	Mean MAPE[b]
Total sulfide	0.641	30.2	-0.073	0.838	-0.006	20.7
Methyl mercaptan	0.673	21.5	-0.074	0.906	-0.025	14.8
Dimethyl sulfide	0.887	18.0	-0.062	1.094	-0.013	14.8
Dimethyl disulfide	0.983	16.8	-0.092	1.385	-0.083	13.0
Dimethyl trisulfide	0.989	16.3	-0.092	1.401	-0.089	12.1

[a] average of eight calibration sets' mean relative response factors

[b] average of fifteen calibration sets' mean absolute percent errors

[c] average of eight calibration sets' y-intercepts from a quadratic regression

[d] average of eight calibration sets' linear constants from a quadratic regression

[e] average of eight calibration sets' quadratic constants from a quadratic regression

Table 6. Retention Time Statistics for RSCs and Sulfur Fraction

Compound	Mean[a] RRT	RSD[b] (%)	Relative Retention Time Window[c]	Fraction Sulfur
Total sulfide	0.192	1.12	0.186 – 0.198	0.9408
Methyl mercaptan	0.318	0.84	0.310 – 0.326	0.6665
Dimethyl sulfide	0.527	0.57	0.518 – 0.536	0.5160
Dimethyl disulfide	1.217	0.11	1.213 – 1.221	0.6808
Dimethyl trisulfide	1.748	0.19	1.738 – 1.758	0.7618
Internal standards	Mean RT[d] (min)	RSD[b] (%)	Retention Time Window	Fraction Sulfur
Thiophene	11.37	0.37	11.24 – 11.49	0.3810
Thioanisole	22.41	0.17	22.52 – 22.29	0.2581

[a] mean relative retention time (relative to thiophene) for 30 calibration standard analyses

[b] relative standard deviation for 30 calibration standard analyses

[c] windows are calculate from the mean value ± three times the standard deviation

[d] mean retention time for 30 calibration standard analyses

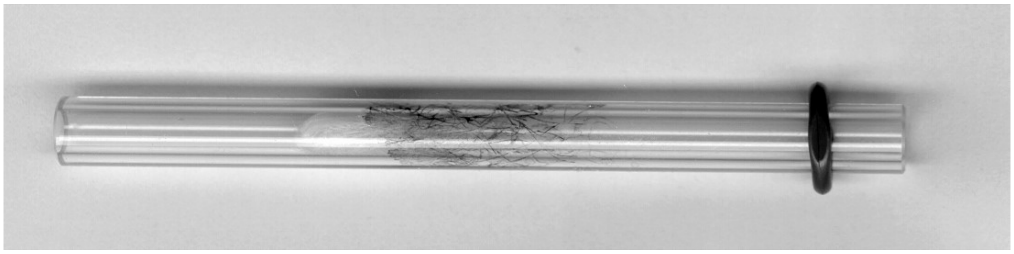


Figure 1. Injection Port Liner with Glass Wool Plug and Deposits from Approximately 20 injections Containing 3 g/L Ascorbic Acid

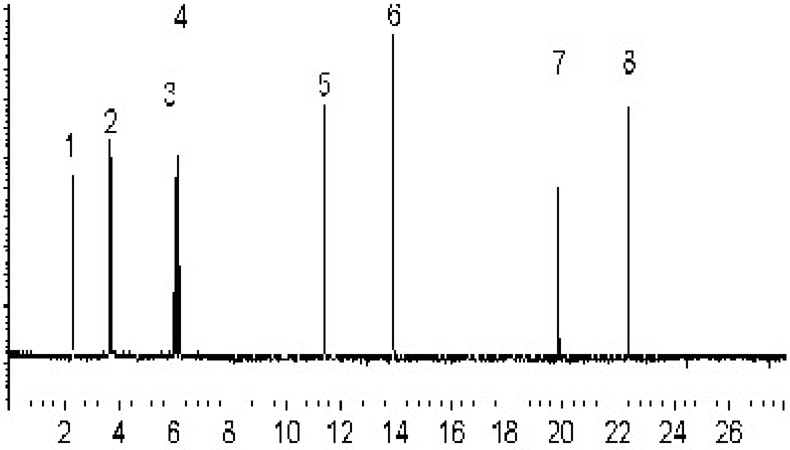


Figure 2. Chromatogram of 200 µg S/L Standard Containing (1) Total Sulfide; (2) MeSH; (3) DMS; (4) CS_2 (resolution check compound); (5) Thiophene (internal standard); (6) DMDS; (7) DMTS; (8) Thioanisole (internal standard)

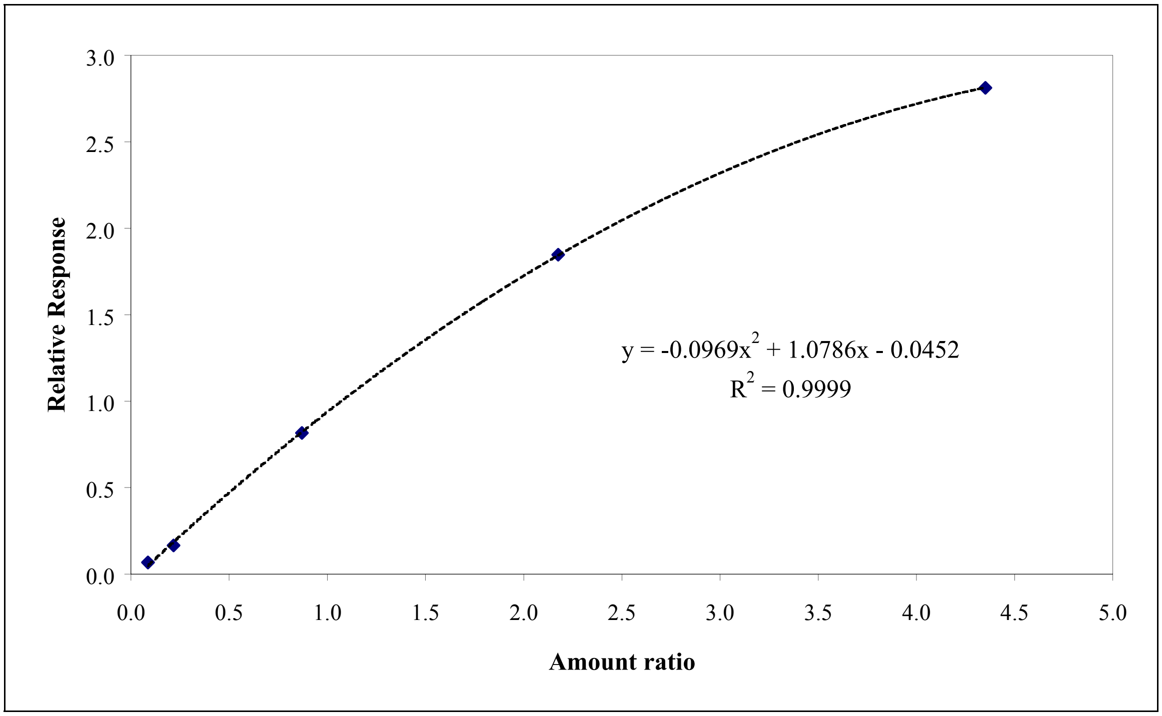


Figure 3. Typical Calibration Curve for Total Sulfide with Quadratic Equation

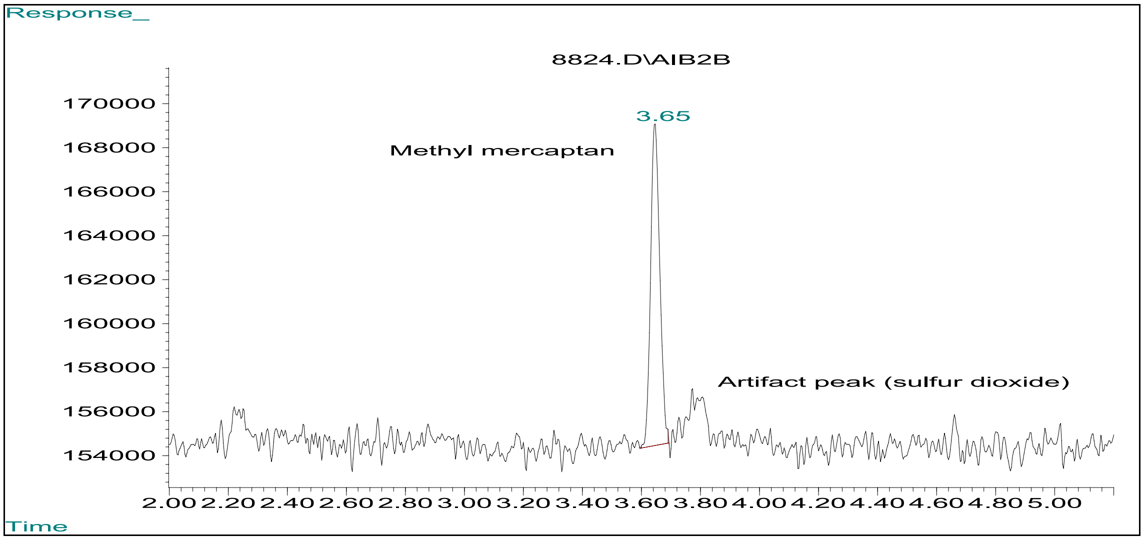


Figure 4. Separation of Methyl Mercaptan (100 µg S/L) from Artifact Peak in Pulp Mill Effluent

APPENDIX B

MILL SUMMARY DATA

MILL A

Mill A’s production is nearly 520 metric tons per day (TPD) of bleached kraft pulp made predominately from softwood, Douglas-fir sawdust, and chips. A schematic of the wastewater treatment plant (WWTP) is provided in Figure B1. This mill hard pipes condensates to the WWTP just prior to the first ASB. Average daily water usage is 11 million gallons per day (MGD). Samples were collected from the primary clarifier outlet, front of the aerated stabilization basin (ASB), midpoint of the ASB, and final effluent. Results are provided in Table B1. Average biological oxygen demand (BOD_5) in the final effluent was 13 mg/L, average pH was 7.41, and total dissolved solids (TSS) were 23 mg/L.

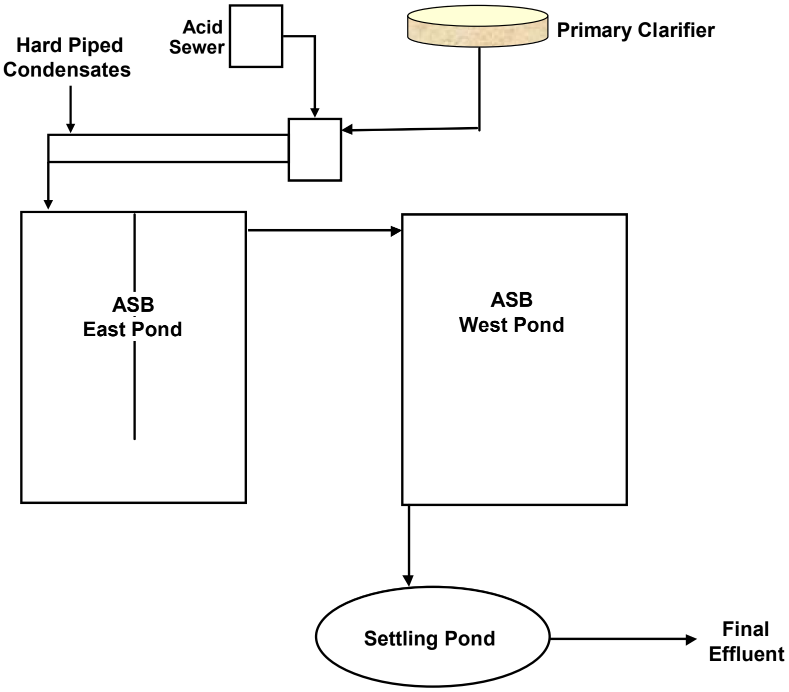


Figure B1. Mill A Wastewater Treatment Plant Schematic

Table B1. Mill A Reduced Sulfur Compound Concentrations (µg S/L)

Compound	Primary Clarifier Outlet	Front of ASB	Midpoint of ASB	Final Effluent
Total sulfide	18100	1030	530	225
MeSH	ND	39.4	232	56.9
DMS	ND	944	2260	33.5
DMDS	ND	1290	2550	113
DMTS	ND	25	353	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL B

This mill produces groundwood (GW), thermomechanical (TMP), and deinked pulp. Average daily production for GW is 8 air dried tons (ADT) of unbleached softwood pulp, TMP production averages 460 ADT, and the deinking facility's average daily production is 600 ADT. Average daily water usage is 11.5 MGD. The WWTP (Figure B2) consists of a 160 ft diameter primary clarifier, followed by a 90 MG ASB, an activated sludge (AS) plant consisting of a 4 MG aeration basin with a secondary clarifier, and a 50 MG ASB prior to discharge. The two ASBs have a total of 2175 horse power (HP) provided by 29 aerators. The retention time (RT) of the treatment system is 3 days. Secondary solids are removed from the secondary clarifier and split to the aeration basin as recirculated activated solids and to the primary clarifier as wasted activated solids. Solids removed from the treatment plant by the primary clarifier are dewatered and burned as fuel. Samples were collected from the primary clarifier outlet, ASB north lagoon, secondary clarifier, dewatering effluent, and final effluent. RSC results are listed in Table B2.

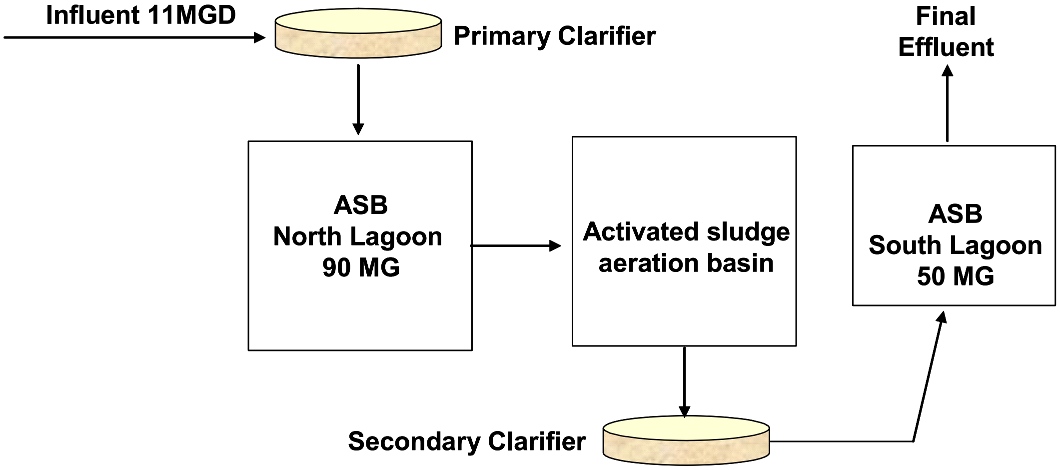


Figure B2. Mill B Wastewater Treatment Plant Schematic

Table B2. Mill B Reduced Sulfur Compound Concentrations (µg S/L)

Compound	Primary Clarifier Outlet	ASB North Lagoon	Secondary Clarifier	Dewatering Effluent	Final Effluent
Total sulfide	5320	52	48	609	ND
MeSH	190	ND	ND	83.3	ND
DMS	ND	ND	ND	ND	ND
DMDS	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL C

Mill C is a kraft mill pulping softwood and old cardboard containers (OCC). It produces about 550 tons of unbleached softwood pulp per day. Average water usage is 12 MGD. The mill is equipped with a primary clarifier, an ASB that has three aerated runs (17 aerators, total of 1275 HP), and a final quiescent run for secondary effluent treatment. The mill hard pipes condensates to the sewer from the primary clarifier prior to the ASB. The system was designed with an RT of 16 days. Further details of the treatment system are provided in Figure B3. Three samplings occurred at this mill. Results are presented in Tables B3, B4, and B5. Data for pH, DO, temperature, TSS, and BOD were provided by mill personnel.

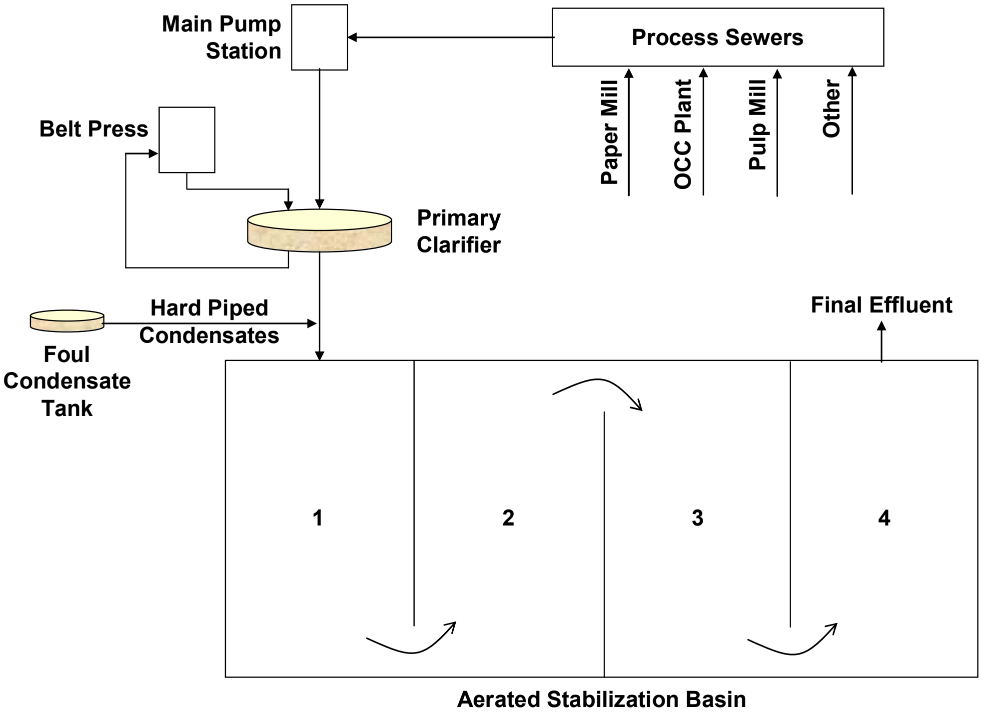


Figure B3. Mill C Wastewater Treatment Plant Schematic

Table B3. Mill C I Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Primary Clarifier Outlet	Front of ASB	Midpoint ASB	Final Effluent	Sludge Dewatering Effluent
Flow (MGD)	8.8	13.2	13.2	13.2	0.46
pH	10.0	8.4	NA	7.3	NA
DO (mg/L)	NA	NA	NA	1.4	NA
Temperature (ºC)	NA	45.8	NA	22.4	NA
TSS (lb/d)	NA	10392	NA	3429	NA
BOD (lb/d)	NA	27517	NA	2007	NA
BOD removal (lb/HP/D)	NA	NA	NA	20	NA
Total sulfide	1310	10800	2810	181	310
MeSH	ND	9260	2370	32.3	ND
DMS	83.5	1430	845	ND	ND
DMDS	ND	2730	1870	ND	ND
DMTS	ND	443	280	ND	ND

NA not applicable; compound not detected in sample

ND not detected above lowest calibration limit: 23.7 μg/L for total sulfide; 31.8 μg/L for MeSH; 38.8 μg/L for DMS; 30.4 μg/L for DMDS; 30.6 μg/L for DMTS

Table B4. Mill C II Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Main Pump Station	Hard Pipe Line	Front of ASB	Midpoint ASB	Final Effluent
Flow (MGD)	8.8	2.0	13.2	13.2	13.2
pH	NA	7.0	9.2	7.4	7.4
DO (mg/L)	NA	NA	1.4	2.0	1.4
Temperature (ºC)	NA	NA	45.8	NA	22.4
Total sulfide	278	12100	12800	6530	54.0
MeSH	ND	2190	5020	910	33.7
DMS	118	2910	3320	570	ND
DMDS	22.6	10000	8280	2000	ND
DMTS	ND	148	112	26.6	ND

NA not applicable; compound not detected in sample

ND not detected above lowest calibration limit: 23.7 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

Table B5. Mill C III Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Main Pump Station	Primary Clarifier Inlet	Primary Clarifier Outlet	Foul Condensate	Hard Pipe Line
Flow (MGD)	8.8	8.8	8.8	NA	4.4
pH	7.4	10.0	10.3	6.9	6.9
DO (mg/L)	NA	NA	NA	NA	NA
Temperature (ºC)	27.4	39.8	37.2	51.8	41.2
Total sulfide	1400	2246	309	55300	38800
MeSH	ND	ND	ND	47300	44300
DMS	ND	ND	ND	524	1890
DMDS	ND	ND	ND	2630	730
DMTS	ND	ND	ND	2750	ND
	Front of ASB	**ASB Run #1**	**ASB Run #2**	**ASB Run #3**	**Final Effluent**
Flow (MGD)	13.2	13.2	13.2	13.2	13.2
pH	9.4	7.4	7.6	7.6	7.6
DO (mg/L)	0.17	2.2	4.0	3.6	3.9
Temperature (ºC)	38.4	27.3	23.1	22.5	21.1
Total sulfide	11400	226	ND	ND	ND
MeSH	13900	ND	ND	ND	ND
DMS	1570	ND	ND	ND	ND
DMDS	8410	680	ND	ND	ND
DMTS	205	ND	ND	ND	ND

NA not applicable; compound not detected in sample

ND not detected above lowest calibration limit: 23.7 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL D

This kraft mill pulps softwood (pine) and produces about 1200 TPD of bleached pulp using a dissolving kraft process. Average water flow through the treatment system is 43 MGD. The mill is equipped with a primary clarifier followed by an ASB. Flow consists of an alkaline waste stream of 14 MGD that goes through primary clarification, and an acid stream of 27 MGD that enters the waste stream at the mix box. Condensates (2 MGD) are hard piped to the waste stream following the mix box. The first cell of the ASB lagoon consists of 15 acres, is 12 ft deep on average, and contains 25 aerators with a total of 1875 HP. The second cell is also 15 acres and 12 ft deep on average, and contains 11 aerators with a total of 825 HP, for 2700 HP overall. Effluent from these cells flows to a 120 acre lagoon. Further details of the treatment system are provided in Figure B4. Different areas of the treatment plant were sampled during three sampling episodes, and results are shown in Tables B6 and B7. The first sampling event occurred during a low odor time, and the second occurred following an odor event.

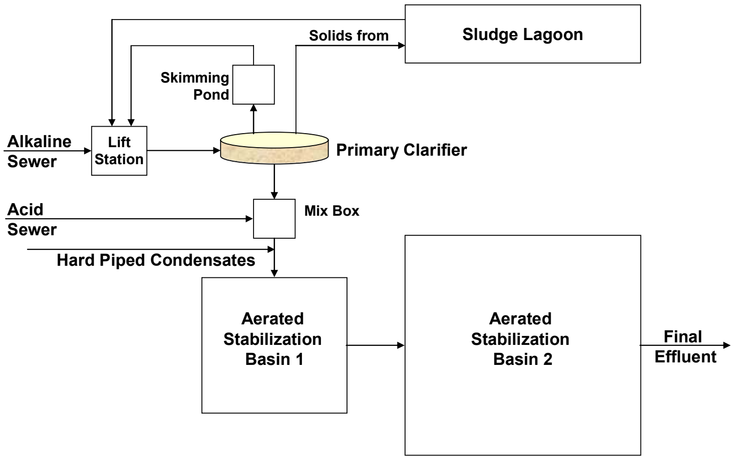


Figure B4. Mill D Wastewater Treatment Plant Schematic

Table B6. Mill D I and II Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Mix Box	Front of ASB	Midpoint ASB	Final Effluent
Mill D I Sampling				
Total sulfide	78.0	1030	446	220
MeSH	31.2	9030	1190	ND
DMS	24.1	4680	1020	ND
DMDS	22.2	587	968	24
DMTS	ND	80.7	24.8	ND
Mill D II Sampling				
Total sulfide	792	66	303	ND
MeSH	24.9	1680	752	24.7
DMS	ND	2580	654	ND
DMDS	ND	1800	1050	ND
DMTS	ND	956	24.8	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

Table B7. Mill D III Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Alkaline Sewer	Acid Sewer	Sludge Lagoon Effluent	Lift Station	Skimming Pond Effluent	Primary Clarifier Outlet
Flow (MGD)	12.4	22.6	2.1	15.1	0.6	15.1
pH	10.7	NA	9.9	NA	9.85	10.5
DO (mg/L)	0.48	NA	0.62	NA	0.56	1.9
Temperature (ºC)	44.4	NA	26.0	NA	28.5	38.1
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	NA	NA	NA	NA	NA	NA
Total sulfide	24700	5470	20900	6560	36000	17000
MeSH	NA	NA	NA	NA	NA	NA
DMS	ND	ND	ND	ND	ND	ND
DMDS	ND	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND	ND
	Hard Pipe Condensate	Mix Box	Front of ASB	ASB Midpoint East Cell	Inlet to Lagoon 2	Final Effluent
Flow (MGD)	3.2	37.7	40.9	40.9	40.9	40.9
pH	NA	6.4	6.3	6.4	6.9	7.2
DO (mg/L)	NA	3.7	0.45	0.45	4.2	2.6
Temperature (ºC)	NA	43.8	45.6	39.8	35.1	26.5
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	NA	NA	NA	NA	NA	NA
Total sulfide	78400	5860	5790	241	89.8	53.6
MeSH	84700	255	5170	261	65.9	NA
DMS	21300	ND	1540	240	40.4	ND
DMDS	9020	ND	2040	1060	223	29.0
DMTS	253	ND	2500	104	ND	ND

NA not available

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL E

Mill E is a kraft and recycle mill that pulps softwood and produces about 1500 TPD of unbleached pulp. Average water flow through the treatment system is 43 MGD. The mill is equipped with a steam stripper for treatment of foul condensates. There are two settling ponds, the second of which is equipped with two injection aerators, followed by an ASB. The treatment system is illustrated in Figure B5. Sample results for RSCs are listed in Table B8.

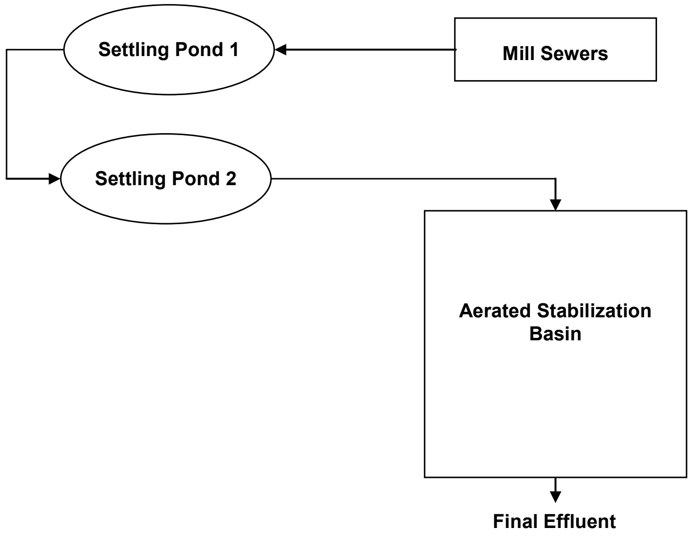


Figure B5. Mill E Wastewater Treatment Plant Schematic

Table B8. Mill E Reduced Sulfur Compound Concentrations (µg S/L)

Compound	Settling Pond 1 Outlet	Front of ASB	Midpoint ASB	Final Effluent
Total sulfide	2670	4500	641	ND
MeSH	26.6	70.2	ND	ND
DMS	22.9	28.7	ND	ND
DMDS	ND	ND	ND	ND
DMTS	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL F

This is a kraft and recycle mill that pulps softwood and produces about 1800 TPD of unbleached pulp. Average water flow through the treatment system is 21 MGD. A stream stripper is used to process foul condensates. The mill is equipped with a primary clarifier followed by a two-stage ASB with twelve 150 HP surface aerators (1800 HP total). The treatment system consists of several waste ponds used for a variety of purposes. This sampling was in support of a project underway by the mill to determine aqueous phase RSC concentrations in selected ponds being monitored for sulfide emissions. Sample results for RSCs are listed in Tables B9 and B10.

Table B9. Mill F Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Pond 17 Outlet	Pond 1 Outlet	Pond 5 Outlet	Pond 8 Outlet
Total sulfide	66900	768	60300	36400
MeSH	ND	ND	ND	81
DMS	ND	ND	ND	ND
DMDS	ND	ND	ND	ND
DMTS	ND	ND	ND	ND

ND not detected above lowest calibration limit: 23.7 µg/L for total sulfide; 31.8 µg/L for MeSH; 38.8 µg/L for DMS; 30.4 µg/L for DMDS; 30.6 µg/L for DMTS

Table B10. Mill F II Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Pond 17 Outlet	Pond 1 Outlet	Pond 5 Outlet	Pond 8 Outlet	Mix Basin
pH	9.68	7.69	9.11	8.9	7.62
DO (mg/L)	3.2	6.8	3.6	2.9	18.5
Temperature (ºC)	18.6	18.1	18.1	18.6	34.8
Specific conductivity (mS/cm)	2.745	2.391	2.757	2.488	2.264
Total sulfide	32900	147	26300	10300	12200
MeSH	ND	ND	ND	41.4	40.4
DMS	ND	ND	ND	ND	20.1
DMDS	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND

ND not detected above lowest calibration limit: : 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL G

Mill G is a kraft mill that pulps softwood and hardwood to produce about 1600 TPD of bleached pulp. It is equipped with a steam stripper for treatment of foul condensates. The mill has a primary clarifier followed by a two-stage ASB. ASB 1 is 53 acres with a depth of 11.5 ft and an RT of 10 days. This lagoon contains 14 aerators with a total capacity of 885 HP. The second lagoon consists of two ponds. ASB 2A is 86 acres with an average depth of 9 ft and a total of 1950 HP of aeration. ASB 2B is a 191 acre pond with a depth of 10 to 11 ft, total aeration of 975 HP, and an RT of 12 days. Details of the treatment system are illustrated in Figure B6. Samples were collected from the input to treatment through both ASBs, with the results for RSCs shown in Table B11.

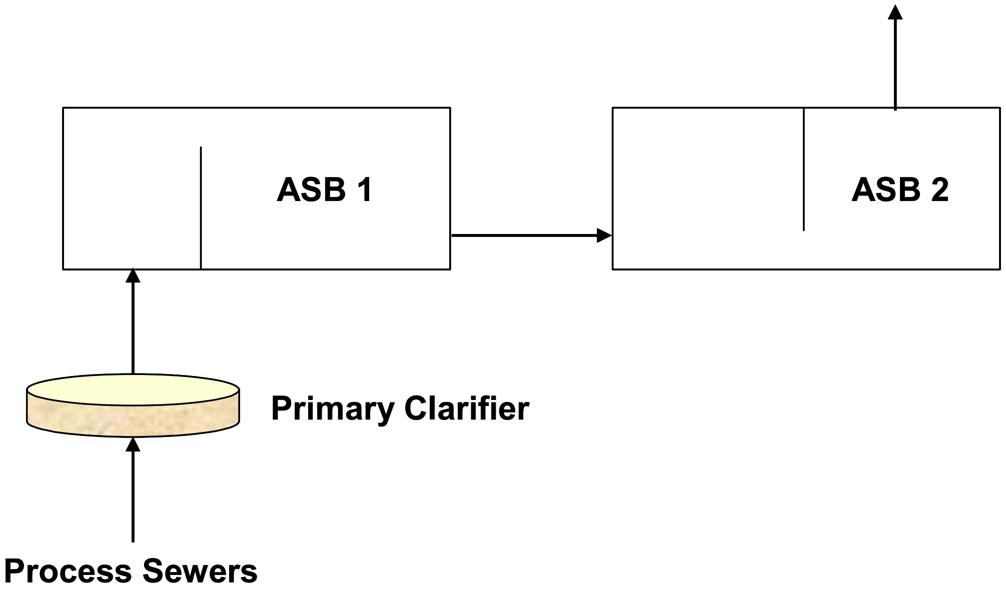


Figure B6. Mill G Wastewater Treatment Plant Schematic

Table B11. Mill G Reduced Sulfur Compound Concentrations (µg S/L)

Compound	Input to ASB	ASB 1 AB Midpoint	ASB 1 AB Effluent	ASB 2AB Midpoint	ASB 2AB Effluent
Total sulfide	19300	146	194	854	56.0
MeSH	282	38.5	57.6	33.9	ND
DMS	116	ND	ND	ND	ND
DMDS	303	ND	ND	ND	ND
DMTS	32.8	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL H

This is a kraft and recycle mill that pulps softwood, hardwood, and recycled fiber to produce about 1600 TPD of bleached and unbleached pulp. Average water flow through the treatment system is 26 MGD. The mill utilizes steam stripping and also hard pipes some foul condensates. The hard pipe inlet is at the front of the ASB. The mill is equipped with a 250 ft diameter primary clarifier followed by a 75 acre ASB with a design volume of 303 MG, equipped with 53 aerators with a total of 3975 HP and a 300 HP fine bubble diffused air system. The current RT is approximately 4 days. Flow from the ASB is directed to a 20 acre, 50 MG pond. This pond has a theoretical residence time of 1 day. Wastewater then flows to a 43 acre, 82 MG hold and release basin equipped with five surface aerators. The system generally operates at a 93% BOD removal efficiency. Details of the treatment system are illustrated in Figure B7. Samples were collected from different areas of the condensate and treatment system during two separate sampling episodes, with the results listed in Table B12.

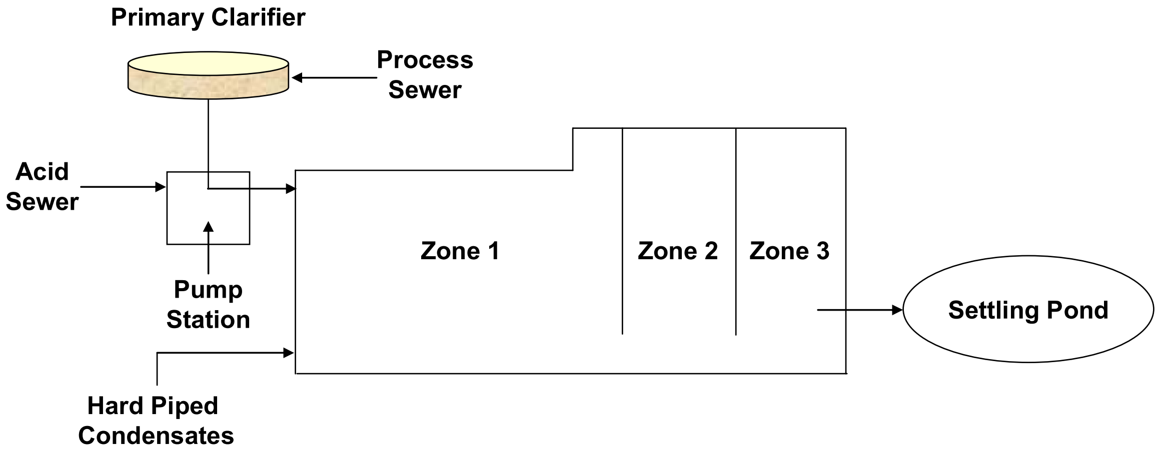


Figure B7. Mill H Wastewater Treatment Plant Schematic

Table B12. Mill H Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Influent to ASB	Zone 1 across ASB	Zone 2 across ASB	Zone 3 across ASB	ASB Effluent	Settling Pond Effluent
Flow (MGD)	26.5	26.5	26.5	26.5	26.5	26.5
Temperature (ºC)	53.3	NA	NA	NA	32.2-35	29.4-31
Mill H I sampling						
Total sulfide	397	16900	29200	20900	224	149
MeSH	2420	ND	ND	ND	ND	ND
DMS	3060	ND	ND	26.3	ND	173
DMDS	377	ND	ND	ND	ND	ND
DMTS	51.2	ND	ND	ND	ND	ND
Mill H II sampling						
Total sulfide	61.7	21700	30000	24000	97.8	73.5
MeSH	175	ND	ND	ND	ND	ND
DMS	2670	ND	ND	ND	ND	119
DMDS	619	ND	ND	ND	ND	ND
DMTS	318	ND	ND	ND	ND	ND

NA not available

ND not detected above lowest calibration limit: 19.6 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL I

Production capacity at Mill I is approximately 475,000 ton per year of unbleached kraft pulp. The mill produces kraft paper and lightweight linerboard. A schematic of the WWTP is provided in Figure B8. The mill utilizes steam stripping and also hard pipes some foul condensates. Effluent from the pulp and paper mill enters the primary clarifier with a combined average flow of 14.7 MGD. Effluent from the primary clarifier is routed to the inlet of a 21.5 acre aeration basin equipped with 1605 HP of aeration and 425 HP of sub-surface aeration. RT in the ASB is approximately 3.8 days. Effluent flows through a spillway to the 60 acre stabilization basin No.1, a single cell pond with an RT of approximately 5 days. Effluent from the first stabilization pond flows into a two cell, 190 acre stabilization pond with an additional 16 day RT. Effluent from the second stabilization pond enters a single cell, 120 acre stabilization pond with a 10 day RT. Samples were collected from the inlet, within, and outlet of the primary clarifier, condensate hard pipe, across the ASB, the retention pond, and the emergency pond. Average results of these analyses are listed in Table B13.

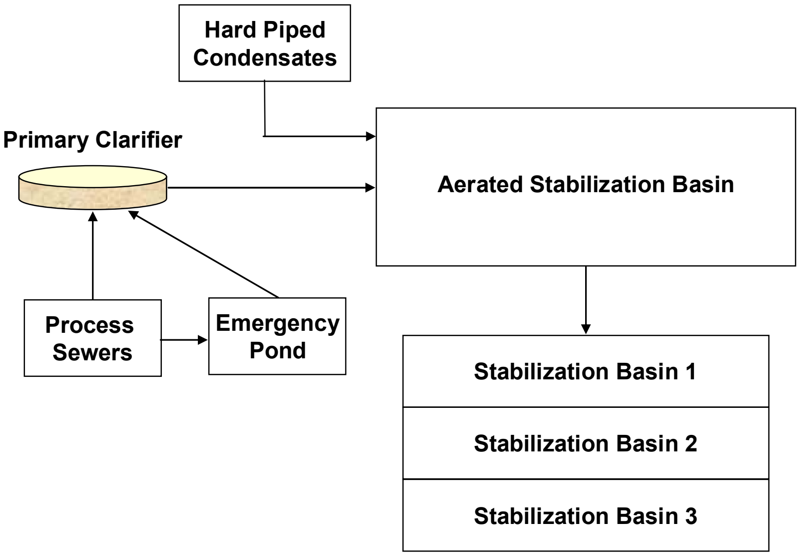


Figure B8. Mill I Wastewater Treatment Plant Schematic

Table B13. Mill I Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Primary Clarifier Inlet	Primary Clarifier Outlet	Condensate Hard Pipe	ASB Outlet	Stabilization Basin 1 Outlet
Total sulfide	617	466	102000	ND	40.9
MeSH	I	I	44100	ND	ND
DMS	19.9	22.6	3680	ND	ND
DMDS	ND	ND	2490	ND	ND
DMTS	ND	ND	374	ND	ND

NA not available
I interference
ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL J

Mill J is a kraft, neutral sulfite semi-chemical (NSSC), and recycle mill that pulps softwood and hardwood and performs nondeink recycling of OCC to produce about 1800 TPD of unbleached pulp. Average water flow through the treatment system is 22.5 MGD. Foul condensates are currently hard piped to the treatment lagoon. The mill is equipped with a 160 ft diameter primary clarifier followed by three equalization ponds in series. The first pond contains four 75 HP aerators, the second and third ponds each contain two 75 HP aerators. These ponds discharge to ASB1, equipped with eight 40 HP aerators and two 75 HP aerators, which discharges to ASB2, equipped with sixteen 75 HP aerators and one 40 HP aerator. Pulp mill effluent enters the system at the front of ASB1 and the hard piped condensate inlet is located at the front of ASB2. The treatment system has an overall RT of 7 days and is diagramed in Figure B9.

Samples from this facility were collected several times during this and other NCASI projects. One project involved an assessment of odorous compounds throughout the treatment system, and another focused on reducing odor related to total sulfide in the primary clarifier and equalization ponds at the front of the WWTP. RSC results for the various samplings are listed in Tables B14, B15, and B16.

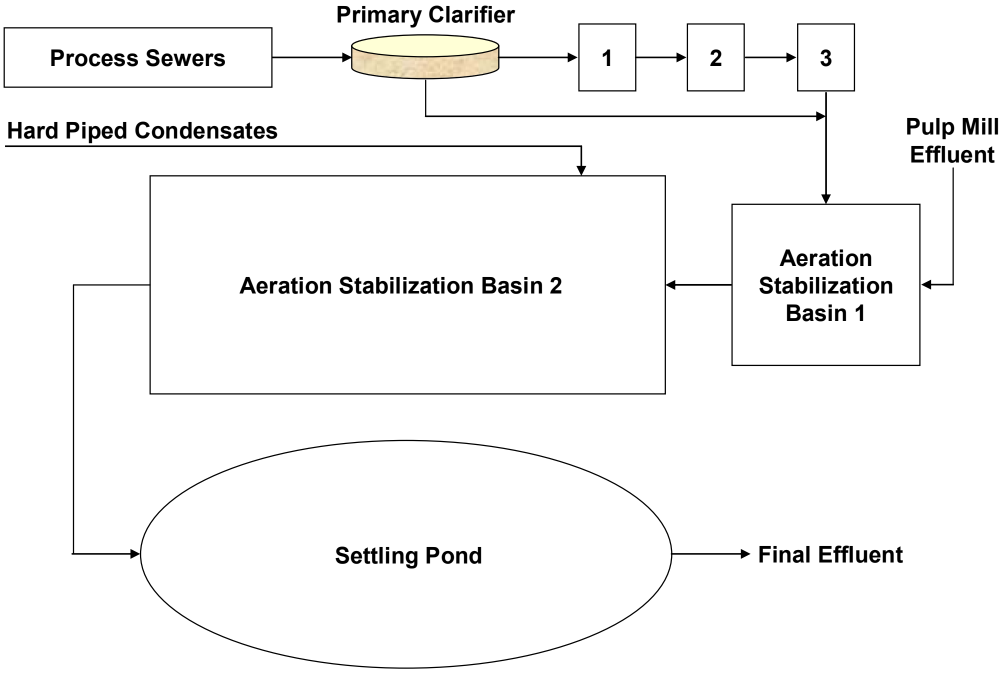


Figure B9. Mill J Wastewater Treatment Plant Schematic

Table B14. Mill J I Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Primary Clarifier Inlet	Primary Clarifier Outlet	Recaust. Sewer	EP 1 Outlet	EP 2 Outlet	EP 3 Outlet
Flow (MGD)	10.14	9.44	0.03	4.72	4.72	4.75
pH	7	7	NA	7	7	7
DO (mg/L)	3	0.42	NA	0.2	0.5	0.28
Temperature (ºC)	46	44.6	NA	36.4	32.5	34
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	72400	50200	100	NA	NA	23300
BOD removal (lb/HP/D)	NA	NA	NA	NA	NA	44.8
COD (ppm)	1640	1216	NA	NA	NA	1144
Total sulfide	406	12600	75400	1690	17300	24400
MeSH	ND	37.3	ND	ND	53	68.8
DMS	ND	34.6	ND	ND	ND	ND
DMDS	ND	25.2	ND	ND	ND	ND
DMTS	ND	29.1	ND	ND	ND	ND
Total sulfur	172	132	653	167	155	136

	Pulp Mill Effluent	ASB1 Outlet	Foul Condensate	ASB2 Midpoint	ASB2 Outlet	Final Effluent
Flow (MGD)	0.98	10.45	0.43	10.88	10.88	10.88
pH	9	7	NA	7	7	7
DO (mg/L)	0.14	1.74	NA	0.56	5.45	0.92
Temperature (ºC)	41	28.5	NA	24.3	22.3	22.4
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	5200	16400	NA	NA	4900	4100
BOD removal (lb/HP/D)	NA	NA	NA	NA	9.3	20
COD (ppm)	1184	910	NA	NA	583	563
Total sulfide	14200	3070	75500	201	112	82.0
MeSH	ND	ND	5390	ND	ND	ND
DMS	ND	ND	990	ND	ND	ND
DMDS	ND	ND	1760	ND	ND	ND
DMTS	ND	ND	176	ND	ND	ND
Total sulfur	86	145	57	141	141	136

NA not available

ND not detected above lowest calibration limit: 30 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

Table B15. Mill J II Reduced Sulfur Compound (µg S/L) and Sulfate, Thiosulfate, and Sulfite (mg/L) Concentrations

Compound or Parameter	Primary Clarifier Inlet	Primary Clarifier Outlet	Recaust. Sewer	Outlet of EP 1	Outlet of EP 2	Outlet of EP 3
Flow (MGD)	10.48	9.83	0.02	6.88	6.88	6.90
pH	7.5	6.0	NA	7.7	7.5	7.8
DO (mg/L)	2.2	0.93	NA	0.2	0.16	0.24
Temperature (ºC)	42.8	42.3	NA	35.7	32.5	30
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	86400	53300	NA	NA	NA	28200
Total sulfide	252	8920	443000	1740	19900	7430
MeSH	139	210	NA	NA	NA	NA
DMS	ND	ND	ND	ND	ND	ND
DMDS	ND	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND	ND
Sulfate	390	390	1000	470	480	490
Thiosulfate	<5	<5	640	9	17	15
Sulfite	<5	<5	200	<5	<5	<5
	EP Sump	ASB1 Outlet	Foul Condensate	ASB 2 Midpoint	ASB 2 Outlet	Final Effluent
Flow (MGD)	9.85	10.93	0.45	11.37	11.37	11.37
pH	8	8.6	NA	7.5	7.6	7.5
DO (mg/L)	0.27	0.16	NA	0.98	3.44	1.22
Temperature (ºC)	33.8	28.9	NA	25.5	22.8	22.4
TSS (lb/d)	NA	NA	NA	NA	NA	NA
BOD (lb/d)	NA	18900	NA	NA	6100	5100
Total sulfide	7880	3730	44300	292	ND	ND
MeSH	NA	NA	2470	ND	ND	ND
DMS	ND	ND	870	ND	ND	ND
DMDS	ND	ND	548	ND	ND	ND
DMTS	ND	ND	127	ND	ND	ND
Sulfate	470	520	<5	540	500	480
Thiosulfate	15	<5	<5	<5	<5	<5
Sulfite	<5	<5	<5	<5	<5	<5

NA not available

ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

Table B16. Mill J III Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Primary Clarifier Inlet	Primary Clarifier Outlet	EP 1 Outlet	EP 2 Outlet
Flow (MGD)	9.7	9.1	3.64	3.64
pH	7.9	6.5	7.7	7.5
DO (g/L)	2.2	1.4	1.3	2.7
Temperature (°C)	45.0	438	27.8	25.6
TSS (lb/d)	NA	NA	NA	NA
BOD (lb/d)[a]	66200	51200	NA	NA
Total sulfide	57.3	5490	ND	ND
MeSH	NA	NA	NA	NA
DMS	NA	NA	NA	NA
DMDS	NA	NA	NA	NA
DMTS	NA	NA	NA	NA

	EP 3 Outlet	EP Outlet and Clarifier Outlet	Pulp Mill Effluent	ASB1 Outlet
Flow (MGD)	3.64	9.1	2.2	11.3
pH	7	7	10.4	7.9
DO (g/L)	4.9	4.6	NA	NA
Temperature (°C)	25.4	25.8	37.5	29.5
TSS (lb/d)	NA	NA	NA	NA
BOD (lb/d)[a]	35000	NA	6500	26400
Total sulfide	2970	2920	4870	1950
MeSH	NA	123	NA	NA
DMS	NA	ND	NA	NA
DMDS	NA	ND	NA	NA
DMTS	NA	ND	NA	NA

[a] data from monthly average April 2004

NA not analyzed for in sample

ND not detected above lowest calibration limit: 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL K

Mill K is a kraft mill that pulps softwood and hardwood to produce from 2000 to 2500 TPD of bleached pulp. Average water flow through the treatment system (Figure B10) is 50 MGD. At the time samples were collected, foul condensates were hard piped to the front of ASB 1. The mill is equipped with a 230 ft diameter primary clarifier (RT 2 to 3 hours) followed by a 5 acre equalization pond that is not aerated. The combined bleach plant sewer enters the waste stream at the equalization pond. The combined flow then goes ¼ mile via an open canal to the ASB. The ASB is made up of three aerated lagoons encompassing 250 acres. ASB 1 (43.5 acres, 2000 ft by 900 ft, 8 ft depth) contains sixteen 60 and 75 HP aerators (990 HP total). ASB 2 (74.2 acres, 2100 ft by 1500 ft, 8 ft depth, RT 1 day) contains eighteen 60 HP aerators. ASB 3 (122 acres, 2650 ft by 1000 ft, 8.5 ft depth, RT 6 days) contains nineteen 60 HP aerators. The system averages 3500 HP overall. This system is followed by a quiescent pond of approximately 300 acres. RT is 14 days. Several samplings were conducted during odor reduction studies. RSC results for WWTP surveys are provided in Tables B17 and B18.

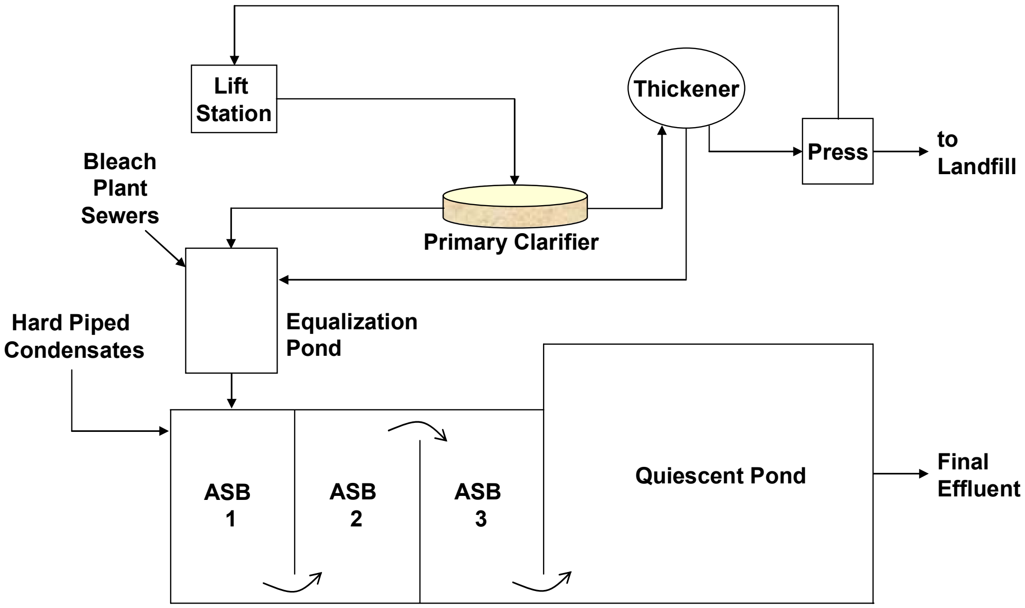


Figure B10. Mill K Wastewater Treatment Plant Schematic

Table B17. Mill K I and II Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Primary Clarifier Inlet	Primary Clarifier Outlet	Hard Pipe Condensate	ASB 1 Inlet	ASB 1 Outlet
Mill K I					
Total sulfide	NS	15800	132000	4540	18800
Mill K II					
Total sulfide	14250	13000	NS	13300	18000
MeSH	6560	370	NS	2720	875
DMS	554	139	NS	1330	383
DMDS	2620	546	NS	935	91
DMTS	170	80.3	NS	171	56.1

NS not sampled

ND not detected above lowest calibration limit: 22.3 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

Table B18. Mill K III Parameters and Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Process Sewer 1	Process Sewer 2	Primary Clarifier Outlet	Bleach Plant Sewer	Equalization Pond	A1 Canal to ASB
Flow (MGD)	7.7	NA[a]	37.5	12.5	50	50
pH	NA	NA	9	3	NA	6.9
BOD removal/HP/d[b]	NA	NA	NA	NA	NA	NA
K V Concentrations (μg S/L)						
Total sulfide	36000	16200	5260	50.2	1320	1220
MeSH	10500	1970	2070	503	612	578
DMS	643	ND	126	330	276	244
DMDS	8250	45.2	186	585	206	161
DMTS	487	ND	60.1	ND	81.2	86.5
K VI Concentrations (μg S/L)						
Total sulfide	NA	6680	22900	ND	5930	6270
MeSH	NA	424	2490	ND	1800	3310
DMS	NA	273	243	ND	181	212
DMDS	NA	4550	2710	120	1580	539
DMTS	NA	264	470	ND	125	405

	Hard Piped Condensate	ASB 1 Outlet	ASB 2 Outlet	ASB 3 Outlet	Quiescent Pond	Final Effluent
Flow (MGD)	3	53	53	53	53	53
pH	9.3	7.1	6.9	7.4	7.4	NA
BOD removal/HP/d[b]	NA	61	52	20	NA	NA
K V Concentrations (μg S/L)						
Total sulfide	96100	15500	318	63.2	28.0	ND
MeSH	99700	1520	133	35	42.3	43.6
DMS	21200	280	37.0	ND	ND	ND
DMDS	12700	137	71.9	ND	ND	ND
DMTS	ND	ND	ND	ND	ND	ND
K VI Concentrations (μg S/L)						
Total sulfide	133000	14364	4150	NA	ND	NA
MeSH	151000	2910	964	NA	221	NA
DMS	21900	383	99.3	NA	ND	NA
DMDS	5750	212	62.2	NA	ND	NA
DMTS	694	ND	31.1	NA	ND	NA

[a] flow data not provided for this location

[b] data from 8 month average, 2003

NA not analyzed

ND not detected above lowest calibration limit: 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL L

This is a recycle (40 to 45%)/TMP (55 to 60%) mill that produces about 450 TPD of directory paper. It utilizes about 6% purchased kraft pulp. Pulp bleaching and brightening uses hydrosulfite as well as hydrogen peroxide with a little hypochlorite. Average water flow through the treatment system (Figure B11) is 8 MGD. The mill is equipped with primary clarification (1.9 MG volume, 21,382 ft^2, RT 5.4 hours) followed by an AS system consisting of a 2.2 MG aeration tank containing ten 40 HP surface aerators with an RT of 4.4 hours, and a secondary clarifier with a volume of 1.2 MG, an area of 13,273 ft^2, and an RT of 2.4 hours. The system has 400 HP of aeration in all and an overall RT of 12.2 hours. Primary and secondary sludge are dewatered by screw presses. RSC samples were collected throughout the WWTP. Sampling sites and analytical results are shown in Table B19.

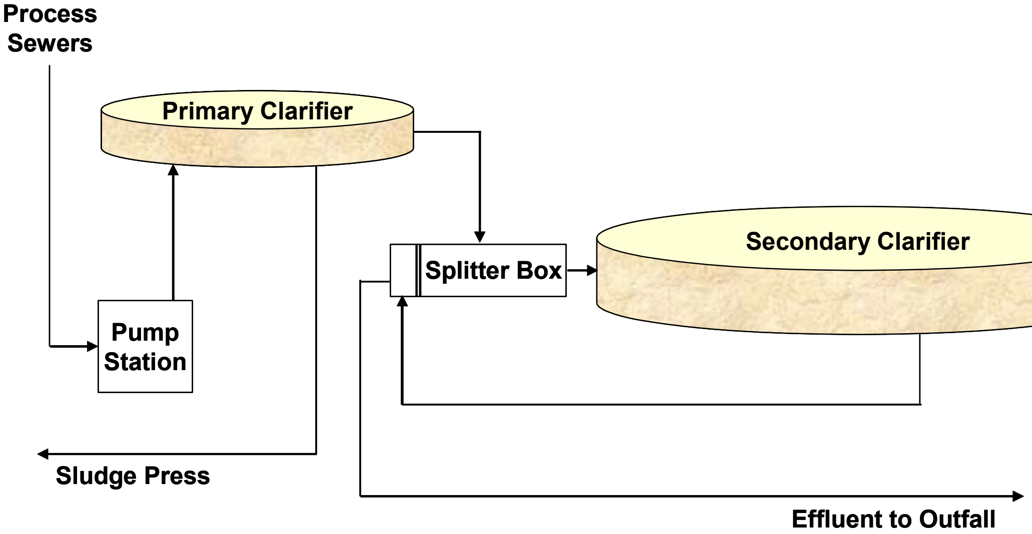


Figure B11. Mill L Wastewater Treatment Plant Schematic

Table B19. Mill L Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Paper Machine Sewer	Recycle Plant Sewer	Screw Press Filtrate	Main Pump Station
Flow (MGD)	5.5	1.88	0.5	8.46
pH	5.42	7.72	7.12	6.99
DO (mg/L)	NA	8.0	7.4	7.1
Temperature (ºC)	35	42	31	36
TSS (lb/d)[a]	NA	NA	NA	156355
BOD (lb/d)[a]	NA	NA	NA	24143
Total sulfide	ND	ND	995	ND
MeSH	ND	ND	74.2	ND
DMS	ND	ND	ND	ND
DMDS	ND	ND	ND	ND
DMTS	ND	ND	ND	ND
	Primary Clarifier Outlet	Aeration Basin Front	Aeration Basin Midpoint	Final Effluent
Flow (MGD)	8.46	8.46	8.46	8.46
pH	6.61	7.14	7.07	7.27
DO (mg/L)	3.5	2.2	2.2	5.4
Temperature (ºC)	36	34	31	30
TSS (lb/d)[a]	4703	NA	NA	2035
BOD (lb/d)[a]	11237	NA	NA	764
Total sulfide	5039	4013	2725	ND
MeSH	133	28.4	ND	ND
DMS	ND	ND	ND	ND
DMDS	ND	ND	ND	ND
DMTS	ND	ND	ND	ND

[a] data provided by mill for March 2004 monthly average

NA not analyzed

ND not detected above lowest calibration limit: 20 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL M

Mill M is an NSSC/recycled fiber mill that produces about 2320 TPD of corrugated medium. The mill does not have a bleach plant. Average water flow through the treatment system is 7 MGD. The mill is equipped with primary clarification followed by an ASB and an activated sludge unit (ASU) with secondary clarification. Condensates are currently hard piped to the ASB prior to the ASU. Further details of the treatment system are provided in Figure B12. RSC results are shown in Table B20.

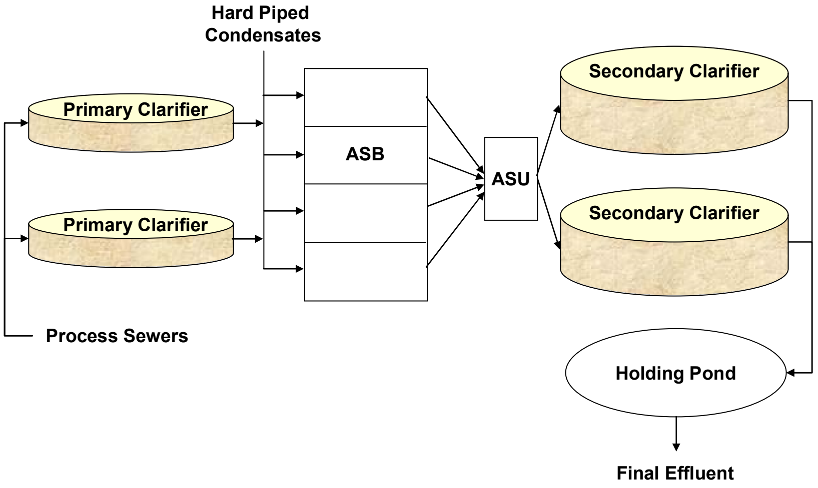


Figure B12. Mill M Wastewater Treatment Plant Schematic

Table B20. Mill M Reduced Sulfur Compound Concentrations (μg S/L)

Sampling Location	Total Sulfide	MeSH[a]	DMS	DMDS	DMTS
Mill process effluent	414	NA	19.9	ND	ND
Screw press filtrate	17100	132	227	ND	ND
Inlet to primary clarifiers	1287	NA	36.5	28.3	ND
#1 Primary clarifier outlet	1810	NA	154	ND	ND
#2 Primary clarifier outlet	2140	NA	87.6	ND	ND
Inlet to ASB	2505	NA	113	ND	ND
Hard piped condensate	95700	18400	25.9	1760	128
ASB pond 1 outlet	545	NA	ND	ND	ND
ASB pond 2 outlet	412	NA	ND	ND	ND
ASB pond 3 outlet	3289	NA	ND	81.4	ND
ASB pond 4 outlet	465	NA	ND	ND	ND
ASU outlet	693	NA	ND	ND	ND
#1 Secondary clarifier outlet	262	NA	ND	ND	ND
#2 Secondary clarifier outlet	197	NA	ND	ND	ND
2nd Clarifier underflow	583	NA	ND	ND	ND
Sludge pond outlet	83000	51.3	27.3	ND	ND
2nd Clarifier overflow	5370	NA	ND	ND	ND

[a] some results not available (NA) due to interference from sulfur dioxide

ND not detected above lowest calibration limit: 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL N

This is a bleached kraft mill producing approximately 660 TPD of pulp. Average water usage is 51,000 m^3/day. The mill runs softwood and hardwood lines. The WWTP receives effluent from a municipal sewage treatment plant that undergoes tertiary treatment in the mill's secondary treatment system. The WWTP consists of primary clarifiers, an equalization basin, and an AS system (Figure B13). Condensates are currently hard piped to the WWTP at the second ASB. Sampling focused on final effluent and hard piped condensates, and results are shown in Table B21.

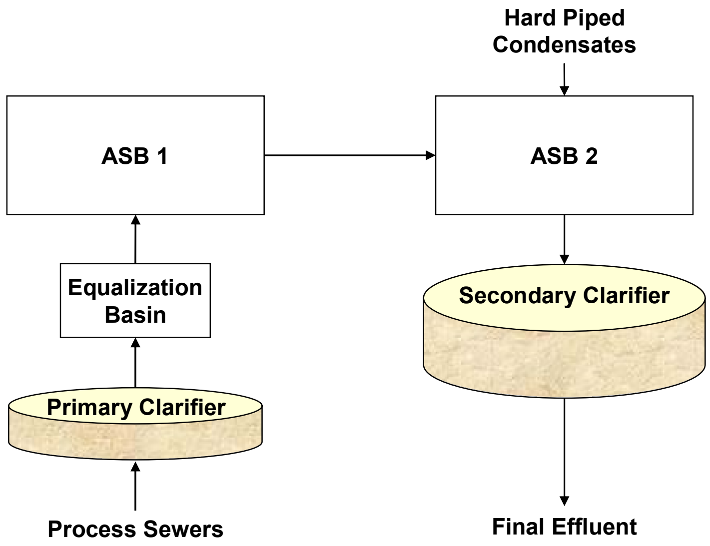


Figure B13. Mill N Wastewater Treatment Plant Schematic

Table B21. Mill N Reduced Sulfur Compound Concentrations (μg S/L)

Compound	Final Effluent	Hard Piped Condensate
Total sulfide	ND	26100
MeSH	ND	70700
DMS	ND	16800
DMDS	ND	1920
DMTS	ND	218

ND not detected above lowest calibration limit: 19.6 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

MILL O

This kraft mill produces approximately 1350 MTPD of bleached kraft pulp from softwood (pine and fir). Average water flow through the treatment system is 115,000 m^3/day. The mill is equipped with primary clarification followed by two settling ponds and an ASB. The ASB has 31 surface aerators that provide a total of 2325 HP across the basin (Figure B14) and a submerged jet injecting oxygen at the front of the ASB. ASB discharge averages a total BOD_5 of 22 mg/L with soluble BOD of 8 mg/L and TSS of 18 mg/L. The mill utilizes steam stripping and treats some foul condensates in the WWTP. The treatment system was surveyed twice to assess RSCs, yielding the results in Table B22.

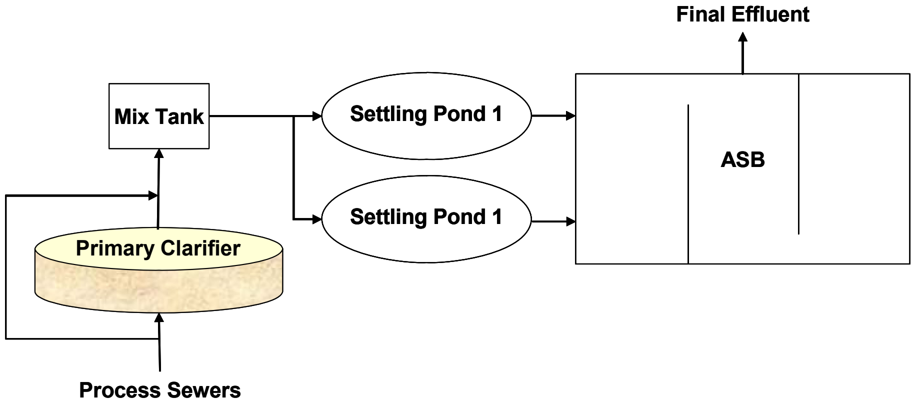


Figure B14. Mill O Wastewater Treatment Plant Schematic

Table B22. Mill O Reduced Sulfur Compound Concentrations (µg S/L)

Sampling Location	Total Sulfide	MeSH	DMS	DMDS	DMTS
Mill O I					
Primary clarifier inlet	113	ND	87.3	149	ND
Primary clarifier outlet	57	37.6	75.6	62.7	ND
Settling pond inlet	ND	ND	ND	46.7	ND
ASB inlet	310	ND	34.1	27.6	ND
ASB section 1 midpoint	57	ND	20.4	ND	ND
ASB section 1 outlet	85	ND	24.5	ND	ND
ASB section 2 outlet	70	ND	26.1	ND	ND
ASB section 3 outlet	39	ND	ND	ND	ND
Final effluent	ND	ND	ND	ND	ND
Mill O II					
Primary clarifier inlet	64.5	ND	61.5	78.8	ND
Primary clarifier outlet	ND	ND	72.2	39.5	ND
Settling pond inlet	58.3	ND	25.9	30.4	ND
ASB inlet	188	ND	31.4	ND	ND
ASB section 1 midpoint	108	ND	24.7	ND	ND
ASB section 1 outlet	89.9	ND	20.6	ND	ND
ASB section 2 outlet	80.1	ND	ND	ND	ND
ASB section 3 outlet	80.8	ND	ND	ND	ND
Final effluent	62.8	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL P

This bleached kraft mill pulps softwood at a capacity of approximately 363,000 tons per year (TPY). A schematic of the WWTP is provided in Figure B15. The mill is equipped with a steam stripper to process foul condensates. The alkaline sewer is routed to the primary clarifier at a flow rate of approximately 11.7 MGD. Effluent from the primary clarifier is mixed with the acid sewer, landfill leachate, and solids dewatering flow from the screw press. The mixed effluent is routed to a four zone, 50 acre aeration pond with a combined flow of 16.7 MGD and equipped with 1275 HP of aeration. Flow from the first pond enters a second ASB utilizing 350 HP in two zones, and approximately 9.2 MGD from the second zone are pumped back to the point where the acid and alkaline streams mix. Effluent from the second ASB enters a 116 acre stabilization pond, followed by a discharge canal that has 80 HP of surface aeration. Samples were collected from the primary clarifier inlet, primary clarifier outlet, ASB inlet, and ASB outlet. Several samples were collected at some of these sites over a three day period and the results listed in Table B23 represent the averages of those measurements.

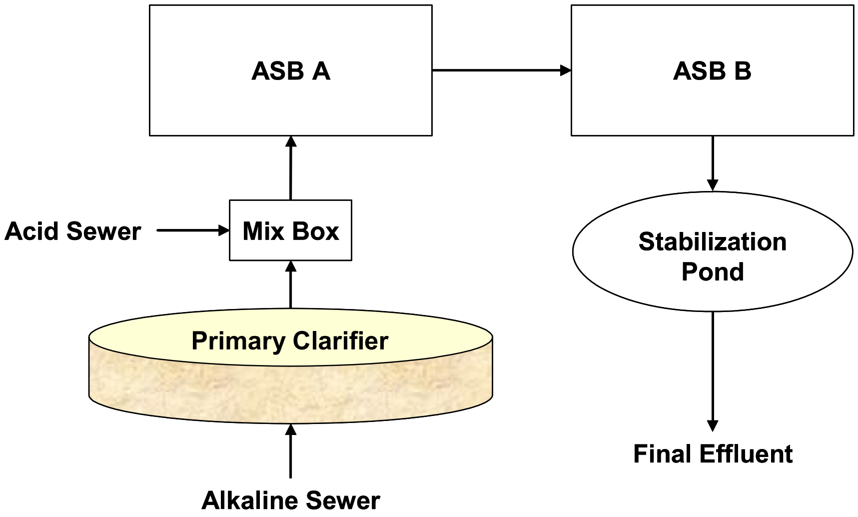


Figure B15. Mill P Wastewater Treatment Plant Schematic

Table B23. Mill P Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Primary Clarifier Inlet (n = 8)	Primary Clarifier Outlet (n = 8)	ASB Inlet (n = 10)	ASB Outlet (n = 5)
Total sulfide	526	637	417	290
MeSH	56.0	86.0	134	49.0
DMS	37.0	34.0	42.0	29.0
DMDS	840	431	217	13.0
DMTS	22.0	94.0	43.3	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL Q

Total production at Mill Q is 748,000 TPY of bleached kraft, with 456,000 tons from softwood and 292,000 tons from hardwood, both from continuous digesters. The mill utilizes a steam stripper to treat foul condensates. The bleach plants associated with the two pulping lines use oxygen delignification and produce 594,000 TPY of bleached paper and 292,000 TPY of recycled liner board. Wastewater enters the WWTP (Figure B16) through either of two 32 acre settling ponds. Approximately 38 MGD of flow enters secondary treatment at a four cell, 67 acre ASB with 3550 HP of aeration. Wastewater then cascades over a riffle to a 39 acre retention pond followed by a 169 acre retention pond. Samples were collected across both settling ponds and across the ASB. The results of these analyses are listed in Table B24.

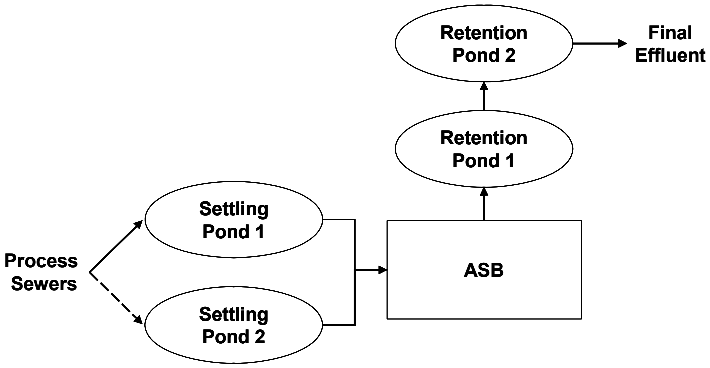


Figure B16. Mill Q Wastewater Treatment Plant Schematic

Table B24. Mill Q Average Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Settling Pond 1 Inlet (n=6)	Settling Pond 1 Outlet (n=4)	Settling Pond 2 Inlet (n=8)	Settling Pond 2 Outlet (n=5)	ASB Inlet (n=7)	ASB Outlet (n=5)
Total sulfide	654	1829	335	1020	2847	221
MeSH	ND	23.5	51.1	21.4	27	ND
DMS	19.4	22.0	60.7	24.5	25	ND
DMDS	30.9	34.7	61.9	ND	ND	ND
DMTS	ND	ND	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL R

Mill R produces 258,000 MTPY of bleached softwood kraft and 406,000 MTPY of bleached hardwood kraft. This mill uses a stream stripper to process foul condensates. The process sewers (25 MGD) go through a bar screen and then into two 180 ft primary clarifiers (12.5 MGD) with RTs of about 4 hours each. The process sewer consists of pulp mill effluent, alkaline sewer, evaporator effluent, powder and recovery area sewers, and the causticizing area sewer. Effluent from the clarifiers goes to the mix box, where 5 to 6 MGD of acid sewer from the bleach plants and about 20,000 GD of a sanitary sewer are added. From the mix box it moves through a splitter box into two ASBs. These consist of two cells, each equipped with nine 75 HP aerators. From the ASBs the wastewater flows to a final settling basin. Samples were collected from the mix box, as well as from the inlet and outlet of the ASB. The results of these analyses are listed in Table B25.

Table B25. Mill R Average Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Mix Box (n=1)	ASB1 Inlet (n=3)	ASB1 Outlet (n=3)	ASB2 Inlet (n=3)	ASB2 Outlet (n=3)
Total sulfide	75.7	70.6	ND	306	ND
MeSH	ND	ND	19.6	ND	ND
DMS	ND	ND	ND	ND	ND
DMDS	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND

ND not detected above lowest calibration limit: 19.6 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL S

Mill S is an unbleached kraft mill producing 821,470 MTPY: 27% specialties, 35% kraft board, and 37% linerboard. Furnish is approximately 25% hardwood and 75% softwood. The mill is equipped with a steam stripper to process foul condensates. Wastewater is treated using primary clarification with oxygen injection followed by AS (Figure B17). Samples were collected during two different sampling events from the forced main prior to the clarifier, primary clarifier center well, primary clarifier outlet, inlet to the aeration basin, and outlet from the aeration basin. Average results for three samples collected throughout the day are listed in Table B26 for the first sampling episode. Average results (n=12) of the RSC analyses, oxidation reduction potential, pH, and temperature for the second sampling episode are shown in Table B27.

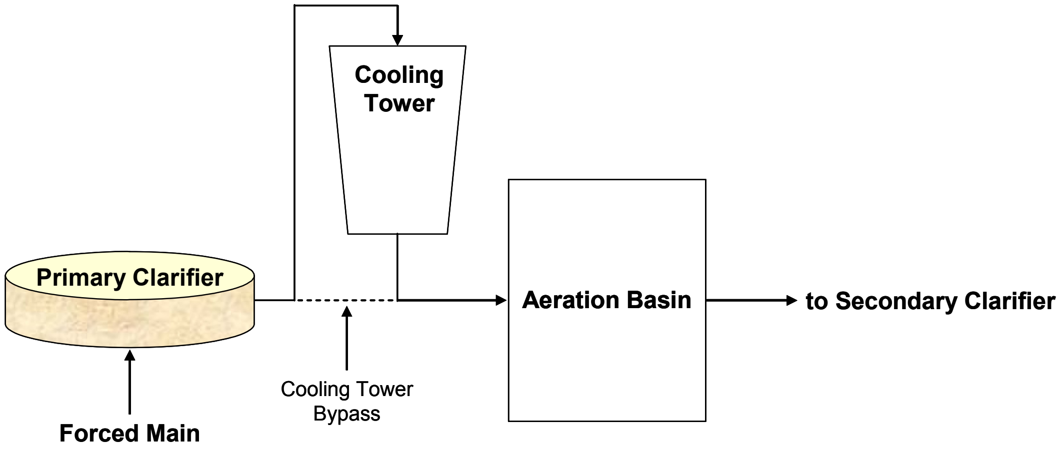


Figure B17. Mill S Wastewater Treatment Plant Schematic

Table B26. Mill S Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Forced Main	Primary Clarifier Center Well	Primary Clarifier Outlet	Aeration Basin Inlet	Aeration Basin Outlet
Total sulfide	1778	4793	15520	12567	69.0
MeSH	1011	972	3960	3753	120
DMS	63	66.0	80.0	77.0	ND
DMDS	2650	2350	289	231	ND
DMTS	319	278	74.0	185	ND

ND not detected above lowest calibration limit: 30 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

Table B27. Mill S Oxidation Reduction Potential, pH, Temperature, and Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Forced Main	Primary Clarifier Center Well	Primary Clarifier Outlet	Aeration Basin Inlet	Aeration Basin Outlet
ORP	-184	-128	-90	-182	119
pH	8.9	9.0	7.8	8.1	7.5
Temperature (ºC)	41	39	37	35	33
Total sulfide	2346	1215	2636	1171	55
MeSH	83	146	466	235	ND
DMS	83	79	66	28	ND
DMDS	1446	1102	479	188	ND
DMTS	114	113	111	94	ND

ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL T

This mill produces approximately 348,500 TPY of air dried pulp consisting of 90% hardwood and 10% softwood bleached kraft. A schematic of the WWTP is provided in Figure B18. The primary clarifier is charged with 8.2 MGD of pulp mill cooling water, 6.1 MGD from the paper mill and coater (non-contact cooling), and smaller amounts from the debarker, pulp drier (non-contact cooling), lime kiln, carbon pit, and stormwater. After primary clarification, effluent is mixed with about 0.14 MGD of sanitary water, 1.2 MGD from the mud ash lagoon, and effluent from the pulp mill bleach pit prior to the mixing chamber. Recovered water from the evaporators and turpentine condensates are treated with peroxide in static mixers and added to the WWTP at the first ASB. ASB 1 (36.8 acres) is followed by a second ASB (25.1 acres) that flows into a 118.8 acre stabilization lagoon prior to final outfall. Samples were collected at the mix box, ASB inlet, and final effluent for three days. Average results of these analyses are listed in Table B28.

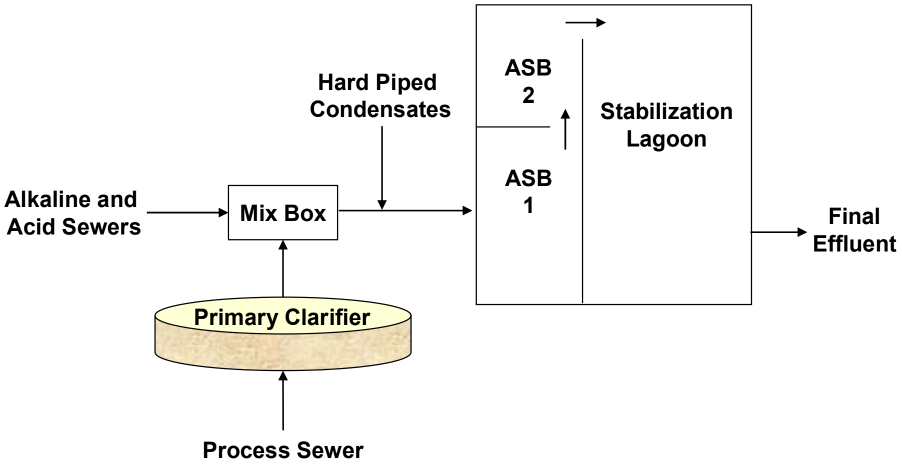


Figure B18. Mill T Wastewater Treatment Plant Schematic

Table B28. Mill T Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Mix Box	Aeration Basin Inlet	Aeration Basin Outlet
Total sulfide	3480	2160	31.4
MeSH	532	605	ND
DMS	541	838	68.1
DMDS	511	1806	110
DMTS	134	177	ND

ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL U

Mill U produces 200,000 MTPD of air dried hardwood kraft and 190,000 MTPD of softwood kraft. Mill production is 7.4% uncoated freesheet, 11.4% specialties, and 81.2% kraft pulp. The wastewater treatment system (Figure B19) consists of two primary settling ponds that are switched back and forth to allow further settling. After settling, the effluent enters an aeration basin that contains two cells with a pinch at about 45% of the total area. Effluent then enters a quiescent basin for final treatment. Samples were collected throughout the south settling basin, ASB cell 1, ASB cell 2, the quiescent basin, and final effluent. Results are listed in Table B29.

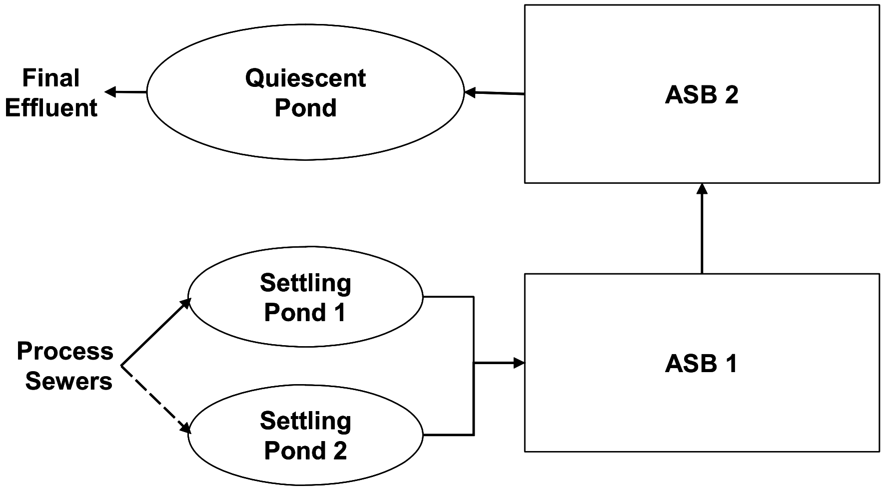


Figure B19. Mill U Wastewater Treatment Plant Schematic

Table B29. Mill U Reduced Sulfur Compound Concentrations (µg S/L)

Compound or Parameter	Settling Pond 2 Inlet	Settling Pond 2 Outlet	ASB 1 Inlet	ASB 1 Outlet	ASB 2 Inlet	ASB 2 Outlet	Quiescent Pond Outlet
Total sulfide	1690	4070	2580	2246	110	498	521
MeSH	59.4	120	49.1	30.2	ND	ND	ND
DMS	177	173	58.5	28.9	ND	ND	ND
DMDS	ND	ND	ND	ND	ND	ND	ND
DMTS	ND	ND	ND	ND	ND	ND	ND

ND not detected above lowest calibration limit: 30 µg/L for total sulfide; 19.4 µg/L for MeSH; 19.2 µg/L for DMS; 19.4 µg/L for DMDS; 19.3 µg/L for DMTS

MILL V

Mill V produces approximately 428,000 MTY of air dried kraft pulp, and 235,000 MTY of hardwood and softwood bleached kraft. The final product is 50% uncoated and 50% kraft board. A schematic of the WWTP is provided in Figure B20. Wastewater is treated using two 200 ft diameter (3.47 MG) and one 125 ft diameter (1.01 MG) primary clarifiers operating in parallel. Effluent from the primary clarifiers is injected with oxygen and nutrients prior to entering an aerobic digester. After digestion the wastewater is treated in three sequential aeration cells with 20 surface aerators. Water then flows into two 200 ft diameter (2.82 MG) and one 150 ft diameter (1.85 MG) clarifiers. Effluent from the secondary clarifiers passes through a reaeration cascade prior to final outfall. Samples were collected from the #3 primary clarifier inlet, three different zones across the clarifier, primary clarifier outlet, aerated digester, three zones of the aeration basin, and final effluent. Results are listed in Table B30.

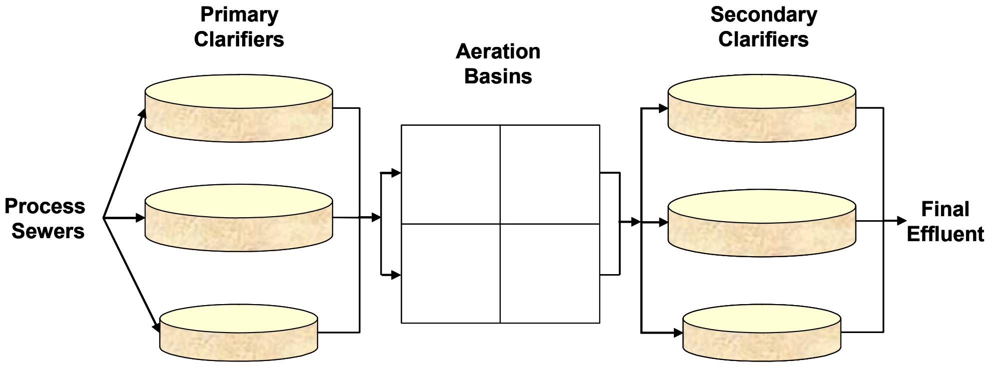


Figure B20. Mill V Wastewater Treatment Plant Schematic

Table B30. Mill V Reduced Sulfur Compound Concentrations (μg S/L)

Compound or Parameter	Primary Clarifier Inlet (n=4)	Primary Clarifier Middle (n=2)	Primary Clarifier Center (n=2)	Primary Clarifier Outlet (n=4)	AST Zone[a] (n=4)	Final Effluent
Mill V I						
Total sulfide	18100	10200	NA	8480	941	ND
MeSH	165	427	NA	168	ND	ND
DMS	404	497	NA	500	ND	ND
DMDS	159	ND	NA	49.0	ND	ND
DMTS	65	ND	NA	37.0	ND	ND
Mill V II						
Total sulfide	13300	7240	7116	19500	613	26.0
MeSH	500	381	309	700	30.7	ND
DMS	1021	486	480	1255	136	ND
DMDS	155	67.6	52.0	247	33.7	ND
DMTS	119	43.0	35.4	151	ND	ND

[a] average across all zones of the aeration basin

NA not analyzed during this sampling episode

ND not detected above lowest calibration limit: 19.6 μg/L for total sulfide; 19.4 μg/L for MeSH; 19.2 μg/L for DMS; 19.4 μg/L for DMDS; 19.3 μg/L for DMTS

APPENDIX E – NCASI TB NO. 949, SUMMARY OF INDUSTRY EXPERIENCE WITH ODOR MINIMIZATION AT WASTEWATER TREATMENT PLANTS

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NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

SUMMARY OF INDUSTRY EXPERIENCE WITH ODOR MINIMIZATION AT WASTEWATER TREATMENT PLANTS

TECHNICAL BULLETIN NO. 949

MAY 2008

by
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NCASI West Coast Regional Center
Corvallis, Oregon

Acknowledgments

This report was written by Diana Cook, Project Leader at NCASI's West Coast Regional Center, with assistance from Vipin Varma, former Project Leader at NCASI's Southern Regional Center. Judith Adamski and Karen Phelps assisted with document formatting.

NCASI appreciates the data and other information on odor reduction anonymously shared by several member companies for use in this report.

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National Council for Air and Stream Improvement, Inc. (NCASI). 2008. *Summary of industry experience with odor minimization at wastewater treatment plants.* Technical Bulletin No. 949. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

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PRESIDENT'S NOTE

Odor minimization is an active goal for many pulp and paper facilities and an important part of mill environmental management programs. As anti-nuisance laws and permit requirements that address fugitive odors have become more prevalent, odor reduction efforts have attracted increased attention within the industry. Historically, most efforts to control odors have focused on minimizing releases of reduced sulfur compounds (RSCs), in particular hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide, from the kraft process. As process emissions have been reduced, RSC emissions from wastewater treatment plants (WWTPs) have become more noticeable at some mills. To assist members in dealing with odor issues related to WWTP operations, NCASI has conducted a multi-year research program that includes development and application of monitoring methods, extensive characterization of odorous compound concentrations and emissions from mill WWTPs, and support of odor control technology evaluations. A considerable body of knowledge has resulted from these efforts and the efforts of member companies that have implemented odor management programs.

This report summarizes important aspects of odor management programs, source characterization study designs, and overviews of available odor control technologies. It will be of interest to mills with WWTP odor issues, especially those that have just begun to formulate odor management programs.

Ronald A. Yeske

May 2008

ncasi

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MOT DU PRÉSIDENT

Pour plusieurs fabriques de pâtes et papiers, la minimisation des odeurs est un objectif constant et constitue une portion importante des programmes de gestion environnementale de l'usine. En réponse à l'apparition de plus en plus fréquente de réglementations et d'exigences contenues dans les permis/autorisations et ayant pour objectif de diminuer les nuisances reliées aux odeurs fugitives, l'industrie a apporté une attention spécifique à la réduction des odeurs. Historiquement, la majorité des efforts visant le contrôle des odeurs était centrée sur la réduction des rejets de composés de soufres réduits (CSR), plus particulièrement, le sulfure d'hydrogène, le méthylmercaptan, le sulfure de diméthyle et le disulfure de diméthyle générés par le procédé kraft. À certaines fabriques, l'effet résultant de la réduction des émissions de procédés, fut que les émissions de CSR des systèmes de traitement des effluents (STE) sont devenues plus perceptibles. Afin d'assister ses membres dans la recherche de solutions aux problématiques d'odeurs reliées aux opérations de STE, NCASI a mené un programme de recherches s'échelonnant sur plusieurs années et qui inclut : le développement et l'application de méthodes de monitoring, la caractérisation exhaustive des concentrations et émissions de composés odorants provenant de STE des fabriques et le support lors d'évaluations de technologies de contrôle des odeurs. Ces efforts, ainsi que ceux des compagnies membres ayant implantés des programmes de gestion des odeurs, ont permis de bâtir une banque importante de connaissances sur le sujet.

Ce rapport résume les aspects les plus importants des programmes de gestion des odeurs et de la planification d'études de caractérisation des sources en plus de procurer un survol des technologies de contrôle des odeurs disponibles. Ce rapport intéressa les fabriques ayant des problématiques reliées aux odeurs de STE et tout particulièrement les fabriques qui commencent à formuler leurs programmes de gestion des odeurs.

Ronald A. Yeske

Mai 2008

SUMMARY OF INDUSTRY EXPERIENCE WITH ODOR MINIMIZATION AT WASTEWATER TREATMENT PLANTS

TECHNICAL BULLETIN NO. 949
MAY 2008

ABSTRACT

Odor emissions at kraft mills have historically been attributed to reduced sulfur gases generated and released from pulp processing areas. Advances in collection and management systems have minimized these releases and their impacts on community odors under normal operating conditions. As these advances have occurred, it has become apparent that at some mills, odors originating in the wastewater treatment plant (WWTP) area may also contribute to community odors. This report has been prepared to assist companies interested in reducing odors associated with WWTPs. Based on available literature, contact with member mills, and NCASI research results, this report provides an overview of a) odor reduction programs within the pulp and paper industry; b) odorous compounds identified in pulp and paper mill WWTPs; c) source identification survey information, including analytical methods and sampling considerations; and d) control methods for hydrogen sulfide in pulp and paper mill wastewater, including chemical precipitation with metal salts, chemical oxidation, biological treatment, pH adjustment, nitrate addition, biostimulants, organic scavengers, enzyme blockers, odor neutralizers, biocides, and vegetative shelterbelts. Examples of applications of these techniques are included when available.

KEYWORDS

analytical methods, biological treatment, biostimulants, enzyme blockers, hydrogen peroxide, hydrogen sulfide, odor, odor reduction, organic scavengers, oxidation, precipitation, pulp mill, reduced sulfur compounds, sulfide, volatile fatty acids, wastewater treatment

RELATED NCASI PUBLICATIONS

Technical Bulletin No. 933 (June 2007). *Development and application of a method for measuring reduced sulfur compounds in pulp and paper mill wastewaters.*

Special Report No. 06-02 (February 2006). *An evaluation of a colorimetric method for the determination of total sulfide in pulp and paper mill wastewaters.*

Special Report No. 05-01 (June 2005). *Evaluation of sulfide ion detector tubes for determining sulfide concentrations in pulp and paper mill wastewaters.*

Technical Bulletin No. 849 (August 2002). *Compilation of speciated reduced sulfur compound and total reduced sulfur emissions data from kraft mill sources.*

Technical Bulletin No. 804 (May 2000). *Laboratory studies of in-digester black liquor oxidation (IDO) for TRS destruction*.

Technical Bulletin No. 691 (February 1995). *Health effects of reduced sulfur gases.*

RÉSUMÉ DE L'EXPÉRIENCE DE L'INDUSTRIE POUR LA MINIMISATION DES ODEURS RELIÉES AUX SYSTÈMES DE TRAITEMENT DES EFFLUENTS

BULLETIN TECHNIQUE NO. 949
MAI 2008

RÉSUMÉ

Historiquement, les émissions d'odeurs de fabriques kraft étaient attribuées aux soufres réduits gazeux générés et rejetés dans les zones de fabrication de la pâte. Des améliorations apportées aux systèmes de collection et de gestion ont permis de minimiser ces rejets ainsi que leurs impacts sur les niveaux d'odeurs dans la communauté (sous des conditions d'opération normales). Au fur et à mesure que ces améliorations étaient apportées, il devenait apparent qu'à certaines usines, les odeurs émanant du système de traitement des effluents (STE) pouvaient aussi contribuer aux niveaux d'odeurs perceptibles dans la communauté. Ce rapport a été préparé afin d'assister les compagnies désirant réduire les odeurs reliées aux STE. En se fondant sur la littérature disponible, sur des communications avec les usines membres et sur des résultats de recherches effectuées par NCASI, ce rapport procure une vue d'ensemble des : a) programmes de réduction d'odeurs en utilisation dans l'industrie des pâtes et papiers; b) composés odorants détectés dans les STE des fabriques de pâtes et papiers; c) informations concernant les études visant l'identification des sources d'odeurs incluant les méthodes analytiques et les précautions à tenir en compte lors des prélèvements; d) les méthodes de contrôle du sulfure d'hydrogène dans les effluents des fabriques de pâtes et papier incluant la précipitation chimique à l'aide de sels métalliques, l'oxydation chimique, le traitement biologique, l'ajustement du pH, l'addition de nitrate, les bio-stimulants, les agents d'épuration organiques, les inhibiteurs enzymatiques, les neutraliseurs d'odeurs, les biocides et les brise-vent végétaux. Des exemples d'applications de ces techniques ont été inclus lorsqu'ils étaient disponibles.

MOTS CLÉS

méthodes analytiques, traitement biologique, bio-stimulants, inhibiteurs enzymatiques, peroxyde d'hydrogène, sulfure d'hydrogène, odeur, réduction d'odeur, agents d'épuration organiques, oxydation, précipitation, fabrique de pâte, composés de soufres réduits, sulfure, acides gras volatils, traitement des effluents

AUTRES PUBLICATIONS DE NCASI DANS CE DOMAINE

Bulletin technique No. 933 (Juin 2007). *Development and application of a method for measuring reduced sulfur compounds in pulp and paper mill wastewaters.*

Rapport spécial No. 06-02 (Février 2006). *An evaluation of a colorimetric method for the determination of total sulfide in pulp and paper mill wastewaters.*

Rapport spécial No. 05-01 (Juin 2005). *Evaluation of sulfide ion detector tubes for determining sulfide concentrations in pulp and paper mill wastewaters.*

Bulletin technique No. 849 (Août 2002). *Compilation of speciated reduced sulfur compound and total reduced sulfur emissions data from kraft mill sources.*

Bulletin technique No. 804 (Mai 2000). *Laboratory studies of in-digester black liquor oxidation (IDO) for TRS destruction*.

Bulletin technique No. 691 (Février 1995). *Health effects of reduced sulfur gases.*

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TABLES

FIGURES

SUMMARY OF INDUSTRY EXPERIENCE WITH ODOR MINIMIZATION AT WASTEWATER TREATMENT PLANTS

1.0 INTRODUCTION

Due primarily to the use of sulfur in pulping processes, the pulp and paper industry has frequently been associated with releases of offensive odors. In recent decades, substantial progress has been made in controlling releases of reduced sulfur compounds (RSCs) from pulping and liquor processing areas. As these controls have been put in place, residual sources of odor have become more apparent, and at some mills, odorous emissions from wastewater treatment and waste handling areas have been identified as important potential contributors to odor observed in surrounding communities.

This report documents pulp and paper industry experience in minimizing odors associated with wastewater treatment plants (WWTPs) and disposal areas. Information included in the report was obtained from published literature, NCASI research work, and member company studies. It provides an overview of key elements of odor reduction programs, a review of odorous compounds identified in mill odor surveys, a summary of NCASI research to characterize odorous compounds and emissions, a brief description of analytical tools, and information on sulfide behavior in WWTPs and odor control methods (focusing on hydrogen sulfide) that have been considered or applied within the industry.

2.0 OVERVIEW OF MILL ODOR REDUCTION PROGRAMS

A number of approaches have been utilized in the pulp and paper industry to minimize odor impacts from WWTPs (Blondeel et al. 2006; Brungardt 2001; Dufresne and Laroche 1998; Marshall 2005; McEwen, Witherspoon, and Chapman 2006; Olendorf, Jacobi, and Bonistall 2000; O’Connor and Ledoux 2002; Ramsay et al. 2001). Some key components of successful programs include use of odor reduction management teams, effective community education and interaction, odor detection surveys, odorous compound and source identification studies, air dispersion modeling, testing and application of odor control techniques, and ongoing performance monitoring.

Odor reduction plans are often formulated and pursued by a team consisting of personnel from various areas of the mill, including engineering, environmental, maintenance, technical, and operations (Olendorf, Jacobi, and Bonistall 2000). Teams may include specialists such as outside consultants with expertise in odor reduction and wastewater treatment system operations (Urbanski, Lister, and Raoul 1998; Ramsay et al. 2001).

Odor is generally the chief complaint among neighbors in mill communities. Therefore, community involvement is a component of many odor reduction programs (Hemmen and Winges 1993). In some cases, a community education and interaction program itself can result in fewer odor complaints (Witherspoon et al. 2004). Interaction can take a variety of forms. Many programs are proactive, ongoing, and based on two-way communication. Facility management provides information to community residents and other stakeholders on environmental issues, health and safety performance, risk, and other factors. Mills often provide avenues through which community concerns and suggestions can be addressed by inviting constructive discussions. One-on-one discussions with residents often work best when dealing with odor complaints. Some suggest that the goal should be to establish and maintain credibility, and to utilize effective communication to educate the public about steps being taken and progress being made to reduce odors (Marshall 2005; CICI 2005).

Many odor reduction programs begin with a subjective survey to ascertain where odors are coming from, how often they are encountered, the times of day odors are observed, and the duration and intensity of odorous events. These surveys often involve interviews with mill personnel and sometimes with community members. Examination of odor complaint histories in conjunction with meteorological data can also help determine likely sources of odors.

Field measurements are sometimes made using total reduced sulfur (TRS) or hydrogen sulfide (H_2S) as the odor surrogate. In addition, normal WWTP process measurements such as temperature, flow rate, pH, dissolved oxygen (DO), oxidation reduction potential (ORP), biochemical oxygen demand (BOD), and total suspended solids (TSS) levels are often compiled. Meteorological measurements such as wind speed and direction taken in conjunction with field measurements of TRS or H_2S may also be useful. A review of available data and information is often completed to determine areas of concern with regard to generation and emission of odorous compounds.

Air dispersion modeling can be used to ascertain the potential contributions of sources within a mill to ambient odor concentrations in the surrounding community (O'Connor and Ledoux 2002; Järvensivu, Mäenpää, and Jämsä-Jounela 2000). Air emission and dispersion modeling results have shown strong correlations to measurements made by sniffing teams during odor investigations (van den Hazel and Waegemaekers 1991).

Reduction techniques that have been applied to odors related to RSCs and volatile fatty acids (VFAs) include chemical precipitation with metal salts, use of oxidizing agents, pH adjustment, biological treatment, alternative electron acceptors, biostimulants, organic scavengers, enzyme blockers, odor neutralizers, biocides, and vegetative shelterbelts (Dyer 1996; WEF 2004; Harshman and Barnette 2000). Most odor reduction plans include a means of measuring progress toward goals. Assessments often involve calculating reductions in sulfide levels or odor complaints.

3.0 ODOROUS COMPOUNDS AND THEIR SOURCES

Odorous compounds can come from many sources in mill environments, including the pulp mill, paper mill, wood pile, bark pile, strong waste pond, primary clarifier, sludge dewatering area, biological treatment system, receiving waters, landfill, leachates, and others (NCASI 2004). Potentially odorous substances include process additives; compounds generated during manufacturing; process-generated compounds derivatized, decomposed, or rearranged in effluent treatment; and products of anaerobic decomposition.

VFAs and aldehydes result from anaerobic decomposition of carbohydrates (in cellulose) and proteins (in biomass). VFAs (acetic, propionic, and butyric acids) can contribute to odor in recycled paper mill systems and paper (Davis and Smith 2001). O'Connor, Buchanan, and Kovacs (2000) indicated that odors associated with effluent treatment system residuals at chemical and non-chemical mills were due to products of anaerobic decomposition, including VFAs, p-cresol, indole, and skatole. VFAs also play a role in sulfide generation by providing substrate for sulfate reducing bacteria (SRB). Extractives released during wood processing and pulping, such as terpenes, are volatile and poorly soluble and can contribute to odor. Because sulfur compounds are utilized in pulping processes (e.g., sodium sulfide in kraft pulping, sulfite in sulfite pulping), sulfur is available for a variety of transformations that can occur during processing and wastewater treatment. RSCs such as methyl mercaptan (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS) are formed during kraft pulping by the reaction of sulfide with methoxy groups of lignin via nucleophilic substitution reactions (Biermann 1996). Certain process wastewaters (e.g., evaporator condensates) may be significant sources of RSCs in kraft mills. The presence of sulfide in wastewater can also result from anaerobic reduction of sulfate by SRB. In addition to RSCs and VFAs, a variety of other odorous compounds have been found in chemical pulp mill effluents, including formic acid, ammonia, sulfur dioxide, and nitric oxide (Goyer and Lavoie 2001). A study conducted to estimate airborne concentrations of odorous compounds from wastewater treatment lagoons at kraft pulp mills identified acetic acid, propionic acid, thiophenol, furfuraldehyde, 2-furan methanol, camphor, 2-butoxyethanol, and others (Lange and Christiansen 2004). These compounds are known to have relatively low odor thresholds.

NCASI has developed and applied a variety of analytical tools to identify and quantify compounds that contribute to odors in waste streams, including NCASI Method RSC-02.02, a direct injection method for quantifying RSCs (NCASI 2007), and a gas chromatography/olfactory-mass spectrometry (GC/O-MS) method (Cook and Hoy 2008).

GC/O-MS was used during an initial industry-wide investigation to help identify compounds in various pulp and paper mill wastewaters that were associated with odors. The method provides simultaneous identification of compounds and characterization of odor traits and intensities by human observers. It was determined that most of the compounds responsible for odor at pulp and paper facilities were amenable to purge and trap methods, so a combination of purge and trap and GC/O-MS was applied to samples collected throughout WWTPs at ten different mills. Personnel who participated as olfactory sniffers were selected based on their ability to detect and describe odors from solutions of standard stocks containing acetic acid, methyl ethyl ketone, propionic acid, isobutyric acid, butyric acid, alpha-pinene, isovaleric acid, valeric acid, beta-pinene, limonene, p-cymene, phenol, o-cresol, m-cresol, p-cresol, guaiacol, iso-borneol, borneol, alpha-terpineol, indole, geosmin, methyl indole, H_2S, MeSH, DMDS, and DMTS. Odor intensity was described as threshold, weak, moderate, or strong during duplicate runs performed on each sample assessed. Compounds identified as contributing to odors via GC/O-MS were confirmed against authentic standards. Concentrations for total sulfide, MeSH, DMS, DMDS, DMTS, and acetic, propionic, isobutyric, butyric, isovaleric, and valeric acid were also assessed using direct injection methods on the same WWTP samples (NCASI 1999, 2007). Based on these investigations and information found in the literature, the main compounds identified as contributing to odors emitted from pulp and paper mill WWTPs are summarized in Table 3.1 along with odor descriptions and odor threshold data (Cook and Hoy 2003; Lange and Christiansen 2004). The odor detection threshold is defined as the odor intensity distinguishable from background.

NCASI studies and Table 3.1 indicate that RSCs continue to be implicated as one of the major classes of odorous compounds emitted from WWTPs (Cook and Hoy 2003). Of the RSCs, H_2S is often the major odor contributor. Therefore, many of the minimization techniques and examples in this report focus on approaches that reduce H_2S-related odors.

Table 3.1 Odorous Compounds Identified in Pulp and Paper Mill Wastewater Treatment Plants

Compound	Odor Description	Odor Detection Threshold (mg/m^3)[a]
Reduced Sulfur Compounds		
hydrogen sulfide	rotten eggs	0.0007 - 0.01
methyl mercaptan	rotten eggs, sulfur-like, pulp mill	0.00004
dimethyl sulfide	rotten vegetables, sour milk	0.0025 - 0.01
dimethyl disulfide	rotten eggs, burnt rubber	0.0001 - 0.03
dimethyl trisulfide	putrid/rancid, rotten eggs, burnt rubber	0.007
3-(methylthio)-1-propene	rotten vegetables, burnt rubber	not available
1-(methylthio)-1-propene	match strike, skunk	not available
ethyl methyl disulfide	not listed	0.062
Volatile Fatty Acids		
acetic acid	vinegar	0.025 - 5.0
propanoic acid (propionic acid)	pungent, rancid	0.003 - 0.89
butyric / isobutyric acid	rancid butter	0.0004 - 3.0
valeric / isovaleric acid	rancid cheese	0.00012 - 0.1
caproic / isocaproic acid	goat or limburger cheese	0.04 - 0.52
2-methylbutyric acid	rancid, fatty	0.3
Terpenes		
alpha-pinene	medicinal, chemical	0.016
beta-pinene	rotten vegetables, skunk-like	140 ppb in water
limonene	woodsy	0.01
p-cymene	medicinal, like a hospital	0.012
Others		
acetaldehyde	solvent-like	0.0002
4-methyl-2-pentanone (MIBK)	sweet, vanilla, phenolic	0.3
guaiacol	phenolic, floral at low conc.	0.0025
skatole	fecal	0.001

SOURCES: Verschueren 2001; Ruth 1986; Van Gemert and Nettenbreijer 1977

[a] detection thresholds in air (unless otherwise stated); ranges shown where reported values differ significantly

4.0 SOURCE IDENTIFICATION SURVEYS

4.1 Analytical Methods

NCASI has participated in a variety of studies involving field measurements at WWTPs to determine odorous compound sources and possible sites at which sulfide and VFAs might be generated and emitted (Cook and Hoy 2003; Crawford 2006, 2007; NCASI 2007). This section discusses some of the methods utilized to measure odorous compounds, focusing on sulfide analyses. These studies often included an assessment of concentrations of the main odorous compounds in air and aqueous phases, along with supporting data such as pH, DO, BOD, TSS, and ORP. Several methods for determining sulfide in aqueous and air samples are summarized herein. It is noteworthy that sulfide is highly reactive and volatile, and therefore presents a substantial analytical challenge. Other compounds of potential interest with respect to treatment plant odors include MeSH, DMS, DMDS, DMTS, and various VFAs.

Sulfide may exist in wastewaters in several chemical forms, including dissolved H_2S gas, hydrosulfide ion (HS^-), acid soluble metal sulfides, and sulfides associated with organic compounds. Sulfide ion (S^{-2}) represents an insignificant fraction of total sulfide at wastewater pHs >8.5 (Section 5.5.1 and

Figure 5.9 provide more details on this relationship). Attempts to develop analytical methods specific to any of these individual forms have been largely unsuccessful due to the active chemical nature of sulfide. Thus, most methods measure total sulfide in the aqueous phase. Total sulfide is usually defined as sulfide that will be released from solution upon acidification of wastewater to pH <2.5. Dissolved sulfide (H_2S and HS^-) may be measured after suspended solids have been removed by flocculation, centrifugation, or filtration. Un-ionized sulfide (dissolved H_2S) may be calculated from the concentration of dissolved sulfide, the pH of the sample, and the practical ionization constant of sulfide (APHA, AWWA, and WPCF 1989). NCASI studies to investigate use of flocculation, centrifugation, and filtration for assessing dissolved sulfide in pulp and paper mill wastewaters showed that those methods result in high variability and losses of sulfide (poor precision and accuracy). When attempting to measure dissolved sulfide, studies to verify the precision and accuracy of the methods in the matrix and experiments to measure known concentrations of quality control standards are highly recommended. Table 4.1 contains a summary of commonly used methods for determining sulfide in aqueous samples. It provides brief method descriptions, applicable ranges, and possible interferences.

Table 4.1 Overview of Sulfide Methods for Aqueous Samples

Method Description	Method Summary	Range	Interferences and Comments
Sulfide ion tubes			
type 1	S^{2-} +$Pb(NO_3)_2$ gives PbS	~1 - 1000 ppm	mercaptans, sulfates, iron, chloride
type 2	S^{2-} +$Pb(CH_3CO_2)_2$ gives PbS	~1 - 110 ppm	false negatives at low levels
Titration (iodine)	iodine oxidizes sulfide to sulfur under acid conditions, excess iodine is back titrated with sodium thiosulfate	above 1 ppm	thiosulfate, sulfite, some organics
Colorimetric (methylene blue)	sulfide reacts with dimethyl-p-phenylenediamine (p-aminodimethyl aniline) in the presence of ferric chloride to produce methylene blue	~1 - 20 ppm	color and turbidity
Capillary zone electrophoresis	electrolyte and indirect UV at 275 nm	not available	issues with sulfide stabilization
Gas chromatography/ sulfur selective detector[a]	sparging or direct injection (NCASI RSC-02.02), or headspace, or solvent extraction followed by GC/SSD	varies depending on detector	coeluting compounds, active surfaces
Electrochemical methods (total sulfide, EPA Method 9215)	silver-silver sulfide electrode test, requires sample distillation; limited data on pulp and paper matrices	1 - 12,000 ppm	colloidal substances

[a] SSDs include pulsed flame photometric detectors (PFPD) and sulfur chemiluminescence detectors (SCD)

Method selection should be based on the level of accuracy and precision required for the task at hand. For example, valuable data regarding general trends can be obtained using screening methods such as sulfide ion detector tubes (NCASI 2005). If better accuracy and precision are required, colorimetric techniques provide good accuracy and precision at concentrations above 40 ppb and are relatively easy and inexpensive to perform (NCASI 2006).

Table 4.2 lists some of the methods that have been utilized to measure sulfide in air during studies to investigate sulfide-related odors and emissions in the pulp and paper industry (http://www.lpes.org/Lessons/Lesson40/40_4_Air_Quality.pdf; Lewis et al. 2004; Racine 2005; NIOSH 1994; Esplin 1989; Natusch, Sewell, and Tanner 1974). A variety of tools such as gas detector tubes, paper tapes, patches, and single gas monitors have been used to detect sulfide in screening efforts. Direct onsite measurements may be preferred, although limited methods are available for such assessments of odorous compounds other than sulfide. Information regarding compounds other than sulfide can be obtained using gas chromatography (GC)/sulfur selective detector (SSD), GC/mass spectrometry (MS), and GC/O-MS (Cook and Hoy 2003).

Table 4.2 Overview of Sulfide Methods for Ambient Air Monitoring

Method Description	Method Summary	Range	Interferences and Comments
Electrochemical methods (Odalog gas logger, gas monitors)	mode of action varies	~0 - 200 ppm; method dependent	
Gold film sensor (Jerome analyzer)	detects change in resistance due to adsorption of H_2S on a thin gold film	0.003 - 50 ppm	MeSH, frequent sensor regeneration required
Paper tape, patches	detects color change in spot on paper tape or patch impregnated with appropriate reagent (e.g., lead acetate)	~0.001 - 50 ppm	average values only; lack precision
Gas detection tubes	media in tube reacts with known volume of air and changes color	~0.2 - 2000 ppm	
Cavity ring-down spectroscopy	optical absorption technology uses laser, optical cavity, and photodetector	ultratrace	
Ambient H_2S analyzers	thermal conversion of H_2S to SO_2, UV fluorescence detection	method dependent	SO_2 yields high bias
GC/MS, GC/O-MS, GC/SSD	air samples collected and often concentrated prior to analysis using a variety of detectors	method dependent	coeluting compounds, losses during sample collection and storage

If samples are to be collected and stored prior to analysis, preservation with zinc acetate at pH >10 is essential. Once a sample is preserved it must be acidified prior to analysis, and will therefore yield a concentration for total sulfide. It is prudent to note that many of the methods that assess sulfide concentrations in aqueous samples (including NCASI Method RSC-02.02) measure total sulfide (sulfide released upon acidification of wastewater to pH <2.5, including metal sulfides and sulfides weakly associated with organics) and may yield overestimates of sulfide available for emission. This is one of the additional challenges in investigating odors related to H_2S because a direct relationship between total sulfide concentration in a water sample and H_2S emissions to the air does not exist.

4.2 Sampling Considerations

Several factors must be considered when developing a sampling plan to characterize odorous compounds. Initial screening studies to identify treatment components for more intensive investigation are recommended to maximize use of resources. Such studies may take advantage of analytical tools such as sulfide detection tubes and gold film air monitors to provide an indication of odor generation and emission sites. Such methods measure concentrations *in situ* and avoid the need for sample preservation. NCASI studies have confirmed that RSC concentrations in the aqueous phase can be quite variable with respect to time. It is therefore important to conduct surveys multiple times to gain a complete understanding of system characteristics (NCASI 2007). Aqueous phase samples can be used to determine changes in wastewater concentrations into and out of treatment units and air phase measurements taken in conjunction with water sampling can be used to indicate emission points.

Screening studies will indicate when more intensive survey work is needed. When additional work is called for, more accurate analytical techniques, such as colorimetric and GC methods, are frequently employed. These methods often require collection of aqueous phase samples for later analysis. Because odor-causing compounds are volatile, proper sampling and preservation techniques must be employed to ensure representativeness of samples. Allowable holding times, even for preserved samples, should be heeded and such timing must be factored into study plans. In some cases sample holding times and available analytical capacity may represent potentially significant constraints on a site survey.

4.3 Summary of NCASI Source Identification Surveys

Only minimal information is available in the literature on RSC emissions from kraft mill WWTPs. This subject is challenging not only because of the complexity of water chemistry, but also because of inherent difficulties in measuring air emissions from these ground-level area sources. NCASI recently completed an extensive and comprehensive study aimed at quantifying RSC emissions from pulp mill WWTP sources. In addition, numerous aqueous phase surveys have been performed at a variety of pulp and paper mills in support of odor reduction studies. Information gleaned from these studies is summarized herein.

4.3.1 *Multi-Mill RSC Emissions Study of Pulp and Paper Mill Wastewater Treatment Plants*

This multi-mill study (Crawford, Crapo, and Jain 2008) was comprehensive in that it generated information on liquid concentrations, system operating parameters, and emissions from a range of WWTP sources such as primary clarifiers, pre-aeration settling ponds, aerated stabilization basins (ASBs), activated sludge treatment (AST) units, and post-aeration polishing ponds. The three primary objectives of the study were to a) quantify RSC emissions via spatial ambient air sampling; b) develop an understanding of factors that affect RSC emissions from kraft mill WWTPs; and c) gather data necessary to calibrate and/or develop mechanistic or semi-empirical models to predict emissions.

An extensive liquid sampling and process data collection program was conducted in conjunction with emissions determinations via spatial ambient air sampling. Liquid samples were collected and analyzed for total sulfide, MeSH, DMS, DMDS, DMTS, sulfate, thiosulfate, and total organic carbon (TOC). Data on wastewater temperature, pH, DO, and conductivity at multiple depths were recorded when grab samples were collected in basins, ponds, and primary clarifiers. The spatial ambient air sampling method used in the study, called boundary layer emission monitoring, was used previously to measure TRS emissions fluxes from three kraft mill ASBs in Canada (Esplin 1988, 1989).

Traditional spatial ambient air sampling methods used to measure emissions from area sources involve a fixed array of towers placed downwind from the source. These towers collect ambient air samples at multiple horizontal and vertical locations, and emissions fluxes are calculated. However, accurate measurements of emissions fluxes from area sources such as ASBs require use of several relatively tall towers, simultaneous operation of several independent sampling trains, and analysis of a multitude of samples. The boundary layer emission monitoring used in this study involved crosswind-integrated downwind sampling at multiple elevations using a mobile cart and helium-filled balloon to hoist sample lines to multiple elevations. Samples were conditioned with a Nafion dryer and collected in evacuated and passivated canisters that were subsequently pressurized with nitrogen. Canister contents were later analyzed off site for TRS compounds using a GC/pulsed flame photometric detector (PFPD) method. Results are summarized below.

1. Primary clarifiers were minor sources of TRS emissions, mainly due to the relatively small surface areas available for emissions.

2. Primary settling ponds at four of the six kraft mills tested were significant sources of H_2S emissions. They are ideal environments for generation of sulfide via biochemical sulfate reduction due to their high organic loadings and typically long residence times relative to primary clarifiers. Their larger exposed surface areas also provide greater opportunity for emissions of sulfide as H_2S. The amount of H_2S emitted versus transferred to downstream secondary treatment processes was found to depend on wind speed, liquid phase pH, and temperature.

3. ASBs with sufficient aeration, especially in the front ends of the systems where oxygen demand is greatest, were minor sources of H_2S emissions. Between 89 and 99.6% of total sulfide in primary effluent appeared to be destroyed, presumably through biological and/or chemical oxidation. However, higher H_2S emissions were measured in one ASB where aeration was marginal or low relative to BOD loading.

4. Post-aeration ponds (polishing ponds) were minor sources of H_2S emissions.

5. MeSH, DMS, and DMDS emissions were primarily related to condensate collection and stripping practices and type of secondary treatment. Organic sulfur compound emissions were higher at ASBs receiving condensates via hard piping. Between 55 and 85% of DMS hard piped to ASBs was accounted for in emissions. As MeSH is known to oxidize to form DMDS, these two compounds were considered together in a mass balance. When considered as a group, between 55 and 65% of the total sulfur in MeSH and DMDS was emitted, with the remainder apparently treated and destroyed.

6. H_2S emissions from ASTs were minimal. ASTs also provided higher apparent destruction of MeSH, DMS, and DMDS, with destruction efficiencies of 91, 79, and 71%, respectively.

4.3.2 *Wastewater Treatment Plant Aqueous Surveys*

NCASI has provided analytical support to a number of mills that were conducting odor reduction studies. Aqueous samples were analyzed for RSCs to help pinpoint treatment units where sulfide generation and loss (emission or oxidation) occurred. Flow and analytical data have been used to develop estimates of mass flows entering and exiting treatment units. These estimates provide a way to determine if RSCs increase or decrease on net across the units. Coupled with data such as pH, DO, ORP, and ambient air measurements, these estimates can provide valuable insights to aid in development of effective odor control programs.

An example of sulfide mass flow estimates is provided in Figure 4.1. The information illustrated in the figure was acquired during odor reduction studies conducted at a bleached kraft mill with a WWTP consisting of a primary clarifier, a non-aerated equalization basin, three ASBs, and a large quiescent basin. Foul condensate was being hard piped to the front end of the first aeration basin when the initial survey occurred. Baseline data suggested that sulfide generation occurred in the primary clarifier and the first ASB. In addition, the foul condensate input (hard pipe inlet) at the front of the first ASB was suspected of being a contributing source of odorous compounds to the basin. Net decreases in sulfide across the equalization basin and second ASB indicated potential emission points, although it is important to consider that some or all of the decreases may have been due to chemical or biochemical oxidation. These findings, in addition to air monitoring results and odor survey work, were utilized by the mill to develop a phased approach that included moving the foul condensate addition point to the second aeration basin and increasing aeration horsepower in the system. Maintaining aerobic conditions throughout the treatment system precludes generation of H_2S via dissimilatory sulfate reduction.

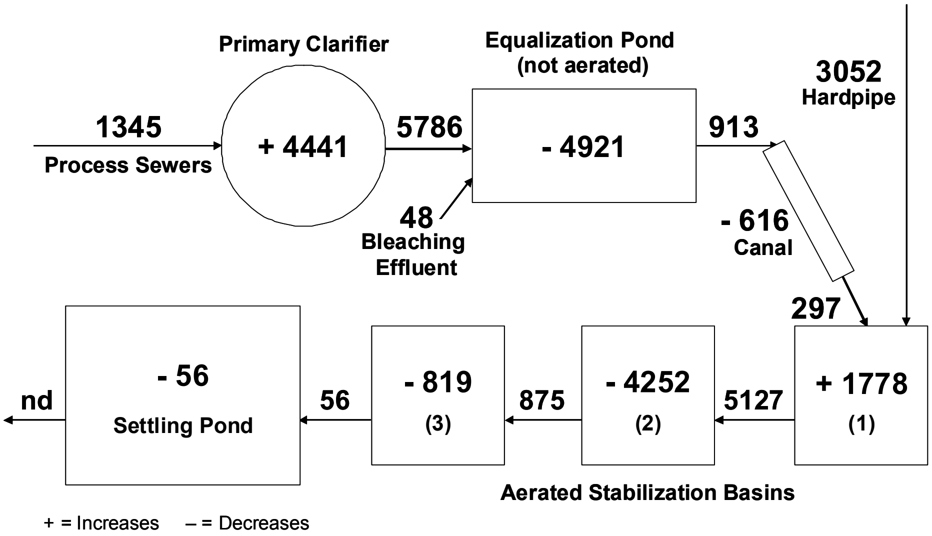

Figure 4.1 Wastewater Treatment Plant Total Sulfide Estimated Mass Flows (lb S/day): Baseline Assessment

These data, and those collected during other WWTP surveys, suggest that sulfide generated during wastewater treatment is usually associated with treatment units in which anoxic conditions occur either by design (primary treatment) or due to insufficiently aerated biological treatment basins. It is likely, based on air monitoring data, that WWTP areas where sulfide generation can occur are also the areas where the potential for emissions is highest. However, actual emission rates depend on several physical properties of the zones, such as surface area to volume ratio and level of turbulence. Loss of RSCs in some treatment zones may be due to volatilization or to oxidation by chemical or biological processes. Several factors influence mass transfer of sulfide in the WWTP. Mass transfer from non-aerated WWTP units such as primary settling ponds and post-aeration stabilization ponds occurs primarily through volatilization, while mass transfer from aerated units such as ASBs occurs through both volatilization and stripping. Therefore, overall mass transfer of sulfide in the WWTP is influenced by aerator characteristics (e.g., impeller diameter, rpm), physical properties (e.g., density and viscosity of air, aeration horsepower, rate and effectiveness of oxygen transfer, diffusivity of oxygen in the water, wind velocity, compound diffusivity in water, unit dimensions such as ratio of fetch to depth), and the Henry's law constant (dependent on pH, temperature, compound hydration, compound concentration, co-solvent and co-solutes, dissolved salts, suspended solids, dissolved organic matter, and surfactants) (Staudinger and Roberts 1996; USEPA 1994). Although aqueous surveys can provide useful information when making odor reduction decisions, additional data may be required to pinpoint zones of generation, oxidation, and volatilization within the WWTP.

5.0 CONTROL METHODS FOR HYDROGEN SULFIDE

NCASI research and published literature regarding WWTP odor reduction indicate that H_2S is a primary cause of odors associated with WWTP operations. Thus, efforts to minimize such odors typically focus on control methods to reduce H_2S generation and emission. A variety of methods have been proposed, many of which have been field-tested and implemented. To better understand the basis for these methods, an overview of major sulfur transformations that can occur in WWTPs is provided. Understanding sulfur chemistry can be challenging and is a lifelong pursuit for some chemists. Sulfur has a total of ten oxidation states, including -2, -1, 0, +1, +2, +2½, +3, +4, +5, and +6, and for this and other reasons, transformation reactions are complex.

This section describes control methods that have been developed and tested in the pulp and paper and other industries to combat and minimize odors arising from RSCs (specifically H_2S) and, to a limited extent, other odor-causing compounds such as VFAs (Zhang et al. 2008). Data acquired from NCASI member company studies are included as examples of techniques that have been utilized at pulp and paper mills in the U.S. and Canada.

5.1 Overview of Sulfide Behavior in Wastewater Systems

H_2S is a weak dibasic acid that will disproportionate in wastewater according to Equation5.1. Of the sulfur species shown, only H_2S is volatile. The reaction is affected by the pH of the wastewater, temperature, and ionic strength. HS^- formation can also result from sulfate and thiosulfate reduction.

$$2H_2S \leftrightarrows H^+ + HS^- \leftrightarrows 2\,H^+ + S^{2-} \qquad \text{(Eq. 5.1)}$$

The chemical fate and transport of sulfur compounds in the WWTP is a complex series of chemical and biochemical reactions and physical transport processes (Tooke 2006; Zhang et al. 2008), as shown in Figure 5.1. They include volatilization, reduction (dissimilatory and assimilatory), oxidation (chemical and biological), and mineralization.

The mechanisms of sulfide generation in wastewater systems may be numerous and complex, but most literature sources indicate that the primary mechanism is dissimilatory sulfate reduction. This biologically mediated reaction occurs under conditions that can develop in many pulp and paper wastewater treatment systems: high temperatures, high BOD and sulfate loads, and an absence of energetically favorable electron acceptors such as oxygen or nitrate (Delgado et al. 1999; Zhang et al. 2008). These conditions are likely to occur in anaerobic sections of the treatment system (Tooke 2006; ASCE 1989) such as primary settling units, the front end of aerated units, and sludge deposits.

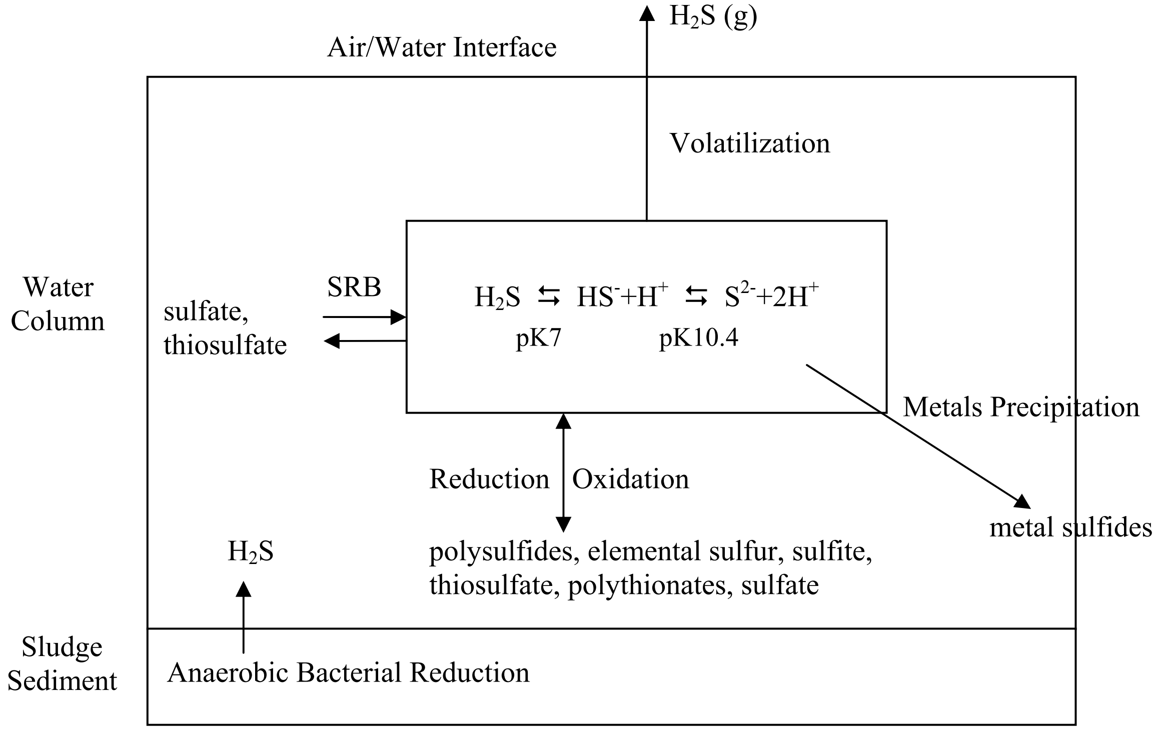

Figure 5.1 Major Sulfide Transitions in the Wastewater Treatment Plant

A typical biologically-mediated reduction is illustrated in Equation 5.2.

$$4H_2 + SO_4^{2-} \rightarrow 4H_2O + S^{2-} \qquad \text{(Eq. 5.2)}$$

Oxidized sulfur is usually not a limiting reactant in pulp and paper mill wastewater because sulfate and other intermediates (sulfite, thiosulfate, polythionates, dimethyl sulfoxide, elemental sulfur) are present (Tooke 2006). The reaction is affected by pH, temperature, available nutrients, absence of SRB, and the ORP of the system (Delgado et al. 1999). Wastes with high BOD_5 concentrations (300 to 1000 mg/L) can enhance sulfide production. Because sulfide generation is dependent on anaerobic conditions, any waste that accelerates the consumption of oxygen tends to produce sulfide (ASCE 1989). Generally, sulfide is present in wastewaters with negative ORP values (<-150). As temperature increases the rate of sulfide formation will increase (Boon 1995). The proportions of H_2S, HS^-, and S^{2-} in the wastewater are significantly affected by pH as well as temperature and ionic strength.

NCASI has generated laboratory data characterizing the rate of sulfide generation in anaerobic waters representative of primary settling units or under-aerated ASBs (Palumbo et al. 2007). These data indicate that sulfide can be generated rapidly in these waters, suggesting the anaerobic water column as a primary source of sulfide in treatment systems. Additionally, field data were collected to estimate the contribution of sludge deposits to H_2S air emissions. These data, from a single treatment system, indicated that a large majority of the gas produced in sludge deposits was methane and carbon dioxide. H_2S was <1% of the gas generated in sludge deposits.

Assimilatory sulfate reduction involves incorporation of the sulfur in sulfate into cellular organic constituents via a sulfide intermediate. Assimilatory reduction often occurs in sediments (Vairavamurthy and Schoonen 1995).

Both chemical and biological sulfide oxidation can occur in the WWTP. Chemical oxidation is typically slower than biological oxidation (ASCE 1989; Tooke 2006), and is influenced by pH, temperature, reactant concentration ratios, ionic strength, and other factors such as the presence of transition metal catalysts. The resulting products (e.g., sulfate, elemental sulfur) depend on these factors. Biological oxidation occurs via sulfur-oxidizing bacteria that use sulfide, elemental sulfur, thiosulfate, or other partially reduced oxides of sulfur as a source of energy, producing sulfate.

Organic compounds that contain sulfur can be decomposed by heterotrophic microorganisms that incorporate some of the sulfur and release some as sulfide. This process of mineralization is illustrated in Equations 5.3 and 5.4. The sulfur-containing organic compound is reduced to MeSH, which in turn is hydrolyzed biochemically to methyl alcohol and sulfide (ASCE 1989).

$$H_2O + CH_3SCH_2CHNH_2COOH \rightarrow CH_3SCH + NH_3 + CH_3CH_2COCOOH \qquad \text{(Eq. 5.3)}$$

$$CH_3SH + H_2O \rightarrow CH_4OH + H_2S \qquad \text{(Eq. 5.4)}$$

The main control methods used to minimize odors due to sulfide encourage processes that reduce or eliminate sulfide generation and encourage its removal via oxidation (chemical and biological) or precipitation (metals and organic scavengers). In addition, methods that encourage sulfide to remain dissolved in solution (e.g., pH adjustment) until oxidation or precipitation can occur are employed. Some control methods (e.g., enzyme blockers, selective use of biocides) attempt to prevent or limit SRB and thus sulfide generation prior to or within the WWTP. Additional methods attempt to neutralize odors and limit or direct their distribution (e.g., vegetative shelter belts) until oxidation can occur in the atmosphere.

5.2 Chemical Precipitation

Odor minimization strategies based on precipitation convert dissolved odor-causing compounds into insoluble salts, thereby precipitating them out of wastewater matrices and rendering them unavailable for volatilization/stripping or for reactions occurring in the liquid column. Sulfide salts of metals such as iron, chromium, copper, zinc, nickel, or cadmium are very sparingly soluble, and addition of metals will cause sulfides to precipitate (Zhang et al. 2008). Iron is the most commonly used metal for sulfide control. Salts such as ferrous chloride ($FeCl_2$), ferric chloride ($FeCl_3$), and ferrous sulfate ($FeSO_4$) have all been tested in several applications to control sulfide-related odors. Addition of any of these compounds results in formation of iron sulfide that has a solubility of 6.2 mg/L of water (FeS) (Lide 1992). The chemical reaction of $FeCl_2$ with sulfide is shown in Equation 5.5. Studies indicate that a mixture of ferrous and ferric iron salts may provide greater reductions in sulfide than either salt individually (Zhang et al. 2008).

$$FeCl_2 + 2HS^- + S^{2-} \rightarrow \text{various Fe sulfide/disulfides} + 2HCl \qquad \text{(Eq. 5.5)}$$

$FeCl_2$ reacts similarly to $FeCl_3$ but has only 65% of the H_2S removal capacity per mole. The reduced cost of $FeCl_2$ relative to $FeCl_3$ can often offset this drawback. Soluble iron salts are usually applied as concentrated liquid solutions that can be stored in totes or tanks and metered into the waste stream using a chemical metering system. Plumbing systems often require use of PVC to minimize corrosion, which can occur with metal pipes. $FeSO_4$ and $FeCl_2$ are mildly corrosive acids and therefore require appropriate precautions during handling.

Disadvantages relate to increased sludge generation and metals that can be problematic when sludge is incinerated in a boiler. They may influence the pH of the solution if the buffering capacity of the wastewater is low. The effectiveness of this approach in WWTP units in which solids may accumulate, such as ASBs and polishing basins, can be limited, as settled metal sulfides may later release H_2S via biochemical reduction of the precipitated compounds.

The effectiveness of $FeCl_3$ as an odor control chemical was tested during a full-scale trial on sludge handling and effluent clarification systems (Crowder, Tinti, and Niedenzu 1992). The facility utilized a primary clarification system and aeration tanks to treat pulp mill effluent. Bleach plant effluent was treated in anaerobic reactors, and anaerobic sludge was combined with primary sludge and dewatered on belt presses. Filtrate from the dewatering system was returned to the primary clarifier. The existing odor control strategy included continuous addition of sodium hypochlorite to the sludge handling system and occasional addition of calcium hypochlorite to the primary clarifier. Odor control performance under the existing strategy was compared to two scenarios: addition of $FeCl_3$ and addition of a proprietary product (Ferrisorb^{TM}, a mix of $FeCl_3$ and other additives) to the sludge handling and effluent treatment systems.

$FeCl_3$ and Ferrisorb were added to the combined (anaerobic + primary) sludge stream just upstream of the dewatering press. Both additives were found to be equally effective in reducing odors at that location. Odor reduction through the use of sodium hypochlorite was also comparable; however, using sodium hypochlorite cost about twice as much as treatment with $FeCl_3$. Additionally, the authors observed an increase in ORP. It was also speculated that $FeCl_3$ benefited sludge dewatering.

In the effluent treatment system, $FeCl_3$ and Ferrisorb were added in a highly turbulent zone ahead of the primary clarifier, thereby promoting rapid mixing. $FeCl_3$ was found to reduce H_2S emissions by 70% at that location, and Ferrisorb was found to be even more effective.

A study to investigate addition of $FeSO_4$ to reduce sulfide in a foul condensate was conducted at a bleached kraft mill pulping softwood and hardwood. Experiments involved adding 17.5 gallons per hour (GPH) of $FeSO_4$ (density not provided) to the foul condensate header, which had a flow of 3.0 million gallons per day (MGD), then measuring sulfide at four drop legs located between the addition point and a point prior to introduction of foul condensate to the WWTP. Dosage and retention time trends were evaluated using a screening technique that involved collecting 25-mL samples in a 500-mL bottle that was closed and agitated for one minute. The cap was removed and a Jerome air monitor was used to measure volatile H_2S in the headspace of the bottle. Using this technique, headspace H_2S concentrations in the foul condensate ranged from 172 to 859 ppm prior to addition of $FeSO_4$ and from <1 to 116 ppm following addition. Reductions in sulfide ranged from 0% at the first drop leg to 60% at the second, third, and fourth drop legs (Figure 5.2), indicating a significant reduction in sulfide once the $FeSO_4$ was well mixed in the foul condensate sewer (NCASI files).

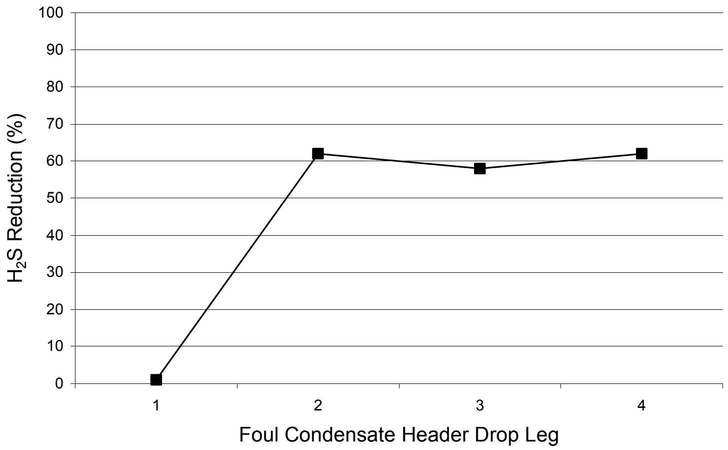

Figure 5.2 Sulfide Reduction after Ferrous Sulfate Addition to a Foul Condensate

5.3 Oxidation

Several oxidizing agents have been used for destruction of odors resulting from H_2S. The approach is to oxidize the sulfide into nonvolatile forms such as elemental sulfur, thiosulfate, sulfite, and sulfate. Chemical oxidation reactions are generally slower than biochemical oxidation reactions (ASCE 1989). In the presence of large organic loads, as with industrial wastewaters, the economics of oxidizing agent use can be prohibitive due to competitive reactions with organic materials. Some of the commonly used oxidizing agents are chlorine, chlorine dioxide, hypochlorite, oxygen, and hydrogen peroxide. Industry experience with use of oxidizing agents is summarized herein.

5.3.1 *Hydrogen Peroxide*

Hydrogen peroxide (H_2O_2) can be used to chemically oxidize H_2S into either elemental sulfur or sulfate (the former at pH <8 to 9; the latter at pH >8 to 9), as shown in Equations 5.6 and 5.7. In the range of pH 7 to 9, both reactions may occur. Excess H_2O_2 can oxidize other wastewater components or decompose to release oxygen and water.

$$H_2O_2 + H_2S \rightarrow S + 2H_2O \qquad \text{(Eq. 5.6)}$$

$$4H_2O_2 + S^{2-} \rightarrow SO_4^{2-} + 4H_2O \qquad \text{(Eq. 5.7)}$$

H_2O_2 is a clear, colorless, nonflammable compound that is miscible with water in all proportions and is normally sold as a solution expressed as a percentage of the solution's weight (e.g., a 35% solution contains 35% H_2O_2 and 65% water by weight). Solutions of >8% are classified as oxidizers by the U.S. Department of Transportation. H_2O_2 can be obtained in small drums or tanks equipped with metering pumps and plumbed to the addition point. Storage containers must be properly vented because contamination or excess heat can accelerate decomposition to oxygen and water. Special safety handling is required, including eye protection and protective clothing.

Davies, Christy, and O'Connor (2000) reported on the effectiveness of using H_2O_2 to control odors resulting from release of H_2S at four locations around the WWTP at a pulp and paper mill in Canada. The specific objectives were to reduce H_2S concentration in an anaerobic spill basin effluent returned to the effluent clarification and treatment system; treat anaerobic sludge from the spill basin; minimize odors arising from sewering condensates; and treat all foul condensates from the mill during a scheduled shutdown of the steam stripper.

H_2O_2 was found to be effective for odor reduction at all the locations. It was added to the anaerobic spill basin effluent at a location that promoted good mixing prior to introduction into the clarifier. The residence time associated with transfer of effluent from the spill basin to the clarifier was sufficient to oxidize H_2S and minimize odor. Sludge dewatering equipment consisted of a screen, an agitation tank, a centrifuge, and a belt press. H_2O_2 was added to the agitation tank. In addition, an odor-controlling spray (Ecosorb) was applied to the air around the screens to capture any residual odors. H_2O_2 was also used to reduce odors during occasional sewering of condensates. Dosage levels were selected based on laboratory studies that indicated that ~200 mg H_2O_2/L of treated condensate was sufficient to remove odors. A solution containing 50% H_2O_2 was also used to reduce odors during steam stripper downtime events when foul condensates were piped directly into the aeration pond.

H_2O_2 and calcium peroxide (CaO_2) have been used in the presence of peroxidase, an enzyme found in horseradish, to remove odors in swine manure. Swine manure is known to contain large amounts of VFAs, phenolic compounds, and indolic compounds that have been implicated in odor. Peroxidase, in the presence of peroxides, has been found to polymerize phenolic odorants, thereby reducing associated odors (Govere et al. 2007).

H_2O_2 has also been used successfully as one element of a multi-pronged approach to control odor attributed to VFA generation in anaerobic environments (Davis and Smith 2001). H_2O_2 would be particularly beneficial for use in mills with high levels of water reuse (e.g., some recycle mills). Oxygen-limited environments in the process water transport system at those facilities can be ideal for anaerobic bacterial growth. Traditional oxidizers such as sodium hypochlorite, chlorine, and chlorine dioxide increase total chloride and conductivity in the reused effluent, which can disrupt process performance and cause corrosion. The multi-pronged approach used at a 100% recycled corrugating medium mill focused on good operating practices aimed at oxygenation, biocide application to control the amount of aerobic bacteria, and H_2O_2 use to prevent anaerobic environments in the secondary treatment system (Davis and Smith 2001).

NCASI assisted a bleached kraft mill that conducted a trial to investigate the effects of adding H_2O_2 to foul condensates. Foul condensates were piped directly to the first basin of a multi-stage ASB. Samples were collected at two locations (just prior to addition of peroxide and just following the addition point) over a five-day period to assess impacts on sulfide concentrations. Samples were analyzed using direct injection GC/PFPD (NCASI Method RSC-02.02; NCASI 2007). H_2O_2 was added as a 50% solution at a rate of 1.78 gallons per minute (GPM) to the foul condensate stream, which had a flow rate of 3 MGD, resulting in a concentration of approximately 0.51 g H_2O_2/L of foul condensate. The average reduction in sulfide concentration was over 79%, as illustrated in Figure 5.3.

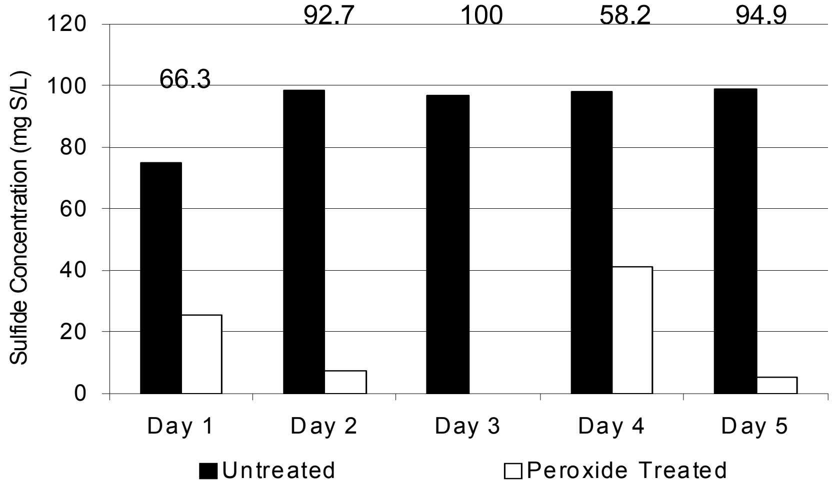

Figure 5.3 Sulfide Concentrations after Peroxide Addition (0.51 g/L) to a Foul Condensate [numbers above bars represent percent reductions in total sulfide observed each day]

Dosage and retention time trends were evaluated using a screening technique that involved collecting 25-mL samples in a 500-mL bottle that was closed and agitated for one minute. The cap was removed and a Jerome air monitor was used to measure volatile H_2S in the headspace. The effect of peroxide dose and retention time are illustrated in Figure 5.4. Reductions of >90% were observed after the first minute, and at some dosage rates they increased modestly with additional retention time. Figure 5.5 illustrates trends for doses of 0.5 and 1.0 GPM of a 50% H_2O_2 solution to the 3 MGD foul condensate at the four sampling locations (drop legs 1 through 4). Although some variability was observed, a significant reduction in sulfide was observed at the first drop leg under both addition rates investigated and increased gradually as the foul condensate progressed through the drop legs.

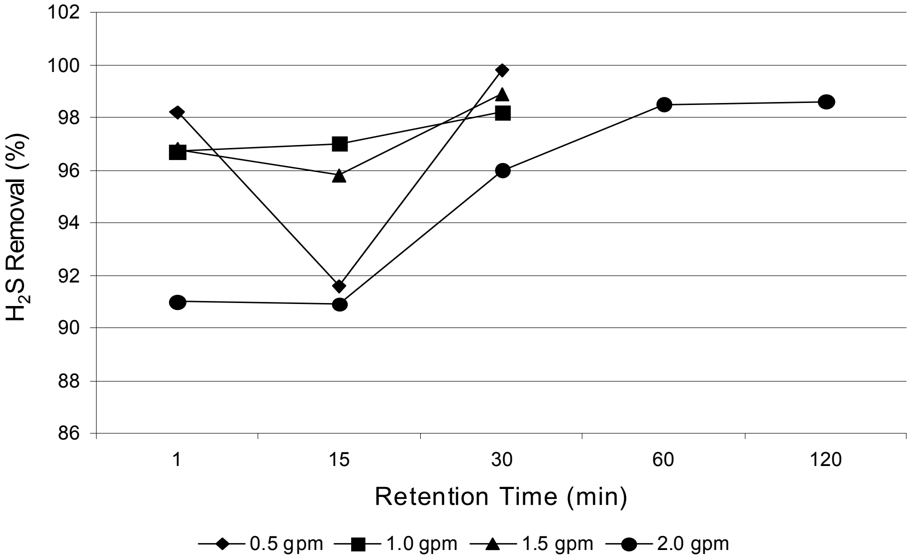

Figure 5.4 Effect of Hydrogen Peroxide Dose (0.14, 0.29, 0.43, and 0.56 g/L) and Retention Time on Sulfide Removal Efficiency [headspace measurements]

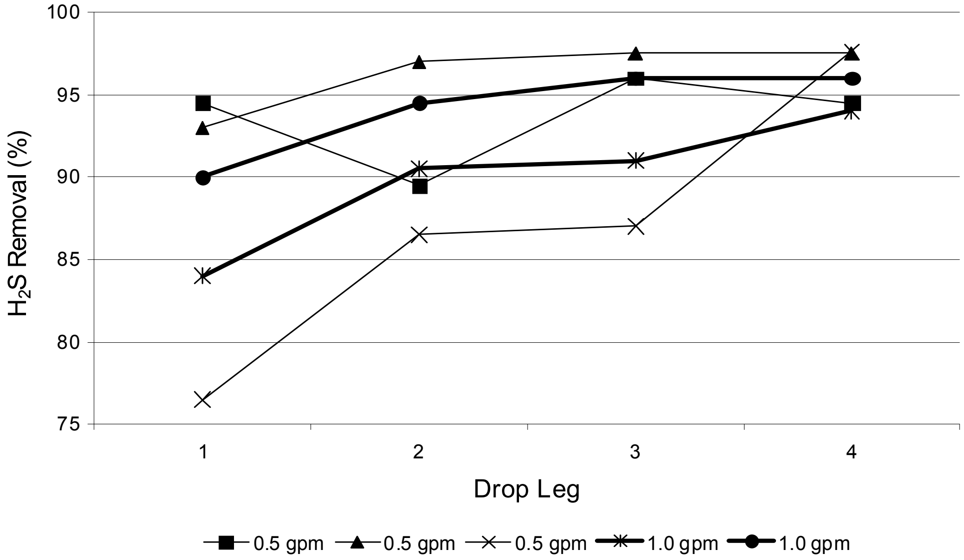

Figure 5.5 Effect of Hydrogen Peroxide Dose (0.14, 0.29, 0.43, and 0.56 g/L) and Sample Location on Sulfide Removal Efficiency [headspace measurements]

Another example of H_2O_2 use at a bleached kraft mill is illustrated in Figure 5.6. The mill conducted a bench study prior to an odor reduction trial to determine the dose-response curve for peroxide addition to foul condensates. Foul condensates were treated with the oxidant (50% H_2O_2; density 1.2 g/mL) volumes shown in the figure (equivalent to 0.14, 0.29, 0.43, and 0.56 g H_2O_2/L of foul condensate) at 50°C for 30 minutes in sealed vials. Samples were removed and analyzed by direct aqueous injection GC/sulfur chemiluminescence detectors (SCD) for sulfide, MeSH, DMS, and

DMDS. The data indicate that sulfide and MeSH were readily removed, but that DMS required significantly higher doses to achieve equivalent levels of removal. DMDS was not removed and in fact increased with peroxide dose, presumably due to oxidation of MeSH.

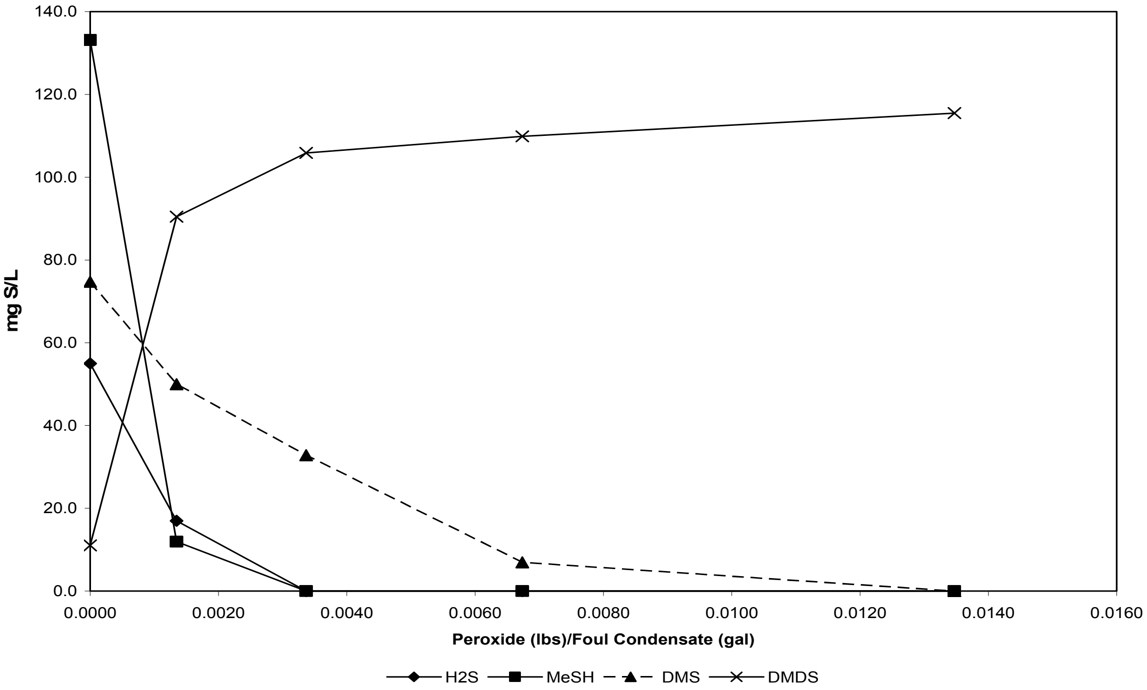

Figure 5.6 Hydrogen Peroxide Dose-Response Curve for Treatment of Foul Condensates

Following the bench studies, a mill trial was conducted over a five day period. H_2O_2 was added to the foul condensate tank (pH 9.0 to 9.3) at a rate of 1 gallon (100% H_2O_2) to every 500 gallons of condensate, which is equivalent to 2.8 g H_2O_2/L of foul condensate. This addition point provided a retention time of ~30 minutes prior to the WWTP. The trial resulted in overall average reductions in sulfide, MeSH, and DMS of 38.8, 64.6, and -3.9%, respectively (Table 5.1). The level of DMDS increased (probably due to oxidation of MeSH to DMDS) during the addition but reportedly did not affect overall odor from the WWTP (NCASI files). The mill continues to feed H_2O_2 to the foul condensate and has reported a reduction in odor at the WWTP.

Table 5.1 Percent Reduction in Hydrogen Sulfide, Methyl Mercaptan, and Dimethyl Sulfide during a Peroxide Addition Trial Conducted in a Foul Condensate

Day of Study	H_2S	MeSH	DMS
1	26.1	67.3	-20.8
2	68.3	74.7	16.5
3	38.1	57.0	1.9
4	36.4	60.0	2.6
5	25.3	63.8	-19.5
Average	38.8	64.6	-3.86

5.3.2 *Chlorine and Chlorine Dioxide*

Both chlorine (Cl_2) and chlorine dioxide (ClO_2) can react with sulfide in wastewater to form dissolved sulfates (sulfuric acid) and, in the case of Cl_2, elemental sulfur. Equations 5.8 and 5.9 illustrate the two different reactions that occur with Cl_2 and H_2S. Hydrochloric acid is also formed in the wastewater matrix as a result of the reaction with Cl_2, reducing the pH of the wastewater. Intermediate reactions between sulfur and sulfate can also occur, including formation of thiosulfate, trithionate, and sulfite, depending on pH, temperature, organic matter in the matrix, and the degree of mixing. Cl_2 and ClO_2 use in full-scale systems is limited by associated safety, storage, and handling problems (Hagen and Hartung 1997). Cl_2 is usually added to the waste stream as either hypochlorite or chlorine gas. Sodium hypochlorite is often used where dosages are small (<100 lb/day) or where chlorine gas is excluded from consideration for safety reasons. These systems often consist of a tank, metering pump, hypochlorite solution feed piping (typically plastic), and diffuser or injection system (ASCE 1989). The proper ratio of chemicals to sulfide is 1.8:1 to 2.0:1 (w/w) when added as an aqueous solution (Zhang et al. 2008).

$$Cl_2 + H_2S + O^{2-} \rightarrow S + H_2O + 2Cl^- \qquad \text{(Eq. 8)}$$

$$H_2S + 4Cl_2 + 4H_2O \rightarrow H_2SO_4 + 8HCl \qquad \text{(Eq. 9)}$$

A laboratory bench trial of sodium hypochlorite (bleach) addition to a foul condensate from a bleached kraft mill yielded the dose-response curve in Figure 5.7. Bleach (129 g Cl_2/L) was added at 1.5 gallons per 500 gallons of condensate. It was determined that reducing sulfide, MeSH, and DMS to levels <100 mg S/L would require 2.5 gallons of bleach (at 129 g Cl_2/L, determined by titration) to every 500 gallons of condensate. Due to prohibitive capital requirements, alternative techniques (H_2O_2 and $FeSO_4$) were employed (NCASI files).

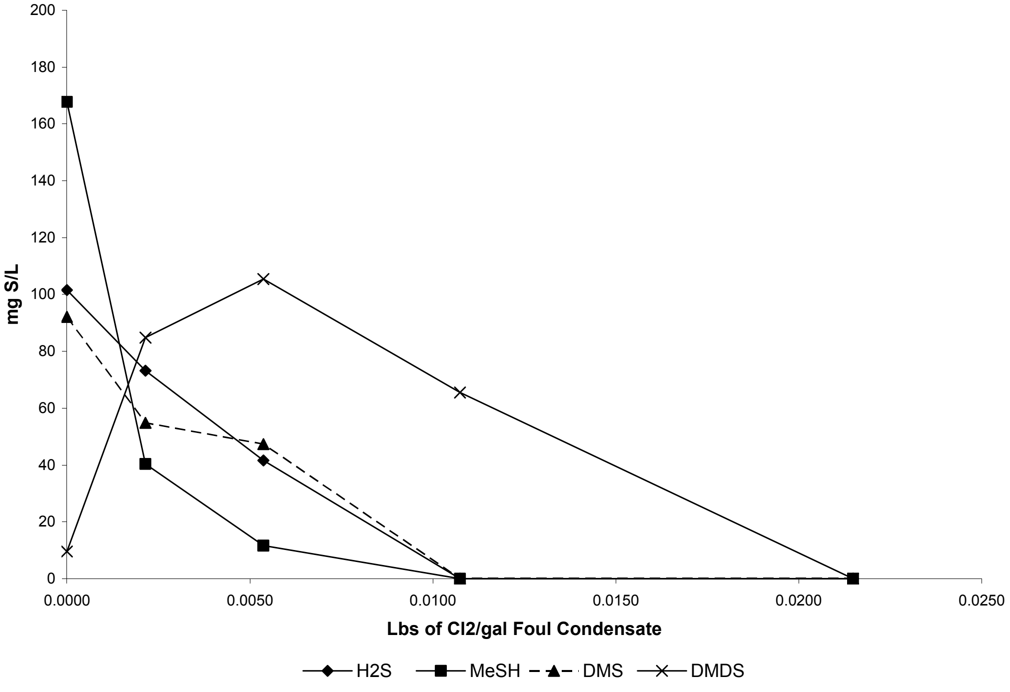

Figure 5.7 Sodium Hypochlorite Dose-Response Curve

5.3.3 *Catalytically Enhanced Oxidation*

Wet scrubbing in conventional packed bed scrubbers has been used to treat TRS gases generated at sewage treatment works. An oxidizing chemical such as sodium hypochlorite is typically used (Norval, Burton, and Kanters 2001). This approach has also been used in pulp mills in the U.S. and Canada to treat both low volume high concentration and high volume low concentration gases (Normandin 2005). One paper mill in Canada uses catalytically enhanced scrubbing with sodium hypochlorite for odor control. The ODORGUARD^{TM} process uses a proprietary nickel catalyst to increase both rate and extent of TRS compound oxidation and has been reported to be effective in treatment of TRS-laden gas streams (Norval, Burton, and Kanters 2001). The ACCENT^{TM} process also uses a nickel catalyst and has been reported to be effective in treatment of foul and clean condensates (Dufresne et al. 2000; Norval, Burton, and Kanters 2001). Laboratory studies indicated that the catalyst completely oxidizes TRS compounds to non-odorous sulfonic acids and sulfones. This approach also reduced chemical oxygen demand (COD) of condensates by 10%.

5.3.4 *Potassium Permanganate*

Potassium permanganate ($KMnO_4$) is a strong oxidizing agent that has been used successfully for odor control at WWTP sources in pulp and paper mills. It reacts with sulfide to form elemental sulfur or potassium sulfate, depending on pH. Elemental sulfur forms under acidic conditions, while potassium sulfate is produced under alkaline conditions (Equation 5.10). It is often supplied as a 6% solution in water.

$$3H_2S + 4KMnO_4 \rightarrow 2K_4SO_4 + S + 3MnO + MnO_2 + 3H_2O \qquad \text{(Eq. 5.10)}$$

An integrated pulp and paper mill in the northeastern U.S. reported successful application of $KMnO_4$ to reduce odors associated with the sludge dewatering area (Jackson 1984). The facility produced bleached kraft pulp and specialty coated paper and generated about 22 MGD of wastewater. Odor was an issue in the sludge dewatering plant, due primarily to generation of sulfide under anaerobic conditions. Furthermore, H_2S was responsible for severe corrosion in wastewater transport pipes. Dissolved sulfides in belt press filtrates were also blamed for increased filamentous bacteria and bulking problems in the AST plant.

Laboratory tests were followed by a plant trial. $KMnO_4$ was found to be very effective in controlling odors around the sludge dewatering plant. Approximately 90% of H_2S generated in the dewatering presses was eliminated, and sulfide in belt press filtrate was reduced to less than 0.1 mg/L. It was also noted that $KMnO_4$ had a beneficial impact on sludge conditioning. The company subsequently installed a dry chemical feeder to add $KMnO_4$ into the blender immediately upstream of the dewatering machines. A dosage rate of 2.6 lb $KMnO_4$ per dry ton of sludge was found to eliminate the odor problem around the dewatering system. Costs associated with $KMnO_4$ use were expected to be offset by reduced demand for polymer aids in the dewatering system. Additionally, elimination of corrosion was expected to add to the economic advantage associated with permanganate use.

5.3.5 *Oxygen*

The importance of oxygen in odor control lies in the fact that it plays a key role in biochemical reactions in which organic matter is oxidized due to the activity of microorganisms. Where such activity occurs, DO is consumed as organic matter is oxidized. In many environments found in wastewater collection and treatment systems, oxygen is not available in sufficient amounts relative to the amount of biodegradable matter present. Where such conditions exist, microorganisms adapt by utilizing alternative electron acceptors (in order of preference nitrate, sulfate, carbon dioxide). When oxygen and nitrate have been depleted from a wastewater, microorganisms utilize sulfate in a process known as dissimilatory sulfate reduction, resulting in generation of sulfide. Thus, avoiding such conditions by ensuring adequate concentrations of DO or nitrate is the basis for many odor control schemes where *in situ* sulfide generation represents a primary source of odors. Research has indicated that sulfide levels increase in areas of the WWTP where DO is <1 mg/L (Mahmood, Banerjee, and Sackellares 1999).

In addition to its role in preventing sulfide generation, oxygen also chemically reacts with sulfide, converting it to various oxidized forms such as elemental sulfur and thiosulfate. Most information available on H_2S oxidation is derived from studies carried out in seawater, water saturated with sulfide, and buffered solutions. Researchers have concluded that chemical oxidation of aqueous sulfide is characterized by an initial induction period followed by a series of reactions that can occur over a relatively long period. It has been demonstrated that use of oxygen to oxidize sulfide can be influenced by certain elements and organics that can inhibit (glycerol, carbitol, EDTA) or act as catalysts for (manganese, nickel, iron, cobalt, copper) oxidation. The initial oxidation rate is inversely proportional to the initial induction period (Chen and Morris 1972). The major products identified are elemental sulfur (S^0), thiosulfate ($S_2O_3^{2-}$), sulfite (SO_3^{2-}), and sulfate (SO_4^{2-}). Reaction rates have been found to be dependent on pH, temperature, reactant concentrations (sulfide and oxygen), ionic strength, and other factors such as the presence of catalysts (transition metals). The rate of chemical sulfide oxidation varies significantly with pH within the mildly acidic to mildly basic range; it was found to increase from pH 6, reach a maximum around pH 8.5, and decline to a minimum around pH 9.3 (Kuhn, Kelsall, and Chana 1983). Inhibitory effects due to the presence of certain organic compounds have also been reported (Cline and Richards 1969; Chen and Morris 1972). In general, at constant pH, temperature, and ionic strength, the reaction rate is expressed as a function of total sulfide and DO concentrations. Overall reaction orders have been calculated to be 1.9 (1.34 with respect to sulfide; 0.56 with respect to DO) in buffered water and seawater (Chen and Morris 1972). Researchers have also utilized rate equations with overall reaction orders of 1.0 to describe sulfide oxidation (Millero et al. 1987). Current evidence indicates that the impact of ionic strength on sulfide oxidation is probably matrix-specific (Nielsen, Vollertsen, and Hvitved-Jacobsen 2003).

Oxidation of sulfide in industrial wastewaters can also be biologically mediated. As a result, some of the chain reactions may involve biological pathways. The relative significance of chemical vs. biological oxidation is not clearly understood. Wilmot et al. (1988) found that biological sulfide oxidation accounted for 12 to 56% of the total oxidation rate in wastewater. They reported a reaction order of 0.6 to 1.2 for total sulfide and 0.2 for DO during combined biological and chemical oxidation. More pronounced contributions from biological oxidation (70%) have also been reported (Kotronarou and Hoffmann 1991).

A variety of techniques have been used to ensure aerobic conditions as a means to control sulfide odors, including installation of conventional aeration devices, application of molecular oxygen, and redistribution of organic loads. The rate and efficiency of oxygen transfer become important parameters to consider for odor reduction strategies relying on oxygen. Conventional system designs that employ aeration equipment such as surface aerators, coarse bubble diffusers, and fine bubble diffusers can maintain aerobic conditions in biological treatment systems. However, DO concentrations vary spatially in these systems and may be inadequate to maintain aerobic conditions in zones that experience high organic loads, such as in the front ends of ASBs and where high strength streams such as foul condensates are introduced. Moreover, untreated or partially treated wastewaters may deplete available DO concentrations in non-aerated vessels and pipes, creating ideal conditions for sulfide generation via biochemical reduction of sulfate. In these situations, oxygen may be added to wastewater to control sulfide levels. Pure oxygen has been used in the industry for this and other purposes for many years. Oxygen gas applied to a wastewater or treated effluent can increase DO to levels well above air saturation values. Gaseous oxygen is typically supplied from a liquid oxygen tank, and the system includes a storage vessel, vaporizer, piping, some means of diffusing the gas into the wastewater, and process controls. Safe handling practices are required because oxygen supports combustion.

A relatively new method to accomplish oxygen addition is the Speece cone (Speece n.d.; Speece and Clidence 2006). It is designed to maximize oxygen dissolution with minimum energy expenditure. An industrial installation of a Speece cone demonstrated a 90% O_2 absorption efficiency by dissolving ~6 tons of oxygen per day into 21 MGD of wastewater. Oxygen concentrations approached 50 mg/L before the effluent entered a force main (Speece and Clidence 2006). This technology has been applied at a paper mill to maintain a positive DO level in a five mile pipe used to transport effluent to the discharge point (EOT 2005). Two eight-foot diameter cones were utilized to raise the DO level to approximately 85 mg/L. This approach might be used to oxygenate effluent entering primary clarifiers, pre-aeration settling ponds, aeration ponds, and even polishing ponds. The technology can be adjusted to ensure that adequate oxygen is always available as effluent moves through the WWTP, thereby preventing sulfide generation due to anoxic conditions.

Oxygen was used effectively at a mill that makes linerboard and medium from kraft, recycled fiber, and neutral sulfite semi-chemical pulps to control generation of sulfide in a primary clarifier. NCASI participated in a study to determine whether oxygen injection at a primary clarifier could reduce sulfide concentrations in the WWTP. Baseline samples were collected prior to initiation of the oxygen addition trial for use in estimating sulfide reduction. Oxygen was injected into the effluent stream ahead of the primary clarifier at the discharge from the lift station at rates of ½, ¾, and 1 ton per day (TPD) for four days at each addition rate. Three different samples were collected throughout each day of testing and were analyzed using NCASI Method RSC-02.02 (NCASI 2007). Figure 5.8 illustrates the variability observed for total sulfide concentrations in aqueous samples collected at the clarifier outlet prior to oxygen addition and at each oxygen addition rate.

Due to associated cost benefits, the facility built a 1 TPD oxygen generator onsite instead of buying and transporting oxygen to the facility (NCASI files). The system has been utilized to help control sulfide levels at the primary clarifier.

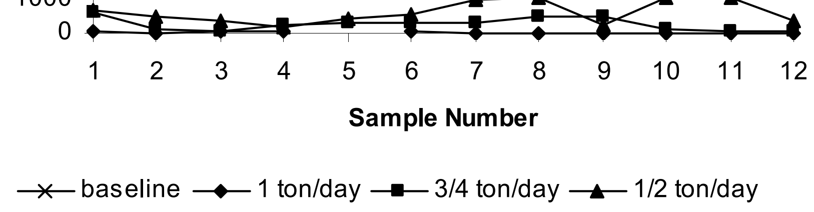

Figure 5.8 Primary Clarifier Effluent Total Sulfide Variability Before and During Oxygen Addition Trials

Many odor reduction programs that have been implemented in the pulp and paper industry utilize a variety of techniques focused on optimization of WWTPs through modifications such as adding aeration capacity and redistributing organic loads to increase DO and minimize anaerobic zones in the treatment system.

One example occurred at a kraft mill in the northern U.S. that was experiencing an increase in odor complaints. The mill used a Jerome ambient air monitor to determine the main sites of H_2S volatilization within its WWTP. The study involved characterizing the WWTP by measuring ambient air H_2S levels, DO, pH, sulfide in the aqueous phase (utilizing a "shaker" test to track H_2S within the system), sulfate, nitrate, microbial populations, and ORP. Data indicated that the first ASB lagoon was the source of odors. The mill instigated a plan in that lagoon that eliminated use of sulfuric acid to control pH, added lime to the inactive side to increase pH, installed baffle curtains to reduce active size and improve the flow pattern, and added aerators to the active side. This increased aeration intensity and decreased anaerobic zones. The average maximum daily H_2S concentration measured in the first ASB lagoon dropped from 265 ppb to 77 ppb after the baffle curtain was installed, and the mill has experienced a decline in odor complaints (Racine 2005).

NCASI participated in a study at a bleached kraft mill pulping softwood and hardwood that also increased aeration capacity and made system modifications to the WWTP to help reduce odors related to sulfide. The WWTP consisted of a primary clarifier and a settling pond followed by an ASB divided into four basins treating approximately 15,000 lb/day of BOD. When the project was initiated, condensates were being routed directly to the first basin of the ASB (hard pipe). The mill examined several options to reduce sulfide emissions at the WWTP. Modifications included redirecting foul condensate to the second ASB and increasing aeration horsepower in the first three ASBs by 74%. Table 5.2 summarizes comparative sulfide concentrations in aqueous samples collected throughout the WWTP prior to and following system modifications. This example illustrates the effectiveness of modifications aimed at minimizing anaerobic conditions in ASBs on sulfide levels and associated odors.

Table 5.2 Aqueous Sulfide Concentrations Before and After Wastewater Treatment Plant Modifications

Sampling Location	Total Sulfide Before Modifications (mg S/L)	Total Sulfide After Modifications (mg S/L)
Lift station	5.86	2.98
Primary clarifier outlet	20.1	6.42
Settling pond	5.20	0.104
Canal to ASB	5.50	0.181
Foul condensate	117	84.2
First ASB basin	12.6	<0.03
Second ASB basin	3.64	<0.03
Third ASB basin	0.28	<0.03
Outlet of ASB	<0.03	<0.03

5.4 Nitrate Addition

Under anoxic (zero DO) conditions microorganisms can utilize nitrate as an electron acceptor, resulting in reduction of nitrate to nitrogen gas (Equation 5.11). Thus, nitrate can be added to wastewaters instead of or in addition to oxygen as a means of precluding sulfate reduction and the accompanying generation of sulfide. Nitrate may also remove H_2S from wastewater by biochemical conversion of sulfide to sulfate (Equation 5.12).

$$6NO_3^- + 5CH_3OH \rightarrow 5CO_2 + 3N_2 + 7H_2O + 6OH^- \qquad \text{(Eq. 5.11)}$$

$$8NO_3^- + 5H_2S \rightarrow 5SO_4^{-2} + 4N_2 + 4H_2O + 2H^+ \qquad \text{(Eq. 5.12)}$$

A nitrate addition system usually consists of a storage tank for the nitrate solution (often either sodium or calcium nitrate), a metering pump, piping, and valves. If the dry form is used, a dry feeder and mixing system is required. The average stoichiometry reported in the literature ranges from 0.6 to 4.5 mg NO_3^-/mg S, with an average sulfide elimination of 90 to 100% (Zhang et al. 2008).

Nitrate compounds have been used to reduce odors at a number of pulp and paper mills (Watson et al. 2001; O'Connor et al. 2003; Groleau et al. 2002). In response to off-site odor complaints, these chemicals were utilized during a trial performed at a WWTP receiving influent from a sulfite and kraft pulp mill. The WWTP consisted of primary clarification, a settling lagoon, and a UNOX activated sludge process. Odor surveys indicated that the major source of sulfide odor was the settling lagoon. It received 16 MGD of wastewater for treatment. Sodium nitrate was added to the front and mid-point of the lagoon. Dosage rates ranged from 2.6 to 1.3 L/min (concentration of biological treatment solution was not provided by the authors); the high dosage was trialed initially, followed by successively lower rates. During the two week trial, sulfide was reduced from a range of 12 to 15 mg/L to <1 mg/L at the outlet of the settling lagoon (Watson et al. 2001).

This approach was also used to control odors from dewatered sludge at a recycled pulp mill producing high quality deinked recycled market pulp (Groleau et al. 2002). It proactively addressed odors and corrosive gases generated during warmer months in a dewatered sludge storage pile located in a temporary outdoor holding area. Odors were most noticeable when stockpiled sludge remained in place for more than a day and after weekends and holidays, and when the pile was being removed or disturbed, indicating anaerobic activity in the inner regions of the sludge pile. After conducting bench tests that yielded a significant reduction in sulfide levels across a range of 0.25 to 4.0 mL of nitrate (density ~1.5 g/mL) for every 250 g of sample (dewatered sludge), a full-scale trial to establish effective dosage rates was pursued. Over a seven-month application period, the average dosage rate was 19 gallons per day (GPD) of product into 205 dry tons of cake solids, a concentration of approximately 0.51g nitrate/kg of cake solids. This resulted in elimination of odor complaints associated with sludge piles and the ability to store dewatered sludge cake for up to seven days. The mill was also able to eliminate use of an odor masking agent around the sludge pile.

Other applications within the industry include a study conducted at a semi-chemical mill with an effluent flow of 7 MGD. The WWTP consisted of a primary clarifier and an AST system. Sodium nitrate was initially added to the primary clarifier and equalization basin. The mill switched to calcium nitrate because it was readily available, reduced costs, and achieved similar results. It began treating one of the paper machine inputs instead of the combined influent to the primary clarifier and equalization basin to reduce the volume of calcium nitrate required. Odor was controlled, as indicated by a reduction in odor complaints (NCASI 2004).

5.5 Miscellaneous Odor Minimization Approaches

5.5.1 *pH Adjustment*

H_2S is moderately acidic, and when dissolved in solution, free H_2S concentrations are dictated by two equilibrium reactions: the equilibrium between H_2S and HS^- and the equilibrium between HS^- and S^{2-}. Concentrations of H_2S, HS^-, and S^{2-} in the associated equilibria depend on the pH of the solution. Under highly basic conditions, HS^- and S^{2-} are predominant, with higher pH favoring S^{2-}. These ionic forms of sulfide are unavailable for volatilization and stripping. Equilibrium shifts to H_2S as pH decreases, thereby increasing the un-ionized fraction and the concentration of H_2S available for volatilization. The dependence of the fraction of H_2S present in undissociated form on pH is shown in Figure 5.9. At a pH of approximately 7.0, H_2S and HS^- are equimolar. Thus, pH adjustment may be used in some situations to help keep sulfide in solution until oxidation can occur.

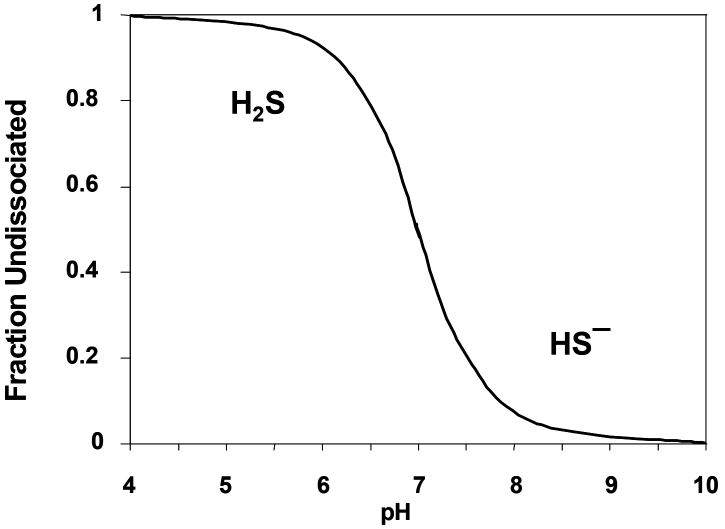

Figure 5.9 Dependence of Sulfide Dissociation on Liquid Phase pH

A softwood kraft mill equipped with settling ponds prior to an ASB added caustic (NaOH) to wastewater entering the settling pond. A target of pH 7.5 was maintained in an effort to keep sulfide in the water column. This pH adjustment, in conjunction with use of nitrates, reduced sulfide odors associated with the settling ponds during a temporary upset of the WWTP (NCASI files).

5.5.2 *In-Digester Treatment*

Research has examined the possibility of oxidizing RSCs formed in the digester prior to the blow. NCASI studies (NCASI 2000) using Douglas fir chips in laboratory batch digesters indicated that for digester configurations tested at high temperatures associated with in-digester oxidation (IDO), all sulfide, MeSH, and DMDS were converted to nonvolatile forms in approximately 4 to 7 minutes. The more oxidation-resistant DMS was reduced about 50% in concentration under the same conditions. At an optimum temperature of 125°C, approximately 2% oxygen was required for the TRS destruction noted. Results also indicated that the oxidized sulfur compounds were not susceptible to reversion to reduced forms, while IDO had no significant impact on pulp yield, physical properties, or bleachability.

Additional studies on IDO of black liquor using oxygen have indicated that MeSH and DMS can be reduced by 90 and 99%, respectively, by addition of 4.5% oxygen on pulp, which corresponds to two moles of oxygen per mole of sodium sulfide (Kringstad et al. 1972). Another study documented that MeSH and DMS formed during pulping can be converted to non-volatile compounds through reactions with polysulfide or polythionate immediately prior to transfer of pulp from the digester (Tormund and Teder 1987). However, neither of these technologies has been implemented in kraft mills. Researchers at the University of Washington and the University of Idaho have reportedly been working on an IDO strategy that injects molecular oxygen at the completion of the pulping cycle, with liquor and pulp still inside the digester. TRS compounds are oxidized at elevated temperature and pressure with this approach.

Research has also examined ways to prevent formation of odor-causing compounds, specifically TRS compounds. Zhu et al. (2002) reported that the extent of formation of organic reduced sulfur compounds (ORSCs) changes significantly when pulping kinetics shift from “bulk phase” to “residual phase” delignification. Residual phase delignification is associated with removal of recalcitrant lignin from the pulp and occurs at lower reaction rates and much lower selectivity (selective removal of lignin without affecting cellulose). That work identified a phase transition point (PTP) associated with the shift from bulk to residual phase delignification below which ORSC formation increased. The PTP was found to occur around kappa numbers 30 for softwoods and 20 for hardwoods. The study suggested that formation of these odor-causing compounds can be minimized if delignification in the digester is truncated at the PTP. Studies have also indicated that anthraquinone (AQ), an additive used in digesters to improve selectivity toward lignin, can be used to reduce formation of RSCs. A 40% reduction in formation of RSCs was expected in full-scale systems when AQ was used and the cook was terminated at the PTP (Yoon et al. 2001).

5.5.3 *Biostimulants*

Biostimulants are chemicals that stimulate the metabolism of bacteria and encourage anaerobic respiration, as well as rapid growth and activity of facultative anaerobes. Biostimulants tested at pulp and paper mills (Volpe et al. 1998; Miller, McMillen, and Sober 1995; Pote and Dwyer 1999) were based on an alkaloid compound derived from two naturally occurring plant extracts combined with a sequestering agent for application to WWTPs in liquid form. Dosage rates ranged from 0.03 to 1 ppm. Treatment was usually accomplished by adding a shock load followed by smaller daily dosages. Two studies in which biostimulants were added to WWTPs are summarized herein.

One of the first reported studies was conducted at a newsprint mill WWTP (11 MGD) consisting of a primary clarifier, an ASB, an activated sludge (AS) plant, and a second ASB. In an effort to eliminate anaerobic odors, reduce sludge volume, and improve treatment efficiency, the mill utilized a biostimulant (Miller, McMillen, and Sober 1995). Initial survey work indicated that odors were emitted from the first ASB, the secondary clarifier, and the sludge press building. Biostimulant application at the first ASB apparently resulted in elimination of offensive odors from that area and reduction of odors in secondary wasted solids. Wasting of secondary solids from the AS plant was also reduced, as well as effluent TSS.

Another study was conducted at a sulfite mill equipped with a WWTP consisting of a primary clarifier followed by three ASBs (Pote and Dwyer 1999). The mill conducted a trial by adding 38 L per day (later reduced to 15 L per day) of biostimulant to the overflow weir between the first lagoon, treating 5.7 million liters per day (MLD) of pulp mill wastewater, and the second lagoon, treating 7.6 MLD of paper mill wastewater. After initial success the mill began adding biostimulant prior to the first lagoon as well. After application was initiated, the number of odor complaints dropped, along with measured concentrations of H_2S. In addition, settleability improved in the lagoons and TSS and BOD dropped to acceptable levels. The mill generated less sludge and stopped using polymers and other chemicals in secondary treatment, resulting in a net cost savings.

5.5.4 *Organic Scavengers*

Organic scavengers are organic-based molecules that selectively react with RSCs containing acidic protons (H_2S and MeSH). Because the scavengers selectively react with these compounds, there is little demand due to other contaminants, and application rates are proportional to the sulfide and MeSH levels present. The reaction forms a water soluble product. Organic scavenger technology avoids some of the problems (corrosion damage to equipment, excess sludge, increased pH levels) associated with other odor control chemicals. An organic scavenger product was applied at a newsprint mill addressing sulfide-related odors at its WWTP (Hagen and Hartung 1997). The WWTP included two parallel primary clarifiers and an AST system. The organic scavenger was added to the primary clarifier influent, and ambient sulfide levels were reduced after 24 hours (Table 5.3).

Table 5.3 Ambient Sulfide Levels Before and After Treatment with an Organic Scavenger

Location	Ambient Sulfide Level Before Treatment (ppm)	Ambient Sulfide Level After Treatment (ppm)
Primary clarifier	50 - 100	2 - 3
Primary sludge press	25 - 50	1 - 2
Secondary sludge press	25 - 50	<1

SOURCE: Hagen and Hartung 1997

Organic scavengers have also been applied at a kraft mill to reduce sulfide odors associated with liquor spills and tank cleaning operations by adding them to the spill containment sump prior to the primary clarifier. The product was manually added to wastewater when pH and conductivity measurements reached specific levels (conductivity was utilized as a surrogate for liquor spills because it often increases during a spill). The organic scavenger helped keep sulfide in solution until oxidation could occur within the WWTP (Hagen and Hartung 1997).

5.5.5 *Enzyme Blockers*

Enzyme blockers affect the action of one of the enzymes that SRB use to metabolize sulfates to sulfide, thereby reducing formation of sulfide. The approach was applied at an integrated pulp and paper mill's 18 MGD WWTP consisting of primary clarification followed by AST. After initial survey studies using sulfide monitors and SRB test kits, it was determined that a majority of sulfide was produced in the thickener that supplied the sludge press. Enzyme inhibitor was added to the thickener mix box (the facility also added $FeSO_4$ for sulfide control). An eight-month trial was conducted during which feed of the enzyme blocker varied from 5 to 10 ppm (in 5 MGD flow to the thickeners). Study results indicated that the primary objective of reducing sulfide loads to the landfill was met. Sulfide levels measured near the belt presses and sludge piles in the press building were reduced. In addition, the mill was able to reduce the amount of $FeSO_4$ used to precipitate sulfide from 4500 lb/d to 500 lb/d, which helped keep overall chemical treatment costs constant (Arthur and Anker 2000).

5.5.6 *Odor Neutralizers*

Odor neutralizers work by absorbing or adsorbing odorous compounds, typically H_2S, MeSH, and VFAs. Neutralizers are applied into the air as vapors or mists and require installation of a delivery system. Many commercially available neutralizers are based on essential oils.

A mill in the central U.S. pulping hardwood and old corrugated containers has been effectively utilizing an odor neutralization system for several years. The mill periodically (when solids loadings are high and oxygen levels are low in the WWTP) has problems with odors associated with the influent pond that receives mill process water and storm water. The odor neutralization system is activated when odor levels increase and wind direction might impact the community. The vaporization system consists of a 2000 ft^3/min blower venting through 2000 feet of eight-inch diameter perforated PVC lines that run horizonally along the edge of the first influent pond and are elevated vertically by approximately three feet. The mill reported that the system was effective in reducing odor complaints (NCASI files).

A similar system was installed around the perimeter of an effluent treatment pond and an emergency spill basin to help control odors at a paper mill in Canada. After installation of the system, which is utilized from May through November, odor complaints declined by 80% (NCASI files).

5.5.7 *Biocides*

Biocides control odors by suppressing the activity of microorganisms. Advantages over chemical oxidants for odor control are that biocides are more persistent in the system, they do not interfere with pulping and papermaking, and lower quantities are required (Dyer 1996). Disadvantages are related to the pH sensitivity of many biocides and that biological wastewater treatment systems may be affected by biocide carryover. Biocides are often used in conjunction with other odor reduction techniques to address odors at recycled paper mills. For example, a multi-pronged approach used at a 100% recycled corrugating medium mill included biocide application at several points in the paper system to control the amount of aerobic bacteria (Davis and Smith 2001). The combined approach to VFA odor control included good operational practices, the biocide program, and system oxygenation using H_2O_2. It resulted in a 17% reduction in acetic acid and a 58% reduction in butyric acid.

5.5.8 *Shelterbelts*

Vegetative shelterbelts have been accepted in the U.S. for control of sulfide-related odors, especially in the livestock industry. Recent investigations have concluded that properly designed and implemented shelterbelts can be effective in odor reduction via four mechanisms (Tyndall and Colletti 2000):

1. mixing and dilution of odorous air with fresh air due to turbulence created by wind;
2. reduction in wind speed across waste ponds, one of the major factors contributing to increased emission rates from pulp and paper mills (Crawford 2006);
3. physical interception of particles (and the odorous compounds attached to them) and other compounds via collection on leaf surfaces; and
4. breakdown of odorous compounds through absorption and adsorption of odorous chemicals on foliage and subsequent breakdown of those chemicals by microbial activity.

Nicolai et al. (2000) conducted studies around a manure storage pond using H_2S as the measurable indicator of odor reduction. They determined that for all wind speeds (averaged) a mature shelterbelt reduced H_2S concentrations by 85%.

A three-row shelterbelt is currently recommended in the dairy industry. This approach incorporates three different tree species: a row of shrubs nearest the odor source to divert air upward and filter the air nearest the ground; a tall conifer row in the middle to provide wind speed reduction on a long-term basis; and a fast-growing deciduous tree row to provide wind reduction on a short-term basis (Bolinger and May 2006). Vegetative buffers should have a porosity of 40 to 60% and a height of 20 to 30 feet to become fully effective (Tyndall and Colletti 2000).

Although shelterbelt effects on odor movement and abatement have yet to be studied in detail around pulp and paper industry WWTPs, they may be worth considering due to significant H_2S reductions reported by the livestock industry. They have the added benefit of being aesthetically pleasing to surrounding communities.

6.0 SUMMARY AND CONCLUSIONS

This report provides a summary of pulp and paper industry experiences with odor minimization methods at WWTPs. Over 100 documents were reviewed, along with NCASI research files and interviews with member companies that have recently conducted odor minimization studies. The key components in many odor reduction programs at pulp and paper mills include formation of an odor reduction team, interactions with communities, subjective surveys of WWTPs, field measurements of ambient air and water, modeling to help predict odor impacts in communities, and selection, application, and assessment of odor control methods.

Hydrogen sulfide is one of the major odorous compounds encountered in WWTPs. A variety of methods can be employed for making field measurements of sulfide in water, including sulfide ion tubes and methods based on titration, colorimetry, capillary zone electrophoresis, GC/SSD, and electrochemistry. Airborne sulfide levels may be assessed using electrochemical methods, gold film sensors, paper tapes and patches, gas detection tubes, cavity ring-down spectroscopy, ambient H_2S analyzers, GC/MS, GC/O-MS, and GC/SSD.

NCASI has conducted several source identification surveys at industry WWTPs. Results indicate that primary clarifiers are typically minor sources of RSC emissions, although significant concentrations of sulfide may be generated in these units. Primary settling ponds and under-aerated ASBs can be significant points of sulfide generation and emissions. ASTs and ASBs with sufficient aeration, especially in the front end of the system, have proven to be minor sources of sulfide emissions, and post-aeration ponds are minor sources. Emissions of MeSH, DMS, and DMDS are often related to condensate collection and stripping practices and the type of secondary treatment employed. Mills that steam stripped foul condensates had low or undetectable levels of ORSCs from all WWTP units assessed, while hard piping of foul condensates to ASBs results in significant ORSC emissions from those basins. Aqueous phase surveys indicate that sulfide generation is associated with anoxic zones where higher concentrations of biodegradable substances are present. Aqueous sulfide surveys can help identify areas where sulfide levels increase and decrease, although interpretation of these data is challenging due to multiple reaction pathways, including oxidation, generation, and volatilization. Once sources have been identified, control methods may be selected and applied.

Odors at most WWTPs are associated with H_2S, and many control methods have been proposed and tested. Effective control methods act on one or more chemical, biochemical, or physical processes that include dissimilatory and assimilatory reduction, chemical and biological oxidation, volatilization, and mineralization. Many methods to reduce odors associated with WWTPs target processes that minimize sulfide generation and encourage its removal via oxidation or precipitation. Table 5.4 summarizes results of studies reported in the literature or conducted by member companies in cooperation with NCASI where the effectiveness of control methods for reducing H_2S were evaluated.

Chemical precipitation using iron salts has been found to reduce H_2S emissions by as much as 70%. The main disadvantage is related to increased sludge generation and metals accumulation. A variety of chemical oxidation approaches have been tested, including addition of oxygen, hydrogen peroxide, chlorine, chlorine dioxide, and potassium permanganate. The effectiveness of these techniques varies depending on doses and application sites, but generally ranges from 60 to 90% reduction in H_2S. Projects that have been effective in reducing odors at pulp and paper mill WWTPs include injecting oxygen at a primary clarifier; adding aeration capacity and redistributing organic loading in an ASB; and adding nitrate compounds as alternative electron acceptors in the primary clarifier, settling pond, or dewatered sludge. Other techniques that have resulted in reductions in odor complaints include pH adjustment to minimize sulfide volatilization, targeted use of biostimulants, organic scavengers, enzyme blockers, odor neutralizers, and biocides. Another concept worthy of consideration is the use of vegetative shelterbelts that have been applied in the swine industry to reduce odors around treatment ponds. Overall, some of the most successful strategies for odor minimization at WWTPs involve elimination of anoxic conditions in treatment basins.

Table 5.4 Summary of Sulfide Control Methods in the Pulp and Paper Industry

Control Method	Application	Average Sulfide Reduction[a]	Reference
Ferric chloride ($FeCl_3$)	sludge dewatering, prior to primary clarifier	70%	Crowder, Tinti, and Niedenzu 1992
Ferrous chloride ($FeCl_2$)	force main	~95%	Wolstenholme and Jabloner 2004
Ferrous sulfate ($FeSO_4$)	foul condensate header	~60%	NCASI files
Hydrogen peroxide (H_2O_2)	foul condensate	79%, 39%	NCASI files
Sodium hypochlorite (NaClO)	foul condensate	75%	NCASI files
Potassium permanganate ($KMnO_4$)	sludge dewatering	~90%	Jackson 1984
Oxygen (O_2)	primary clarifier inlet	~70 – 99%	NCASI files
Increased aeration HP	ASB	reduced odor complaints	Racine 2005
Sodium nitrate ($NaNO_3$)	settling lagoon, sludge dewatering	~90% eliminated odor complaints	Watson et al. 2001; Groleau et al. 2002
Calcium nitrate ($CaNO_3$)	paper machine sewer	reduced odor complaints	NCASI files
Caustic for pH control	settling pond prior to ASB	reduced odor complaints	NCASI files
Anthraquinone and pulping modifications	in digester	40%	Yoon et al. 2001
Biostimulants	ASB lagoon	reduced sulfide concentrations and odor complaints	Pote and Dwyer 1999
Organic scavengers	primary clarifier, sludge press	>90%	Hagen and Hartung 1997
Enzyme blockers	sludge thickener mix box	reduced sulfide and odor	Arthur and Anker 2000
Odor neutralizers	emergency spill basin	80%	NCASI files
Biocides	paper system	~40% reduction in VFAs	Davis and Smith 2001

[a] values are for sulfide unless otherwise noted

REFERENCES

American Public Health Association (APHA), American Water Works Association (AWWA), and Water Pollution Control Federation (WPCF). 1989. 4500-S^{2-} F. Calculation on un-ionized hydrogen sulfide. In *Standard methods for the examination of water and wastewater*, 17th ed., 4-198-4-1999. Washington, DC: American Public Health Association.

American Society of Civil Engineers (ASCE). 1989. *Sulfide in wastewater collection and treatment systems*. New York: American Society of Civil Engineers.

Arthur, P.J., and Anker, L.S. 2000. Hydrogen sulfide odor control technology. In *Proceedings of the TAPPI International Environmental Conference*, 219-222. Atlanta, GA: TAPPI Press.

Biermann, C.J. 1996. *Handbook of pulping and papermaking*, 2nd ed. San Diego, CA: Academic Press.

Blondeel, M., François, F., Bernaert, P., and Baert, R. 2006. Solving odour problems together with the neighbourhood. In *Proceedings, WEF/AWWA Odors and Air Emissions Conference*, 813-824. April 9-12, Hartford, CT. Water Environment Federation and American Water Works Association.

Bolinger, D., and May, G. 2006. Odor: Give your neighbors a break–A windbreak. *Michigan Dairy Review* 11(1):19-21.

Boon, A.G. 1995. Septicity in sewers: Causes, consequences, and containment. *Water Science and Technology* 31(7):237-253.

Brungardt, J. 2001. Odor reduction – Identification and control. Presented at NCASI Central-Lake States Regional Meeting. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Chemical Industry Council of Illinois (CICI). 2005. *Recommendations for effective community outreach from Chemical Industry Council of Illinois Responsible Care® state outreach panel.* Rosemont, IL: Chemical Industry Council of Illinois, Inc.

Chen, K.Y., and Morris, J.C. 1972. Kinetics of oxidation of aqueous sulfide by O_2. *Environmental Science and Technology* 6(6):529-537.

Cline, J.D., and Richards, F.A. 1969. Oxygenation of hydrogen sulfide in seawater at constant salinity, temperature, and pH. *Environmental Science and Technology* 3(9):838-843.

Cook, D.L., and Hoy, D.R. 2003. Analytical techniques for investigating odors at pulp and paper facilities: Preliminary results. In *Proceedings from the 2003 TAPPI Environmental Conference*, Portland, OR. Atlanta, GA: TAPPI Press

———. 2008. What's that smell? Analytical measurements for odorous compounds in pulp and paper mill wastewaters. *WEF/A&WMA Odors and Air Emissions 2008*, April 6-9, Phoenix, AZ (on CD). Water Environment Federation and Air & Waste Management Association.

Crawford, R. 2006. Measurement of reduced sulfur compounds and methane emissions from kraft mill wastewater treatment plants. In *WEF/A&WMA Odors and Air Emissions*, April 9-11, Hartford, CT. Water Environment Federation and Air & Waste Management Association.

———. 2007. Results of wastewater treatment plant reduced sulfur compound emission studies. Presented at NCASI Southern Regional Meeting, June 12-14, Nashville, TN. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Crawford, R.J., Crapo, A.M., and Jain, A.K. 2008. Reduced sulfur compound and methane emissions from kraft pulp and paper mill wastewater treatment plants. Presented at WEF/A&WMA Odors and Air Emissions 2008. April 6-9, Phoenix, AZ. Water Environment Federation and Air & Waste Management Association.

Crowder, J.R., Jr., Tinti, G.A., and Niedenzu, P.M. 1992. Wastewater odor control using ferric chloride. In *Proceedings of the TAPPI International Environmental Conference*, 63-79. Atlanta, GA: TAPPI Press.

Davies, D.T., Christy, T., and O'Connor, B. 2000. Combatting odour problems in a kraft mill using hydrogen peroxide. *Pulp and Paper Canada* 101(1):78-81.

Davis, C.K., and Smith, K.S. 2001. Controlling odor from volatile fatty acids in closed, recycle paper mill systems. *Pulp and Paper* 75(12):42-44.

Delgado, S., Alvarez, M., Rodriguez-Gomez, L.E., and Aguiar, E. 1999. H_2S generation in a reclaimed urban wastewater pipe. Case study: Tenerife (Spain). *Water Research* 33(2):539-547.

Dufresne, R., Caouette, L., Norval, G.W., and Kanters, C.J. 2000. Treatment of clean condensate using catalytically enhanced oxidation. In *Proceedings of the TAPPI International Environmental Conference*, 89-101. Atlanta, GA: TAPPI Press.

Dufresne, R., and Laroche, I. 1998. Evaluation of sulfur source emission around the wastewater treatment of a kraft mill. In *Proceedings of the TAPPI International Environmental Conference*., 1429-1435. Atlanta, GA: TAPPI Press.

Dyer, J. 1996. Odor control in recycled fiber mills. *Progress in Paper Recycling* August:87-90.

Eco-Oxygen Technologies, LLC (EOT). 2005. ECO_2 system defeats hydrogen sulfide. *Paper Industry* (December). http://www.eco2tech.com.

Esplin, G.J. 1988. Boundary layer emission monitoring. *Air Pollution Control Association Journal* 38(9):1158-1161.

———. 1989. Total reduced sulphur (TRS) emissions from effluent lagoons. *Pulp & Paper Canada* 90(10):105.

Govere, E.M., Tonegawa, M., Bruns, M.A., Wheeler, E.F., Kephart, K.B., Voigt, J.W., and Dec, J. 2007. Using mince horseradish roots and peroxides for the deodorization of swine manure: A pilot scale study. *Bioresource Technology* 98:1191-1198.

Goyer, N., and Lavoie, J. 2001. Emissions of chemical compounds and bioaerosols during the secondary treatment of paper mill effluents. *American Industrial Hygiene Association Journal* 62:330-341.

Groleau, J., Clausen, T., Hunniford, D., Ellis, K., and Huza, S. 2002. Bioxide improves air quality, controls odors and corrosive gas generation in dewatered sludge. In *Proceedings of the TAPPI International Environmental Conference*. Atlanta, GA: TAPPI Press.

Hagen, C.E., and Hartung, R.W. 1997. New chemical treatment method controls wastewater system odor. *Pulp and Paper* November:81-89.

Harshman, V., and Barnette, T. 2000. Wastewater odor control: An evaluation of technologies. *Water Engineering and Management* 147(5):34-46.

Hemmen, M., and Winges, K. 1993. Community participation in a mill sponsored odor survey. In *TAPPI International Environmental Conference and Exhibit*, 233-237. Atlanta, GA: TAPPI Press.

Jackson, J.H. 1984. Potassium permanganate solves odor problem at Consolidated mill. *Pulp and Paper* April:147-149.

Järvensivu, M., Mäenpää, T., and Jämsä-Jounela, S.-L. 2000. Field survey of reduced-sulfur emissions from a modern Finnish pulp mill. *Environmental Progress* 19(3):147-156.

Kotronarou, A., and Hoffmann, M.R. 1991. Catalytic autooxidation of hydrogen sulfide in wastewater. *Environmental Science and Technology* 25(6):1153-1160.

Kringstad, K.P., McKean, W.T., Libert, J., Kleppe, P.J., and Laishong, C. 1972. Odor reduction by IDO of kraft black liquor with oxygen. *TAPPI Journal* 55(10):1528.

Kuhn, A.T., Kelsall, G.H., and Chana, M.S. 1983. A review of air oxidation of aqueous sulfide solutions. *Journal of Chemical Technology and Biotechnology* 33A:406-414.

Lange, C.R., and Christiansen, J. 2004. Characterization of odors originating from pulp and paper wastewater lagoons. In *TAPPI International Environmental Conference and Exhibit*. May 2-5, Atlanta, GA. Atlanta, GA: TAPPI Press.

Lewis, R., Magers, K., Sattler, A., Khoury J., McCaw, K., Mathison, S., and Lee, J. 2004. Detection, identification and quantitation of odorous emissions using whole air sampling, gas chromatography/mass spectrometry and semiquantitative olfactometry. In *WEF/A&WMA Odors and Air Emissions*, April 18-21, Bellevue, WA. Water Environment Federation and Air & Waste Management Association.

Lide, D.R. (ed.-in-ch.). 1992. Physical constants of inorganic compounds. In *Handbook of chemistry and physics*, 73rd ed., 4-36-4-114. Boca Raton, FL: CRC Press.

Mahmood, T., Banerjee, S., and Sackellares, R.W. 1999. Sources and fate of TRS compounds in a pulp mill ASB. *Water Science and Technology* 40(11-12):289-295.

Marshall, K. 2005. Being part of the community: Mill odors and public response. Presented at NCASI West Coast Regional Meeting. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

McEwen, D., Witherspoon, J., and Chapman, P. 2006. Odor control master planning and biotechnology applications at Delta Diablo Sanitation District. In *Proceedings, WEF/AWWA Odors and Air Emissions Conference*, 825-849. April 9-12, Hartford, CT. Water Environment Federation and American Water Works Association.

Miller, S., McMillen, D.D., and Sober, G. 1995. A method to eliminate anaerobic odors, reduce sludge volumes and increase biologic treatment efficiency in effluent treatment plants. In *Proceedings of the TAPPI International Environmental Conference*, 941-946. Atlanta, GA: TAPPI Press.

Millero, F.J., Hublinger, S., Fernandez, M., and Garnett, S. 1987. Oxidation of H_2S in seawater as a function of temperature, pH, and ionic strength. *Environmental Science and Technology* 21(5):439-443.

National Council [of the Paper Industry] for Air and Stream Improvement, Inc. (NCASI). 1999. *Process water quality and water reuse practices at low-and zero-discharge recycled paperboard mills*. Technical Bulletin No. 796. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

———. 2000. *Laboratory studies of in-digester black liquor oxidation (IDO) for TRS destruction.* Technical Bulletin No. 804. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

———. 2004. *Understanding odor from wastewater treatment systems*. Webcast. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

———. 2005. *Evaluation of sulfide ion detector tubes for determining sulfide concentrations in pulp and paper mill wastewaters.* Special Report No. 05-01. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

———. 2006. *An evaluation of a colorimetric method for the determination of sulfide in pulp and paper mill wastewaters.* Special Report No. 06-02. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

———. 2007. *Development and application of a method for measuring reduced sulfur compounds in pulp and paper mill wastewaters*. Technical Bulletin No. 933. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

National Institute for Occupational Safety and Health (NIOSH). 1994. Hydrogen sulfide 6013. In *NIOSH Manual of Analytical Methods*, 4th ed. United States Center for Disease Control, National Institute for Occupational Safety and Health.

Natusch, D.F.S., Sewell, J.R., and Tanner, R.L. 1974. Determination of hydrogen sulfide in air–An assessment of impregnated paper tape methods. *Analytical Chemistry* 46(3):410-415.

Nicolai, R.E., Phol, S.H., Lefers, R., and Dittbenner, A. 2000. *Natural windbreak effect on livestock hydrogen sulfide reduction and adapting an odor model to South Dakota weather conditions*. Project funded by South Dakota Pork Producers. South Dakota State University.

Nielsen, A.H., Vollertsen, J., and Hvitved-Jacobsen, T. 2003. Determination of kinetics and stoichiometry of chemical sulfide oxidation in wastewater of sewer networks. *Environmental Science and Technology* 37(17):3853-3858.

Normandin, A. 2005. Comparative annual cost efficiency between thermal and chemical oxidation of TRS in kraft mills. *TAPPI Journal* 4(7):3.

Norval, G., Burton, T., and Kanters, C. 2001. The removal of pulp mill odours by novel catalytic environmental technology. *Pulp and Paper Canada* 102(4):53.

O'Connor, B.I., Buchanan, B.E., and Kovacs, T.G. 2000. Compounds contributing to odors from pulp and paper mill biosolids. *Pulp and Paper Canada* 101(2):57-61.

O'Connor, B., Craig, D.C., Huza, S., and Box, B. 2003. Use of a commercial additive for sludge odour control. In *Proceedings of the TAPPI International Environmental Conference*. Atlanta, GA: TAPPI Press.

O'Connor, B., and Ledoux, C. 2002. TRS inventories and air dispersion modeling for odour reduction at a kraft mill with an activated sludge treatment plant. *TAPPI Journal* 1(2):3-8.

Olendorf, S., Jacobi, K., and Bonistall, D. 2000. Kraft mill odor monitoring and operational results. In *TAPPI International Environmental Conference and Exhibit*. Atlanta, GA: TAPPI Press.

Palumbo, J., Ramage, K., Stratton, S., and Upton, B. 2007. Update on NCASI investigations into sulfide generation in wastewater treatment plants. In *Advance Summaries of Presentations, 2007 West Coast Regional Meeting*, G-11–G-14. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Pote, R.P., and Dwyer, E.J. 1999. Microbial biostimulant use in resolving waste water treatment issues at Lyons Falls Pulp and Paper. In *Proceedings of the TAPPI International Environmental Conference*, 415-423. Atlanta, GA: TAPPI Press.

Racine, B. 2005. Measuring H_2S down to 3 ppb. Presented at the NCASI Northern Regional Meeting, May 24. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Ramsay, K., Manolescu, D., Wentzell, P., and Winik, C. 2001. Economic benefits achieved from an odour reduction project. In *Proceedings of the TAPPI International Environmental Conference*, 793-797. Atlanta, GA: TAPPI Press.

Ruth, J.H. 1986. Odor thresholds and irritation levels of several chemical substances: A review. *American Industrial Hygiene Association Journal* 47:142-151.

Speece, R.E. n.d. Cost effective odor/corrosion prevention in wastewater collection systems by superoxygenation. *WEF cMOM*. http://www.cmom.net.

Speece, R.E., and Clidence, D. 2006. Superoxygenation: A prescription for odor and corrosion prevention. *Water Environment and Technology* March:2-5.

Staudinger, J., and Roberts, P.V. 1996. A critical review of Henry's law constants for environmental applications. *Critical Reviews in Environmental Science and Technology* 26(3):205-297.

Tooke, D.L. 2006. *Sulfur transport and fate in a pulp mill wastewater treatment system*. PhD thesis. University of Montana.

Tormund, D., and Teder, A. 1987. Elimination of malodorous organic sulfur compounds from the kraft pulping process with polysulfide and polythuinate. *Nordic Pulp and Paper Research Journal* 2(3):97.

Tyndall, J., and Colletti, J. 2000. *Air quality and shelterbelts: Odor mitigation and livestock production–A literature review*. Project No. 4124-4521-48-3209 for the United States Department of Agriculture, National Agroforestry Center. Ames, IA: Iowa State University, Forestry Department.

United States Environmental Protection Agency (USEPA). 1994. *Air emissions models for waste and wastewater*. EPA-453/R-94-080A. Research Triangle Park, NC: United States Environmental Protection Agency.

Urbanski R., Lister, S., and Raoul, D. 1998. Development of an effective TRS and odor reduction program. *Pulp and Paper Canada* 99(8):70-73.

Vairavamurthy, M.A., and Schoonen, M.A.A. (eds.). 1995. *Geochemical transformations of sedimentary sulfur*. ACS Symposium Series 612. Washington, DC: American Chemical Society.

van den Hazel, P.J., and Waegemaekers, C.H.F.M. 1991. Odour annoyance in a residential area near a papermill. *Public Health Reviews* 19:251-262.

Van Gemert, L.J., and Nettenbreijer, A.H. 1977. *Compilation of odour threshold values in air and water*. Voorburg, Netherlands: National Institute for Water Supply; and Zeist, Netherlands: Central Institute for Nutrition and Food Research TNO.

Verschueren K. 2001. *Handbook of environmental data on organic chemicals*, 2nd ed. New York: Van Nostrand Reinhold.

Volpe, G., Christiansen, J.A., Wescott, J., Lejeur, R., and Rumbaugh, E. 1998. Use of a slime producing microorganism to enhance biomass settleability in activated sludge and ASB systems. In *Proceedings of the TAPPI International Environmental Conference*, 789-809. Atlanta, GA: TAPPI Press.

Water Environment Federation (WEF). 2004. *Control of odors and emissions from wastewater treatment plants*. Manual of Practice No. 25. Alexandria, VA: Water Environment Federation.

Watson, A., Goggins, R., Hunniford, D., Overton, B., and Huza, S. 2001. Odor control and sulfide removal from a wastewater treatment plant lagoon. In *TAPPI International Environmental Health and Safety Conference and Exhibit*. April 21-25, Charlotte, NC. Atlanta, GA: TAPPI Press.

Wilmot, P.D., Cadee, K., Katinic, J.J., and Kavanaugh, B.V. 1988. Kinetics of sulfide oxidation by dissolved oxygen. *Journal of the Water Pollution Control Federation* 60(7):1264-1270.

Witherspoon, J.R., Mann, J., Cesca, J., Barnes, J., and Allen, E. 2004. Balancing community odor control demands with innovation in odor assessment and control strategies and approaches. In *WEF/A&WMA Odors and Air Emissions*, April 18-21, Bellevue, WA. Water Environment Federation and Air & Waste Management Association.

Wolstenholme, P.L., and Jabloner, M.L. 2004. Sulfide and odor control at Naval Station Everett. In *WEF/A&WMA Odors and Air Emissions Conference Proceedings*. Water Environment Federation and Air & Waste Management Association.

Yoon, S.H., Chai, X.-S., Zhu, J.Y., Li, J., and Malcolm, E.W. 2001. In-digester reduction of organic sulfur compounds in kraft pulping. *Advances in Environmental Research* 5(1):91-98.

Zhang, L., De Schryver, P., De Gusseme, B., De Muynck, W., Boon, N., and Verstraete, W. 2008. Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review. *Water Research* 42(2008):1-12.

Zhu, J.Y., Chai, X.-S., Pan, X.J., Luo, Q., and Li, J. 2002. Quantification and reduction of organic sulfur compound formation in a commercial wood pulping process. *Environmental Science and Technology* 36(10):2269-2272.

APPENDIX F – NCASI TB NO. 956, EMISSIONS OF REDUCED SULFUR COMPOUNDS AND METHANE FROM KRAFT MILL WASTEWATER TREATMENT PLANTS

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NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

EMISSIONS OF REDUCED SULFUR COMPOUNDS AND METHANE FROM KRAFT MILL WASTEWATER TREATMENT PLANTS

TECHNICAL BULLETIN NO. 956

SEPTEMBER 2008

by

Robert Crawford
NCASI Southern Regional Center
Gainesville, Florida

Acknowledgments

The accomplishment of this large, complex project required the dedicated efforts of many people. The staff at the NCASI Southern Regional Center in Newberry, Florida, with significant contributions to this project included Ashok Jain, Rob Crawford, Ann Crapo, Jim Stainfield, Vipin Varma, Derek Sain, Jeff Drese, Raulie Raulerson, Ganka Slavova, Lee Carlson, Ben Fair, Bill Rice, Tracy Stubbs and Susan Kirkland. Diana Cook and Dean Hoy at the NCASI West Coast Regional Center in Corvallis, Oregon, also made very significant contributions to this project. John Pinkerton (Vice President, Air Quality) at the NCASI headquarters in Research Triangle Park, North Carolina, provided oversight for this project.

Finally, the authors would like to thank the mill and corporate staff of the companies that participated in this study.

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National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). 2008. *Emissions of reduced sulfur compounds and methane from kraft mill wastewater treatment plants*. Technical Bulletin No. 956. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.

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PRESIDENT'S NOTE

Reducing the odor impact of kraft pulp mills remains one of the top environmental priorities for the pulp and paper industry. With the widespread implementation of in-mill control measures to minimize emissions of reduced sulfur compounds from pulp mill sources, attention has shifted to the wastewater treatment plant as the most significant remaining odor source at kraft mills. For the most part, wastewater treatment plant odor problems have been viewed as site-specific situations requiring corresponding site-specific solutions. In the absence of a fundamental understanding of reduced sulfur compound emissions from various components of wastewater treatment plants and the factors affecting those emissions, mills faced with odor issues have often had to resort to trial-and-error approaches for identifying the causes and finding a workable solution.

Developing a better understanding of reduced sulfur compound emissions from kraft mill wastewater treatment plants has been a long-standing NCASI goal. Two major impediments existed that prevented progress towards this goal. First, analytical methods had to be found for quantifying reduced sulfur compounds in ambient air and wastewater. Second, a cost-effective technique was required to directly measure reduced sulfur emissions from individual components of actual treatment plants. After considerable effort, we believe these two obstacles have now been overcome. A separate technical bulletin describing the analytical methods and emission measurement technique is now being prepared.

This technical bulletin contains the results of applying the new methods and sampling technique to wastewater treatment plants at six kraft mills. Emission rates of the four reduced sulfur compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) were determined for numerous components of these plants: sewer vents; primary clarifiers; pre-aeration settling basins, equalization basins, and spill ponds; aerated stabilization basins; activated sludge treatment units; and various types of post-aeration basins. The concurrent collection of wastewater samples allowed determination of concentrations of these compounds, plus other physical and chemical properties, at various points within these components. The wastewater data were critical to identifying potential factors affecting the observed emission rates.

Based on the six wastewater treatment plants sampled, primary clarifiers, well-aerated basins (either aerated stabilization basins or activated sludge treatment reactors) and post-aeration retention basins were found to be minor sources of H_2S emissions. The largest sources were multi-acre anaerobic pre-aeration basins such as primary settling ponds or spill ponds. Aerated stabilization basins where foul condensates were directly introduced via a submerged enclosed pipe were found to be the most significant source of emissions of the three organic reduced sulfur compounds. Emission rates for the same unit often varied considerably over time, and similar units at different plants generally did not have equivalent emission rates. Variables affecting emission rates included incoming loadings of sulfide and organic compounds, effluent pH, effluent temperature, dissolved oxygen levels, amount of aeration, wind speed, and atmospheric stability.

Although this investigation was initially focused on reduced sulfur compounds, it presented an opportunity to obtain methane information with modest additional effort. Methane concentration measurements were used to estimate methane emission rates from the wastewater treatment plants. This additional work was undertaken to see if current greenhouse gas emission factors being used to estimate methane emissions from pulp mill wastewater treatment systems are realistic. It appears that these factors are unrealistically high.

The field work described in this technical bulletin represents a significant step forward in quantifying reduced sulfur compound emissions from kraft mill wastewater treatment plants and identifying factors that affect emission rates in different components of the plant. The ultimate goal for NCASI is to develop a model for predicting these emissions using site-specific treatment plant design characteristics, operating parameters, and measurable effluent properties. To formulate this model, we will be drawing on the results of this field work and additional laboratory studies that are now in progress to address the fate of sulfur-containing compounds in effluent.

Ronald A. Yeske

September 2008

MOT DU PRÉSIDENT

La réduction de l'impact des odeurs issues des fabriques de pâte kraft demeure une des priorités environnementales des plus importantes pour l'industrie des pâtes et papiers. Suite à l'adoption à grande échelle de mesures de contrôle dans les usines pour la minimisation des émissions de composés de soufre réduits des différentes sources des fabriques de pâtes, l'attention s'est tournée vers les systèmes de traitement des effluents qui sont maintenant considérés comme étant les sources résiduelles les plus importantes d'odeurs des fabriques kraft. Dans la majorité des cas, les problématiques d'odeurs de systèmes de traitement des effluents ont été abordées comme étant spécifiques à chaque site et nécessitant des solutions tout aussi spécifiques. Étant donné l'absence d'une compréhension fondamentale des émissions de composés de soufre réduit provenant des diverses composantes des systèmes de traitement des effluents ainsi que des facteurs affectant ces émissions, les fabriques confrontées à des problématiques d'odeurs n'ont pas eu d'autres choix que d'utiliser des approches essais-erreurs afin d'identifier les causes des problèmes pour ensuite identifier des solutions réalisables.

Le développement d'une meilleure compréhension des émissions de composés de soufre réduit provenant des systèmes de traitement des effluents des fabriques de pâte kraft demeure un objectif de longue date de NCASI. La progression vers l'atteinte de cet objectif s'est heurtée à deux grands obstacles. Premièrement, des méthodes analytiques pour quantifier les composés de soufre réduit dans l'air ambiant et dans les effluents devaient être trouvées. Deuxièmement, une technique efficiente et économique était nécessaire pour mesurer les émissions de soufre réduit de composantes spécifiques des systèmes de traitement des effluents en place. Suite à des efforts considérables, nous croyons que ces deux obstacles ont maintenant été surmontés. Un bulletin technique distinct est présentement en cours de préparation et ce dernier décrira les méthodes d'analyses et la méthode d'échantillonnage des émissions pour les systèmes de traitement des effluents.

Ce bulletin technique contient les résultats de l'utilisation des nouvelles méthodes d'analyses et de la méthode d'échantillonnage pour caractériser les systèmes de traitement des effluents de six fabriques de pâte kraft. Les taux d'émissions des quatre composés de soufre réduit (sulfure d'hydrogène, méthylmercaptan, sulfure de diméthyle et disulfure de diméthyle) ont été déterminés pour plusieurs composantes de ces systèmes de traitement : évents d'égouts, clarificateurs primaires, bassins de sédimentation précédant l'aération, bassins d'égalisation et étangs de rétention de déversements, bassins de stabilisation aérés, systèmes de traitement par boues activées et divers types de bassins en aval des étapes d'aération. Les prélèvements simultanés d'échantillons d'eaux usées ont permis de déterminer les concentrations de ces composés, ainsi que d'autres propriétés physiques et chimiques, en divers points de ces composantes. Les données sur les eaux usées étaient essentielles à l'identification des facteurs pouvant potentiellement affecter les taux d'émissions observés.

En s'appuyant sur les échantillonnages effectués à six systèmes de traitement des effluents, les auteurs ont déterminé que les clarificateurs primaires, les bassins aérés (que ce soit les bassins de stabilisation aérés ou les systèmes de traitement par boues activées) et les divers types de bassins de rétention en aval des étapes d'aération sont des sources d'émissions mineures de H_2S. Les sources d'émissions les plus importantes se sont avérés être les bassins anaérobiques à grande superficie, précédant l'aération tels que les bassins de sédimentation primaires et les étangs de rétention de déversements. Les auteurs ont aussi déterminé que la source la plus importante d'émission des trois composés de soufre réduit organiques étaient les bassins d'égalisation aérés dans lesquels des condensats contaminés sont introduits directement par l'entremise d'une conduite submergée. Les taux d'émissions pour un même bassin pouvaient varier de manière significative dans le temps et de manière générale, des bassins comparables situés dans des fabriques différentes ne présentaient pas des taux d'émissions équivalents. Parmi les variables affectant les taux d'émissions, mentionnons les charges à l'entrée de composés soufrés et organiques, le pH de l'effluent, la température de l'effluent, les niveaux d'oxygène dissout, le taux d'aération, la vitesse des vents et la stabilité des conditions atmosphériques.

Même si les recherches effectuées dans le cadre de ce projet étaient initialement orientées vers les composés de soufre réduit, elles présentaient la possibilité d'obtenir des informations sur le méthane et ce, sans nécessiter d'efforts supplémentaires significatifs. Des mesures de concentration de méthane ont été utilisées pour estimer les taux d'émission de méthane des systèmes de traitement des effluents. Cette tâche additionnelle a été entreprise afin d'évaluer si les facteurs d'émissions de gaz à effet de serre présentement utilisés pour estimer les émissions de méthane de systèmes de traitement des effluents des fabriques de pâtes sont réalistes. Il appert que ces facteurs d'émissions sont anormalement élevés.

Le travail de terrain décrit dans ce bulletin technique représente un grand pas en avant en ce qui a trait à la quantification des émissions de composés de soufre réduit venant des systèmes de traitement des effluents de fabriques kraft ainsi qu'à l'identification des facteurs qui affectent les taux d'émissions dans les différentes composantes du système de traitement. L'objectif ultime de NCASI est de développer un modèle pour prévoir ces émissions en utilisant les paramètres spécifiques des systèmes de traitement des effluents tels que : les critères de conception, les paramètres d'opération et les propriétés mesurables des effluents. Pour formuler ce modèle, nous utiliserons les résultats des travaux de terrain décrits dans ce rapport ainsi que les résultats d'études de laboratoire supplémentaires qui sont présentement en cours pour établir le sort des composés soufrés contenus dans les effluents.

Ronald A. Yeske

Septembre 2008

EMISSIONS OF REDUCED SULFUR COMPOUNDS AND METHANE FROM KRAFT MILL WASTEWATER TREATMENT PLANTS

TECHNICAL BULLETIN NO. 956
SEPTEMBER 2008

ABSTRACT

A spatial ambient air sampling technique was used to quantify emissions of four reduced sulfur compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) and methane from the various components of wastewater treatment plants at six kraft mills. Components tested included primary clarifiers, primary settling ponds, spill ponds, aerated basins, activated sludge treatment reactors, and post-aeration retention ponds. Concurrent liquid sampling was conducted, and relevant process information was gathered. For a given component, emissions of hydrogen sulfide were dependent mainly on the inlet sulfide loading, in-basin pH, and the level of in-basin sulfide generation, which was apparently due to anaerobic biological activity. Quiescent pre-aeration settling ponds and spill basins had the largest emissions of hydrogen sulfide, with wind speed also being a significant factor affecting emissions from these components. Emissions of organic reduced sulfur compounds were largely a function of mill condensate handling practices. Methane emissions appeared to be related to the level of apparent anaerobic biological activity and sludge accumulation.

KEYWORDS

ambient air, analysis, dimethyl disulfide, dimethyl sulfide, emissions, hydrogen sulfide, kraft pulp mill, methane, methyl mercaptan, reduced sulfur compounds, sampling, wastewater treatment plant

RELATED NCASI PUBLICATIONS

Spatial ambient air sampling and analysis methods for quantifying reduced sulfur compound and methane emissions from kraft mill wastewater treatment plants. (Forthcoming).

ÉMISSIONS DE COMPOSÉS DE SOUFRE RÉDUIT ET DE MÉTHANE DES SYSTÈMES DE TRAITEMENT DES EFFLUENTS DE FABRIQUES KRAFT

BULLETIN TECHNIQUE N^{O}. 956
SEPTEMBRE 2008

RÉSUMÉ

Les auteurs ont utilisés une technique spatiale d'échantillonnage d'air ambiant pour quantifier les émissions de quatre composés de soufre réduit (sulfure d'hydrogène, méthylmercaptan, sulfure de diméthyle et disulfure de diméthyle) et de méthane des différentes composantes de systèmes de traitement des effluents situés dans six fabriques kraft. Parmi les composantes testées, mentionnons les clarificateurs primaires, les bassins de sédimentation primaires, les étangs de rétention de déversements, les bassins de stabilisation aérés, les systèmes de traitement par boues activées et les divers types de bassins suivant les étapes d'aération. Des prélèvements simultanés d'échantillons aqueux ont été effectués et des informations pertinentes concernant les procédés ont été recueillies. Pour chaque composante étudiée, les émissions de sulfure d'hydrogène étaient principalement fonction de la charge de sulfure à l'entrée, du pH dans le bassin et du taux de génération de sulfure dans le bassin, celui-ci étant apparemment relié au taux d'activité biologique anaérobique. Les bassins de sédimentation sans agitation situés en amont des sections d'aération et les étangs de rétention de déversement (sans agitation) présentaient les taux d'émission de sulfure d'hydrogène les plus élevés; la vitesse du vent étant un facteur déterminant pour l'amplitude de ces émissions. Les émissions de composés de soufre réduit organiques sont principalement reliées aux pratiques de la fabrique en ce qui concerne la gestion des condensats. Les émissions de méthane semblent être reliées au taux apparent d'activité biologique anaérobique et à l'accumulation de boues.

MOTS CLÉS

air ambiant, analyse, sulfure de diméthyle, disulfure de diméthyle, émissions, sulfure d'hydrogène, fabrique de pâte kraft, méthane, méthylmercaptan, composés de soufre réduit, échantillonnage, système de traitement des effluents

AUTRES PUBLICATIONS DE NCASI DANS CE DOMAINE

Spatial ambient air sampling and analysis methods for quantifying reduced sulfur compound and methane emissions from kraft mill wastewater treatment plants. (À venir).

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EMISSIONS OF REDUCED SULFUR COMPOUNDS AND METHANE FROM KRAFT MILL WASTEWATER TREATMENT PLANTS

1.0 INTRODUCTION

1.1 Background

Odor associated with emissions of reduced sulfur compounds from kraft pulp mills has been of long-standing concern. As total reduced sulfur (TRS) emissions from pulp mill and chemical recovery area sources such as digesters, evaporators, recovery furnaces, lime kilns and smelt dissolving tanks have been dramatically reduced over the last 40 years, attention has gradually shifted to mill wastewater treatment systems as the main remaining source of TRS emissions and community odor impacts. Although a great deal of information exists on TRS emissions from pulp mill sources, this is unfortunately not the case for wastewater treatment systems.

There are two main mechanisms that can give rise to TRS emissions from wastewater treatment systems. First, reduced sulfur compounds present in the effluent may volatilize when exposed to ambient air, especially when the effluent is in a turbulent state. This mechanism is the main source of organic reduced sulfur compound emissions (methyl mercaptan, dimethyl sulfide, dimethyl disulfide), and can be a significant source of hydrogen sulfide. Second, biological activity in the sediment results in release of gases such as methane, carbon dioxide and hydrogen sulfide. These gases form bubbles which rise through the water column and are released to the atmosphere, thus contributing to reduced sulfur compound (RSC) emissions from the treatment system. This mechanism is particularly important when high levels of anaerobic activity are present.

On-site wastewater treatment systems at kraft mills typically involve solids removal (clarification), biological treatment of dissolved organics, and settling of biological solids. Many different configurations exist for these systems, operating characteristics vary widely, and raw effluent properties differ from mill to mill. Because of the uniqueness of each system, it has proven nearly impossible to make generalizations about TRS emissions from them. Even though modeling is a useful tool for estimating emissions of volatile organic from wastewater treatment systems, it is not yet a viable approach for reduced sulfur compounds because there is insufficient understanding of the complex reactions occurring within the systems involving sulfur-containing compounds.

Given this situation, it would appear that site-specific measurements, including direct measurement of TRS emissions, for a number of wastewater treatment systems are essential to identifying and understanding the factors affecting TRS releases. However, direct measurement of TRS emissions from wastewater treatment systems is a challenging task since these systems are comprised of multiple area sources, some of which can have surface areas on the order of 100 acres. Besides large surface areas, the spatial and temporal variability of releases, surface turbulence caused by mechanical aeration, and existence of surface foam pose additional sampling issues. The task is further complicated when attempting to isolate emissions from various components of the system, e.g., primary clarifiers, aerated stabilization basins, settling basins, etc.

One approach for sampling of gaseous emissions from area sources such as landfills, agricultural operations, animal feed lots, material storage piles, and lagoons involves direct measurement of vertical fluxes from the surface using flux chambers or micrometeorological instrumentation. This approach is best suited for relatively small area sources with spatially uniform emissions. It would be impractical for large kraft mill wastewater treatment systems. Also, flux chambers do not lend themselves to measuring emissions from large surface aerators used in pulp and paper industry wastewater treatment plants.

Another approach for determining area source emissions relies on measuring ambient concentrations and meteorological data. The emission rate from the area source is then back-calculated with an atmospheric dispersion model using the measurements to estimate the total amount of material passing through a vertical plane downwind of the area source. Concentration measurements must be made at a sufficient number of downwind points (both horizontally and vertically) to obtain a reasonable approximation of the total flux through the plane. In this approach, sampling devices are typically deployed on towers. An alternative is to make horizontal path-integrated measurements at several heights (generally requiring the use of one or more towers) employing Fourier Transform Infrared Spectroscopy (FTIR) or other remote sensing technologies. The former approach is not suitable for use at pulp and paper mills because of the presence of multiple sources of reduced sulfur gases at each site which cannot be isolated and the difficulty of installing multiple towers. The use of long-path instruments, although attractive, is not feasible at this point as the reduced sulfur gas concentrations around wastewater treatment systems are too low to be reliably measured with currently available long-path instruments.

Recognizing the difficulties associated with measuring reduced sulfur gas emissions from wastewater treatment systems at pulp and paper mills, Esplin reported on a novel measurement approach which utilized a mobile cart with a tethered balloon (Esplin 1988). In his approach, the sampling lines were lifted to the appropriate height with the balloon, while the cart was moved along a crosswind path downwind of the basin being sampled. Gas sampling was conducted at regularly spaced intervals along the path, with one horizontally integrated sample obtained for each sampling height. Sampling heights and times were governed by wind direction and atmospheric stability. Esplin called his technique “boundary layer emission monitoring” and presented results for several aerated stabilization basins and a spill lagoon located at kraft mills in British Columbia (Esplin 1988, 1989).

Given Esplin’s apparent success with his technique, and considering the expected difficulties and logistical limitations of applying other available techniques, NCASI decided to adapt Esplin’s “boundary layer emission monitoring” methodology to determine emissions from the various components of kraft mill wastewater treatment systems. However, the scope of the NCASI investigations included measurement of individual reduced sulfur compounds—hydrogen sulfide (H_2S), methyl mercaptan (MM), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS)—and methane (CH_4). Also, extensive liquid sampling was conducted in conjunction with the air sampling for the purposes of identifying factors that may influence emission rates and for use in developing empirical and mechanistic simulation models for reduced sulfur compounds.

This technical bulletin describes a multi-mill sampling effort conducted by NCASI to determine emission rates of individual reduced sulfur compounds and methane. To the extent possible, factors influencing the emission rates have been identified using the data gathered. A companion technical bulletin contains comprehensive documentation of the sampling equipment, sampling procedures, quality assurance criteria for data acceptability, and emission rate calculation methodology. Complete details for the individual mill studies are available in separate mill-specific reports, which can be obtained from the NCASI members only web site.

1.2 Additional Factors Considered in Sampling Program Design

One goal of the sampling program undertaken by NCASI was to quantify the emission rate of reduced sulfur compounds and methane from the various components of kraft mill wastewater treatment plants. This goal could be accomplished with a combination of ambient concentration and meteorological measurements using Esplin’s methodology. Another goal was to concurrently obtain additional wastewater data that might help explain the observed emission rates and be used in the development of simulation models for emission predictions.

There are two types of mechanisms by which gaseous compounds may be released from kraft mill wastewater treatment plants: surface mass transfer and sediment releases in the form of bubbles rising through the water column. The emission of volatile or semi-volatile compounds from exposed water bodies into the atmosphere through surface mass transfer can be represented by the two resistance model for mass transfer (Treybal 1980). In this model, mass transfer is represented by the following sequential processes (Liss and Slater 1974):

- transfer from the liquid phase to the interface separating the liquid from air
- transfer from the interface to the air

The emission rate of a volatile compound through surface mass transfer is expressed in terms of an overall mass transfer coefficient as follows:

$$E = K_L (A) (C_L - C_G) \qquad \text{(Equation 1)}$$

where

E = Emission rate, gm/sec
K_L = Overall mass transfer coefficient, m/sec
A = Area for mass transfer (Exposed surface area), m^2
C_L = Concentration of compound in liquid, gm/m^3
C_G = Concentration of compound in air, gm/m^3
($C_G \sim 0$ for environmental volatilization due to constant surface renewal of air)

In the two resistance model, the overall mass transfer coefficient for the compound is further expressed as a function of the individual mass transfer coefficients in the liquid and gas phases. Equation 2 below represents the "overall" resistance for mass transfer of the compound as a sum of the individual resistances in the liquid phase ($1/k_l$) and gas phase (RT/Hk_g).

$$1/K_L = (1/k_l) + (1/ K_{eq} k_g) \qquad \text{(Equation 2)}$$

where

k_l = Liquid phase mass transfer coefficient, m/sec
k_g = Gas phase mass transfer coefficient, m/sec
K_{eq} = Partition Coefficient (= H/RT)
H = Henry's law constant, atm-m^3/mol
R = Universal gas constant, atm-m^3/mol. °K
T = Temperature, K

The individual liquid and gas phase mass transfer coefficients for the compound (k_l and k_g) depend on system characteristics (such as basin dimensions, aeration and temperature), atmospheric conditions, and compound properties.

Surface mass transfer from non-aerated systems like primary settling ponds and post-aeration stabilization ponds occurs through volatilization (surface/wind effects). Surface mass transfer from aerated systems like ASBs occurs both through volatilization and stripping (attributed to aeration). The gas phase and liquid phase mass transfer coefficients for volatilization and stripping and Henry's law constant, all of which impact the overall mass transfer rate K_L, depend on the following parameters.

- Gas phase and liquid phase mass transfer coefficients for stripping depend on aerator characteristics (impellor diameter, rpm etc.), physical properties like the density and viscosity of air, aeration HP, the rate and effectiveness of oxygen transfer, and the diffusivity of oxygen in water.
- Gas phase and liquid phase mass transfer coefficients from non-aerated systems depend on the viscosity of air, density of air, wind velocity, compound diffusivity in water, and system dimensions, specifically, the ratio of fetch to depth.
- The Henry's law constant (H), which represents the partitioning coefficient for the compound between the liquid and gas phases when present at dilute concentrations, is related to liquid temperature.

The area of mass transfer in Equation 1 above is determined directly from the dimensions of the treatment pond/basin. According to Equation 1, as the surface area available for mass transfer increases, the emission rate is expected to increase proportionally.

Finally, according to Equation 1, the emission rates of reduced sulfur compounds would be a function of the concentration of each compound in the liquid phase. For compounds such as dimethyl sulfide and dimethyl disulfide, which do not dissociate in water, C_L is determined directly through liquid analysis. However, hydrogen sulfide and methyl mercaptan dissociate in water according to the following equations.

$$H_2S \xrightleftharpoons{k_1} H^+ + HS^- \qquad \text{(Equation 3)}$$

$$HS^- \xrightleftharpoons{k_2} H^+ + S^= \qquad \text{(Equation 4)}$$

$$CH_3HS \xrightleftharpoons{k_3} H^+ + CH_3S^- \qquad \text{(Equation 5)}$$

Since the values of equilibrium constants k_1, k_2, k_3 as function of temperature are known, knowing the total sulfide ($[H_2S] + [HS^-] + [S^=]$) and total mercaptan ($[CH_3SH] + [CH_3S^-]$) concentrations and the pH, one can calculate the values of undissociated H_2S and methyl mercaptan in Equation 1 to estimate the impact of concentration, pH and temperature changes on the rates of emission. In general, increasing the pH would increase dissociation and decrease the availability of H_2S and methyl mercaptan for volatilization and stripping.

In addition to releases as a result of mass transfer from the surface, gases generated in the sediment as a result of anaerobic activity can also contribute to H_2S emissions from wastewater treatment system components. Wastewaters from pulp and paper mills contain organic settleable solids which accumulate at the bottoms of the basins in the treatment system. Depending upon the prevailing conditions, there can be significant anaerobic activity in the sediment, resulting in the generation of methane and hydrogen sulfide. The volume of the gases generated in pre- and post-aeration basins is large enough for the rising bubbles to be clearly visible. As described earlier, during this study, the rates of emission of methane from various components of wastewater treatment systems were also measured along with the reduced sulfur gas emissions. Separate NCASI studies are being carried out to better understand the generation of methane and H_2S in the sediment. Therefore, liquid samples were collected at several locations within each component of the wastewater treatment plants. Analyses were conducted for total sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, sulfate and thiosulfate. In addition, measurements were made in the water column for several parameters, including temperature, pH, conductivity, dissolved oxygen, and, in some cases, oxidation reduction potential (ORP). Information was gathered on the physical dimensions of each component, along with liquid flow rates and aerator parameters including location, motor horsepower, and oxygen transfer rates.

2.0 METHODS

The study had three major components: 1) emission screening, 2) liquid sampling, and 3) emission measurement and quantitation. These components are discussed in Sections 2.1 through 2.3.

2.1 Emissions Screening Tests

Kraft mill wastewater treatment plants (WWTPs) can consist of many components, including multiple, sequential post-aeration retention ponds. At the outset of this study, the significance of emissions from these ponds was not known. If the emissions from these ponds, or any of the other WWTP components, were very low or not quantifiable via the spatial ambient air sampling technique (NCASI's adaptation of Esplin's methodology), then a very considerable amount of effort would have been wasted by testing these sources. To avoid this possibility, a screening study was conducted at several of the WWTPs before the spatial ambient air sampling technique was used to quantify emissions in conjunction with liquid sample collection. In addition to providing information about the significance of emissions from the various WWTP components, the screening study generated useful information for planning the full study and determination of emissions rates, such as approximate ground-level ambient air concentrations.

During the screening tests, measurements were taken with a Jerome H_2S analyzer, upwind and downwind of the source. The wind direction observed at an on-site meteorological station and a site plan were used to select three sample collection locations on the upwind and downwind sides of the source. For both sides, one of the sampling locations was at the point where a line representing the wind direction, and passing through the geographical center of the basin, intersected the edges of the basin. The other two sampling points were at the edge of the basin, approximately halfway between the line through the center and the lines which represent the wind direction and intersect the crosswind edges of the basin. Figure 2.1 is an example of a site plan used for emissions screening sample point selection. At each sample point, three consecutive measurements were made with the H_2S analyzer.

The Jerome H_2S analyzer has a sensitive linear response to H_2S, with a detection limit of 1 ppbv. However, it is not specific to H_2S, and responds to other reduced sulfur compounds to varying degrees. Therefore, to obtain speciated reduced sulfur compound data, at one or more downwind sampling locations, canister samples were collected for gas chromatograph/pulsed flame photometric detector (GC/PFPD) analysis, which provided speciated concentration measurements for H_2S, MM, DMS and DMDS.

Following the screening study, full-scale source emission measurement tests, with the associated liquid sampling programs, were carried out at selected sources.

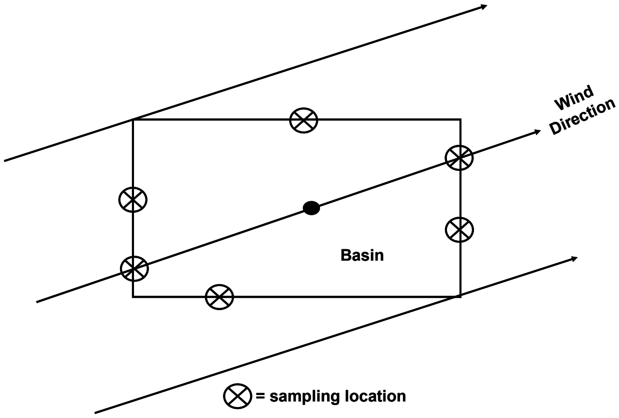

Figure 2.1 Emissions Screening Procedure Sample Point Selection

2.2 Liquid Sampling and Analysis

Liquid samples were collected for three purposes: 1) to develop an understanding of factors that affect emissions of reduced sulfur compounds from WWTPs, 2) to relate liquid phase concentrations to air concentrations for material balance purposes, and 3) to obtain data for the development and calibration of emissions models.

2.2.1 *Sample Collection Strategy and Methods*

At each WWTP, there were two groups of liquid samples collected in conjunction with atmospheric emissions testing: inlet/outlet and surface liquid. Inlet/outlet samples were collected for characterization of the WWTP and material balance purposes. Surface liquid samples were collected one foot below the surface in basins, ponds and primary clarifiers for source characterization and to obtain data for the development and calibration of emission models.

Inlet/outlet samples were generally collected three times a day (morning, mid-day, and evening) on each day before and during emissions testing at each source. Temperature and pH were always measured in conjunction with inlet/outlet liquid sample collection. When conditions permitted, dissolved oxygen and conductivity were also measured in conjunction with inlet/outlet liquid sample collection.

Surface liquid samples were collected from each source once on each day during which emissions testing was conducted at that source. Surface liquid samples were generally collected from four locations in basins and ponds. In primary clarifiers, surface liquid samples were collected at three locations: outside of the centerwell, inside of the weir, and midway between those locations. Figure 2.2 is a generic schematic representation of a primary clarifier, which shows the locations for surface liquid sampling. Temperature, pH, dissolved oxygen and conductivity were always measured in conjunction with surface liquid sample collection. In addition, where it was possible to do so, those physical/chemical parameters were measured at three depths at the locations where surface liquid samples were collected. The three measurement depths were one foot above the bottom, one foot below the water surface, and midway between those two measurement depths.

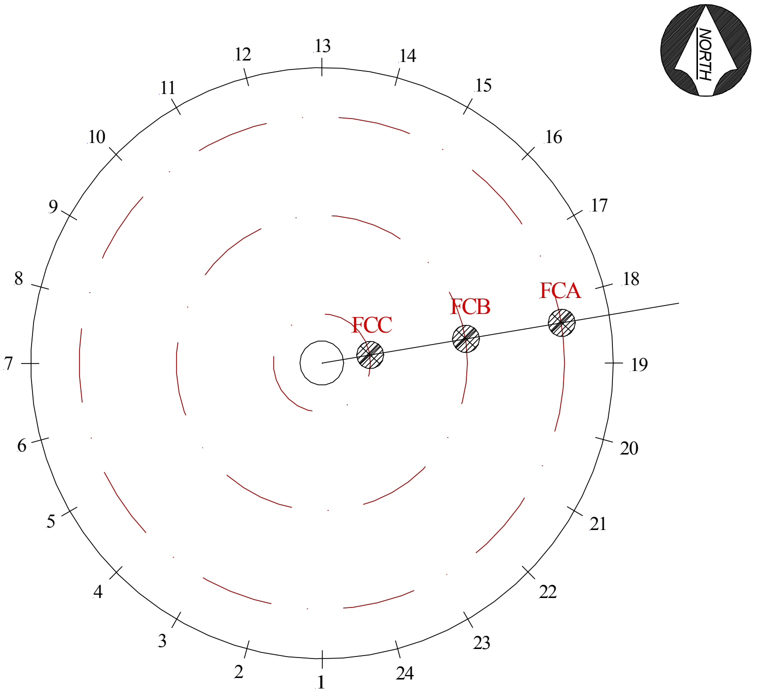

Figure 2.2 Surface Liquid Sampling Locations for a Primary Clarifier

Liquid sampling consisted of collecting grab samples in labeled zero-headspace VOA (volatile organic analysis) vials, preloaded with the appropriate preservative for the target analytes. Samples were analyzed for total sulfide, methyl mercaptan (MM), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS), sulfate, thiosulfate and total organic carbon (TOC). In addition to the grab samples collected for laboratory analysis, in-situ determinations of dissolved sulfide ion concentration were conducted using sulfide ion detector tubes. Because each collection vial was preloaded with a specific quantity of preservative, a dipper constructed of inert material was used to draw the liquid sample from beneath the liquid surface. In locations where the dipper handle length was insufficient to reach below the water surface or samples were drawn from automatic peristaltic samplers, a bucket was used to collect a larger volume from which sample vials could be filled. All sample vials were filled to the top without overflowing, then capped and inverted several times to promote mixing of the sample and preservative solution. Collected samples were then carried back to the field trailer where the preserved sample pH was checked and adjusted if necessary. Collected samples were stored in coolers with ice for transport and/or shipment to the laboratory for analysis. For quality assurance purposes, one set of field duplicates was collected for approximately every 10 sample sets with at least one set of field duplicates per day.

2.2.2 *Sample Analysis Methods*

2.2.2.1 *Total Sulfide*

Liquid samples for the analysis of total sulfide were collected, preserved and stored for analysis following the procedure outlined in NCASI Method RSC-02.02, “Reduced Sulfur Compounds by Direct Injection GC/PFPD” (NCASI 2005a). The sample collection vials for total sulfide analysis were preloaded with a zinc acetate/NaOH preservative solution. All vials were amber to minimize the potential for photochemical oxidation. Once collected, the pH of the preserved sample was checked, and adjusted if necessary, with additional 1N NaOH to assure that the final pH of the preserved sample was greater than 10.

Samples to be analyzed for total sulfide were shipped to NCASI's West Coast Regional Center laboratory for analysis. Per method requirements, samples were analyzed within 14 days of sample collection.

For analysis, an aliquot of the preserved sample is acidified prior to injection. NCASI Method RSC-02.02 measures the total amount of sulfide in a sample volatile at pH 2.5. It is believed that this includes all freely dissolved sulfide, plus sulfide weakly associated with dissolved organic matter or certain transition metals.

2.2.2.2 *Sulfide Ion*

Gastec 211 sulfide ion detector tubes with a measuring range of 1 to 100 ppm were used to provide an in-situ field measurement of dissolved sulfide ion concentration. The measurement is made by cutting both ends of a fresh detector tube and partially immersing it in a freshly drawn wastewater sample. As the wastewater is drawn into the tube by capillary forces, an indicator compound (lead acetate) reacts with the dissolved sulfide ions and changes in color from white to light brown. The concentration value is read directly from the scale on the detector tube.

Gastec 211 tubes have a working pH range of 3.5 to 12 and a working temperature range of 0 to 40°C. Use of these tubes above the maximum recommended temperature is reported by the manufacturer to result in lower values and false non-detects. An NCASI study of sulfide ion detector tubes (NCASI 2005b), reported a higher sensitivity to pH for detector tubes based on the reaction of lead acetate with sulfide ion to form lead sulfide. Additionally, a number of coexisting substances are known to interfere with the measurement of sulfide with detector tubes. Carbonate and chloride ion are two known interferences. Refer to NCASI Special Report No. 05-01 (NCASI 2005b) and manufacturer's instructions for further information.

Dissolved sulfide ion concentration was measured at the same sampling frequency as liquid grab sample collection. A duplicate determination was made for every 10 sample collections with at least one duplicate determination made per day.

2.2.2.3 *Organic Reduced Sulfur Compounds*

Liquid samples for the analysis of organic reduced sulfur compounds (RSC) were collected, preserved, and stored for analysis following the procedure outlined in NCASI Method RSC-02.02, "Reduced Sulfur Compounds by Direct Injection GC/PFPD" (NCASI 2005a).

The sample collection vial for RSC analysis is preloaded with 120 mg ± 5 mg of ascorbic acid. All vials were amber to minimize the potential for photochemical oxidation. Once collected, the pH of the preserved sample was checked, and adjusted if necessary, with 1:3 phosphoric acid solution to ensure that the final pH of the preserved sample is between 2 and 3.

Samples to be analyzed for organic reduced sulfur compounds (MeSH, DMS, DMDS, and DMTS) were shipped to NCASI's West Coast Regional Center laboratory for analysis. Per method requirements, samples were analyzed within 14 days of sample collection.

2.2.2.4 *Sulfate and Thiosulfate*

Samples to be analyzed for sulfate and thiosulfate were collected in 40-mL amber VOA vials preloaded with 120 mg ± 5 mg of ascorbic acid. The pH of the preserved sample was checked after collection and adjusted, if necessary, with 1:3 phosphoric acid solution to ensure that the final pH of the preserved sample was between 2 and 3.

Samples to be analyzed for sulfate and thiosulfate were returned to NCASI's Southern Regional Center laboratory for analysis. Samples were maintained at a temperature of approximately 4°C until analysis. Analysis for sulfate and thiosulfate followed the ion chromatographic method (4110) described in *Standard Methods for the Examination of Water and Wastewater*, 20th edition (APHA 1998).

2.2.2.5 *Total Organic Carbon*

Samples to be analyzed for total organic carbon (TOC) were collected in 40-mL amber VOA vials. Vials were filled to the top without overflowing, capped and then carried back to the field trailer. Samples not requiring filtration were acidified with 1:3 phosphoric acid solution to preserve the sample at a pH less than 2.

Samples to be analyzed for TOC were shipped overnight to NCASI's West Coast Regional Center laboratory. All samples were then forwarded to CH_2M Hill in Corvallis, Oregon for analysis. Analyses were conducted on an OI Model 700 Total Organic Carbon Analyzer using EPA Method 415.1/415.2. In this method, samples are sparged under slightly acidic conditions to remove inorganic carbon prior to oxidization with persulfate in a digestion vessel at 100°C. The carbon dioxide formed is measured using non-dispersive infrared spectroscopy. Inorganic or purgeable carbon is not measured. Concentrations for each sample are determined by comparing the measurement with a standard curve prepared from solutions of anhydrous potassium biphthalate. Per method requirements, samples were analyzed within 30 days of collection and preservation.

2.2.2.6 *Physical Parameter Data Collection*

Wastewater temperature and pH were measured with stand-alone thermocouples and pH meters, or with a portable YSI 556 MPS Multi Probe System. All dissolved oxygen and conductivity measurements were made with the portable YSI 556 MPS Multi Probe System. This field instrument is equipped with a pH probe, combined temperature/conductivity probe, and dissolved oxygen sensor. In locations where the probe cable length was insufficient to reach below the water surface, or when the wastewater was accessed through an automatic peristaltic sampler, a bucket was used to collect sufficient sample volume to immerse the probe. Measurements at all other locations were made directly in the pond or basin under test.

The YSI multiprobe used in liquid sampling was maintained and calibrated daily while in use. The probe system was rinsed with fresh water after each use and kept moist without being immersed. The pH sensor was removed from the probe module at the end of sampling each day and stored overnight in electrode storage solution. Due to the potential for fouling in the presence of hydrogen sulfide, the response of the dissolved oxygen sensor was monitored during each daily calibration, and the membrane and solution were replaced when a significant deterioration in output current was seen.

2.3 Determination of Source Emission Rates

2.3.1 *Air Sampling for Source Characterization*

The approach taken in this study was to quantify average emission rates of reduced sulfur compounds from kraft pulp mill WWTP components through measuring wind velocity and concentration values over the area of the downwind dispersion plume. To this end, the general procedure for spatial ambient air sampling, or boundary layer emission monitoring, outlined by Esplin (Esplin 1988, 1989) was followed.

This procedure for spatial ambient air sampling is a variation on the transect technique, but instead of employing a permanent or semi-permanent array of masts and instruments downwind of a source to measure velocity and concentration values, a mobile cart with sample lines set at multiple elevations is used to traverse the dispersion plume and collect an integrated sample. As shown in Figure 2.3, a helium-filled balloon (Vaisala TTB327), which is aerodynamically shaped to fly essentially directly over the cart, was used to raise the sample lines to the desired elevations. The system was designed to be able to hoist three sample lines with the high line up to 91 meters; however, the highest elevation at which it was used was 55 meters. An advantage of this method over the "traditional" transect technique is its flexibility, which allows for continual adjustment with changes in wind direction, speed and atmospheric stability.

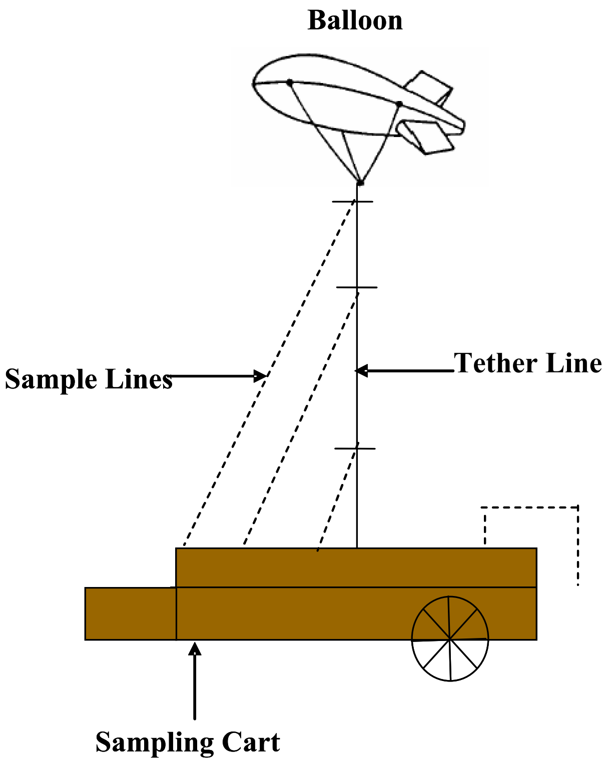

Figure 2.3 Downwind Ambient Air Mobile Sampling System

This spatial ambient air sampling procedure allows for the determination of horizontal and vertical emission flux profiles. As shown in Figure 2.4, the sample cart is moved along the downwind sample path and collects a downwind composite crosswind sample at each of four elevations, one of which is set at essentially ground level. The sample path was generally a road around the perimeter of the basin. The crosswind emission flux profile is integrated by partially filling sample containers at equally spaced sampling locations along the downwind sample path. The amount of sample collected at each location is proportional to the sine of the angle between the wind direction and the sample path (θ). Flow controllers are used to fill the containers at a constant rate, so the amount of sample collected at each location is controlled by the amount of time the container valves are opened at each location. In the work reported herein, the total sample collection time was set to 45 minutes. When the time required to move between the sampling stations was included, the total time elapsed during sample collection was generally in the range of 50 to 60 minutes. Generally, approximately 10 downwind sample collection locations were used, and the sample collection times at each location would range from approximately 1 to 6 minutes, depending on the sine of the angle between the wind direction and sample path for each location. An additional sampling system was located upwind of the source under test to correct the downwind sample concentrations for potential background concentrations.

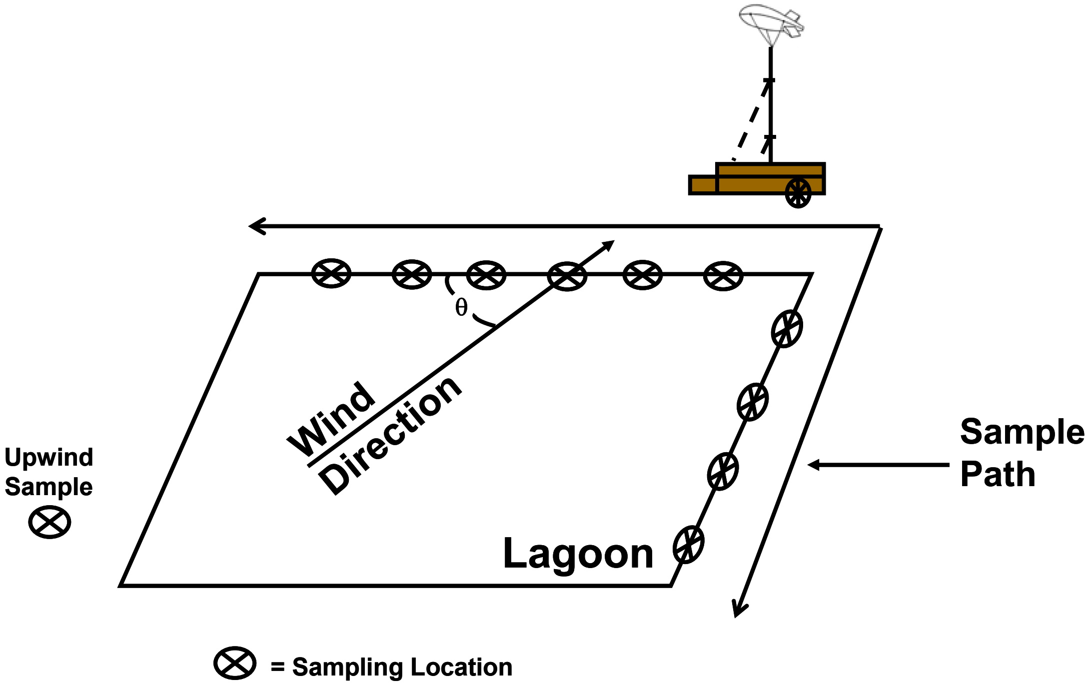

Figure 2.4 Ambient Air Sampling Scheme

During this study, upwind samples from the ground level and downwind samples from various elevations were collected in evacuated 6 L canisters for subsequent analysis. Figure 2.5 is a schematic representation of the ambient air sampling system. A Teflon head pump (KNF Neuberger diaphragm pump Model N86KTDC 12 volt DC) continuously pulls the sample through a black rubber-coated one-eighth inch outside diameter Teflon sample line. When the valve on the evacuated canister is open, a portion of the gas exiting the pump is pulled through a Nafion dryer (Perma Pure MD-Series gas dryer with Nafion polymer membrane) and then through a mechanical mass flow controller (Entech CS1200) before entering the canister. The apparatus for collecting the upwind or background sample had only one sampling system. The cart used for collecting the downwind horizontally integrated samples at four elevations had four sampling systems—one for each elevation. For both the upwind and downwind sampling systems, appropriately sized 12 volt lead-acid batteries were used to power the pumps.

To collect the necessary meteorological data, a field station was erected in the area of the WWTP. Three-dimensional wind speed and direction were measured at heights of 10 meters and 2 meters above ground level using sonic anemometers. Barometric pressure and temperature were also measured. Data from the anemometers were collected throughout the duration of the tests and stored for later retrieval on a portable computer.

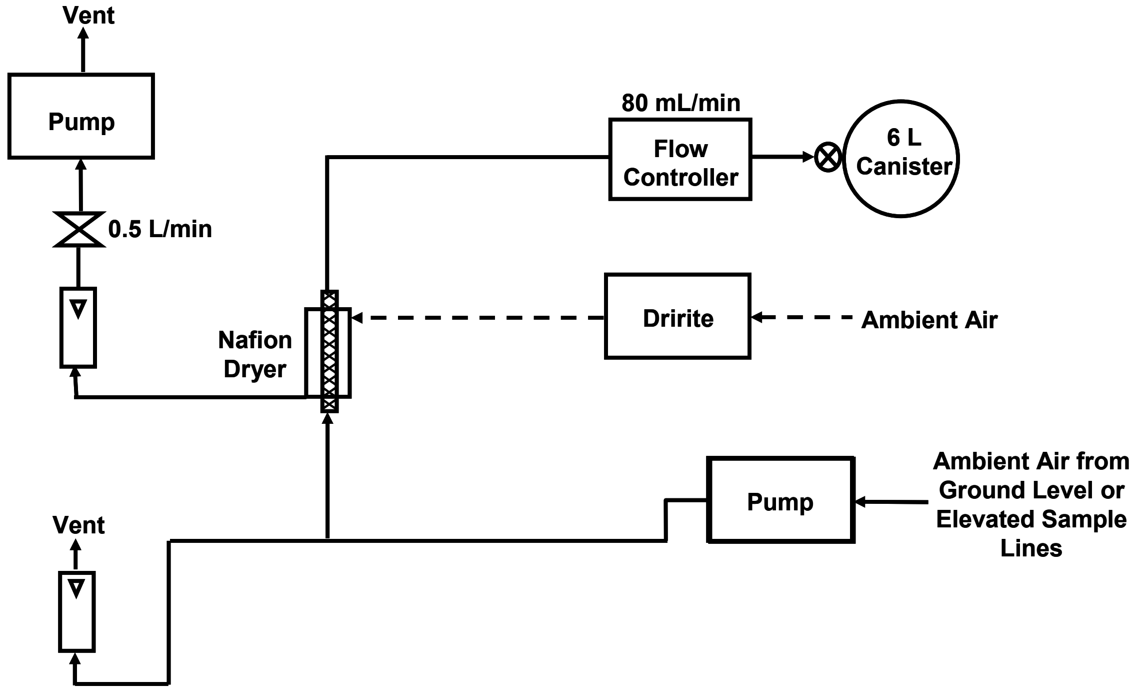

Figure 2.5 Ambient Air Sampling System

To extend the analytical portion of the method for off-site speciated analysis of reduced sulfur compounds, the ambient air samples were collected in evacuated six liter stainless steel canisters (Entech 29-10622), which were coated with a special sulfur-inert coating (Silonite™). All metal components in the sampling and analytical systems that came in contact with the sample had this coating. As shown in Figure 2.5, the sample was conditioned before collection in a canister by first passing through a Nafion dryer. Additionally, immediately following sample collection, the canister contents were diluted with nitrogen. This is done by pressurizing the canister with nitrogen to achieve a dilution ratio of approximately 3.75. The canister samples were shipped via overnight courier to the laboratory where they were analyzed.

2.3.2 *Determination of Analyte Concentrations in Canisters*

The canister samples were analyzed in the laboratory to determine the concentration of reduced sulfur gases and methane for calculation of emission rates. A gas chromatograph initially equipped with a flame photometric detector and cryogenic pre-concentration was used to measure the concentration of reduced sulfur gases in the sample canister. The flame photometric detector was only used for the first study, which was conducted at Mill A. For the remainder of the studies, a pulsed flame photometric detector was substituted for the flame photometric detector. The gas chromatograph used for methane determination was equipped with a flame ionization detector.

There were some differences in the manner in which the reduced sulfur compound concentrations were determined over the course of the study. For the purpose of describing the analysis methods used over the course of the study, the study can be separated into the following categories: 1) Mill A, which was tested over the period of June through October 2004; 2) the Phase I studies at Mills E, D and B, which were carried out during the period of April through August, 2005; 3) the Phase II studies a Mills E and B, which were conducted during March and April, 2006; and 4) Mill F, which was tested during April, 2006.

During the studies at Mill A and the Phase I studies, the calibration curves for individual reduced sulfur compounds were initially prepared using approximately 10 data points. For most of the analyses at Mill A, at least one check standard was analyzed for each 10 sample analyses. With the conditions used for the GC-FPD analyses, correction for check standard recovery was not considered necessary. During the Phase I GC-PFPD sample analyses, following initial calibration, at least two check standard samples were analyzed before and after each set of 10 samples. The resulting average recovery of the check standards was used to correct the measured analyte concentrations. For the Mill A and Phase I data, no correction factor was used to correct for sample loss due to delay in sample analysis; however, the samples were analyzed within five days of collection. During the Phase II and Mill F studies, a different protocol was followed. Instead of using check standards, the instrument was calibrated daily and no check standard correction was needed. However, based on a separate study of sample loss during storage in canisters, a correction factor for sample loss during storage, for periods of up to 10 days, was applied. The details of the analytical equipment and procedure will be included in a separate methods technical bulletin.

2.3.2.1. ***Detection and Quantitation Limits***

Since the study was carried out over a long period of time, there were changes in analytical methods. These changes resulted in different detection and quantitation limits during the study for the reduced sulfur compounds. For the Mill A and Phase I studies, statistically derived method detection limits (MDLs) were determined along with practical quantitation limits (PQLs), which were defined as being equal to 10 times the MDLs. Concentration values between the MDL and PQL were used similarly in the calculation of emission rates; however, those values were flagged in the individual mill reports (NCASI 2008a-i). For the Phase II and Mill F studies, method quantitation limits (MQLs) were used. The MQL was defined as being equal to the value of the lowest calibration standard. Values above the MQL were handled in the same manner.

Mill A Quantitation Limits

The method detection and practical quantitation limits for the GC-FPD analysis of the reduced sulfur compounds in ambient air are shown in Table 2.1. Method detection limits were determined following revision 1.11 of the EPA procedure for the determination of the method detection limit (40 CFR (7-1-95 edition) Part 136, Appendix B). Because the canister samples are pressurized with nitrogen in the field to enhance sample stability prior to analysis, a factor of 3.75 has been applied to the detection limit of the canister analysis, in order to provide an estimate of the method detection limit for each compound in ambient air.

Table 2.1 Detection and Practical Quantitation Limits for RSC Concentrations in Ambient Air, Mill A

Compound	Method Detection Limit (ppbv)	Practical Quantitation Limit (ppbv)
Hydrogen sulfide	4.69	46.9
Methyl mercaptan	14.18	141.8
Dimethyl sulfide	0.31	3.1
Dimethyl disulfide	0.29	2.9

Phase I Mill Reports Quantitation Limits

The method detection and practical quantitation limits for the GC-PFPD analysis of the reduced sulfur compounds in ambient air are shown in Table 2.2. Method detection limits were determined following revision 1.11 of the EPA procedure for the determination of the method detection limit (40 CFR (7-1-95 edition) Part 136, Appendix B). Because the canister samples are pressurized with nitrogen in the field to enhance sample stability prior to analysis, a factor of 3.75 has been applied to the detection limit of the canister analysis, in order to provide an estimate of the method detection limit for each compound in ambient air.

Table 2.2 Detection and Practical Quantitation Limits for RSC Concentrations in Ambient Air, Phase I

Compound	Method Detection Limit (ppbv)	Practical Quantitation Limit (ppbv)
Hydrogen sulfide	1.0	10
Methyl mercaptan	2.3	23
Dimethyl sulfide	1.7	17
Dimethyl disulfide	1.2	12

Phase II Mill Reports Quantitation Limits

The approximate method quantitation limits (MQLs) for the GC-PFPD canister analysis are contained in Table 2.3. The values shown in the table are derived by multiplying the lowest calibration point value by the dilution ratio. The exact MQLs will vary depending on the specific conditions for each calibration curve. The canister samples are pressurized with nitrogen in the field to enhance sample stability prior to analysis to yield a dilution ratio of approximately 3.75.

Table 2.3 Approximate Quantitation Limits for RSC Concentrations in Ambient Air, Phase II

Compound	Approximate Method Quantitation Limit (ppbv)
Hydrogen sulfide	4.1
Methyl mercaptan	3.9
Dimethyl sulfide	3.9
Dimethyl disulfide	1.4

Mill F Quantitation Limits

The approximate method quantitation limits (MQLs) for the GC-PFPD canister analysis are contained in Table 2.4. The values shown in the table are derived by multiplying the lowest calibration point value by the dilution ratio. The exact MQLs will vary depending on the specific conditions for each calibration curve. The canister samples are pressurized with nitrogen in the field to enhance sample stability prior to analysis to yield a dilution ratio of approximately of 3.75.

Table 2.4 Approximate Quantitation Limits for RSC Concentrations in Ambient Air, Mill F

Compound	Approximate Method Quantitation Limit (ppbv)
Hydrogen sulfide	1.2
Methyl mercaptan	0.23
Dimethyl sulfide	0.57
Dimethyl disulfide	0.16

2.3.3 *Calculation of Emission Rates*

Emission rates were determined according to the approach described by Esplin (1988). Concentration and wind direction and speed measurements are used to estimate the spatial distribution of flux of a gas, e.g., H_2S, passing through an imaginary vertical plane downwind of an area source such as a wastewater basin. By integrating over the entire area of the vertical plane, the total amount of the gaseous compound passing through the plane can be computed. This amount is assumed to be equal to the amount of the gas emitted per unit time from the surface of the basin.

The horizontal path and heights for the concentration measurements must be selected before each sampling run so that essentially all of the gaseous releases from the basin surface will pass through the downwind plane of sampling locations. Due to the unique circumstances surrounding each test, it was not possible to establish an objective set of criteria for acceptable lateral plume coverage; however, each test was evaluated for the reasonableness of the plume coverage and the calculated emission rate. The details surrounding each test can be found in the individual mill test reports (NCASI 2008a-i). Gaussian dispersion of the released gases is assumed, implying the gas plume expands vertically and horizontally due to atmospheric turbulence as it travels downwind. The amount of expansion depends on the degree of turbulence, with more turbulent (unstable) conditions resulting in greater expansion. Thus, the height and width of the vertical plane for concentration measurements will increase with downwind distance and with increasing instability.

In order to perform the flux integration calculation over the vertical plane, several assumptions are made.

1. Wind direction is uniform within the plane.
2. Wind speed at a given height is horizontally uniform across the plane.
3. The vertical profile of wind speed u can be described by a power law function, $u(z)=u_r(z/z_r)^p$, where z is height above ground, z_r is the height above ground of the wind speed measurement u_r, and p is a stability-dependent parameter.
4. The vertical profile of the horizontally averaged concentration c(z) is of the following power law form, $c(z)=C_o(1-z/Z_b)^b$, where z is the height above ground, C_o is the concentration at z=0, b is an empirical constant, and Z_b is the boundary layer height, i.e. $c(Z_b)=0$.
5. Emission rates, winds, and atmospheric stability are constant over the duration of a sampling run.

2.3.3.1 *Emission Rate Calculation Equation*

Emission rates were calculated using the following equation.

$$E = C_o W U_{10} \int_0^{Zb} \left(\frac{Z}{10}\right)^p \left(1-\frac{Z}{Z_b}\right)^b dz \qquad \text{(Equation 7)}$$

where

E = emission rate, g/s
C_o = horizontally averaged ground-level (Z=0) compound concentration, g/m^3
W = crosswind length of the sample path, m
U_{10} = average wind velocity at 10 meters, m/s
Z_b = pollutant boundary layer height, m
p = wind profile exponent whose value is a function of atmospheric turbulence
b = concentration profile exponent

To compute E, values for C_o, p, Z_b, and b must first be calculated. W and U_{10} are measured. Then the integral was numerically evaluated using 0.1 meter increments for Z. The following sections describe the procedures used in the calculations.

2.3.3.2 *Determination of Atmospheric Stability Class and Z_b*

The pollutant boundary layer height Z_b is a function of atmospheric stability and downwind distance from the emission source. Atmospheric stability is typically characterized in terms of a stability class, which is estimated from meteorological parameters. There are several different approaches for determining the stability class.

In this study, an estimate of the stability class was made prior to each sampling run following the approach outlined by Turner (Turner 1994) which assigns a Pasquill-Gifford stability category (A, B, C, D, E, or F) based on wind speed at 10 meters, incoming solar radiation, and cloud cover. The standard deviation of the Gaussian concentration distribution in the vertical direction, σ_Z, was then calculated with a formula, $\sigma_z = ax^d$, where x is the downwind distance from the upwind edge of the basin to be sampled to the sampling path for the cart and balloon apparatus, and a and d are stability dependent parameters. As recommended by Esplin (1988), Z_b was assumed to be $2.15\sigma_z$. This value of Z_b was used to set the heights for the concentration measurements.

After the sampling run, two other approaches using wind data collected during the sampling run were used to recalculate the stability class, σ_z, and Z_b. The fluctuations in the horizontal wind direction (azimuth angle), vertical wind direction (elevation angle), and vertical velocity measured by the sonic anemometer at the 10 meter height were used to compute σ_A, σ_E, and σ_w, respectively. The relationship between Pasquill-Gifford stability class and the standard deviation of the azimuth and elevation angles over a 60-minute averaging period is shown in Table 2.5 (Gifford 1976; Kunkel 1985). When the sampling period was different from 60 minutes, the σ_A value was adjusted to a 60 minute mean σ_A value with the following equation (Kunkel 1985): $(\sigma_A)_{60} = (\sigma_A)_t\,(60/t)^{0.2}$, where t is in minutes. A minimum of 360 values obtained during the averaging period should be used for calculating the standard deviations (USEPA 2000).

Table 2.5 Relationship between Pasquill-Gifford (P-G) Stability Class and the Standard Deviation of the Azimuth and Elevation Angles (σ_A and σ_E) of the Horizontal and Vertical Wind Components

Stability Description	P-G Stability Class	σ_A, deg.	σ_E, deg.
Very unstable	A	25	10
Moderately unstable	B	20	–
Slightly unstable	C	15	–
Neutral	D	10	2 – 5
Moderately stable	E	5	–
Very stable	F	2.5	1

In the first approach, the computed σ_A values were used to determine the stability class. σ_z and Z_b were then determined with the same relationships as before, i.e. $\sigma_z = ax^d$ and $Z_b = 2.15\sigma_z$.

In the second approach, σ_Z was directly calculated from the standard deviation of the vertical component of the wind velocity (σ_w) using Irwin's model (Irwin 1983). This model relates the two parameters through the following equation.

$$\sigma_z = \sigma_w\, T\, f_z \qquad \text{(Equation 8)}$$

where

σ_w = standard deviation of the vertical component of the wind velocity, m/s

T = travel time (seconds) = $\dfrac{x(meters)}{U_{10}(m/s)}$

$f_z = 1.88\left(\dfrac{T}{100} - 0.4\right)^2 + 0.7$ for unstable conditions, and

$$= \frac{1}{1+0.9(T/50)^{0.5}} \quad \text{for stable conditions.}$$

If measurements of σ_w are not available, it can be approximated from σ_E and $\bar{U}_{10}$ by using the following equation (USEPA 2000).

$$\sigma_w = \sigma_E \cdot \overline{U_{10}} \qquad \text{(Equation 9)}$$

where

σ_E = standard deviation of the elevation angle, radians
$\bar{U}_{10}$ = average 10-meter wind velocity, m/s

Again, Z_b was assumed to be $2.15\sigma_z$.

Normally the value of σ_z calculated from σ_w was used to determine Z_b. However, this method can yield unrealistically large values for σ_z when wind speeds are low. Thus, if σ_Z calculated from σ_w was approximately two or more times the value of σ_Z based on σ_A, then other factors were evaluated to determine which value of σ_z should be used for calculating Z_b. First, the meteorological conditions and associated atmospheric stability were examined before, during, and after the sampling run to determine if there were any trends, and if so, whether the trend in vertical stability was better represented by σ_z based on the σ_A or σ_w method. Second, emission fluxes were calculated using values of σ_z determined from both the σ_A and σ_w methods, and the resulting flux profiles were examined to determine which Z_b value appeared to give the most reasonable profile. If the trends and flux profiles both suggested σ_z calculated from the σ_A method resulted in the best fit to the observations, then the σ_z value based on the σ_A method was used to calculate Z_b. Otherwise, σ_z and Z_b were based on the σ_w method.

2.3.3.3 *Calculation of the Wind Velocity Profile Exponent (p)*

The value of p was calculated from the site-specific horizontal wind velocities measured at 2 meters and at 10 meters using the following equation.

$$p = \frac{\ln(U_{10}) - \ln(U_2)}{\ln(10) - \ln(2)} \qquad \text{(Equation 10)}$$

On rare occasions, the mean wind speed at 2 meters slightly exceeded that at 10 meters. In that circumstance, p was set to zero. When wind speed values were not available for both levels, a default p value (USEPA 2000) based on the atmospheric stability class was assigned. The stability class was determined from σ_A. The p values are shown in Table 2.6, and represent “rural” conditions with a modest surface roughness.

Table 2.6 Wind Profile Exponent as a Function of Atmospheric Stability Class for Rural Sites

Stability Class	p
A	0.07
B	0.07
C	0.10
D	0.15
E	0.35
F	0.55

2.3.3.4 *Background Concentration Correction*

Normally, the measured background RSC concentrations were subtracted from the downwind sample concentrations only if they were considered to represent relatively three-dimensionally homogeneous background concentrations. If the results of screening studies indicated that a three-dimensionally non-homogeneous background concentration profile existed in a given situation, then emission testing was only done in that situation if the relative concentration levels, considering dispersion conditions, indicated that ignoring the background would not significantly bias the calculated emission fluxes. When a correction for upwind background concentration was to be applied to the downwind canister RSC concentrations, then the pre-dilution concentration of the background canister was subtracted from the pre-dilution concentrations in the canisters collected downwind from the source at multiple elevations. After the downwind sample RSC concentrations had been corrected for the background concentration, or the decision was made not to correct for background concentration, the resulting concentration values were considered the downwind ambient air concentrations due to source emissions.

For methane, all downwind concentrations were corrected for background concentrations because background methane concentrations were always a significant portion of the downwind concentrations. Background methane concentrations, in the absence of any nearby upwind sources, were assumed to be spatially uniform. Data in the literature indicate that this is a reasonable assumption. A study of the vertical distribution of ambient air methane concentrations in the lower troposphere showed no significant variation (Sugawara et al. 1997). Interference from nearby upwind sources was not expected to be a significant problem in the study reported herein, because methane emissions quantitation was only performed when the sources could be tested without interference from upwind anthropogenic methane emission sources. Additionally, given the distance of the tested sources to natural methane emissions from upwind wetlands, and the maximum estimated emissions from natural wetlands (Ehhalt and Heidt 1973; Walter, Heimann, and Matthews 2001), methane emissions from natural sources would not be expected to significantly affect the measured downwind methane vertical concentration profiles.

2.3.3.5 *Calculation of C_0 and b*

The balloon sampling system provided horizontally averaged ambient concentrations for each of the four reduced sulfur compounds and methane at three or four heights. The vertical concentration distribution was assumed to be of the form

$$C(z) = C_o \left(1 - \frac{Z}{Z_b} \right)^b \qquad \text{(Equation 11)}$$

In order to solve for b and C_0, the natural logarithm was taken of both sides of the equation to yield

$$\ln[C(z)] = \ln C_o + b \ln \left[1 - \frac{Z}{Z_b} \right] \qquad \text{(Equation 12)}$$

As this equation represents a straight line in log-log space, linear regression can be used to obtain values for the slope b and intercept ln C_0, provided that values of C are available for at least three heights. However, there were many sampling runs where less than three concentrations were above method detection limits, especially for the reduced sulfur compounds at the elevated sampling heights. Thus procedures had to be developed to handle these situations, as described in the following sections. These procedures were used to calculate compound-specific C_0 values, compound-specific b values and average b values. Occasionally deviations from these procedures were necessary to accommodate data sets with unusual characteristics. Any such departures have been identified in the individual mill reports (NCASI 2008a-g).

If all five compounds were released uniformly over the surface of a basin at a constant rate, then in theory, the slope of the horizontally averaged vertical concentration profile (in log-log space) would be the same for all five compounds. However, it is likely the releases of each compound vary horizontally over the basin surface and vary over time. Furthermore, slopes determined from field data for individual compounds are subject to considerable uncertainties due to measurement inaccuracies, non-steady state meteorological conditions, non-uniform background concentrations, and non-Gaussian concentration distributions. Thus, the calculated slopes for the five different compounds are not expected to be in agreement with each other.

Because of the uncertainties inherent in the individual compound concentration profiles obtained through linear regression, use of the average of the b exponents determined for each of the five compounds was believed to be the most reasonable approach for calculating emissions, with some rare exceptions. If any compound lacked sufficient concentration measurements to calculate a b exponent from detectable values, it was not included in the calculation of the average b value.

Because Esplin's (1988) measurements were limited to a single parameter (TRS), only one vertical concentration profile could be computed. Also, he apparently did not encounter any TRS concentrations below his method detection limits. Procedures to handle non-detects and compute vertical profiles with less than three data points were therefore unnecessary in his study.

2.3.3.6 *Calculation of Compound-Specific b and C_0 for RSC Compounds*

If measured concentrations of a given compound were above the quantitation limit at three or four elevations, then all of the concentration values above the quantitation limit were used for linear regression to calculate the compound-specific b and C_0 values.

If measured concentrations of a given compound were above the quantitation limit at only two elevations, then the two quantified values and one-half of the quantitation limit at the next highest elevation were used to calculate compound-specific b and C_0 values. If the two above quantitation limit concentrations were the ground level (0.5 meters) and the high level, then the quantitated ground level (0.5 meter) and high level concentrations were used in conjunction with an assumed value of 0.001 ppbv at 95% Z_b to calculate compound-specific b and C_0 values.

Assigning a 0.001 ppbv value at 95% of Z_b was somewhat arbitrary. The assumed form of the vertical concentration profile implies $C(Z_b) = 0$. However, the b exponent is calculated by linear regression using the logarithmic form of the profile where the term $\ln(1\text{-}z/Z_b)$ becomes infinitely large as z approaches Z_b, as shown in Figure 2.6. Through trial and error, it was found that using a concentration value of 0.001 ppbv at $0.95Z_b$ appeared to give reasonable flux profiles and fit what was known about the vertical concentration profiles for the area sources and atmospheric stability conditions encountered in this study in almost all situations. Nevertheless, there were a few situations where alternative calculation procedures were necessary.

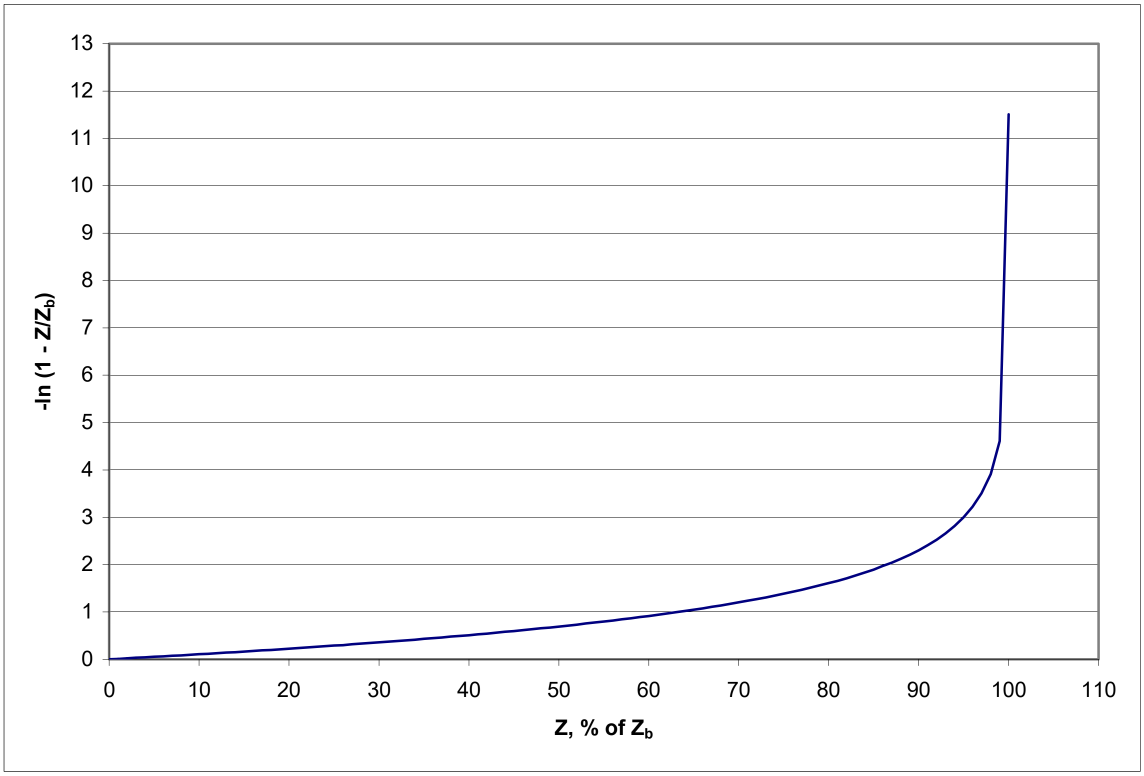

Figure 2.6 Effect of Z Approaching the Pollutant Boundary Layer Height, Z_b

When only three sampling elevations were used (mainly at the beginning of the study), and the highest elevation exceeded Z_b, then the concentrations at the lower two sampling elevations were used in conjunction with 0.001 ppbv at 95% Zb for calculation of the compound-specific b and C_0 values.

In situations where concentrations for one compound were above the quantitation limit only at the ground level, then the measured 0.5 meter concentration was used as C_0. If duplicate concentration values were available for the 0.5 meter level and both of those values were above the quantitation limit, then the average of the duplicate values were used as C_0. However, if one of those duplicate values was less than one-half the other, then the lower value was not used. Also, if the 0.5 meter level concentration was measured in duplicate, but only one of the two values was above the quantitation limit, then only the value that was above the quantitation limit was used as C_0. In the preceding cases, it was assumed that the lower duplicate values were due to the development of active sites on the interior canister surfaces. Compound-specific b values were not calculated when only the 0.5 meter concentration was above the quantitation limit unless vertical concentration profiles could not be computed for any of the other compounds, including methane. If b had to be calculated because it was not available from any of the other compounds, then one-half of the detection limit at the low level and 0.001 ppbv at 95% of Z_b were used to determine b and C_o.

If concentrations at all elevations were below the quantitation limit, then the quantitation limit was used as C_0, the emission rate was reported as ND[xxxx] and a compound-specific b was not calculated. If measured vertical concentration profile data were not available for any of the other compounds, including methane, then one-half of the detection limit at the low level and 0.001 ppbv at 95% Z_b were used to calculate b.

In all cases where a concentration value of 0.001 ppbv at 95% of Z_b was used to estimate b for a reduced sulfur compound, the resulting vertical concentration profile curve fit was visually inspected. If the fit with the known concentration data was poor, then the vertical concentration profile was refitted using the measured ground-level concentration and one-half of the quantitation limit at the low, mid and, in some cases, the high sampling elevations in the regression calculation for the determination of the b and C_o values.

2.3.3.7 *Calculation of b and C_0 for Methane*

If the background-corrected concentrations were above zero at three or four levels, then all of the positive values were used for linear regression to calculate b and C_0 for methane.

If the background-corrected methane concentrations were above zero at two elevations and the highest of those two elevations was less than 80% of Z_b, then all of the detect values were used in conjunction with 0.001 ppbv at 95% Z_b to calculate b and C_0.

Whenever a concentration value of 0.001 ppbv at 95% of Z_b was used to estimate b for methane, the resulting vertical concentration profile curve fit was visually inspected. If the fit with the known concentration data was poor, then a value for b was not calculated for methane, the measured ground-level concentration was used as C_o, and the average b value for the reduced sulfur compounds was used to calculate the methane emission rate.

If only the ground level (0.5 meter) background-corrected concentration was positive, then the 0.5 meter concentration was used as the C_0 value, and a compound-specific b value was not calculated.

If the ground level (0.5 meter) background-corrected concentration was negative, no values for methane were calculated and the emission rate was report as NA (not available).

2.3.3.8 *Calculation of Average b*

In the average b calculation, all of the compounds were included for which above quantitation limit (or for methane, above zero) concentrations were measured at a minimum of two levels.

If none of the compounds were detected at two or more levels, then the average b was computed from the compound-specific b values for those compounds detected at ground-level. Compound-specific b values less than one were not used when calculating the average.

2.3.3.9 *Use of Average b vs. Compound-Specific b in the Emission Rate Calculation*

The average b value was used in all emission rate calculations, unless there was evidence indicating specific source characteristics and meteorological conditions resulted in significantly different compound-specific vertical concentration profiles. Examples of this situation are the data from test run nos. 1, 7, 8, 9, 10 and 11 at the Mill D no. 1 ASB. During these test runs, a portion of the sample path passed close to the area where the acidic mill effluent was entering the basin. The acidic area near the basin inlet was relatively small, due to the buffering effect of aerobic biological activity as the mill effluent moved through the basin. The acidic conditions resulted in a relatively high hydrogen sulfide emission rate in that area; however, it had little effect on the emission rates of the organic reduced sulfur compounds or methane. Therefore, in this situation, the use of compound-specific b exponents yielded the most accurate vertical concentration profiles and emission rates.

2.3.4 *Calculation of Average Source Emission Rates*

To compute the emission rate for a source, results from multiple test runs on the source were averaged. The following procedure was used for averaging multiple test run results in this report. When emission rates could be calculated for all test runs on a given source, then the average emission rate was calculated using all test runs. If emission rates could not be calculated from any of the test runs on a given source, then the emission rate was based on the lowest concentration detection limits for that source. In mixed data sets, i.e., with some emission rates based on above the detection limit data and some on below detection limit data, one-half of the detection limit for each test run with an emission rate below the detection limit was averaged with the above detection limit emission rate values to calculate the average source emission rate.

In the detailed individual mill test reports (NCASI 2008a-i), emission rate values below the detection limit were simply excluded from the calculation of average emission rates. The calculation of average source emission rates was done differently in the individual mill reports because those reports were prepared earlier, and for different purposes.

3.0 SOURCE DESCRIPTION AND RESULTS OF TESTS AT MILL A

The wastewater treatment plant components at Mill A were tested during three separate time periods: June 22–24, 2004, July 27–29, 2004, and October 11–13, 2004. The results of this testing are detailed in the Mill A Test Report (NCASI 2008a). During the first test period, emissions measurement testing was done at the primary clarifier and the no. 1 ASB. During the second test period, emissions measurement testing was conducted at the no. 1 ASB. During the third test period, emissions measurement testing was conducted with associated inlet/outlet liquid sample collection at the no. 1 ASB.

3.1 Wastewater Treatment Plant Description, Mill A

Mill A produces approximately 1400 tons per day of bleached softwood kraft pulp for specialty applications. Mill A does not have a steam stripper, so the foul condensates are hard-piped to secondary wastewater treatment.

As shown in Figure 3.1, the major components of the wastewater treatment plant at Mill A are the primary clarifier, the no. 1 ASB and the no. 2 ASB. Figure 3.2 is a flow diagram for the WWTP. Most of the secondary treatment is accomplished in the no. 1 ASB, although significant aeration, about one-half as much as in the no. 1 ASB, is applied in the no. 2 ASB.

The primary clarifier is 100 meters in diameter. Material skimmed off the surface of the primary clarifier flows into the skimming pond, which roughly forms the shape of a horseshoe around the primary clarifier. The sludge removed from the bottom of the primary clarifier is pumped to the sludge pond. Drainage from both the skimming and sludge ponds flows back to the inlet of the primary clarifier.

Effluent from the primary clarifier flows to the mix box, where it joins first with the acid sewer and then the hard-piped condensates. The mixed effluent flows to the no. 1 ASB at a rate of approximately 43 MGD. The no. 1 ASB has an area of approximately 28 acres, it is concrete lined, has a water depth of approximately 12 ft, and almost no settled sludge accumulation. It has 36 75-HP high-speed surface aerators; therefore, the maximum power available for aeration is 2700 HP. Effluent from the no. 1 ASB flows to the inlet of the 120-acre no. 2 ASB, from which the final effluent is discharged.

Mill and WWTP process operating information for the test periods is summarized in Table 3.1.

Figure 3.1 Aerial View of the Mill A WWTP

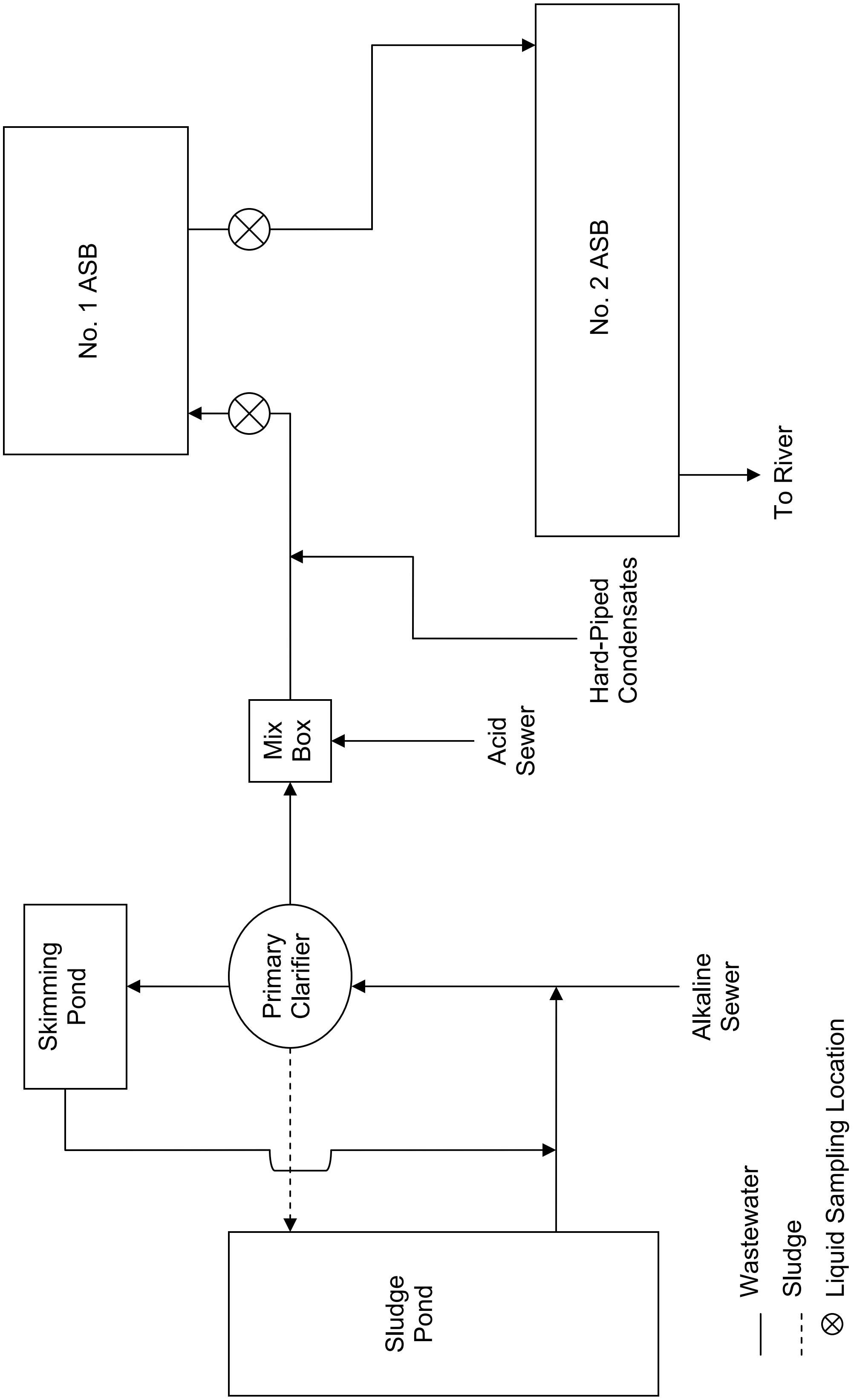

Figure 3.2 Mill A WWTP Flow Diagram

Table 3.1 Summary Process Operation Information, Mill A

		Primary Clarifier		No. 1 ASB							
Date	Production Rate, ADBTPD	Inlet Flow, MGD	Inlet pH	Hard Pipe Flow, MGD	Inlet Flow Rate, MGD	Aerator HP	Inlet pH	Outlet pH	Inlet Temp., °C	Midway Temp., °C	Outlet Temp., °C
6/21/04	1,513	17.2	10.5	2.80	44.0	2650	5.4	7.2	45.0	38.9	37.8
6/22/04	1,433	16.4	10.7	2.75	43.1	2625	6.6	7.7	42.8	38.9	37.2
6/23/04	1,530	17.2	11.0	3.24	44.4	2625	5.6	6.8	NA	41.1	40.0
6/24/04	1,421	16.1	11.5	3.21	43.3	2625	7.3	7.5	45.0	42.2	41.1
7/26/04	1,557	17.3	11.4	3.14	44.4	2650	4.6	7.2	43.9	38.9	37.2
7/27/04	1,560	16.4	10.9	3.07	43.5	2625	4.9	7.2	42.8	38.9	37.2
7/28/04	1,391	17.2	10.8	3.15	44.3	2625	5.1	7.1	43.9	37.8	36.1
7/29/04	1,207	15.1	11.3	2.78	41.9	2625	6.6	7.3	38.9	37.8	37.2
10/10/04	1,413	13.3	11.2	3.11	40.4	2700	6.3	7.3	45.0	37.2	36.1
10/11/04	1,528	16.4	11.1	3.14	43.5	2700	6.1	7.3	42.8	37.2	36.1
10/12/04	1,346	15.2	11.2	2.90	42.1	2700	5.8	7.4	43.9	37.2	36.1
10/13/04	1,399	14.5	11.0	3.11	41.6	2625	4.9	7.4	42.8	37.2	36.1

(Continued on next page. See notes at end of table)

Table 3.1 Continued

	No. 1 ASB						
Date	Inlet BOD*, lb/day	Outlet BOD*, lb/day	Inlet DO mg/L	Midway DO mg/L	Outlet DO mg/L	Inlet TSS mg/L	Outlet TSS mg/L
6/21/04	123,849	11,009	3.1	1.9	1.7	24	70
6/22/04	133,632	11,034	0.7	0.8	1.1	49	104
6/23/04	123,919	5,745	NA	0.7	0.5	29	62
6/24/04	135,829	11,996	3.4	0.9	0.8	55	102
7/26/04	96,219	14,191	1.3	0.6	0.6	22	78
7/27/04	100,853	15,302	0.9	0.7	0.5	39	76
7/28/04	95,977	11,910	1.3	0.7	0.8	44	90
7/29/04	88,967	11,342	0.4	0.1	0.2	29	68
10/10/04	121,642	11,324	0.3	0.5	1.0	32	64
10/11/04	131,097	24,179	0.5	0.5	0.9	31	62
10/12/04	104,964	25,148	0.7	0.5	0.7	24	38
10/13/04	105,377	20,519	0.6	0.5	1.2	29	56

NA = Not Available
*From the 5-Day BOD Test

3.2 Emissions Measurement and Liquid Sampling Results, Mill A

At Mill A, emission testing was conducted at the primary clarifier and the no. 1 ASB. The emission rates determined from that testing are summarized in Tables 3.2 and 3.3. Meteorological and RSC concentration data associated with the emissions tests are summarized in Table 3.4.

For the two test runs at the primary clarifier, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide emissions averaged 0.03 g/s, ND[0.02] g/s, 0.02 g/s, and 0.001 g/s, respectively.

For the 22 test runs at the no. 1 ASB, which were conducted on eight different test days over a five-month period, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide emissions averaged 0.4 g/s, 0.9 g/s, 3.1 g/s and 5.5 g/s, respectively. Figure 3.3 shows the average hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide emissions for each test day. Overall, the highest emissions were measured on 6/23/04. Since the emissions of all four compounds were high, the most likely cause was relatively high RSC concentrations in the liquid input, although no liquid sampling was conducted on this date.

As indicated on Figure 3.2, process unit inlet/outlet liquid sampling was conducted at the no. 1 ASB inlet and outlet during the October test period. The average analysis results for the liquid samples are summarized in Table 3.5. The average physical/chemical parameter data associated with liquid sample collection are summarized in Table 3.6.

Table 3.7 shows the results of a material balance conducted to calculate the apparent generation/ destruction of the reduced sulfur compounds in the no. 1 ASB for the 10/11-13/04 test period. The results of the material balance indicate the apparent destruction of 93% of the sulfide entering the ASB with the liquid inputs. Thus, only 7% of the total sulfide entering the ASB with the liquid inputs was emitted to the atmosphere as H_2S. Forty-four percent of the DMS entering the ASB with the liquid input was apparently destroyed and 56% was emitted to the atmosphere. Less than 3% of the DMS entering the ASB with the influent left the ASB with the liquid effluent. Most of the methyl mercaptan entering the ASB (91%) was apparently destroyed. However, the material balance for DMDS indicates generation that was 75% of the amount entering the ASB with the liquid inputs. This can be explained by the oxidation of methyl mercaptan to DMDS, which is one of the primary oxidation reactions for methyl mercaptan (Morrison and Boyd 1973). Also included in Table 3.7 is a material balance for the sum of methyl mercaptan and DMDS as sulfur. The results of this material balance indicate that 44% of the sum of the methyl mercaptan and DMDS (as sulfur) entering the ASB was apparently destroyed in the ASB, 5% left the ASB with the liquid effluent, and 51% was emitted to the atmosphere.

In Table 3.8, the BOD removal across the no. 1 ASB is compared to the methane emissions. BOD and methane emissions data were available for seven days of testing. For those seven days, the methane emissions averaged 3.9 g/s, and the average BOD removal across the basin was 419 g/s.

Table 3.2 Summary of Emission Rates for the Primary Clarifier at Mill A

Run No.	Date	Emissions, g/s H_2S	MeSH	DMS	DMDS
1	6/24/2004	2.44E-02	ND[2.10E-02]	1.71E-02	1.07E-03
2	6/24/2004	3.93E-02	ND[2.87E-02]	1.36E-02	2.65E-04
	Average	3.19E-02	ND[2.10E-02]	1.54E-02	6.68E-04

ND[xxxx] = the estimated maximum emission rate calculated from non-detect ambient air concentration data using the procedures outlined in Section 2.3.3.

Table 3.3 Summary of Emission Rates for the No. 1 ASB at Mill A

No.	Date	Emissions, g/s H_2S	MeSH	DMS	DMDS	CH_4
1	6/22/2004	ND[7.64E-02]	ND[3.26E+00]	4.05E+00	8.52E+00	6.21E+00
2	6/22/2004	ND[6.58E-02]	ND[2.81E+00]	2.94E+00	5.64E+00	4.77E+00
Average	6/22/2004	ND[6.58E-02]	ND[2.81E+00]	3.50E+00	7.08E+00	5.49E+00
3	6/23/2004	ND[7.51E-01]	ND[3.21E+00]	4.41E+00	9.05E+00	2.80E+00
4	6/23/2004	3.41E+00	ND[7.52E+00]	9.55E+00	1.10E+01	NA
5	6/23/2004	1.82E+00	ND[2.75E+00]	6.03E+00	7.09E+00	3.39E+00
Average	6/23/2004	1.87E+00	2.03E+00	6.66E+00	9.05E+00	3.10E+00
6	7/27/2004	1.21E-01	2.33E+00	3.38E+00	4.14E+00	2.54E+00
7	7/28/2004	ND[7.73E-02]	ND[3.30E-01]	1.11E+00	2.00E+00	2.98E+00
8	7/29/2004	ND[3.59E-01]	ND[1.54E+00]	4.11E+00	7.17E+00	1.12E+01
9	7/29/2004	ND[1.70E-01]	ND[7.26E-01]	2.39E+00	4.08E+00	5.54E+00
10	7/29/2004	ND[2.28E-01]	ND[9.73E-02]	2.83E+00	5.48E+00	7.10E+00
11	7/29/2004	ND[1.69E-01]	ND[7.19E-01]	3.34E+00	6.19E+00	4.18E+00
12	7/29/2004	ND[2.21E-01]	ND[9.45E-02]	3.22E+00	5.86E+00	1.20E+01
Average	7/29/2004	ND[1.69E-01]	ND[9.45E-02]	3.18E+00	5.76E+00	8.00E+00
13	10/11/2004	ND[1.78E-01]	ND[7.59E-01]	1.72E+00	2.28E+00	NA
14	10/12/2004	ND[2.75E-02]	ND[1.18E+00]	2.94E+00	4.47E+00	6.69E+00
15	10/12/2004	3.37E-01	6.46E-01	1.74E+00	2.69E+00	1.88E+00
16	10/12/2004	3.53E-01	8.01E-01	2.82E+00	4.29E+00	2.69E+00

(Continued on next page. See note at end of table.)

Table 3.3 Continued

No.	Date	Emissions, g/s				
		H_2S	MeSH	DMS	DMDS	CH_4
Average	10/12/2004	2.35E-01	6.79E-01	2.50E+00	3.82E+00	3.75E+00
17	10/13/2004	2.65E-01	5.21E-01	1.99E+00	4.67E+00	1.01E+00
18	10/13/2004	2.84E-01	5.77E-01	1.43E+00	4.47E+00	7.68E-01
19	10/13/2004	5.56E-01	8.06E-01	2.20E+00	5.39E+00	8.46E-01
20	10/13/2004	3.14E-01	8.95E-01	2.71E+00	6.99E+00	2.39E+00
21	10/13/2004	2.66E-01	5.51E-01	2.07E+00	4.68E+00	1.94E+00
22	10/13/2004	3.35E-01	6.75E-01	2.11E+00	5.14E+00	NA
Average	10/13/2004	3.37E-01	6.71E-01	2.09E+00	5.22E+00	1.39E+00
Overall Average		4.16E-01	9.23E-01	3.14E+00	5.51E+00	4.26E+00

ND[xxxx] = the estimated maximum emission rate calculated from non-detect ambient air concentration data using the procedures outlined in Section 2.3.3.

Table 3.4 Meteorological and Concentration Summary Data for Emission Tests, Mill A

Source	Run No.	Date	Horizontal Wind Direction*, degrees	Horizontal Wind Velocity*, m/s	P-G Stability Class*	Integrated Downwind Ground-Level Concentration**, ppbv			
						H_2S	MM	DMS	DMDS
No. 1 ASB	1	6/22/2004	226	5.06	D	ND[45.8]	ND[138.4]	133.3	184.8
	2	6/22/2004	252	3.34	D	ND[46.3]	ND[140.4]	114.1	144.2
	3	6/23/2004	226	6.07	D	ND[46.5]	ND[140.7]	149.6	203.0
	4	6/23/2004	224	5.95	C	93.3	ND[145.8]	143.4	109.3
	5	6/23/2004	226	4.84	D	133.3	ND[142.4]	242.2	187.7
	6	7/27/2004	246	3.6	A	7.0	95.2	107.0	86.3
	7	7/28/2004	106	2.13	A	ND[4.8]	ND[14.5]	37.7	45.0
	8	7/29/2004	94	2.37	A	ND[4.8]	ND[14.6]	30.2	34.8
	9	7/29/2004	99	2.33	A	ND[4.8]	ND[14.5]	37.0	41.5
	10	7/29/2004	103	2.48	A	ND[4.7]	ND[14.3]	32.2	41.1
	11	7/29/2004	107	2.89	A	ND[4.8]	ND[14.5]	52.3	63.9
	12	7/29/2004	122	2.87	A	ND[4.7]	ND[14.2]	37.4	45.0
	13	10/11/2004	93	3.51	A	ND[4.7]	ND[14.2]	24.9	21.8
	14	10/12/2004	138	1.98	A	ND[4.7]	ND[14.2]	27.5	27.6
	15	10/12/2004	202	4.05	B	26.7	36.2	75.5	77.2
	16	10/12/2004	215	4.78	C	21.3	34.3	93.4	93.7
	17	10/13/2004	278	2.83	A	20.2	28.1	83.2	128.7
	18	10/13/2004	281	2.69	A	17.5	25.2	48.4	99.6
	19	10/13/2004	266	4.68	B	57.0	58.5	123.9	200.0
	20	10/13/2004	255	5.84	C	16.8	33.9	79.6	135.1
	21	10/13/2004	247	5.73	C	18.8	27.6	80.6	119.8
	22	10/13/2004	250	5.39	D	19.3	27.6	67.0	107.5
Primary Clarifier	1	6/24/2004	222	3.67	C	23.8	ND[14.5]	5.8	0.2
	2	6/24/2004	224	4.41	C	27.9	ND[14.5]	5.4	0.1

ND[xxx] = Not detected at a detection limit of xxx.

*Determined from the anemometer at 10 meter height.

**Determined via the procedures outlined in Section 2.3.3.

Table 3.5 Average Liquid Sample Concentrations, Mill A

Location	Date	Total Sulfide, µg S/L	MM, µg S/L	DMS, µg S/L	DMDS, µg S/L	DMTS, µg S/L
No. 1 ASB Inlet	10/11 - 13/04	2570	2740	1120	950	996
No. 1 ASB Outlet	10/11 - 13/04	48	21	31	154	ND[20]

ND[xx] = Not detected at a quantitation limit of xx

Table 3.6 Average Physical/Chemical Parameter Measurement Data Associated with Liquid Sample Collection, Mill A

Location	Date	Temp., ° C	Specific Conductance, mS/cm	DO, mg/L	pH
No. 1 ASB Inlet	10/11 - 13/04	47.4	2.59	0.51	4.9
No. 1 ASB Outlet	10/11 - 13/04	35.9	2.58	3.08	7.0

Table 3.7 Apparent Destruction or (Generation) of RSC Compounds in the Mill A ASB

Compound	Influent, g/s	Effluent, g/s	Air Emissions, g/s	Apparent Destruction or (Generation) as Percent of Input, %
H_2S	5.1*	0.1*	0.3	93
DMS	4.0	0.1	2.2	44
MM	7.7	0.1	0.6	91
DMDS	2.6	0.1	4.5	(75)
MM + DMDS (as S)	6.9	0.4	3.5	44

*total sulfide as H_2S

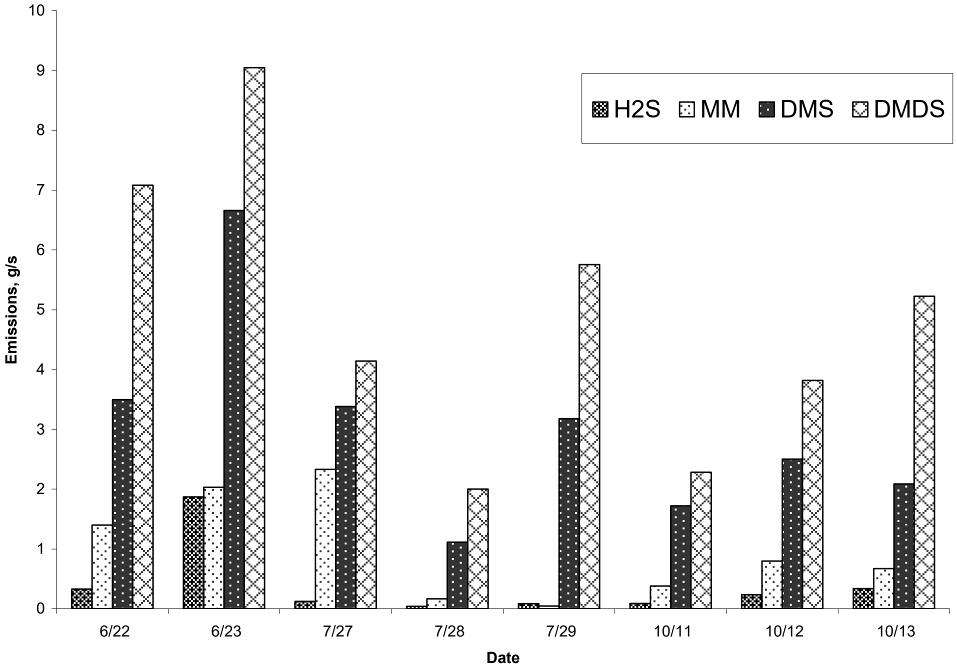

Figure 3.3 Average RSC Emission Rates for Each Test Day at the No. 1 ASB, Mill A

Table 3.8 ASB BOD Removal and Methane Emissions, Mill A

Date	BOD Removal,* g/s	Average CH_4 Emissions, g CH_4/s
6/22/2004	441	5.49
6/23/2004	440	3.10
7/27/2004	409	2.54
7/28/2004	408	2.98
7/29/2004	404	8.00
10/11/2004	416	NA
10/12/2004	418	3.75
10/13/2004	418	1.39
Average	419	3.89

*Inlet-outlet for the 60 day period prior to emissions testing ; BOD was determined from the 5-day BOD test.

4.0 SOURCE DESCRIPTION AND RESULTS OF TESTS AT MILL B

The wastewater treatment plant components at Mill B were tested during three separate time periods. The first two time periods were considered the Phase I Study. The third time period was considered the Phase II Study. In this report the results of both the Phase I and Phase II Studies are presented. The results of the Phase I study are detailed in one test report (NCASI 2008b), whereas the results of the Phase II Study are detailed in another test report (NCASI 2008c). In Phase I a screening study was conducted with data collection on August 3, 4 and 17, 2005, and emissions measurement testing with the associated liquid sample collection program was conducted on August 17 - 21, 2005. In Phase II, additional emissions measurement testing with the associated liquid sample collection program was conducted on April 25 and 26, 2006.

4.1 Wastewater Treatment Plant Description, Mill B

The kraft pulp mill has a total pulp production capacity of approximately 475,000 tons per year of kraft pulp. The paperboard mill has two paper machines producing unbleached kraft paper and lightweight linerboard.

The wastewater treatment plant consists of a series of earthen ponds or basins, and a primary clarifier, as shown in Figure 4.1. Figure 4.2 diagrams the flow sequence and approximate flow rates through the WWTP. Inlet/outlet liquid sampling locations are indicated on Figure 4.2. Effluent from the pulp and paper mills and a minor stream from the fly ash pond, with a combined average flow of approximately 14.7 MGD, is routed to the primary clarifier. Sludge from the primary clarifier is dewatered and sent to an on-site landfill. In the event of an upset in the mill, effluent can bypass the primary clarifier and be routed to a 19.6-acre spill pond. Overflow from the woodyard's storm water pond is also routed to the spill pond. Figure 4.3 is a scale drawing of the spill pond, on which the four surface liquid sampling locations are marked. Wastewater that was diverted to the spill pond is pumped to the primary clarifier at approximately 2.2 MGD when operation of the mill returns to normal.

Effluent from the primary clarifier is routed to the inlet of the 20.7-acre aerated stabilization basin. A portion of the foul condensates is treated in a small steam stripper and reused in the mill. The remainder of the foul condensates is hard-piped to the ASB. Installed surface aeration on the ASB totals 1605 horsepower and installed sub-surface aeration totals 425 horsepower. Retention time in the ASB is approximately 3.8 days. Figure 4.4 is a scale drawing of the ASB, on which the four surface liquid sampling locations are marked.

Effluent from the ASB flows through a spillway into the 61.8-acre no. 1 retention pond. The no. 1 retention pond is a single-cell pond, with an approximate retention time of 5 days. Figure 4.5 is a scale drawing of the no. 1 retention pond, on which the four surface liquid sampling locations are marked. Effluent from the no. 1 retention pond flows through culverts in an earthen dike into the nos. 2 and 3 retention ponds, which are divided by an earthen dike, and have a combined area of 128 acres. The nos. 2 and 3 retention ponds have an approximate retention time of 16 days. Effluent from the no. 3 retention pond flows through culverts in an earthen dike into the 97.4-acre no. 4 retention pond. The no. 4 retention pond is a single-cell pond, with an approximate retention time of 10.1 days. Secondary sludge which is periodically dredged from the retention ponds is placed in the 27.3-acre sludge lagoon, which is located immediately south of the ASB. Supernatant from the sludge lagoon is routed to the ASB. Secondary sludge had not been deposited in the sludge lagoon for at least two years before the testing reported herein was conducted.

Summarized mill and WWTP process operating information is contained in Table 4.1.

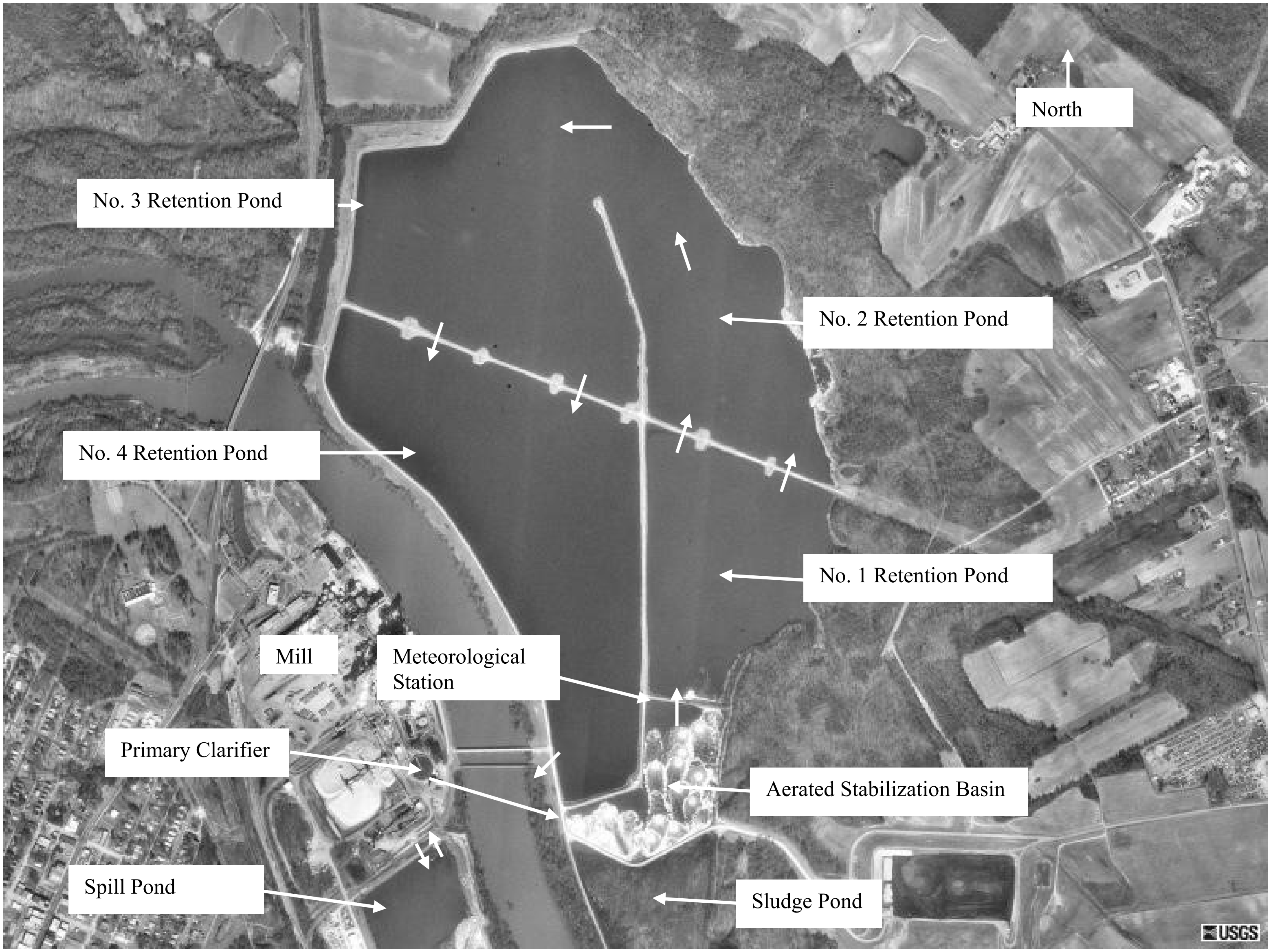

Figure 4.1 Aerial View of the Mill B WWTP

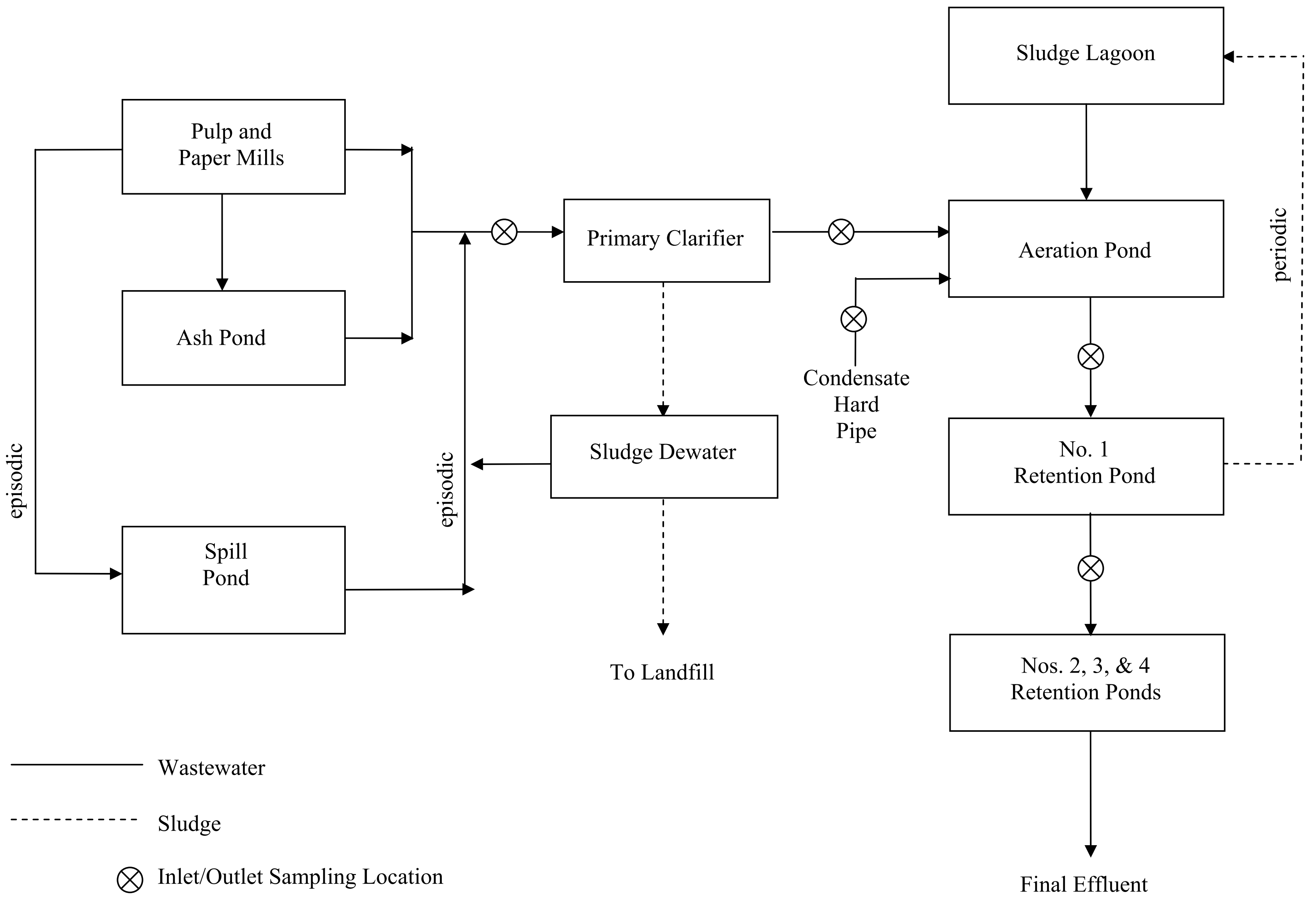

Figure 4.2 Mill B WWTP Flow Diagram

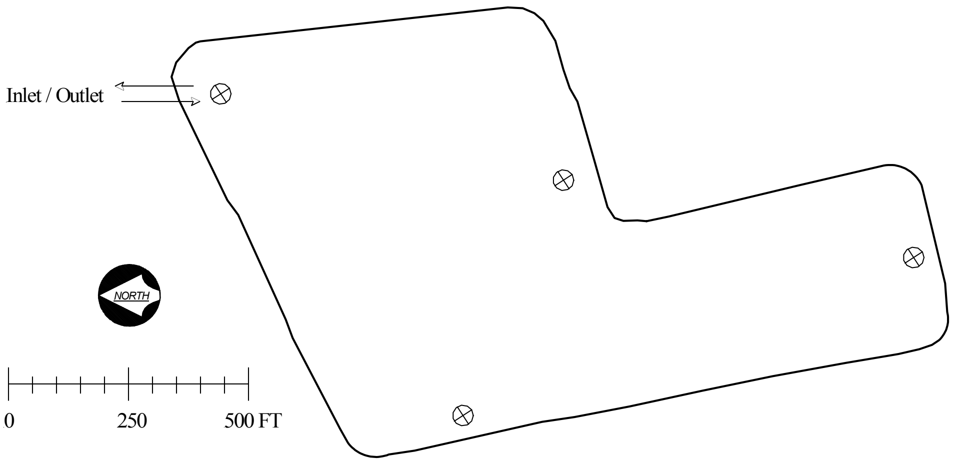

Figure 4.3 Scale Drawing of the Spill Pond with Surface Liquid Sampling Locations, Mill B

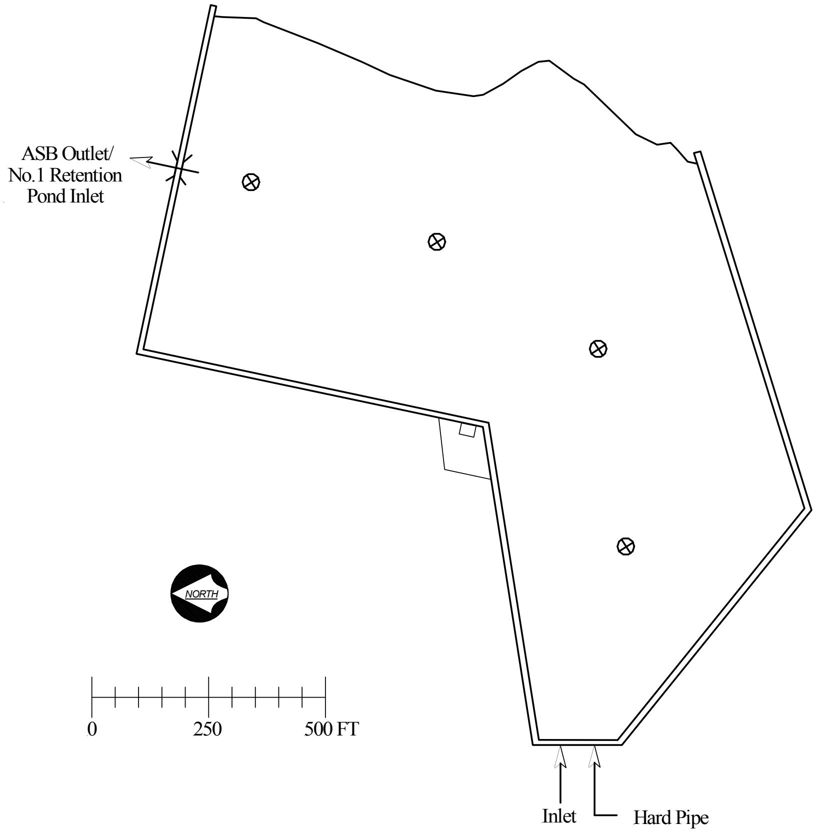

Figure 4.4 Scale Drawing of the ASB with Surface Liquid Sampling Locations, Mill B

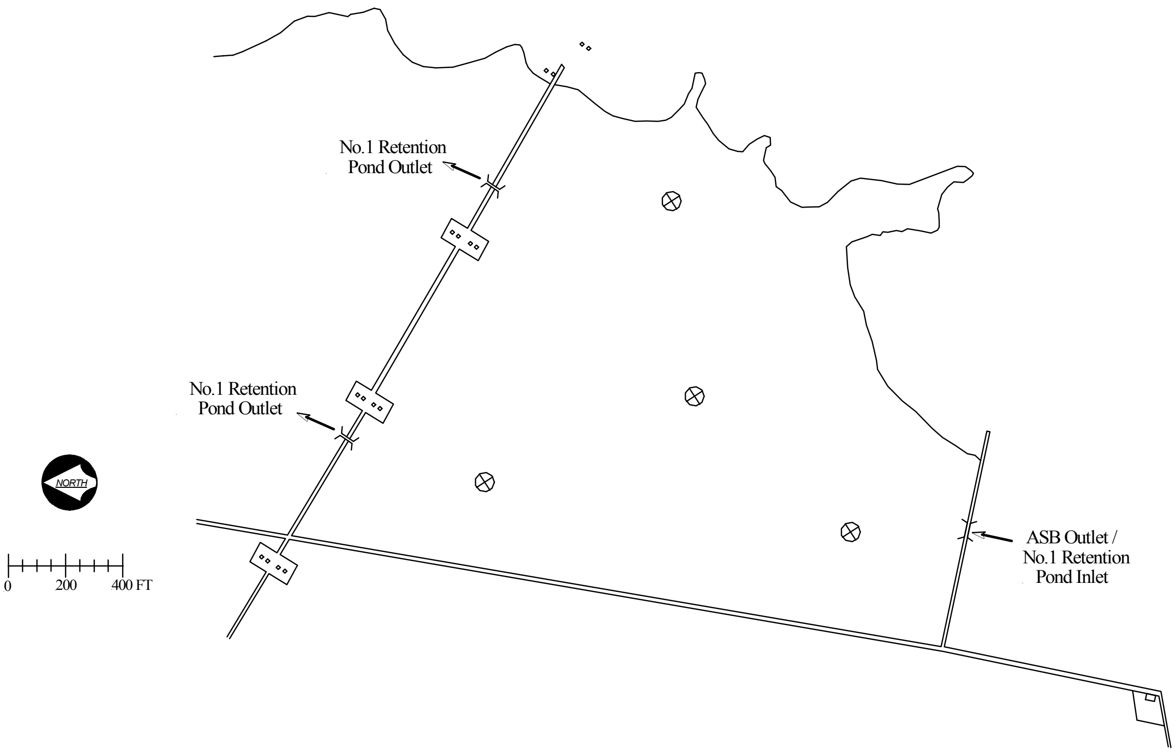

Figure 4.5 Scale Drawing of the No. 1 Retention Pond with Surface Liquid Sampling Locations, Mill B

Table 4.1 Summary Process Operating Parameter Information, Mill B

Date	Pulp Mill Production (midnight to midnight), ODTPD	Main Sewer Flow MGD	Main Sewer BOD**, lb./day	Main Sewer TOC ppm	Bypass to Spill Pond, Minutes (7 am to 7 am)	Spill Pond Level	Clarifier Influent BOD**, ppm	Clarifier Effluent BOD**, ppm	Clarifier Effluent BOD**, lb/day	Clarifier Effluent TOC, ppm	Hard Pipe TOC, ppm
8/16/2005	1015	14.4	21617	92	0	3' 8"	153	67	8022	50	704
8/17/2005	1139	13.8	30212	112	298	4' 2"	229	91	10485	61	777
8/18/2005	1139	13.6	31135	133	87	4' 3"	249	107	12114	75	713
8/19/2005	1026	15.5		92	273	4' 7"	232			64	804
8/20/2005	1072	14.1		76	201	4' 10"	192			71	743
8/21/2005	1102	14.5	18805	71	3	4' 8"	194	93	11271	46	695
8/22/2005	1138	14.4	15612	62	43	4' 6"	314	105	12634	62	673
4/25/2006	1345*	13.5	43460	329	116	3' 2"	143		16134	134	675
4/26/2006	1237*	13.4	29448	205	36	3' 3"	117		13053	133	579

Date	Hard Pipe BOD**, ppm	Hard Pipe Flow, GPD	Hard Pipe BOD**, lb/day	Total BOD to the ASB, lb/day	No. Aerators Running	Total ASB HP	ASB Effluent TSS	ASB Influent BOD*, ppm	ASB Effluent BOD*, ppm	Flow to the River, MGD
8/16/2005	2152	854467	15336	23358	25	1595	84.0	101.0	41.1	0.0
8/17/2005	2368	899143	17757	28242	25	1595	88	180	33.6	0.0
8/18/2005	2216	762850	14099	26212	25	1595	68	263	22.6	14.1
8/19/2005		740246			25	1595	136	275	23.7	14.0
8/20/2005		642340			25	1595				15.0
8/21/2005	2286	837430	15966	27236	25	1595				14.4
8/22/2005	1880	843000	13218	25852	24	1545	96	156	21.6	14.4
4/25/2006	1630	821000	11161	27295	30	NA	128	207	52.4	13.8
4/26/2006	1268	716500	7577	20630	28	NA	148	386	45.3	13.2

*Total Paper Machine Production

**From the 5-Day BOD Test

4.2 Screening Study Results, Mill B

The Jerome H_2S analyzer and canister downwind speciated screening study results for Mill B are summarized in Tables 4.2 and 4.3. The initial screening study data were collected on August 3-5, 2005. Additional screening study data were collected for nos. 1 and 2 retention ponds on August 17, 2005 during the full emissions measurement study with concurrent liquid sample collection. Therefore, only the data collected during the initial screening study were available for planning the full study.

The results of limited work during the initial screening study indicated that the ASB and the spill pond were clearly significant sources of reduced sulfur compound emissions, which was as expected based on an initial analysis of the WWTP configuration and operating practices. Additionally, based on experience gained at other WWTPs, it was decided to add the primary clarifier to the full study plans without any screening work. Therefore, the bulk of the initial screening study work was focused on determining whether or not the four large post-aeration retention ponds were significant sources of reduced sulfur compound emissions.

Examination of the initial screening study data clearly indicated that the nos. 2, 3 and 4 retention ponds were not significant sources of reduced sulfur compound emissions. However, the data indicated that the no. 1 retention pond may have been a significant source of H_2S emissions, so it was included in the full emissions measurement and liquid sample collection study. Because of sludge accumulation in the no. 1 settling pond, the liquid level had to be raised to allow the use of a boat for liquid sample collection. Therefore, the liquid level was raised in the no. 1 retention pond during the approximately 10 day period between the initial screening study and the start of the full emissions measurement and liquid sample collection study. Additional screening study work during the full emissions measurement study, and the results of the full emissions measurement study indicated lower emissions than what were expected based on the initial screening study results. It is not known whether or not the increase in the liquid level was related to lower H_2S emissions from the no. 1 retention pond than what were expected based on the initial screening study results.

The canister screening study results indicated that H_2S accounted for most of the reduced sulfur compound emissions from the spill pond, whereas the organic reduced sulfur compounds accounted for most of the emissions from the ASB.

Table 4.2 Jerome Analyzer Upwind/Downwind Screening Study Results, Mill B

Source	Run No.	Date	Start Time	Stop Time	Avg. Meteorological Cond.* Wind Direction, degrees	Wind Speed, m/s	P-G Atmos. Stability Class	Average Conc., ppbv Upwind	Downwind
ASB	1	8-3-05	13:07	14:34	11	2.74	A	12	92
No. 1 Retention Pond	1	8-3-05	8:40	9:46	341	2.1	D-E	1	10
	2	8-3-05	16:36	17:44	23	3.9	A	5	70
	3	8-4-05	8:27	8:49	1	1.3	D	6	15
	4	8-17-05	9:39	10:40	36	5.4	D-E	11	10
No. 2 Retention Pond	1	8-3-05	8:40	9:46	341	2.1	D-E	5	15
	2	8-3-05	16:36	17:44	23	3.9	A	4	5
	3	8-17-05	9:39	10:40	36	5.4	D-E	8	11
No. 3 Retention Pond	1	8-3-05	8:40	9:46	341	2.1	D-E	5	2
	2	8-3-05	16:36	17:44	23	3.9	A	4	5
No. 4 Retention Pond	1	8-3-05	8:40	9:46	341	2.1	D-E	2	1
	2	8-3-05	16:36	17:44	23	3.9	A	5	6

*Determined from the anemometer at 10 meter height.

Table 4.3 Canister Downwind Speciated Screening Study Results, Mill B

Source	Run No.	Date	Start Time	Stop Time	Avg. Meteorological Cond.* Wind Direction, degrees	Wind Speed, m/s	P-G Atmos. Stability Class	Downwind Concentration, ppbv H_2S	MM	DMS	DMDS
ASB	1	8-3-05	8:27	9:12	332	2.1	C-D	ND[1]	3	4	28
Spill Pond	1	8-3-05	13:13	13:58	9	2.6	A	46	ND[2]	ND[2]	3
No. 1 Retention Pond	1	8-3-05	9:28	10:13	346	1.8	A	11	ND[2]	ND[2]	1
	2	8-3-05	14:20	15:05	357	3.5	B	13	ND[2]	ND[2]	ND[1]
	3	8-17-05	8:43	9:37	29	5.2	D-E	4	ND[2]	ND[2]	ND[1]
	4	8-17-05	9:49	10:42	37	5.7	D-E	4	ND[2]	ND[2]	ND[1]
	5	8-17-05	10:53	11:46	35	3.2	C	4	ND[2]	ND[2]	ND[1]
No. 2 Retention Pond	1	8-3-05	15:18	16:03	7	3.8	A	ND[1]	ND[2]	ND[2]	ND[1]
No. 3 Retention Pond	1	8-3-05	16:11	16:56	16	4.2	A	ND[1]	ND[2]	ND[2]	ND[1]

ND[x] = Not detected at a detection limit of x.

*Determined from the anemometer at 10 meter height.

4.3 Emissions Measurement and Liquid Sampling Results, Mill B

At Mill B emissions testing with associated liquid sampling was conducted at the spill pond, primary clarifier, ASB and the no. 1 retention pond. The emission rates determined from that testing are summarized in Table 4.4. Meteorological and RSC concentration data associated with the emissions tests are summarized in Table 4.5.

As shown in Figure 4.2, liquid sampling was conducted at the primary clarifier inlet, primary clarifier outlet (which was the same as the ASB inlet), ASB outlet (which was the same as no. 1 retention pond inlet), and no. 1 retention pond outlet. Condensates being hard-piped to the ASB were also sampled. The average analysis results for the liquid samples are summarized in Table 4.6. Surface liquid samples (one foot below the surface) were collected from the spill pond, primary clarifier, ASB and no. 1 retention pond. Figure 2.2 is a generic schematic diagram showing the three surface liquid sampling locations for the primary clarifier. The surface liquid sampling locations for the spill pond, ASB and no. 1 retention pond are shown in Figures 4.3 through 4.5.

The average physical/chemical parameter data associated with liquid sample collection are summarized in Table 4.7. At the primary clarifier and ASB, physical/chemical parameter data associated with surface liquid sample collection were obtained at two additional depths, which were one foot above the bottom and midway between the surface and bottom. Due to the shallow nature of the no. 1 retention pond, physical/chemical parameter data associated with liquid sample collection were collected at only one additional depth, which was one foot above the bottom. Physical/chemical parameter data associated with liquid sample collection were only collected at the surface level of the spill pond because it was not accessible via boat.

As shown in Table 4.4, for the spill pond, H_2S emissions averaged 2.7 g/s during the August 2005 tests, and 5.9 g/s during the April 2006 tests. Organic reduced sulfur compound emissions were not detected, except for a small amount of methyl mercaptan (0.01 g/s) during the second test period. The spill pond H_2S emissions from the second test period were over twice what they were during the first test period. The higher emissions from the second test period may be related to higher horizontal wind velocities. The average wind velocity at an elevation of 10 meters was 2.7 m/s for the first test period and 5.0 m/s for the second test period. Wind velocity is expected to have a significant effect on emissions from quiescent basins (USEPA 1994). The average level of total sulfide in the pond was also higher during the second tests (29 mg/L versus 24 mg/L). However, the pH during the second test was 8.8 compared to 8.0 during the first test period. The methane emissions from the spill pond averaged 2.7 g/s for the first test period, and 0.4 g/s during the second test period. There are two known possible reasons for the reduced methane emissions from the spill pond during the second test period: 1) accumulated sludge near the inlet/outlet was dredged from the spill pond shortly before the second test period, and 2) the liquid temperature was much lower during the second test period (22°C versus 32°C during the first test period).

At the primary clarifier, emissions of the organic reduced sulfur compounds were not detected, except for a small DMS emission rate of 0.001 g/s during the first test period, and a small DMDS emission rate of 0.0004 g/s during the second test period. The average H_2S emission rate for the first test period was 0.014 g/s, whereas it was 0.060 g/s for the second test period. Liquid total sulfide concentration was the parameter that was most different between the two test periods, and most likely to have been related to the higher H_2S emissions during the second test period. The average surface liquid total sulfide concentrations in the clarifier were 0.7 mg/L and 8.2 mg/L for the first and second test periods, respectively. The average total sulfide concentrations in the primary clarifier inlet samples (0.8 mg/L and 6.9 mg/L for the first and second test periods, respectively) indicate that most of the total sulfide in the primary clarifier originates from input with the wastewater rather than in-clarifier anaerobic generation. The pH of the effluent in the clarifier was 9.7 during the first test and 10.2 during the second test. Methane emissions were similar for both test periods, with average emission rates of 0.02 g/s for both test periods. In Table 4.8, the methane emissions from the primary clarifier are tabulated along with the measured BOD and TOC removals or gains across the clarifier. Variability in BOD and TOC removal or gains measured across the clarifier may be related to differences between the two methods in the way the solid material, which is removed during clarification, is handled in the inlet samples. For example, fiber, which may lead to oxygen consumption during the 5-day BOD test, would not be included as part of the organic carbon-containing material in the TOC test.

Emissions from the ASB were only measured during the first test period. Since process condensates which also contain significant levels of organic reduced sulfur compounds were being hard-piped directly to the front of the ASB, there were significant emissions of organic reduced sulfur compounds. The average rates of emissions of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide were 0.3, 0.9 0.2 and 0.7 g/s, respectively. The physical/chemical parameter data in Table 4.7 indicate that dissolved oxygen was present in the ASB; therefore, significant anaerobic activity would not be expected. It was not possible to quantify the methane emissions from the ASB because of upwind methane emissions from the no. 1 retention pond.

Table 4.9 shows the results of a material balance conducted at the ASB to calculate the apparent destruction or generation of the reduced sulfur compounds in the ASB. Most of the total sulfide and essentially all of the organic reduced sulfur compounds that entered the ASB with the liquid inputs originated from the hard-piped condensates. The results of the material balance indicate an apparent destruction of 94% of the sulfide entering the ASB with the liquid inputs. Thus, only 6% of the total sulfide entering the ASB with the liquid inputs was emitted to the atmosphere as H_2S. Only 14% of the DMS entering the ASB with the liquid inputs was apparently destroyed; therefore, most (86%) of the DMS was emitted to the atmosphere. Most of the methyl mercaptan entering the ASB (60%) was apparently destroyed. However, the material balance for DMDS indicates generation that was 320% of the amount entering the ASB with the liquid inputs. This can be explained by the oxidation of methyl mercaptan to DMDS, which is one of the primary oxidation reactions for methyl mercaptan (Morrison and Boyd 1973). Also included in Table 4.8 is a material balance for the sum of methyl mercaptan and DMDS as sulfur. The results of this material balance indicate that 35% of the sum of the methyl mercaptan and DMDS (as sulfur) entering the ASB was apparently destroyed in the ASB.

Emissions from the no. 1 retention pond were only measured during the first test period. No significant emissions of the organic reduced sulfur compounds were detected at the no. 1 retention pond. The average H_2S emissions were 0.04 g/s. The average liquid total sulfide concentrations were 25 μg/L at the inlet, 93 μg/L in the pond, and 41 μg/L at the outlet. Therefore, the indications are that most of the sulfide in pond, which resulted in the H_2S emissions, was anaerobically generated, rather than entering with the liquid input. The average methane emissions were 2.0 g/s. In Table 4.8, the methane emissions from the no. 1 retention pond are tabulated along with the measured TOC gain across the pond. The increase in the amount of TOC as the wastewater flows through the pond may be due to 1) the formation of water soluble carbon-containing compounds from biological degradation of the settled secondary sludge and/or 2) fixation of atmospheric carbon dioxide via photosynthetic or other biological means in this large, shallow basin.

Table 4.4 Summary of Emission Rates for Mill B

	Run		Emissions, g/s				
Source	No.	Date	H_2S	MeSH	DMS	DMDS	CH4
ASB	1	8/17/2005	5.20E-01	1.26E+00	2.74E-01	2.34E-01	NA
	2	8/17/2005	1.64E-01	7.81E-01	2.14E-01	1.43E+00	NA
	3	8/17/2005	1.31E-01	8.05E-01	2.24E-01	4.84E-01	NA
	Avg.		2.72E-01	9.49E-01	2.37E-01	7.16E-01	NA
No. 1 Retention Pond	1	8/18/2005	5.83E-02	ND[1.61E-01]	ND[1.54E-01]	ND[1.58E-01]	2.12E+00
	2	8/18/2005	1.77E-02	ND[3.82E-02]	ND[3.66E-02]	ND[3.74E-02]	1.53E+00
	3	8/19/2005	4.12E-02	ND[3.28E-02]	ND[3.14E-02]	ND[3.21E-02]	2.41E+00
	Avg.		3.91E-02	ND[3.28E-02]	ND[3.14E-02]	ND[3.21E-02]	2.02E+00
Spill Pond	1	8/19/2005	2.47E+00	ND[3.63E-02]	ND[3.48E-02]	ND[3.55E-02]	2.30E+00
	2	8/19/2005	2.51E+00	ND[2.57E-02]	ND[2.46E-02]	ND[2.52E-02]	1.90E+00
	3	8/20/2005	2.88E+00	ND[3.70E-02]	ND[3.55E-02]	ND[3.62E-02]	2.90E+00
	4	8/20/2005	3.08E+00	ND[2.30E-02]	ND[2.21E-02]	ND[2.25E-02]	3.77E+00
	Avg.		2.74E+00	ND[2.30E-02]	ND[2.21E-02]	ND[2.25E-02]	2.72E+00
	5	4/26/2006	6.74E+00	1.58E-02	ND[2.01E-02]	ND[6.41E-03]	4.52E-01
	6	4/26/2006	7.46E+00	1.16E-02	ND[1.87E-02]	ND[5.97E-03]	3.58E-01
	7	4/26/2006	3.52E+00	1.07E-02	ND[1.59E-02]	ND[5.98E-03]	3.13E-01
	Avg.		5.91E+00	1.27E-02	ND[1.59E-02]	ND[5.97E-03]	3.74E-01
Primary Clarifier	1	8/21/2005	9.58E-03	ND[9.24E-04]	ND[8.84E-04]	ND[9.04E-04]	3.19E-03
	2	8/21/2005	9.23E-03	ND[8.09E-04]	ND[7.74E-04]	ND[7.91E-04]	9.25E-03
	3	8/21/2005	2.61E-02	ND[1.88E-03]	2.08E-03	ND[1.84E-03]	3.51E-02
	4	8/21/2005	1.21E-02	ND[7.13E-04]	7.94E-04	ND[6.98E-04]	2.14E-02
	Avg.		1.43E-02	ND[7.13E-04]	9.26E-04	ND[6.98E-04]	1.72E-02
	5	4/25/2006	1.04E-01	ND[2.42E-04]	ND[7.01E-04]	3.54E-04	1.03E-02
	6	4/25/2006	4.36E-02	ND[2.73E-04]	ND[8.36E-04]	3.35E-04	3.80E-02
	7	4/25/2006	3.20E-02	ND[2.84E-04]	ND[6.52E-04]	3.70E-04	2.36E-02
	Avg.		5.99E-02	ND[2.42E-04]	ND[6.52E-04]	3.53E-04	2.40E-02

NA = not available

ND[xxxx] = the estimated maximum emission rate calculated from non-detect ambient air concentration data using the procedures outlined in Section 2.3.3.

Table 4.5 Meteorological and Concentration Summary Data for Emission Tests, Mill B

Source	Run No.	Date	Horizontal Wind Direction*, degrees	Horizontal Wind Velocity*, m/s	P-G Stability Class*	Integrated Downwind Ground-Level Concentration**, ppbv			
						H_2S	MM	DMS	DMDS
Aeration Pond	1	8/17/2005	29	5.22	D-E	42.67	73.05	12.34	6.94
	2	8/17/2005	37	5.69	D-E	15.97	53.79	11.44	50.25
	3	8/17/2005	35	3.23	C	12.13	52.82	11.41	16.25
No. 1 Retention Pond	1	8/18/2005	103	1.94	A	1.18	[2.32]	[1.72]	[1.16]
	2	8/18/2005	142	2.59	A	1.54	[2.36]	[1.75]	[1.18]
	3	8/19/2005	153	1.73	A-B	4.13	[2.33]	[1.73]	[1.17]
Spill Pond	1	8/19/2005	226	3.02	B-C	223.50	[2.33]	[1.73]	[1.17]
	2	8/19/2005	237	2.63	B-C	322.48	[2.34]	[1.74]	[1.17]
	3	8/20/2005	286	2.45	A	255.49	[2.33]	[1.73]	[1.16]
	4	8/20/2005	271	2.83	A	439.41	[2.33]	[1.73]	[1.16]
	5	4/26/2006	38	6.09	D	436.50	0.73	[0.71]	[0.15]
	6	4/26/2006	25	5.14	D	526.04	0.58	[0.72]	[0.15]
	7	4/26/2006	54	3.9	C - D	287.34	0.62	[0.71]	[0.15]
Primary Clarifier	1	8/21/2005	291	2.38	C	34.15	[2.33]	[1.73]	[1.17]
	2	8/21/2005	286	2.41	C	37.65	[2.34]	[1.73]	[1.17]
	3	8/21/2005	312	2.59	C	45.47	[2.32]	1.98	[1.16]
	4	8/21/2005	310	2.38	C	55.65	[2.32]	2.00	[1.16]
	5	4/25/2006	245	4.15	C	181.62	[0.30]	[0.67]	0.22
	6	4/25/2006	238	3.46	C	67.83	[0.30]	[0.72]	0.19
	7	4/25/2006	212	3.18	C	53.60	[0.34]	[0.60]	0.22

[x.xx] = Not detected at a detection limit of x.xx.
*Determined from the anemometer at 10 meter height.
**Determined via the procedures outlined in Section 2.3.3.

Table 4.6 Average Liquid Sample Concentrations, Mill B

Location	Date	Sulfide Ion, mg/L	Total Sulfide, µg S/L	MM, µg S/L	DMS, µg S/L	DMDS, µg S/L	DMTS, µg S/L	Sulfate, mg S/L	Thio-Sulfate, mg S/L	TOC, mg C/L	TOC Filtered, mg C/L
Spill Pond*	8/19-20/05	>100	23925	179	19.0	ND[10.8]	ND[11.5]	185	ND[1.4]	NA	NA
	4/26/06	>100	29025	131	ND[10.5]	ND[10.0]	ND[10.9]	140	ND[0.7]	NA	NA
Primary Clarifier Inlet	8/16-21/05	4.1**	802	NA	20.0	58.2	17.7	122	ND[1.4]	98.8	NA
	4/25/06	70	6930	NA	16	30.1	ND[10.9]	189	6.2	398	NA
Primary Clarifier *	8/21/05	1	699	NA	19.6	ND[10.8]	ND[11.5]	133	ND[1.4]	NA	NA
	4/25/06	60	8152	NA	ND[10.5]	19.9	ND[10.9]	185	6.1	NA	NA
Primary Clarifier Outlet	8/16-21/05	2.0**	511	NA	23.9	23.7	ND[11.5]	151	ND[1.4]	111	89.4
	4/25/06	33	5265	NA	ND[10.5]	ND[10.0]	ND[10.9]	202	5.1	269	NA
Condensate Hard Pipe	8/16-19/05	>94**	102825	46769	3895	2598	374	144	ND[1.4]	778	741
Aeration Pond*	8-17-05	ND[0.5]	70.6	27.2	22.7	38.0	13.8	164	ND[1.4]	NA	NA
Aeration Pond Outlet	8/16-19/05	ND[0.5]**	24.8	24.8	17.9	25.3	ND[11.5]	164	ND[1.4]	66.9	50.4
No. 1 Retention Pond*	8/18-19/05	ND[0.5]	92.8	65.3	ND[9.5]	18.7	18.1	163	ND[1.4]	NA	NA
No. 1 Retention Pond Outlet	8/16-19/05	ND[0.5]	41.3	13.4	ND[9.5]	13.7	ND[11.5]	167	ND[1.4]	71.7	54.4

* Average of Three to Four Surface Liquid Sampling Locations

NA = Not Available

ND[xxx] = non-detect with xxx equal to one-half of the lowest calibration limit

**Includes values for samples not analyzed via total sulfide method, so the average values are not directly comparable.

>xxx indicates that one or more of the sulfide ion detection tube readings were greater than 100

Table 4.7 Average Physical/Chemical Parameter Measurement Data Associated with Liquid Sample Collection, Mill B

Location	Date	Depth, ft	Temp., °C	Specific Conductance, mS/cm	DO, mg/l	pH
Spill Pond*	8/19-20/05	1	31.9	NA	NA	8.0
	4/26/06	1	21.9	NA	NA	8.8
Primary Clarifier Inlet	8/16-21/05	1	46.5	1.62	1.45	9.7
	4/25/06	1	43.4	NA	NA	10.2
Primary Clarifier *	8/21/05	1	47.0	1.54	0.25	9.0
		6-9	46.6	1.58	0.13	9.0
		12-17	45.9	1.73	0.14	7.5
	4/25/06	1	43.9	1.42	0.10	10.1
		6-9	43.3	1.38	0.08	9.8
		12-17	42.6	1.39	0.08	8.8
Primary Clarifier Outlet	8/16-21/05	NA	42.6	1.66	0.88	7.9
	4/25/06	NA	41.7	NA	NA	8.7
Condensate Hard Pipe	8/16-19/05	NA	56.5	0.58	1.16	7.1
Aeration Pond*	8-17-05	1	39.7	1.90	0.32	7.5
		4-6	39.0	1.92	0.35	7.4
		7-12	38.7	1.93	0.56	7.3
Aeration Pond Outlet	8/16-19/05	1	37.7	1.88	1.47	7.4
No. 1 Retention Pond*	8/18-19/05	1	NA	NA	0.22	NA
		3	30.0	1.80	0.14	7.0
No. 1 Retention Pond Outlet	8/16-19/05	1	31.5	1.88	0.23	7.3

* Average of three to four liquid sampling locations

Table 4.8 Methane Emissions and the BOD and TOC Liquid Material Balances at Mill B

Source	Date	Parameter	Inlet, g/s	Outlet, g/s	Removal or (Gain), g/s	Methane Emissions, g/s
Primary Clarifier	8/21/2005	BOD	142.1	68.1	74.0	1.72E-02
Primary Clarifier	8/21/2005	TOC	68.5	78.0	(9.5)	1.72E-02
Primary Clarifier	4/25/2006	TOC	274.2	185.3	88.9	2.40E-02
No. 1 Ret. Pond	8/16-19/2005	TOC	49.0	52.5	(3.5)	2.02E+00

(xx) indicates gain in the liquid parameter between the inlet and outlet
*From the 5-day BOD test

Table 4.9 Apparent Destruction or (Generation) of RSC Compounds in the Mill B ASB

Compound	Influent Main, Sewer g/s	Influent Cond. Hard Pipe, g/s	Total Influent, g/s	Effluent, g/s	Air Emissions, g/s	Apparent Destruction or (Generation), %
H_2S	0.6*	4.2*	4.8*	0.0*	0.3	94
DMS	0.0	0.3	0.3	0.0	0.2	14
MM	0.0	2.4	2.4	0.0	0.9	60
DMDS	0.0	0.2	0.2	0.0	0.7	(320)
MM + DMDS (as S)	0.0	1.7	1.7	0.0	1.1	35

*total sulfide as H_2S

5.0 SOURCE DESCRIPTION AND RESULTS OF TESTS AT MILL D

Tests were conducted at Mill D during two separate time periods. The results obtained from testing during both of the periods are detailed in the Mill D Test Report (NCASI 2008d). The first study was only a screening study conducted on March 11-13, 2005. The second study, conducted on May 10-15, 2005, included emissions measurement testing and the associated liquid sampling.

5.1 Wastewater Treatment Plant Description, Mill D

The kraft pulp mill has a production capacity of approximately 363,000 tons per year of bleached softwood kraft pulp. This facility has a single pulping line with one continuous digester. The single bleach plant uses O_2 delignification. All pulp produced at this facility is market pulp and is processed on a single air float dryer. This facility utilizes a steam stripper to comply with MACT I requirements. Condensates are not hard-piped to the ASB.

The wastewater treatment plant at Mill D is comprised of a primary clarifier and a series of earthen ponds, as shown in Figure 5.1. Figure 5.2 diagrams the flow sequence and approximate flow rates through the WWTP. The alkaline mill sewer is routed to the 250 ft. diameter primary clarifier. Effluent from the primary clarifier enters the mix channel where it combines with the acid sewer and two minor streams consisting of the landfill leachate and the solids dewatering flow from the screw press. A Parshall flume is used to continuously measure flow in the mix channel. For the sampling period, the alkaline sewer flow averaged 64% of the mix channel flow, and the acid sewer flow averaged 36% of the mix channel flow. The mix channel flow, which is the influent to the no. 1 ASB, was approximately 15 MGD.

The no. 1 ASB has an area of 46.6 acres and is curtained into four cells in series. Installed surface aeration in the no. 1 ASB totals 1275 horsepower. During the test period, approximately 80% of the aerators were operated at partial load as part of an energy saving measure. Operating horsepower in the no. 1 ASB averaged 737 hp during the test period. Figure 5.3 is a scale drawing of the no. 1 ASB, on which the four surface liquid sampling locations are marked.

Effluent from the no. 1 ASB flows over a weir into the 41.5-acre aeration no. 2 ASB. The no. 2 ASB is divided into two serial zones by means of an earthen dike. Installed surface aeration on the no. 2 ASB totals 350 horsepower. During the test period, an average 200 hp was used.

At the beginning of the second zone in the no. 2 ASB, approximately 8 MGD of wastewater is recirculated back to the no. 1 ASB. Thus, the total wastewater flow through the no. 1 ASB is approximately 23 MGD. The recirculated flow enters the no. 1 ASB in the same general vicinity as the influent.

Wastewater exits the no. 2 ASB over a weir and enters the 80.8-acre retention pond at a flow rate of approximately 15 MGD. The retention pond is divided into four zones by two earthen dikes. Flow is parallel in the first two zones and serial in the last two zones. During times of high water, the second dike is short-circuited. Effluent from the retention pond enters the effluent canal before final discharge to the river. The discharge canal has 80 horsepower of surface aeration and a side-stream oxygenation system.

Summarized mill and WWTP process operating information is contained in Table 5.1.

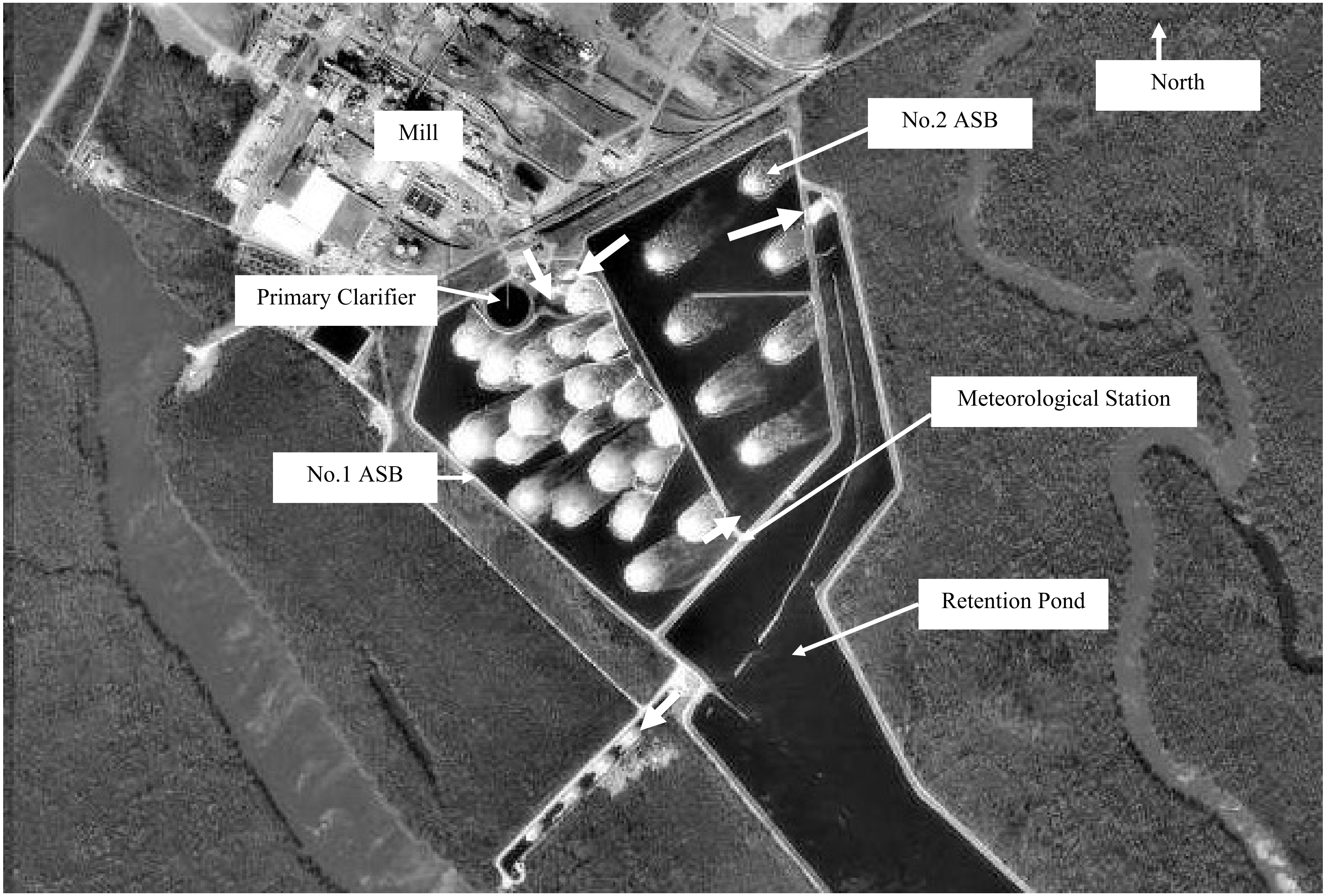

Figure 5.1 Aerial View of the Mill D WWTP

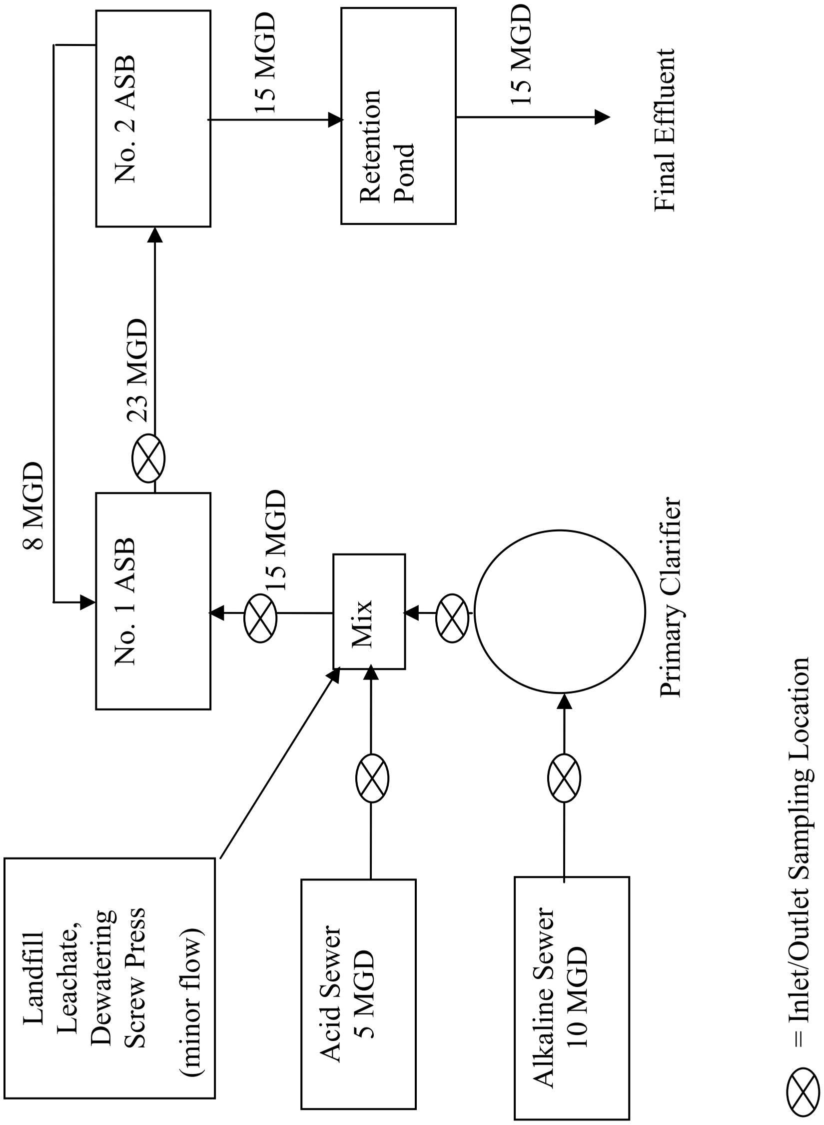

Figure 5.2 WWTP Flow Diagram, Mill D

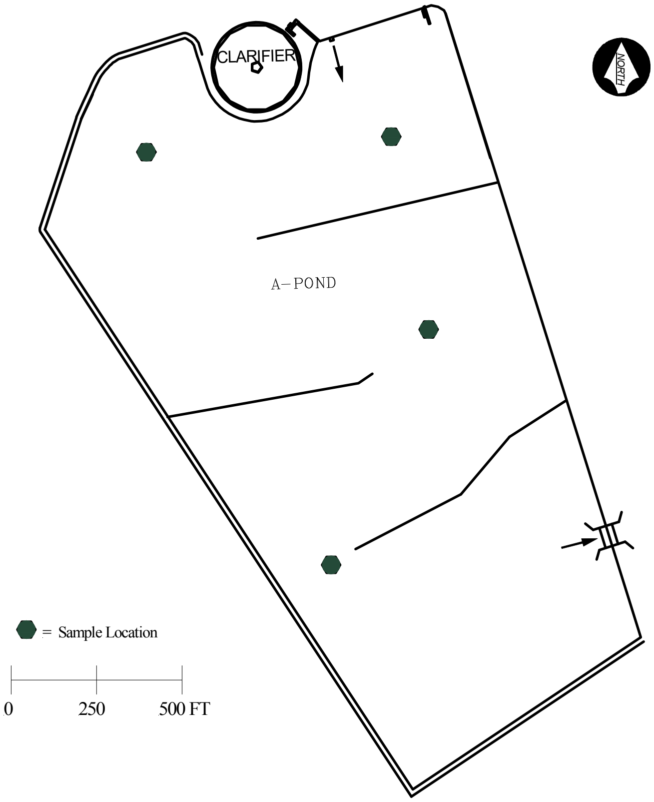

Figure 5.3 Surface Liquid Sampling Locations for the No. 1 ASB at Mill D

Table 5.1 Summary Process Operating Information, Mill D

Date	Pulp Production Rate, ADTPD	Alkaline Sewer Flow, MGD	Acid Sewer Flow, MGD	Combined Sewer Flow, MGD	No. 1 ASB Influent BOD*, mg/L	No. 1 ASB Influent TSS, mg/L	No. 1 ASB Effluent BOD*, mg/L	No. 1 ASB Effluent TSS, mg/L
5/10/2005	1055	9.4	4.8	14.2	258	15	48	32
5/11/2005	853	9.9	5.1	15.0	261	29	51	34
5/12/2005	752	10.0	5.2	15.2	237	28	50	34
5/13/2005	994	9.9	5.1	15.0	235	26	45	35
5/14/2005	1056	9.9	5.1	15.0	NA	NA	NA	NA
5/15/2005	1056	10.3	5.3	15.6	NA	NA	NA	NA

NA = Not Available
*From the 5-day BOD test

5.2 Screening Study Results, Mill D

The Jerome H_2S analyzer screening study results for Mill D are summarized in Table 5.2. These results indicate that the significant sources of reduced sulfur compound emissions are the primary clarifier and no. 1 ASB. The no. 2 ASB and the post-aeration retention pond were not significant emitters of reduced sulfur compounds. No canister sampling was carried out during the screening study.

Table 5.2 Jerome Analyzer Upwind/Downwind Screening Study Results, Mill D

Source	Run No.	Date	Start Time	Stop Time	Avg. Meteorological Cond.*			Average Conc., ppbv	
					Wind Direction, degrees	Wind Speed, m/s	P-G Atmos. Stability Class	Upwind	Downwind
Primary Clarifier	1	3-12-05	13:32	13:56	268	8.0	B	13	164
No. 1 ASB	1	3-12-05	15:51	17:10	255	7.4	C-D	3	20
	2	3-13-05	8:47	9:49	105	3.4	B	2	20
	3	3-13-05	10:36	11:39	159	2.7	A	5	31
No. 2 ASB	1	3-12-05	15:51	17:10	255	7.4	C-D	20	5
	2	3-13-05	8:47	9:49	105	3.4	B	3	3
	3	3-13-05	10:36	11:39	159	2.7	A	3	5
Retention Pond	1	3-12-05	14:12	14:56	267	8.6	B	3	4
	2	3-13-05	8:47	9:49	105	3.4	B	NA	3
	3	3-13-05	10:36	11:39	159	2.7	A	NA	3

*Determined from the anemometer at 10 meter height.

5.3 Emissions Measurement and Liquid Sampling Results, Mill D

At Mill D, emission testing with associated liquid sampling was conducted at the primary clarifier, no. 1 ASB and the acid sewer vent. The emission rates determined from that testing are summarized in Table 5.3. Meteorological and RSC concentration data associated with the emissions tests are summarized in Table 5.4.

As shown on Figure 5.2, liquid sampling was conducted at the primary clarifier inlet and outlet, acid sewer, and the no. 1 ASB inlet and outlet. Surface liquid samples (one foot below the surface) were collected from the primary clarifier and the no. 1 ASB. Figure 2.2 is a schematic diagram showing the three surface liquid sampling locations for primary clarifiers. The surface liquid sampling locations for the no. 1 ASB are shown in Figure 5.3. The results of liquid sample analyses are summarized in Table 5.5. The values in Table 5.5 represent the average values of multiple samples.

The values of the average physical/chemical parameter data associated with liquid sample collection are summarized in Table 5.6. At the primary clarifier and the no. 1 ASB, physical/chemical parameter data associated with surface liquid sample collection were obtained at two additional depths, which were one foot above the bottom and midway between the surface and bottom.

For the five test runs on the primary clarifier, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide emissions averaged 0.05, 0.02, 0.01, and 0.1 g/s, respectively. All four of these compounds were also detected at significant levels in all of the liquid samples associated with the primary clarifier, despite the fact that Mill D utilizes a condensate steam stripper. Methane emissions from the clarifier averaged 0.2 g/s. In Table 5.7, the methane emissions from the primary clarifier are tabulated along with the measured TOC removal across the clarifier.

For the 11 test runs on the no. 1 ASB, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide emissions averaged 0.6, 0.4, 0.2 and 0.3 g/s, respectively. Methane emissions averaged 1.5 g/s. The sample path used for test run nos. 2 through 6 included emissions from the primary clarifier; therefore, the average measured primary clarifier emissions were subtracted from the measured total emissions to calculate the no. 1 ASB emissions for those runs. This approach is reasonable since the primary clarifier emissions are relatively small in comparison to the no. 1 ASB emissions.

In Table 5.8, the liquid material balances for the reduced sulfur compounds in the no. 1 ASB are compared to the measured emissions of those compounds. This comparison shows that most of the reduced sulfur compound air emissions from the no. 1 ASB were not accounted for in the liquid material balance, which is simply the RSC mass input associated with the influent minus the RSC mass output associated with the effluent. Therefore, this indicates that all four of the reduced sulfur compounds were being anaerobically generated in the no. 1 ASB. Inspection of the liquid sample data in Tables 5.5 and 5.6 supports the hypothesis of anaerobic RSC generation in the no. 1 ASB. The concentration data in Table 5.5 shows relatively steady RSC concentrations from zone 1 through the no. 1 ASB outlet. This is in contrast to the other ASBs in this study where RSC compound destruction, rather than generation, was indicated from the material balances, and in which the liquid RSC concentrations diminished rapidly in the ASBs to the point that they were generally non-detect at the outlet. Also, the dissolved oxygen data in Table 5.6 indicates very low levels at all three depths in all four zones. Other studies have shown that all four of the reduced sulfur compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) can be generated in settled anaerobic sludge/soil layers (Devai and DeLaune 1995; Higgins et al. 2002).

The methane emissions from the ASB are tabulated along with the BOD and TOC removal rates in Table 5.9.

Flow and concentration data for the acid sewer vent are summarized in Table 5.10. The acid sewer vent is a 10 inch diameter fiberglass stack, which is approximately 15 feet tall, attached to a hood over the area where the acid sewer transitions from a closed pipe to an open ditch. The bottom of the hood is open to the atmosphere on the side over the ditch. There is no fan on this vent. Due to low gaseous flow rates and low concentrations, the emissions of H_2S, MM, DMS and DMDS were very low, with average emission rates of 2E-04, 3E-05, 1E-06, and 6E-05 g/s, respectively.

Table 5.3 Summary of Emission Rates for Mill D

	Run		Emissions, g/s				
Source	No.	Date	H_2S	MeSH	DMS	DMDS	CH_4
Primary Clarifier	1	5/12/2005	4.18E-02	2.70E-02	1.18E-02	1.25E-01	1.28E-01
	2	5/12/2005	6.57E-02	3.59E-02	1.33E-02	1.58E-01	3.18E-01
	3	5/12/2005	2.12E-02	1.13E-02	6.76E-03	1.09E-01	1.26E-01
	4	5/12/2005	7.13E-02	1.16E-02	8.06E-03	5.47E-02	1.13E-01
	5	5/12/2005	4.45E-02	1.36E-02	7.48E-03	8.88E-02	8.80E-02
	Avg.		4.89E-02	1.99E-02	9.48E-03	1.07E-01	1.55E-01
No. 1 ASB	1	5/11/2005	5.06E-01	3.19E-01	1.85E-01	5.36E-01	6.78E-01
	2	5/13/2005	8.49E-02	1.34E-01	6.90E-02	5.30E-02	NA
	3	5/13/2005	7.28E-01	3.19E-01	1.62E-01	2.33E-01	NA
	4	5/13/2005	1.05E+00	3.68E-01	1.96E-01	2.77E-01	NA
	5	5/13/2005	1.21E+00	7.47E-01	3.77E-01	6.28E-01	NA
	6	5/13/2005	5.84E-01	5.14E-01	2.43E-01	1.62E-01	NA
	7	5/14/2005	2.40E-01	5.97E-01	3.08E-01	5.21E-01	NA
	8	5/14/2005	6.40E-01	3.12E-01	2.49E-01	2.31E-01	1.62E+00
	9	5/14/2005	5.25E-01	2.58E-01	2.16E-01	2.80E-01	1.45E+00
	10	5/14/2005	6.24E-01	3.13E-01	1.92E-01	1.25E-01	2.85E+00
	11	5/14/2005	4.24E-01	2.46E-01	1.32E-01	1.10E-01	2.92E+00
	Avg.		6.01E-01	3.75E-01	2.16E-01	2.87E-01	1.90E+00
Acid Sewer Vent		5/15/2005	2.51E-05	3.78E-05	1.52E-06	6.95E-05	NA
		5/15/2005	2.63E-04	1.98E-05	1.17E-06	2.61E-05	NA
		5/15/2005	2.33E-04	3.30E-05	1.70E-06	9.55E-05	NA
	Avg.		1.74E-04	3.02E-05	1.46E-06	6.37E-05	NA

NA = not available

Table 5.4 Meteorological and Concentration Summary Data for Emissions Tests at Mill D

Source	Run No.	Date	Horizontal Wind Direction*, degrees	Horizontal Wind Velocity*, m/s	P-G Stability Class*	Integrated Downwind Ground-Level Concentration**, ppbv H_2S	MM	DMS	DMDS
Primary Clarifier	1	5/12/2005	258	3.27	C-D	45.50	20.81	7.06	49.09
	2	5/12/2005	286	3.59	C	39.40	15.28	4.37	34.23
	3	5/12/2005	284	3.33	C-D	27.58	10.37	4.83	51.28
	4	5/12/2005	293	3.63	D-E	95.33	10.97	5.92	26.47
	5	5/12/2005	285	3.50	D-E	53.69	11.59	4.95	38.79
No. 1 ASB	1	5/11/2005	159	1.25	A	13.08	5.32	2.39	4.57
	2	5/13/2005	29	3.85	A	11.54	9.76	3.85	5.30
	3	5/13/2005	48	3.48	A	37.70	11.76	4.62	6.08
	4	5/13/2005	50	3.37	A	57.86	14.69	6.01	7.48
	5	5/13/2005	50	4.26	A	24.61	10.69	4.17	5.25
	6	5/13/2005	57	4.41	A-B	36.47	22.04	8.07	5.74
	7	5/14/2005	185	3.50	B-C	26.79	11.34	4.53	5.05
	8	5/14/2005	204	3.87	A	77.06	10.09	6.24	3.82
	9	5/14/2005	223	3.73	A	45.34	7.61	4.94	4.24
	10	5/14/2005	217	3.56	A	59.37	6.94	3.29	1.42
	11	5/14/2005	191	3.18	B-C	58.34	9.17	3.82	2.10

*Determined from the anemometer at 10 meter height.

**Determined via the procedures outlined in Section 2.3.3.

Table 5.5 Average Liquid Sample Concentrations, Mill D

Location	Date	Sulfide Ion, mg/L	Total Sulfide, µg S/L	MM, µg S/L	DMS, µg S/L	DMDS, µg S/L	DMTS, µg S/L	Sulfate, mg S/L	Thio-Sulfate, mg S/L	TOC, mg C/L	Nitrate mg/L
Primary Clarifier Inlet	5/10-14/05	1.3	1030	52.6	36.2	838	20.5	153	ND[1.4]	239	NA
Primary Clarifier*	5/12/05	1.8	1349	117	48.7	535	125	170	ND[1.4]	NA	NA
Primary Clarifier Outlet	5/10-14/05	0.7	587	83.6	33.7	432	92.4	159	ND[1.4]	213	NA
Acid Sewer	5/10-14/05	NA	1260	217	19.3	164	12.6	305	ND[1.4]	NA	NA
No. 1 ASB Inlet	5/10-14/05	0.5	409	134	42.5	222	46.3	267	ND[1.4]	267	0.48
No. 1 ASB, Zone 1	5/10,11,14/05	ND[0.5]	110	47.3	32.7	58.3	20.8	307	ND[1.4]	142	0.08
No. 1 ASB, Zone 2	5/10,11,14/05	ND[0.5]	148	48.8	30.5	26.4	ND[11.5]	310	ND[1.4]	132	0.02
No. 1 ASB, Zone 3	5/10,11,14/05	ND[0.5]	152	47.4	24.4	29.9	ND[11.5]	286	ND[1.4]	NA	NA
No. 1 ASB, Zone 4	5/10,11,14/05	ND[0.5]	161	43.8	23.8	21.6	ND[11.5]	279	ND[1.4]	NA	NA
No. 1 ASB Outlet	5/10-14/05	ND[0.5]	296	51.2	29.4	13.2	ND[11.5]	281	ND[1.4]	118	NA

* Average of three surface liquid sampling locations

NA = Not Available

ND[xxx] = non-detect with xxx equal to one-half of the lowest calibration limit

Table 5.6 Average Physical/Chemical Parameter Measurement Data Associated with Liquid Sample Collection, Mill D

Location	Depth, ft	Temp., °C	Specific Conductance, mS/cm	DO, mg/L	pH
Primary Clarifier Inlet	1	55.7	1.65	1.42	9.0
Primary Clarifier*	1	52.9	1.75	1.14	9.0
	6	50.9	1.70	0.10	8.5
	11	50.1	1.66	0.10	8.1
Primary Clarifier Outlet	1	50.8	1.52	2.43	8.1
Acid Sewer	1	56.5	2.93	2.27	2.6
No. 1 ASB Inlet	1	52.0	1.88	3.94	4.3
No. 1 ASB, Zone 1	1	36.1	1.93	0.23	6.4
	6 - 7	34.3	1.93	0.23	6.6
	10 - 13	33.5	1.92	0.23	6.7
No. 1 ASB, Zone 2	1	34.4	1.94	0.24	6.6
	6 - 7	33.7	1.94	0.21	6.6
	10 - 13	32.9	1.88	0.20	6.7
No. 1 ASB, Zone 3	1	33.0	1.91	0.22	6.7
	6 - 7	31.9	1.91	0.19	6.7
	10 - 13	31.1	1.88	0.18	6.8
No. 1 ASB, Zone 4	1	32.0	1.91	0.22	6.7
	6 - 7	31.1	1.91	0.19	6.7
	10 - 13	30.1	1.90	0.19	6.8
No. 1 ASB Outlet	1	30.7	1.90	0.29	6.7

*Average of Three Surface Liquid Sampling Locations
NA = Not Available
ND[xxx] = non-detect with xxx equal to one-half of the lowest calibration limit

Table 5.7 Methane Emissions and the TOC Liquid Material Balance for the Primary Clarifier at Mill D

Date	Inlet, g C/s	Outlet, g C/s	Removal, g C/s	Methane Emissions, g/s
5/12/2005	106.6	95.7	11.0	0.155

Table 5.8 Apparent Generation of RSC Compounds in the Mill D No. 1 ASB

Compound	Influent, g/s	Effluent, g/s	Liquid Balance, g/s	Air Emissions, g/s	Apparent Generation Rate g/s	Apparent Generation Rate as % of Input, %
H_2S	0.28*	0.21*	0.08	0.58	0.50	178
DMS	0.05	0.04	0.02	0.21	0.20	363
MM	0.13	0.05	0.08	0.37	0.29	221
DMDS	0.21	0.01	0.20	0.29	0.09	42
MM + DMDS (as S)	0.23	0.04	0.19	0.44	0.25	109

*total sulfide as sulfur

Table 5.9 ASB BOD and TOC Liquid Material Balance and Methane Emissions, Mill D

Parameter	Liquid Balance*	Units	Methane Emissions, g/s
TOC	94.3*	g C/s	1.90
BOD**	123.6***	g/s	1.90

*Inlet-outlet during the period of emissions testing
**From the 5-day BOD test.
***Inlet-outlet for the 60 day period prior to emissions testing

Table 5.10 Flow and Concentration Summary for the Acid Sewer Vent, Mill D

Run No.	Temp., °F	Moisture, %	Flow, ACFM	Flow, DSCFM	Vent Concentration, ppbv H_2S	MM	DMS	DMDS
1	81	3.6	239	221	164	175	5	164
2	83	3.8	251	234	1617	86	4	58
3	85	4.1	256	237	1412	141	6	209

6.0 SOURCE DESCRIPTION AND RESULTS OF TESTS AT MILL E

Testing was conducted at the Mill E wastewater treatment plant during four separate time periods. The first two periods were considered the Phase I Study. The third period was considered the Phase II Study, and the fourth period was considered the Phase III Study. In this report, the results of the Phase I, II, and III Studies are presented. The results of the Phase I study are detailed in one test report (NCASI 2008e), whereas the results of the Phase II Study are detailed in another test report (NCASI 2008f). Details of the Phase III study not discussed in this section are contained in the Phase III Study test report (NCASI 2008g). In Phase I, a screening study was conducted with data collection on March 9 and 10, 2005, and emissions measurement testing with the associated liquid sample collection program was conducted on April 12 - 19, 2005. In Phases II and III, additional emissions measurement testing with the associated liquid sample collection program were conducted on February 28 – March 2, 2006, and June 18-20, 2007, respectively.

6.1 Wastewater Treatment Plant Description, Mill E

The kraft pulp mill at Mill E has a total permitted, unbleached pulp production capacity of approximately 748,000 oven dry tons per year, of which approximately 60% is softwood and 40% is hardwood. Bleached pulp yields from unbleached production range between 95 and 96%. There are two pulping lines with two continuous digesters. The bleach plants associated with the two pulping lines both use O_2 delignification.

A recycled fiber facility was operated at Mill E until February 12, 2006. It was operating during the screening study and first test period (March and April 2005), but not during the second and third test periods. The recycled fiber facility produced approximately 1000 tons per day of pulp from old corrugated containers (OCC). One paper machine was also shut down when the recycled fiber facility ceased operations. These changes resulted in less primary sludge generation, so the primary sludge dewatering plant operation was reduced from continuous to only the morning and evening shifts (16 hr/day) on Monday through Friday.

The paper mill at Mill E currently produces approximately 470,000 air-dried tons per year of bleached paper, and approximately 160,000 air-dried metric tons per year of fluff pulp. Two of three operating paper machines at this facility produce uncoated free-sheet (fine paper), and one machine produces fluff pulp.

The wastewater treatment plant at Mill E is comprised of a series of earthen ponds and basins, as shown in Figure 6.1. Figure 6.2 schematically diagrams the flow sequence through the WWTP during the Phase I and II periods. Figure 6.3 shows the flow sequence for the Phase III test period. Inlet/outlet liquid sampling locations are also shown on Figures 6.2 and 6.3. Primary treatment is effected through the routing of wastewater through two serpentine settling ponds. The no. 1 settling pond has a surface area of 21.1 acres, and the no. 2 settling pond has a surface area of 32.0 acres. As shown in Figure 6.2, during the Phase I and II test periods effluent from the bleach plants, power and recovery, and papermaking areas flowed to the inlet of the no. 1 settling pond at a rate of approximately 32 MGD during Phase I and 28 MGD during the Phase II. As shown in Figure 6.3, during the Phase III test period, effluent from the bleach plants, power and recovery, and papermaking areas bypassed the no. 1 settling pond and flowed to the inlet of the no. 2 settling pond at a flow rate of approximately 30 MGD. Additionally, a minor stream of wastewater from secondary sludge dewatering and leachate from the landfilled secondary sludge enters near the end of the no. 1 settling pond at a flow rate of less than 1 MGD. As shown in Figures 6.2 and 6.3, during the Phase I test period combined effluent from primary sludge dewatering and the OCC fiber recycling facility flowed to the inlet of the no. 2 settling pond at an estimated rate of less than 1 MGD. Between the Phase I and II test periods, the OCC recycling facility was shut down; therefore, during the Phase II and III test periods this minor stream flowing to the inlet of the no. 2 settling pond only contained effluent from primary sludge dewatering. Effluent from the fiberlines, with a flow rate of approximately 8 MGD, entered the no. 2 settling pond at a point approximately halfway through the pond.

The effluent from the nos. 1 and/or 2 settling ponds is combined and flows to the ASB via an open canal which contains a Parshall flume. At the end of the open canal is the no. 2 lift station from which the wastewater is pumped into the ASB. Figure 6.1 shows the location of the flume area within the WWTP. As shown in Figures 6.2 and 6.3, flow, which averaged approximately 41 MGD during the Phase I test period, and 37 MGD during the Phase II and II tests periods, was pumped to the approximately 72-acre aeration basin, which is curtained into three cells in series. During the Phase I and II test periods, surface aeration totaled 3250 horsepower with 750 HP in zone 1, 1400 HP in zone 2, and 1100 HP in zone 3. During the Phase III test period, surface aeration totaled 2250 horsepower with the 800 HP in zone 1, 800 HP in zone 2, and 650 HP in zone 3.

Wastewater flows from the ASB to the 36-acre no. 1 retention pond, and then through the serpentine 282-acre no. 2 retention pond. Following the no. 2 retention pond, the wastewater flows through a polishing canal with additional installed aeration before it is discharged to the river.

Summarized mill and WWTP process operating information is contained in Table 6.1. Figure 6.4 shows the flow configuration and the in-basin liquid sampling locations for the no. 1 settling pond during the Phase I and II test periods. Figures 6.5 and 6.7 show the flow configurations and in-basin liquid sampling locations used during the Phase I and II test periods for the no. 2 settling pond and ASB, respectively. Figures 6.6 and 6.8 are similar representations for the Phase III test period. As shown in Figure 6.6, during the Phase III test period, large portions of the no. 2 settling pond were covered by a hard, dry layer of fibrous material which originated from the fiberline sewer.

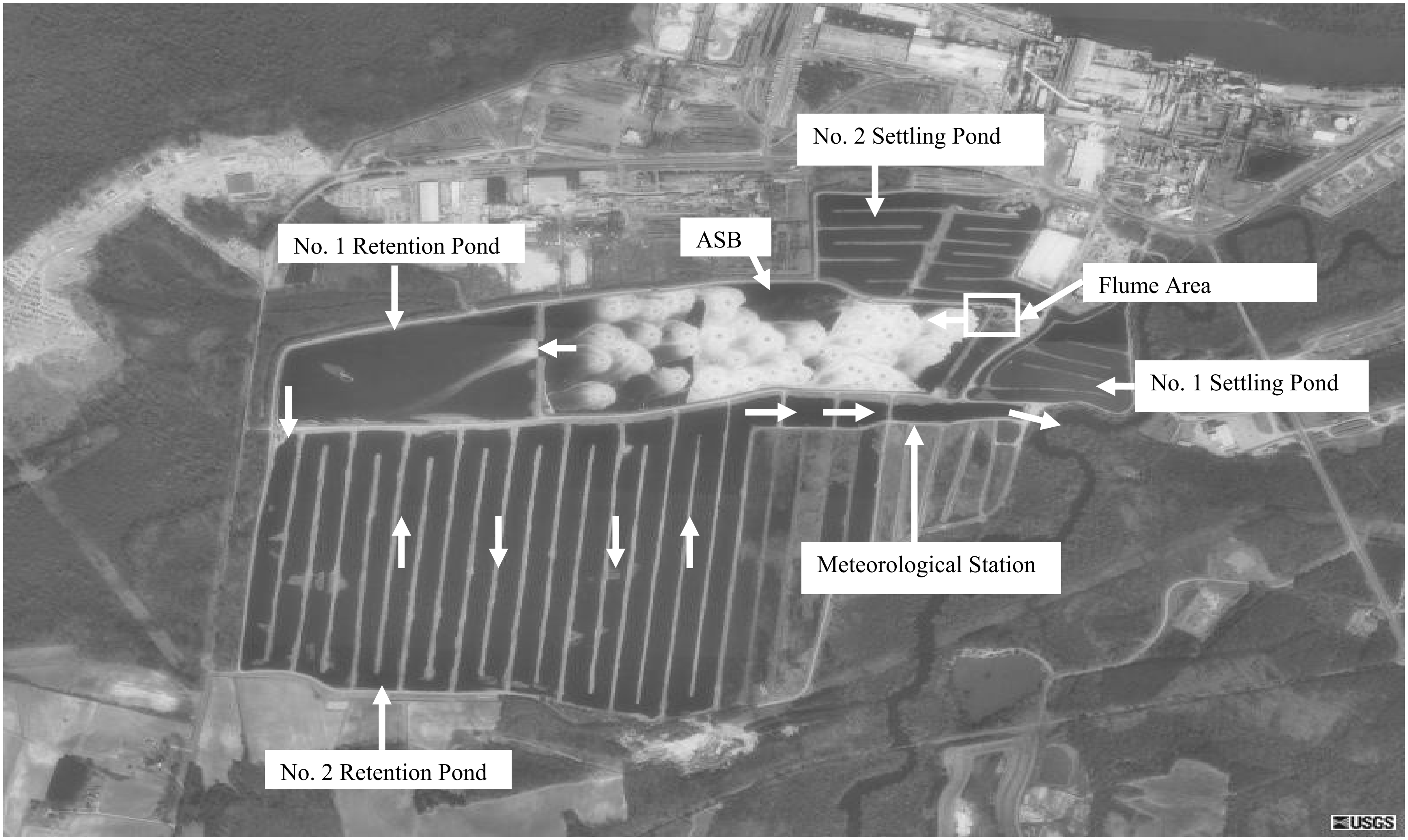

Figure 6.1 Aerial View of the Mill E WWTP

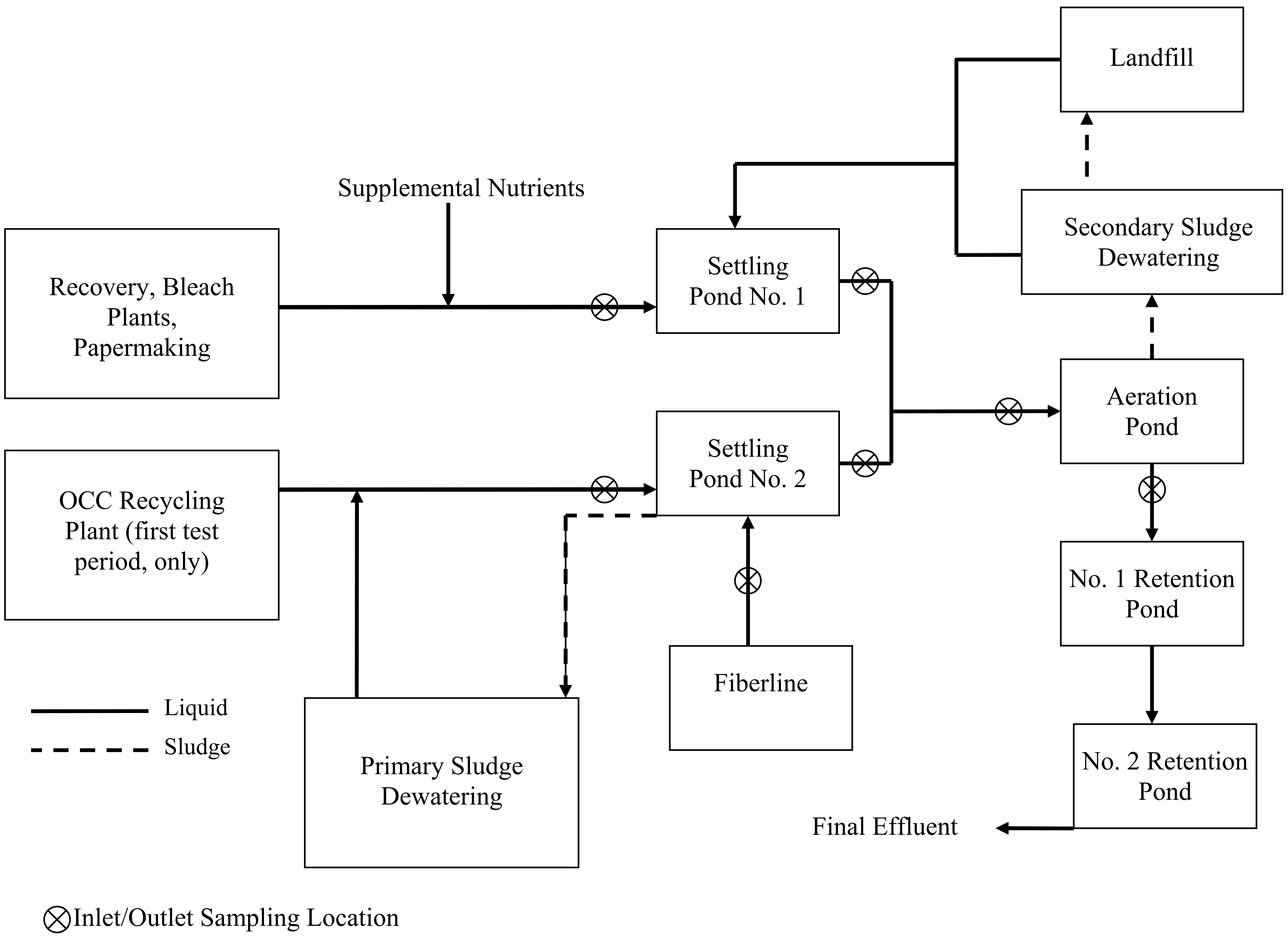

Figure 6.2 Phase I and II WWTP Flow Diagram, Mill E

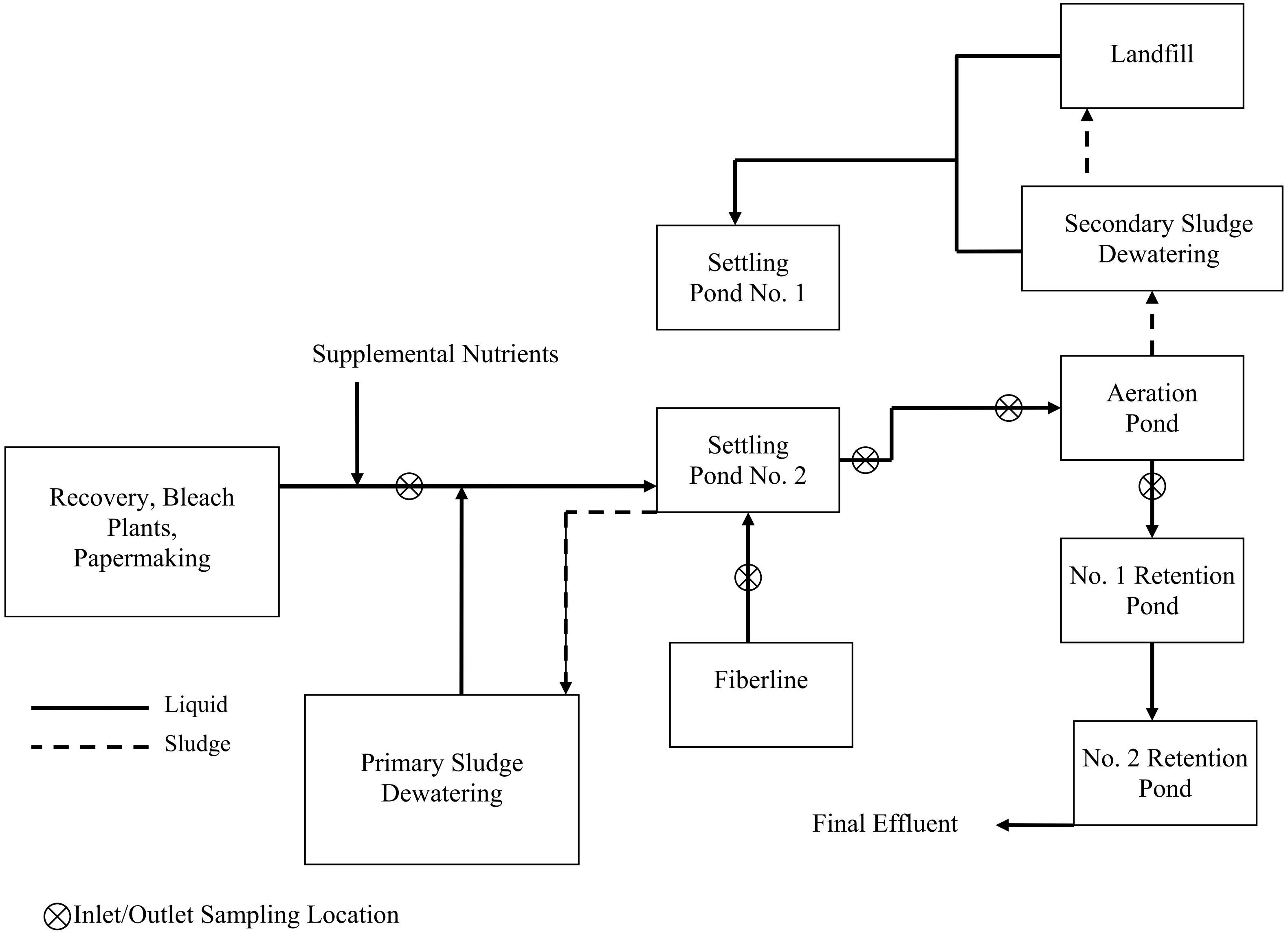

Figure 6.3 Phase III WWTP Flow Diagram, Mill E

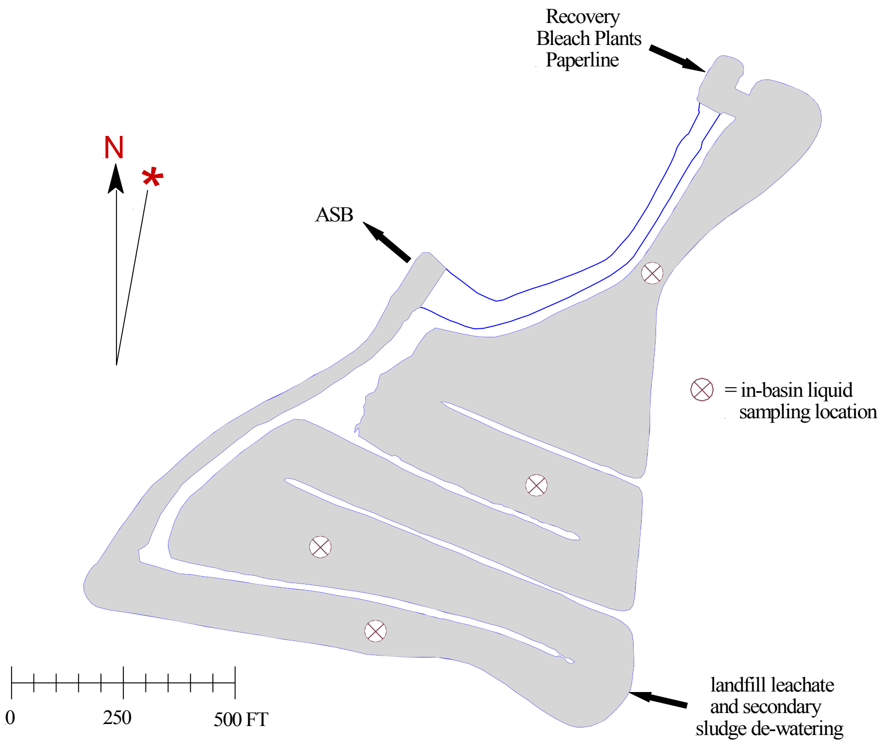

Figure 6.4 In-Basin Liquid Sampling Locations for the No. 1 Settling Pond at Mill E

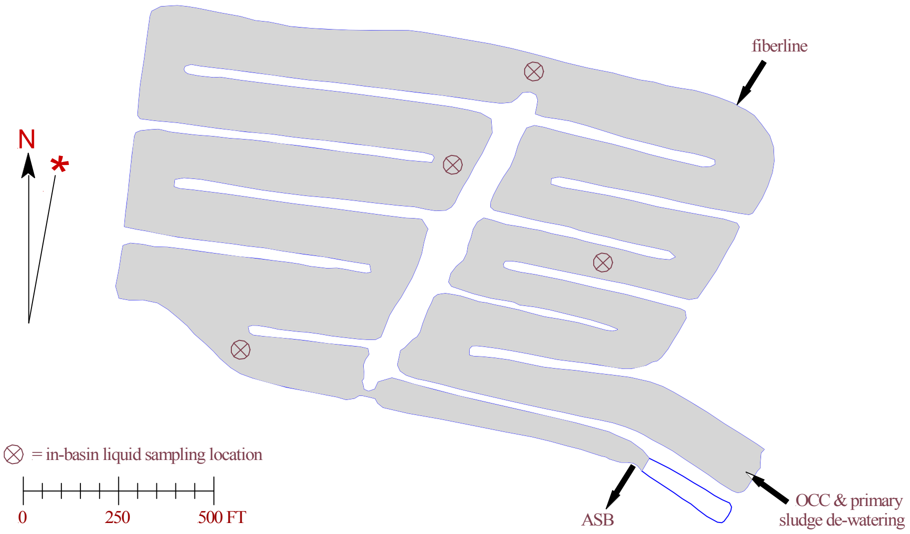

Figure 6.5 Phase I and II In-Basin Surface Liquid Sampling Locations for the No. 2 Settling Pond at Mill E

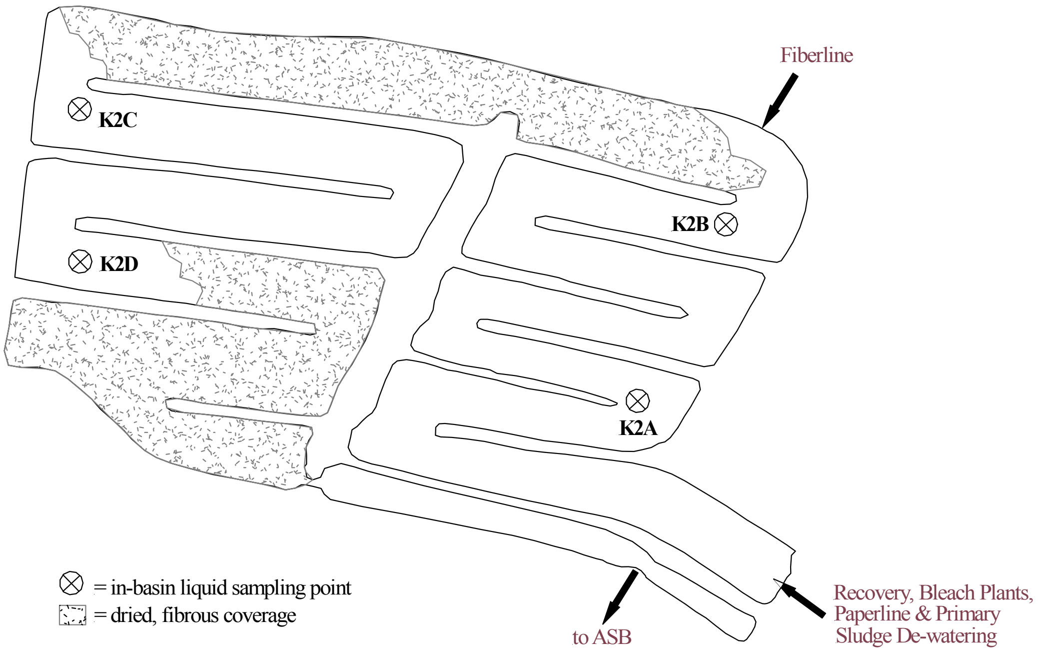

Figure 6.6 Phase III In-Basin Liquid Sampling Locations and Approximate Sludge Coverage on the No. 2 Settling Pond at Mill E

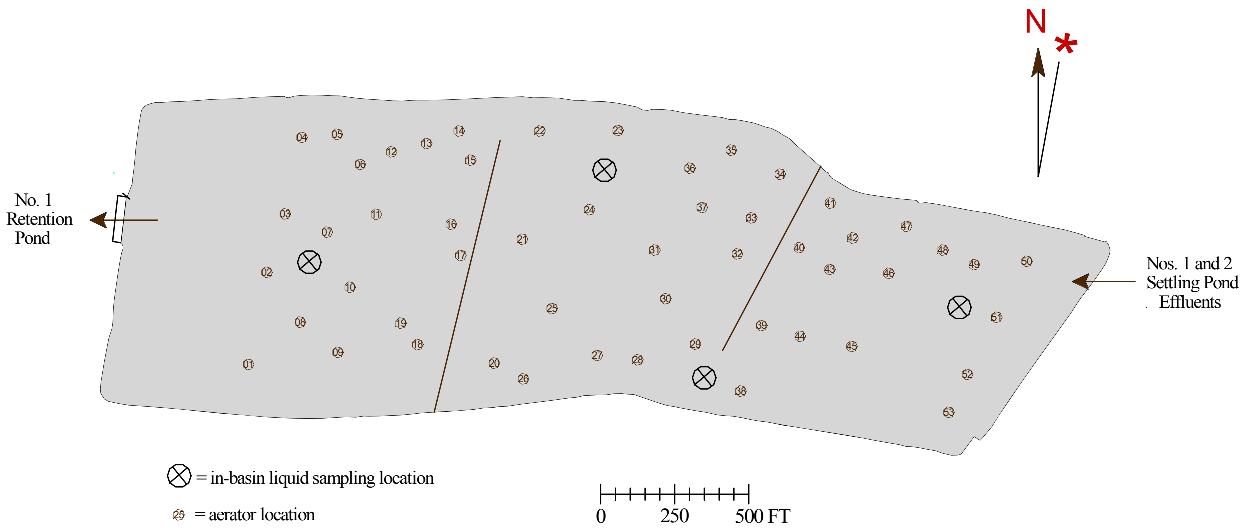

Figure 6.7 Phase I and II In-Basin Surface Liquid Sampling Locations for the ASB at Mill E

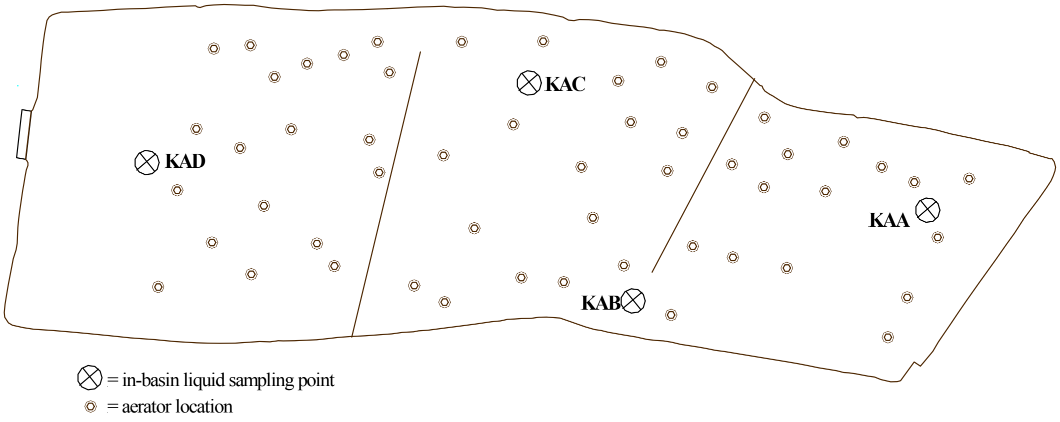

Figure 6.8 Phase III In-Basin Liquid Sampling Locations for the ASB at Mill E

Table 6.1 Summary Process Operating Information, Mill E

Source	Parameter	4/12-19/2005			3/7/06	3/8/06	3/9/06	6/19/07	6/20/07
		Average*	Min.	Max.					
Mill	Pulp Production, UBODT/day	1604	1346	1677	1443	1308	1353	1394	1400
No. 1 Settling Pond	Influent Flow, MGD	33	32	35	29	29	28	0	0
	Influent BOD**, mg/L	349	264	558	291	297	226	NA	NA
	Influent TSS, mg/L	563	327	1054	741	1058	939	NA	NA
No. 2 Settling Pond	Influent Flow, MGD	1	1	1	1	1	1	30	30
	Fiberline Flow, MGD	8	8	8	8	8	8	8	8
	Fiberline BOD**, mg/L	201	121	276	397	320	283	505	470
	Fiberline TSS, mg/L	233	143	331	664	550	452	-	-
ASB	Influent Flow, MGD	41	40	43	37	38	36	38	38
	Influent BOD**, mg/l	337	276	548	313	261	291	180	180
	Influent TSS, mg/L	46	30	63	231	289	244	-	-
	Influent DO, mg/L	0.6	0.4	1.3	0.3	0.2	0.2	0.4	0.2
	Effluent BOD**, mg/L	64	52	93	90	104	76	-	-
	Effluent TSS, mg/L	61	30	96	35	165	32	-	-
Effluent to River	BOD**, mg/L	28	23	33	35	31	21	-	-
	TSS, mg/L	15	13	20	20	23	15	-	-
	DO, mg/L	4.4	1.8	5.4	3.2	5.2	4.4	-	-

*Calculated from daily averages
NA = Not Applicable
**From the 5-day BOD test.

6.2 Screening Study Results, Mill E

Two screening studies, one during March 9-10, 2005 and the other during April 7-18, 2005, were carried out at Mill E. The studies utilized the Jerome H_2S analyzer and canisters downwind sampling. The results of these tests are summarized in Tables 6.2 and 6.3. These results indicate that the significant sources of reduced sulfur compound emissions were the nos. 1 and 2 settling ponds and the ASB. The canister results show that H_2S was the only reduced sulfur compound with significant emissions from these basins. Additionally, both the Jerome H_2S analyzer and canister results indicate that the nos. 1 and 2 post-aeration retention ponds were not significant emitters of reduced sulfur compounds.

Table 6.2 Jerome Analyzer Upwind/Downwind Screening Study Results, Mill E

Source	Run No.	Date	Start Time	Stop Time	Avg. Meteorological Cond.** Wind Direction, degrees	Wind Speed, m/s	P-G Atmos. Stability Class	Average Conc., ppbv Upwind	Downwind
No. 1 Settling Pond	1	3-10-05	7:57	8:20	71	4.0	C	58	195
	2	3-10-05	8:26	8:48	74	2.8	C	11	144
	9	6-20-07	9:20	9:39	266	3.3	C	NA	385*
No. 2 Settling Pond	1	3-9-05	13:25	13:56	266	5.1	C-D	4	31
	2	3-9-05	14:18	14:50	270	5.4	C-D	2	25
	3	3-10-05	11:16	11:39	343	3.0	C	3	28
	9	6-19-07	8:00	9:00	260	2.3	C-D	NA	182*
	10	6-20-07	7:55	8:30	226	3.3	C-D	NA	214*
ASB	1	3-9-05	15:29	16:10	277	5.2	D	3	38
	2	3-10-05	14:49	15:17	268	4.1	C	11	80
	3	3-10-05	15:21	15:47	257	4.3	C	6	40
	7	6-19-07	8:00	9:00	260	2.3	C-D	NA	100*
No. 1 Retention Pond	1	3-9-05	10:32	10:59	300	5.5	D	2	3
	2	4-17-05	10:48	11:16	39	4.7	C	4	4
No. 2 Retention Pond	1	4-17-05	13:40	14:08	80	4.0	C	13	6

NA = not available

*These concentration values were determined from pseudo-integration across the width of the linear sample path perpendicular to the wind direction, rather than from a straight average calculation. This procedure is described in Section 6.3

**Determined from the anemometer at 10 meter height.

Table 6.3 Canister Downwind Speciated Screening Study Results, Mill E

					Avg. Meteorological Cond.*			Downwind Concentration, ppbv			
Source	Run No.	Date	Start Time	Stop Time	Wind Direction, degrees	Wind Speed, m/s	P-G Atmos. Stability Class	H_2S	MM	DMS	DMDS
No. 1 Settling Pond	1	3-10-05	7:57	8:48	72	3.4	C	342	ND[2]	ND[2]	ND[1]
No. 2 Settling Pond	1	3-9-05	14:18	14:50	286	5.4	D	9	ND[2]	ND[2]	3
ASB	1	3-10-05	13:42	14:27	291	4.1	C	337	ND[2]	ND[2]	ND[1]
	2	3-10-05	14:32	15:17	275	3.8	C	264	ND[2]	ND[2]	ND[1]
No. 2 Retention Pond	1	4-18-05	8:03	9:00	237	3.4	E	ND[1]	ND[2]	ND[2]	ND[1]
	2	4-18-05	9:15	10:10	225	2.7	D	ND[1]	ND[2]	ND[2]	ND[1]
	3	4-18-05	13:44	14:49	232	3.0	A	ND[1]	ND[2]	ND[2]	ND[1]
	4	4-18-05	15:35	16:36	242	2.6	A	ND[1]	ND[2]	ND[2]	ND[1]
	5	4-19-05	7:51	8:43	219	2.3	E	ND[1]	ND[2]	ND[2]	ND[1]
	6	4-19-05	8:55	9:46	241	1.4	A	ND[1]	ND[2]	ND[2]	ND[1]
	7	3-9-06	8:11	9:09	213	4.8	D	ND[1]	ND[2]	ND[2]	ND[1]
	8	3-9-06	9:20	10:16	231	5.9	E	ND[1]	ND[2]	ND[2]	ND[1]
	9	3-9-06	10:34	11:37	219	6.3	C	ND[1]	ND[2]	ND[2]	ND[1]

ND[x] = Not detected at a detection limit of x

*Determined from the anemometer at 10 meter height.

6.3 Emissions Measurement and Liquid Sampling Results, Mill E

Following the screening study at Mill E, air emissions testing and associated liquid sampling were conducted in three phases at the no. 1 and no. 2 settling ponds, the ASB, and the flume and canal area between the settling ponds and ASB.

For the Phase III study, which was conducted on June 19 and 20 of 2007, Jerome analyzer ground-level H_2S concentration measurements were made with the intention of using that data to estimate emission rates. The information required to calculate a source emission rate from the spatial ambient air sampling technique used in this study includes meteorological data, geographical data, horizontally integrated ground-level concentrations and horizontally integrated vertical concentration profile data. The meteorological data and geographical data were obtained from a portable meteorological station and a site plan in a fashion similar to what was used for all of the other emission rate calculations in this study. The following discussion describes the manner by which estimates were obtained for the horizontal and vertical concentration profiles so that emission rates could be calculated for the Phase III study.

Although the Jerome analyzer did not directly provide horizontally integrated ground-level H_2S concentration data, it did provide enough information to make reasonable estimates. As discussed in Section 2, the Jerome analyzer has been shown to yield accurate, linear responses to H_2S challenge gases at the concentration levels found downwind of kraft mill WWTPs (NCASI forthcoming). If other reduced sulfur compounds are present in the ambient air, their presence will result in a positive bias of the Jerome analyzer measurement. However, extensive spatial ambient air and liquid testing for reduced sulfur compound concentrations indicated that H_2S was the only reduced sulfur compound found consistently in the vicinity of this WWTP. Additionally, Jerome analyzer measurements concurrent with collection of canister samples for gas chromatographic analysis at this WWTP in 2006 (NCASI forthcoming) showed very good comparison between the methods for samples collected downwind from all three basins (nos. 1 and 2 settling ponds, and ASB).

The average Jerome responses from the downwind sampling locations were used to estimate the horizontally integrated ground-level downwind concentration. To generate ground-level crosswind path-averaged downwind H_2S concentrations for use as C_o values in the emission rate calculation equation, the measured concentrations were adjusted in the average calculation proportional to their spacing across the crosswind sample path (W). This yields average values similar to what would have been obtained from ground-level integrated canister sampling. These “pseudo-integrated” downwind ground-level concentrations are shown in Table 6.2.

The other requirement for the emission rate calculation is the vertical concentration distribution. Vertical concentration profiles developed from previous testing during this study were examined. The exponent b, which governs the concentration profile, exhibited a very wide range. Values were especially variable for unstable conditions (Pasquill-Gilford categories A and B). If only b values derived for P-G categories C, D, and E were considered, the range was much narrower. For stability classes C, D, and E, there were 51 test runs, for 15 different sources at five WWTPs. For these 51 runs, the b exponent averaged 3.9 with a standard deviation of 1.8. Therefore, a decision was made to use a b exponent of 3.9 in emission rate calculations for the C through E stability classes. Emission rates were also calculated with b exponents plus and minus one standard deviation (2.1 and 5.7) as an indication of the uncertainty in these emission estimates. The bar chart (Figure 6.9) shows the estimated emission rates, for each test run at the three sources, for the three different b values. The computed emission rates are provided in Table 6.4.

The emission rates determined from all three phases are summarized in Table 6.5. Meteorological and RSC concentration data associated with the emissions tests are summarized in Table 6.6.

The liquid sample collection locations at Mill E are shown in Figure 6.2. Samples were collected at the inlet and outlet of the no. 1 settling pond. The no. 2 settling pond had two inlet streams and one outlet stream. The two inlet streams included 1) a stream, with differing composition for each test period, which entered at the beginning of the pond; and 2) effluent from the fiber line sewer, which entered approximately midway through the pond. Samples were collected at all of the settling pond inlet/outlet locations. At the ASB, samples were collected at both the inlet and outlet. Surface liquid samples (one foot below the surface) were collected from four locations in each of the three basins, as shown in Figures 6.3 through 6.5. The results of analysis of these samples are in Tables 6.8 through 6.10. These results are average values for multiple samples.

The average values of the physical/chemical parameter data gathered for the liquid samples collected during the study are summarized in Tables 6.11 through 6.13 for the no. 1 settling pond, no. 2 settling pond and the ASB. Physical/chemical parameter data associated with liquid sample collection were obtained at one or two additional depths, depending on the depth of the pond at the sampling location. The lowest depth was always one foot above the bottom, and, if an intermediate depth was used, then it was always midway between the surface and the bottom.

Emission testing was conducted at the no. 1 settling pond, while it was on line with the main mill sewer flowing through it, on three separate days (April 12, 2005, April 14, 2005 and March 9, 2006). Except for run no. 3 conducted on April 14, 2005, the emissions of all of the organic reduced sulfur compounds were non-detect. In run no. 3, an emission rate of 0.2 g/s was calculated for DMDS. Overall, for all 8 runs, the average methane emissions were 14 g/s, indicating significant anaerobic biological activity. For run nos. 1 and 2 conducted on April 12, 2005, the average H_2S emissions were 1.7 g/s. For run nos. 3, 4 and 5 conducted on April 14, 2005, the average H_2S emissions were 0.53 g/s. For run nos. 6, 7 and 8 conducted on March 9, 2006, the average H_2S emission rate was 3.0 g/s.

Parameters influencing H_2S emission rates include horizontal wind velocity, surface liquid sulfide concentration, pH, and the Henry's Law constant at the prevailing conditions. The average wind velocities measured at 10 meters elevation on April 12, 2005, April 14, 2005 and March 9, 2006 were 3.7 m/s, 6.0 m/s and 7.1 m/s, respectively. Liquid to gas phase mass transfer considerations suggest emissions of H_2S from large, shallow quiescent basins would increase with wind velocity (USEPA 1994). According to Springer, emission rates begin to steeply increase once wind speeds exceed 3.25 m/s at a 10 m height. Based on wind velocity alone, higher emissions would have been expected on April 14, 2005 than on April 12, 2005; however, on 4/14/0 April 14, 2005 the in-basin liquid total sulfide concentration was lower, and the average in-basin pH was higher. Together, these two parameters would cause lower aqueous free H_2S concentrations, implying lower H_2S emissions to the atmosphere. On April 12, 2005, the average in-basin total sulfide concentration and pH values were 3.0 mg/L and 6.74, respectively, whereas on 4/14/05 they were 1.0 mg/L and 7.10, respectively. The concentration difference, as measured by the sulfide ion detector tubes, was even greater with average concentrations of 7.1 mg/L and 1.2 mg/L on April 12, 2005 and 4/14/05, respectively.

H_2S is a weak acid that dissociates in water according to the following formula (Rydholm 1967):

$$H_2S \xrightleftharpoons{pKa=7.0} H^+ + HS^- \xrightleftharpoons{pKa=13.5} H^+ + S^{-2} \qquad \text{(Equation 13)}$$

The total sulfide measurement, as discussed in Section 2, is believed to measure all freely dissolved sulfide (HS^-), plus sulfide that is weakly associated with dissolved organic matter or certain transition metals. Therefore, the in-basin pH must be considered to estimate the concentration of undissociated H_2S in the wastewater. The acid dissociation constants shown above are for H_2S in pure water. Kraft pulp and paper mill wastewater is a very complex aqueous solution of inorganic and organic compounds; thus, the dissociation constants shown above may not provide a means of accurately estimating liquid phase undissociated H_2S concentrations from the total sulfide measurements. However, it is useful interpreting trends in measured data, i.e., increasing the pH will decrease the ratio of H_2S to "total sulfide." Thus, even though the wind velocity was higher on April 14, 2005 than on April 12, 2005, the combination of lower in-basin total sulfide concentration and higher pH could explain the lower emission rate on April 14, 2005.

The highest emissions from the no. 1 settling pond, while it was on line with the main mill sewer flowing through it, were observed on March 9, 2006, in conjunction with the highest wind velocity and highest in-basin liquid phase sulfide concentrations. The average total in-basin sulfide concentration was 57 mg/L, and the average concentration measured by the sulfide ion detector tubes was 73 mg/L. Due to problems in the causticizing area, the average in-basin pH was much higher on March 9, 2006 with a value of 10.4. However, the high wind velocity combined with the high in-basin average total sulfide concentration apparently counteracted the effect of the higher pH.

On June 20, 2007, H_2S emissions from the no. 1 settling pond were estimated as described at the beginning of this section. At that time, the no. 1 settling pond had been off line without any flow through it for almost five months. The H_2S emissions were estimated to be 3.1 g/s. Since there was no input of sulfur to the pond, the emissions must have resulted from anaerobic reduction of sulfate and/or elemental sulfur associated with the water and/or sludge. Oxidized sulfur may have still been present in the pond at the time of sampling because the stagnant pond would have been much cooler in the winter and spring months, so there may not have been much anaerobic activity until it got warmer with the approach of summertime. Additionally, with no flow through the pond, the only significant mechanism for sulfur removal is H_2S emissions to the atmosphere; therefore, it may take a relatively long period of time for all of the sulfur stored in the pond to be removed.

At the no. 2 settling pond, emissions measurements were made on April 14, 2005, April 16, 2005, March 7, 2006, and March 8, 2006 with the pond in the off-line configuration, i.e., with the main mill sewer flowing through the no. 1 settling pond. For the eight emissions test runs at the no. 2 settling pond carried out on April 14, 2005, April 16, 2005, March 7, 2006, and March 8, 2006, except for a DMS emission rate of 0.3 g/s measured during run no. 3, all of the organic reduced sulfur compound results were non-detect. For the five emissions measurements on April 14, 2005 and April 16, 2005, there was no obvious trend in the H_2S emissions measurements, and there were no significant meteorological, in-basin chemical or process differences between these days that would have been expected to result in identifiably different H_2S emissions. The average H_2S emissions for those two days in April 2005 were 3.4 g/s. For the one test run conducted on March 7, 2006, the H_2S emission rate was 0.66 g/s, whereas for the two test runs conducted on March 8, 2006, the H_2S emission rates were 0.26 g/s and 0.20 g/s. The higher H_2S emission rate on March 7, 2006 was most likely due to the higher wind velocity which was 5.5 m/s versus an average of 2.3 m/s on March 8, 2006.

Overall, the no. 2 settling pond average H_2S emission rate measured in March 2006 (0.37 g/s) was much less than the average H_2S emission rate measured in April 2005 (3.4 g/s). As previously discussed in this section, wind velocity is the primary factor most likely to have been related to this difference in emission rates. The average wind velocity was 8.3 m/s for the April 2005 test period versus 3.3 m/s for the March 2006 test period.

During the Phase III study on June 19 and 20, 2007, H_2S emissions from the no. 2 settling pond were estimated as described at the beginning of this section. During the Phase III study period, the no. 2 settling pond was in the on-line configuration, i.e., the main mill sewer was flowing to the no. 2 settling pond inlet, along with the effluent from primary sludge dewatering. The average H_2S emission rate determined for this two day period was 1.4 g/s.

The anaerobic sulfide generation rates for the nos. 1 and 2 settling ponds during all three test phases are calculated in Table 6.12. During Phase I and II with the no. 1 settling pond in the on-line configuration and the no. 2 settling pond in the off-line configuration, the sulfide generation rates for the no. 2 settling pond were relatively similar, with values of 3.4 g/s and 5.0 g/s. For the no. 1 settling pond, the sulfide generation rate was apparently much higher during Phase II than during Phase I, with values of 25.5 g/s and 3.3 g/s, respectively. Inspection of the average physical/chemical parameter data associated with surface liquid sampling in Table 6.10 indicates that in-basin pH might be associated with the higher sulfide generation rate during Phase II, since it was 10.4 during Phase II versus 7.0 during Phase I. However, the detailed pH and liquid sulfide concentration data summarized in Table 6.14 indicate that the generation rate was already high, before the pH began to increase in the basin. From March 7, 2006 to March 8, 2006, the pH and sulfide concentration of the influent to the no. 1 settling pond increased and then stayed fairly steady through 3/9/06. At mid-day on March 7, 2006, the inlet and outlet pH values were 6.6 and 8.2, respectively, and the sulfide ion detector tubes indicated that the sulfide concentration in the basin was increasing from non-detect (<1 mg/L) at the inlet to 14 mg S/L at the outlet, which corresponds to a sulfide generation rate of 16.6 g/s, without the inclusion of the additional sulfide generation being emitted as H_2S. Therefore, since pH does not seem to be responsible for the apparent increase in sulfide generation between Phase I and Phase II, other the potential causes were investigated. Inspection of the process operation records indicated that additional sludge which accumulated in the no. 1 settling pond between Phase I and Phase II was the most likely factor to have been responsible for increased sulfide generation. The no. 1 settling pond had been dredged approximately four months before Phase I in April 2005; therefore, by Phase II in March 2006, it had been approximately 15 months since it had been dredged. The no. 2 settling pond had been continuously dredged over the same 15 month period.

During Phase III in June 2007, the no. 2 settling pond was in the on-line configuration, i.e., the main mill sewer was flowing directly to the no. 2 settling pond inlet, along with the effluent from primary sludge dewatering. The no. 1 settling pond was off-line with no flow through it. In this configuration, the H_2S generation rate in the no. 2 settling pond was 25.3 g S/s. This is approximately 5 to 10 times higher than it was with the WWTP in the previous configuration. Possible explanations for this increase include 1) the higher BOD and total sulfur load associated with the main mill sewer flow, and 2) the higher temperature in the pond which was associated with a) seasonal variation, b) the main mill sewer flow, and c) the dried, fibrous covering over much of the pond. For the no. 1 settling pond, the H_2S generation rate was 2.9 g S/s. In this case, the generation rate was the same as the emission rate, since there was no liquid flow through the pond. Therefore, the significance of this emission/generation rate has already been addressed in the discussion relative to emission rate measurement.

As shown in Table 6.4, methane emissions from the no. 2 settling pond averaged 32 g/s during the April 2005 test period but dropped to 9 g/s during the March 2006 tests. Since yet to be published NCASI studies have shown that settled sludge is the primary source of methane emissions from settling basins at pulp and paper mills, and methane has extremely low solubility in water and thus methane emissions from the basin would directly be affected by the methane generation rate and not by gas-liquid mass transfer phenomenon, the study results suggests that there was significantly less anaerobic activity in the no. 2 settling pond during the March 2006 sampling period. This is consistent with the earlier observation that the no. 2 settling pond was being continuously dredged between April 2005 and March 2006 and would have had greatly reduced levels of sludge at the time of March 2006 testing.

In Table 6.4, the methane emissions from the no. 1 and no. 2 settling ponds are tabulated along with the measured TOC gains across the ponds. The increase in the amounts of TOC as the wastewater flows through the ponds may be due to 1) formation of water soluble carbon-containing compounds from biological degradation of the settled primary sludge, and/or 2) fixation of atmospheric carbon dioxide via photosynthetic or other biological means in these large, shallow basins.

The ASB was tested during all three phases: April 18 and 19, 2005, March 9, 2006, and June 19, 2007. The ASB is curtained into three zones. The results of the screening study had indicated that the H_2S emissions from the ASB would be low – possibly too low to quantify – and that most of the small amount of emissions originated from zone 1. Due to the mechanics of the test method, testing just the area where most of the emissions were expected to occur could allow emissions quantitation, even if the emissions from the full ASB were too low to quantify. Therefore, the plan for the first test period included three tests on the full ASB and three tests on zone 1. The results from the Phase I study confirmed that the ASB H_2S emissions were low; however, they were quantifiable, so only the full ASB was tested during the Phase II and III Studies.

During the Phase I Study, all three of the full ASB test runs and the first test run on zone 1 were conducted on April 18, 2005. On that day, the average H_2S emissions from the full ASB were 0.12 g/s, whereas the emissions from zone 1 were 0.17 g/s for the one run, suggesting most of the emissions were from zone 1. Wind velocity is not expected to have a large effect on emissions from relatively well-mixed basins such as ASBs with surface aerators; therefore, only liquid chemical and physical parameters should influence emission rates. For the two runs conducted at zone 1 on April 19, 2005, the emissions were less (0.03 g/s and ND); however, between the two days the in-basin total sulfide concentration had dropped from 114 μg S/L to non-detect at less than 33 μg S/L, with the same in-basin pH. Therefore, the lower measured emissions from zone 1 on 4/19/05 are consistent with the reduction in sulfide concentration.

The average H_2S emissions from the full ASB during the Phase II Study were higher than from the Phase I Study. The average emissions from Phase I were 0.12 g/s versus 0.27 g/s for the Phase II; however, average in-basin sulfide concentration was also much higher during Phase II: 329 μg S/L versus 85 μg S/L for Phase I. The average in-basin pH (@ 1 foot depth) was higher during Phase II (pH = 8.3) than during Phase I (pH = 7.7), although, as discussed earlier in this section, how much this will tend to decrease the aqueous H_2S concentration in this chemically complex wastewater is not known. Also, the inlet total sulfide concentration was much greater during Phase II (41 mg/L versus 3 mg/L for the first period), which may have contributed to emissions at the front of zone 1, before the effluent reached the first surface liquid sampling location. For Phase III Study, the average in-basin total sulfide concentration and pH values were similar to the Phase I Study; however, the emissions were estimated to be significantly higher (0.8-2.3 g/s versus 0.12 g/s). One possible explanation for this is increased H_2S volatilization due to higher average in-basin temperature, which was approximately 11°C higher during the third test period. The higher temperature was due to seasonal variation and the WWTP configuration during the Phase III, which had all of the mill effluent flowing through the no. 2 settling pond. This configuration does not allow as much cooling as when the effluent flow is split between the two settling ponds.

Table 6.16 contains the results of a material balance which shows that the apparent destruction of liquid total sulfide was 91.4% during Phase I, and was even higher at 99.6% during Phase II even though the inlet total sulfide concentration was over an order of magnitude higher than during Phase I. The higher apparent destruction of sulfide during Phase II may have been related to the higher inlet pH, which was 10.3 during Phase II, and 7.0 during Phase I. During the Phase III Study, the calculated apparent destruction of total sulfide in the inlet stream was slightly lower at 94.5%.

As shown in Table 6.4, no organic reduced sulfur compounds were found to be present in the ASB emissions. This is consistent with the observation that significant quantities of the organic reduced sulfur compounds were not found in any of the liquid samples collected during these studies.

The emissions of methane from the ASB ranged from 2.1 to 10.3 g/s. The average methane emission rate was 5.8 g/s. In Table 6.17 the BOD and TOC removal across the ASB are tabulated along with the methane emissions.

During the Phase III study, emission rate estimates for the flume area were made using a procedure similar to what was used to estimate emission rates from the settling ponds and ASB, except downwind ambient air H_2S concentrations data were obtained from an open path tunable diode laser (OP-TDL)* as shown in Figure 6.10, instead from a Jerome H_2S analyzer. Additionally, the average OP-TDL beam height was approximately one meter above ground-level, whereas the Jerome analyzer measurements were taken at a height of 5 cm above the ground. Therefore, ground-level concentrations were calculated from the OP-TDL measurements using the relationship between elevation and concentration for area emission sources adapted by Esplin (Esplin 1988, 1989), from work done by Horst and Slinn (Horst and Slinn 1984) on sprayed-field pesticide emissions. The equations for this relationship are discussed in Section 2.3.3.5 of this report. Table 6.18 shows the input data used to estimate flume emission rates on June 19, 2007 and June 20, 2007. The reported path-integrated H_2S concentrations from the OP-TDL $C(z = 1\ m)$ were 3.0 and 1.5 ppmv, on the two days, respectively. The maximum plume height (Z_b) at the sampling path was estimated to be in the range of 2.5 to 3.0 meters. As for the settling ponds and ASB, the vertical concentration profile exponent (b) was estimated at 3.9 plus or minus one standard deviation of 1.8. As previously discussed in this section, 3.9 was the average value of the b exponent for vertical profile concentration data measured during relatively stable P-G atmospheric stability classes (C, D and E). The concentration measurements for the flume were made with C atmospheric stability on June 19, 2007 and B atmospheric stability on June 20, 2007. Even though the B stability class was not included in the development of the 3.9 average b exponent value, in the absence of any better estimate, it still seemed reasonable to use it for the following reason. In the case of the flume measurement, the fetch is so short (only several meters) that vertical atmospheric dispersion will not have much of an effect on the shape of the vertical concentration profile. The 3.9 value for the vertical concentration profile exponent (b) is simply used to generate a reasonable estimate of the vertical concentration profile shape. Emission rates were calculated for two values of Z_b (2.5 and 3.0 m), and three values of b (2.1, 3.9 and 5.7). Emissions from the ASB, which was upwind of flume, would be expected to add a positive bias to the H_2S concentration measured downwind of the flume; however, the ambient air H_2S concentrations measured downwind of the ASB were only a small fraction of concentrations measured downwind of the flume. Therefore, the upwind ASB did not significantly bias the tests conducted at the flume.

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[*] This instrument was operated by EPA and its contractor; concentrations cited in this report were provided by EPA (USEPA 2008)

The flume emission rate calculations are tabulated in Table 6.19. The range of the estimated H_2S emissions from the canal and Parshall flume between the combined settling pond exit and the ASB was considerable, from 0.4 to 1.8 g/s, reflecting a good deal of uncertainty in the estimating procedures. Emission testing in the flume and canal area was not conducted during the Phase I and Phase II studies because measurements made during the screening study indicated that the canal and flume area was not a significant source of emissions. Additionally, during the screening study and the Phase I and II studies, the staging area for all of the WWTP measurement work was set up immediately adjacent to the flume. Throughout those studies, evidence from measurements with the Jerome analyzer, personal H_2S exposure monitors, and human olfactory odor detection indicated that H_2S emissions were not significant. However, when staff arrived on site for the Phase III Study, it was immediately obvious, from the Jerome analyzer, personal H_2S exposure monitors, and human olfactory odor detection, that the flume conditions had changed and that it would not have been possible to use that location as a staging area. The most probable explanation for the dramatically increased H_2S emissions during the third test period is the combination of relatively high liquid total sulfide concentration, in conjunction with near neutral pH and relatively high liquid temperature. As previously discussed, the relatively high liquid total sulfide concentration and temperature were apparently due to seasonal variation, and the change in WWTP configuration, which put all of the mill effluent flow through the no. 2 settling pond. Additionally, the large areas of dried fibrous covering over much of the surface of the no. 2 settling pond probably exacerbated the condition.

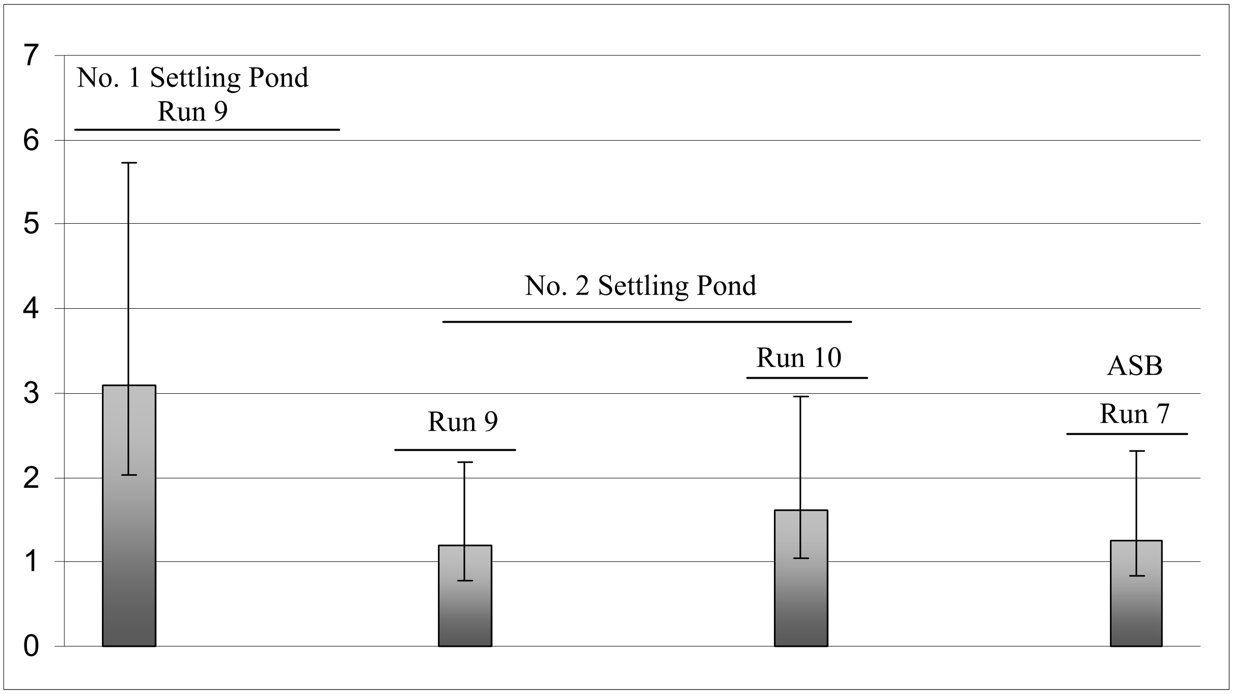


Figure 6.9 Emission Rates Estimated from Ground-Level Jerome Analyzer Measurements

Table 6.4 Emission Rates Estimated from Ground-Level Jerome Analyzer Measurements

Source	Run No.	H_2S Emission Rate, g/s b = 5.7	b = 3.9	b = 2.1
No. 1 Settling Pond	9	2.0	3.1	5.7
No. 2 Settling Pond	9	0.8	1.2	2.2
No. 2 Settling Pond	10	1.1	1.6	3.0
ASB	7	0.8	1.3	2.3

Table 6.5 Summary of Emission Rates for Mill E

Source	Run No.	Date	Emissions, g/s				
			H_2S	MeSH	DMS	DMDS	CH_4
No. 1 Settling Pond	1	4/12/2005	1.36E+00	[5.86E-02]	[5.61E-02]	[5.73E-02]	8.40E+00
	2	4/12/2005	2.09E+00	[1.28E-01]	[1.22E-01]	[1.25E-01]	2.16E+01
	Avg.		1.73E+00	[5.86E-02]	[5.61E-02]	[5.73E-02]	1.50E+01
	3	4/14/2005	3.40E-01	[6.76E-02]	[6.47E-02]	1.50E-01	9.88E+00
	4	4/14/2005	6.92E-01	[1.16E-01]	[1.11E-01]	[1.14E-01]	1.76E+01
	5	4/14/2005	5.70E-01	[4.49E-02]	[4.30E-02]	[4.40E-02]	NA
	Avg.		5.34E-01	[4.49E-02]	[4.30E-02]	7.63E-02	1.37E+01
	6	3/9/2006	3.81E+00	[1.62E-01]	[1.86E-01]	[8.21E-02]	1.65E+01
	7	3/9/2006	2.05E+00	[1.40E-01]	[1.58E-01]	[6.89E-02]	1.11E+01
	8	3/9/2006	2.99E+00	[1.55E-01]	[1.74E-01]	[7.38E-02]	1.16E+01
	Avg.		2.95E+00	[1.40E-01]	[1.58E-01]	[6.89E-02]	1.31E+01
	9	6/20/2007	3.10E+00*	NA	NA	NA	NA
No. 2 Settling Pond	1	4/14/2005	4.42E+00	[2.26E-01]	[2.16E-01]	[2.21E-01]	4.77E+01
	2	4/14/2005	2.65E+00	[1.85E-01]	[1.77E-01]	[1.81E-01]	3.80E+01
	3	4/14/2005	3.13E+00	[1.52E-01]	2.66E-01	[1.48E-01]	NA
	4	4/16/2005	1.83E+00	[1.25E-01]	[1.20E-01]	[1.22E-01]	2.02E+01
	5	4/16/2005	4.82E+00	[1.04E-01]	[9.91E-02]	[1.01E-02]	2.05E+01
	Avg.		3.37E+00	[1.04E-01]	[1.14E-01]	[1.01E-01]	3.16E+01
	6	3/7/2006	6.64E-01	[5.76E-02]	[6.23E-02]	[2.45E-02]	8.56E+00
	7	3/8/2006	2.63E-01	[3.48E-02]	[3.77E-02]	[1.51E-02]	7.26E+00
	8	3/8/2006	1.96E-01	[3.65E-02]	[4.28E-02]	[2.00E-02]	1.13E+01
	Avg.		3.74E-01	[3.48E-02]	[3.77E-02]	[1.51E-02]	9.04E+00
	9	6/19/2007	1.19E+00*	NA	NA	NA	NA
	10	6/20/2007	1.61E+00*	NA	NA	NA	NA
	Avg.		1.40E+00*	NA	NA	NA	NA
ASB	1	4/18/2005	9.54E-02	[4.65E-02]	[4.46E-02]	[4.55E-02]	2.10E+00
	2	4/18/2005	6.13E-02	[7.65E-02]	[7.33E-02]	[7.49E-02]	9.08E+00
	3	4/18/2005	2.01E-01	[7.17E-02]	[6.86E-02]	[7.01E-02]	1.03E+01
	Avg.		1.19E-01	[4.65E-02]	[4.46E-02]	[4.55E-02]	7.16E+00

(Continued on next page. See notes at end of table.)

Table 6.5 Continued

Source	Run No.	Date	Emissions, g/s H_2S	MeSH	DMS	DMDS	CH_4
ASB	4	3/9/2006	5.01E-01	[1.19E-01]	[1.42E-01]	[6.75E-02]	5.71E+00
	5	3/9/2006	1.52E-01	[4.96E-02]	[5.90E-02]	[2.78E-02]	3.42E+00
	6	3/9/2006	1.60E-01	[8.68E-02]	[1.02E-01]	[4.76E-02]	4.31E+00
	Avg.		2.71E-01	[4.96E-02]	[5.90E-02]	[2.78E-02]	4.48E+00
	7	6/19/2007	1.26E+00*	NA	NA	NA	NA
ASB Zone 1	1	4/18/2005	1.71E-01	[1.15E-02]	[1.10E-02]	[1.12E-02]	3.32E+00
	2	4/19/2005	2.73E-02	[1.04E-02]	[9.99E-03]	[1.02E-02]	3.71E+00
	3	4/19/2005	[2.00E-02]	[6.78E-02]	[6.48E-02]	[6.61E-02]	1.22E+01
	Avg.		1.51E-01	[1.04E-02]	[9.99E-03]	[1.02E-02]	6.41E+00
Flume Area	1	6/19/2007	1.01E-00**	NA	NA	NA	NA
	2	6/20/2007	5.29E-01**	NA	NA	NA	NA
	Avg.		7.68E-01**	NA	NA	NA	NA

ND[xxxx] = The estimated maximum emission rate calculated from non-detect ambient air concentration data using the procedures outlined in Section 2.3.3.

*Calculated from ground-level Jerome Analyzer data and an estimated vertical concentration profile exponent (b) of 3.9.

**Calculated from open-path tuneable diode laser H_2S concentration data, and an estimated b exponent of 3.9.

Table 6.6 Meteorological and Concentration Summary Data for Emissions Tests at Mill E

Source	Run No.	Date	Horizontal Wind Direction*, degrees	Horizontal Wind Velocity*, m/s	P-G Stability Class*	Integrated Downwind Ground Level Concentration**, ppbv			
						H_2S	MM	DMS	DMDS
No. 1 Settling Pond	1	4/12/2005	84	4.59	B	76.30	[2.33]	[1.73]	[1.17]
	2	4/12/2005	92	2.88	A	57.22	[2.47]	[1.84]	[1.24]
	3	4/14/2005	31	5.57	D	17.00	[2.40]	[1.78]	2.72
	4	4/14/2005	39	5.64	C-D	19.63	[2.33]	[1.73]	[1.17]
	5	4/14/2005	48	6.74	D	42.50	[2.37]	[1.76]	[1.19]
	6	3/9/2006	210	7.4	C-D	178.73	[5.40]	[4.79]	[1.40]
	7	3/9/2006	202	6.55	D	114.12	[5.52]	[4.84]	[1.39]
	8	3/9/2006	202	7.49	D	155.49	[5.71]	[4.96]	[1.39]
No. 2 Settling Pond	1	4/14/2005	49	8.48	D	77.85	[2.82]	[2.09]	[1.41]
	2	4/14/2005	46	8.39	C-D	47.49	[2.35]	[1.74]	[1.17]
	3	4/14/2005	38	8.32	C-D	68.14	[2.34]	3.66	[1.17]
	4	4/16/2005	29	7.69	C-D	54.47	[2.57]	[1.91]	[1.29]
	5	4/16/2005	33	8.63	C-D	171.91	[2.52]	[1.87]	[1.26]
	6	3/7/2006	360	5.51	E	103.89	[6.39]	[5.36]	[1.39]
	7	3/8/2006	314	1.66	A	67.03	[6.27]	[5.27]	[1.39]
	8	3/8/2006	274	2.86	A	37.70	[4.96]	[4.51]	[1.39]
ASB	1	4/18/2005	237	3.39	E	6.87	[2.38]	[1.76]	[1.19]
	2	4/18/2005	225	2.74	D	2.33	[2.33]	[1.73]	[1.17]
	3	4/18/2005	232	2.99	A	9.88	[2.50]	[1.85]	[1.25]
	4	3/9/2006	213	4.79	D	28.41	[4.80]	[4.42]	[1.39]
	5	3/9/2006	231	5.94	E	21.05	[4.87]	[4.49]	[1.40]
	6	3/9/2006	219	6.34	C	13.08	[5.02]	[4.59]	[1.41]

(Continued on next page. See notes at end of table.)

Table 6.6 Continued

Source	Run No.	Date	Horizontal Wind Direction*, degrees	Horizontal Wind Velocity*, m/s	P-G Stability Class*	Integrated Downwind Ground-Level Concentration**, ppbv			
						H_2S	MM	DMS	DMDS
ASB Zone 1	5	4/18/2005	242	2.62	A	49.22	[2.34]	[1.73]	[1.17]
	6	4/19/2005	219	2.33	E	11.57	[2.34]	[1.73]	[1.17]
	7	4/19/2005	241	1.42	A	[1.67]	[4.36]	[3.14]	[2.03]

[xxx] = Not Detected at a Detection Limit of xxx; NA = Not Available

*Determined from the anemometer at 10 meter height.

**Determined via the procedures outlined in Section 2.3.3.

Table 6.7 No. 1 Settling Pond Average Liquid Sample Concentrations, Mill E

Location	Date	Sulfide Ion, mg/L	Total Sulfide, µg S/L	MM, µg S/L	DMS, µg S/L	DMDS, µg S/L	DMTS, µg S/L	Sulfate, mg S/L	Thio-Sulfate, mg S/L	TOC, mg C/L	TOC, (filtered) mg C/L
No. 1 SP Inlet	4/12-14/05	1.3	573	[9.6]	15.1	29.3	[11.5]	271	ND[1.4]	NA	NA
	3/8-9/06	30.4	33600	NA	NA	NA	NA	149	2.6	165.0	NA
No. 1 SP (in-basin)*	4/12/05	7.1	3008	19.4	14.3	15.6	[11.5]	248**	ND[1.4]	NA	NA
	4/14/05	1.2	998	13.6	13.3	[10.75]	[11.5]	248**	ND[1.4]	NA	NA
	3/9/06	>72.7	57417	NA	NA	NA	NA	164	3.7	NA	NA
No. 1 SP Outlet	4/12-14/05	8.7	2170	18.7	21.4	[10.75]	[11.5]	263	ND[1.4]	NA	NA
	3/8-9/06	>52.0	51950	NA	NA	NA	NA	157	4.4	200	202

* Average of Four Surface Liquid Sampling Locations

** Average of 4/12/05 and 4/14/05 Concentrations

NA = Not Available

ND[xxx] = non-detect with xxx equal to one-half of the lowest calibration limit

>xx.x indicates that one or more of the sulfide ion detector tube readings were greater than 100

Table 6.8 No. 2 Settling Pond Average Liquid Sample Concentrations, Mill E

Location	Date	Sulfide Ion, mg/L	Total Sulfide, µg S/L	MM, µg S/L	DMS, µg S/L	DMDS, µg S/L	DMTS, µg S/L	Sulfate, mg S/L	Thio-Sulfate, mg S/L	TOC, mg C/L	TOC, (filtered) mg C/L
No. 2 SP Inlet**	4/13-16/05	[0.5]	335	19.9	59.5	23.5	[11.5]	260	[1.4]	NA	NA
	3/7-8/06	[0.5]	120	NA	NA	NA	NA	34	[1.4]	159	NA
	6/18-20/07	[0.5]	76	[12.3]	[12.2]	[10.4]	[12.2]	117	[1.4]	NA	NA
No. 2 SP Inlet (Fiberline)	4/13-16/05	0.8	456	15.8	73.6	13.7	[11.5]	197	[1.4]	NA	NA
	3/7-8/06	[0.5]	63	NA	NA	NA	NA	14	[1.4]	123	NA
	6/18-20/07	15.8	8855	44.6	75.7	[10.4]	[12.2]	32	4.8	NA	NA
No. 2 SP (in-basin)*	4/14-16/05	8.6	5319	61.7	38.5	12.2	[11.5]	229	[1.4]	NA	NA
	3/7-8/06	10.3	11596	NA	NA	NA	NA	5	[1.4]	NA	NA
	6/18-20/07	9.0	6572	34.9	[12.2]	[10.4]	[12.2]	95	[1.4]	NA	NA
No. 2 SP Outlet	4/13-16/05	0.9	1007	14.3	23.3	[10.75]	[11.5]	233	[1.4]	NA	NA
	3/7-8/06	7.3	11925	NA	NA	NA	NA	2	[1.4]	184	162
	6/18-20/07	25.2	16370	34.1	[12.2]	[10.4]	[12.2]	95	[1.4]	NA	NA

* Average of Four Surface Liquid Sampling Locations

** The no. 2 SP inlet included the effluent from primary sludge dewatering and the OCC Plant Sewer during the 4/13-16/05 Sampling Period. During the 3/7-8/06 sampling period the no. 2 SP inlet only included the effluent from primary sludge dewatering. For the 6/18-20/07 sampling period, the no. 2 settling pond inlet included the effluent from primary sludge dewatering and the main mill sewer, which includes the effluent from recovery, bleaching and papermaking.

NA = Not Available

ND[xxx] = non-detect with xxx equal to one-half of the lowest calibration limit

Table 6.9 ASB Average Liquid Sample Concentrations, Mill E

Location	Date	Sulfide Ion, mg/L	Total Sulfide, µg S/L	MM, µg S/L	DMS, µg S/L	DMDS, µg S/L	DMTS, µg S/L	Sulfate, mg S/L	Thio-Sulfate, mg S/L	TOC, mg C/L	TOC, (filtered) mg C/L
ASB Inlet	4/17-19/05	4.1	3019	25.9	24.4	[10.75]	[11.5]	199	[1.4]	NA	NA
	3/8-9/06	43.0	41217	NA	NA	NA	NA	146	3.0	186	NA
	6/18-20/07	20.7	13783	36.9	[12.2]	[10.4]	[12.2]	94	[1.4]	NA	NA
Full ASB (in-basin)*	4/18/05	[0.5]	85	[9.6]	[9.5]	[10.78]	[11.5]	203**	[1.4]	NA	NA
	4/19/05	[0.5]	28	[9.6]	[9.5]	[10.78]	[11.5]	203**	[1.4]	NA	NA
	3/8-9/06	0.8	329	NA	NA	NA	NA	168	[1.4]	NA	NA
	6/18-20/07	[0.5]	81	[12.3]	[12.2]	[10.4]	[12.2]	113	[1.4]	NA	NA
ASB (Zone 1, in-basin)	4/18/05	[0.5]	114	[9.6]	[9.5]	[10.8]	[11.5]	206	[1.4]	NA	NA
	4/19/05	[0.5]	[16.5]	[9.6]	[9.5]	[10.8]	[11.5]	199	[1.4]	NA	NA
ASB Outlet	4/17-19/05	[0.5]	196	[9.6]	[9.5]	[10.8]	[11.5]	193	[1.4]	NA	NA
	3/8-9/06	[0.5]	[16.2]	NA	NA	NA	NA	171	[1.4]	105	109
	6/18-20/07	[0.5]	46	NA	NA	NA	NA	116	[1.4]	NA	NA

* Average of Four Surface Liquid Sampling Locations

** Average of 4/18/05 and 4/19/05 Concentrations

NA = Not Available

[xxx] = non-detect with xxx equal to one-half of the lowest calibration limit

Table 6.10 Average Physical/Chemical Parameter Measurement Data Associated with Liquid Sample Collection at the No. 1 Settling Pond, Mill E

Location	Date	Depth, ft	Temp., ° C	Specific Conductance, mS/cm	DO, mg/L	pH
No. 1 SP Inlet	4/12-14/05	1	45.7	NA	NA	6.6
	3/8-9/06	1	45.1	NA	NA	10.7
No. 1 SP (in-basin)*	4/12/05	1	42.0	2.77	0.59	6.8
		3-4	41.8	2.79	0.16	6.7
	4/14/05	1	40.8	2.70	0.10	7.1
		3-4	40.2	2.63	0.09	7.1
	3/9/06	1	39.5	3.79	0.11	10.4
		4	39.2	3.43	0.09	10.5
No. 1 SP Outlet	4/12-14/05	1	35.4	NA	NA	7.0
	3/8-9/06	1	37.3	NA	NA	9.4

* Average of Four Surface Liquid Sampling Locations
NA = Not Available

Table 6.11 Average Physical/Chemical Parameter Measurement Data Associated with Liquid Sample Collection at the No. 2 Settling Pond, Mill E

Location	Date	Depth, ft	Temp., °C	Specific Conductance, mS/cm	DO, mg/L	pH	ORP
No. 2 SP Inlet**	4/13-16/05	1	31.8	NA	NA	7.3	NA
	3/7-8/06	1	12.7	NA	NA	7.7	NA
	6/18-20/07	1	49.8	1.90	4.03	7.3	24
No. 2 SP Inlet (Fiberline)	4/13-16/05	1	32.0	NA	NA	9.2	NA
	3/7-8/06	1	31.6	NA	NA	9.8	NA
	6/18-20/07	1	42.1	2.02	0.29	10.7	-224
No. 2 SP (in-basin)*	4/14-16/05	1	18.8	1.37	0.53	6.9	NA
		2-4	18.2	1.31	0.20	6.7	NA
		5	17.6	1.61	0.22	6.7	NA
	3/7-8/06	1	20.2	1.33	0.19	6.7	NA
		3-4	19.6	1.33	0.18	6.7	NA
		5-7	18.4	1.32	0.18	6.6	NA
	6/19/07	1	43.9	1.91	0.31	6.9	27
		3	43.3	1.98	0.32	6.6	-17
		6	44.2	2.08	0.25	6.6	-51
No. 2 SP Outlet	4/13-16/05	1	16.7	NA	NA	7.1	NA
	3/7-8/06	1	17.6	NA	NA	6.8	NA
	6/18-20/07	1	40.7	2.03	0.31	7.0	-172

* Average of Four Surface Liquid Sampling Locations

** The no. 2 SP inlet included the effluent from primary sludge dewatering and the OCC Plant Sewer during the 4/13-16/05 Sampling Period. During the 3/7-8/07 sampling period the no. 2 SP inlet only included the effluent from primary sludge dewatering. For the 6/18-20/07 sampling period, the no. 2 settling pond inlet included the effluent from primary sludge dewatering and the main mill sewer, which includes the effluent from recovery, bleaching and papermaking.

NA = Not Available

Table 6.12 Average Physical/Chemical Parameter Measurement Data Associated with Liquid Sample Collection at the ASB, Mill E

Location	Date	Depth, ft	Temp., °C	Specific Conductance, mS/cm	DO, mg/L	pH	ORP
ASB Inlet	4/17-19/05	1	34.7	NA	NA	7.0	NA
	3/8-9/06	1	35.6	NA	NA	7.8	NA
	6/18-20/07	1	40.8	2.02	0.32	7.0	-142
Full ASB (in-basin)*	4/18/05	1	22.7	2.40	2.91	7.7	NA
		3-6	23.0	2.40	2.57	7.7	NA
		9-12	22.1	2.40	3.21	7.2	NA
	4/19/05	1	24.3	2.42	2.75	7.8	NA
		3-6	24.6	2.42	2.12	7.6	NA
		9-12	23.6	2.42	2.92	7.1	NA
	3/8-9/06	1	22.5	2.50	2.04	8.3	NA
		3-7	22.4	2.50	1.97	7.8	NA
		6-12	22.2	2.47	0.23	6.7	NA
	6/19/07	1	34.2	2.02	0.95	7.7	61
		3-5	33.6	2.05	0.77	7.3	6
		5-10	33.4	2.19	0.80	7.2	1
ASB (Zone 1, in-basin)*	4/18/05	1	25.0	2.42	0.53	7.6	NA
		3-6	24.5	2.42	1.63	7.6	NA
		9-12	24.2	2.44	0.60	6.9	NA
	4/19/05	1	26.4	2.43	0.34	7.6	NA
		3-6	26.0	2.42	0.31	7.5	NA
		9-12	25.4	2.41	0.19	7.0	NA
ASB Outlet	4/17-19/05	1	24.8	NA	NA	7.7	NA
	3/8-9/06	1	25.1	NA	NA	8.0	NA
	6/18-20/07	1	33.7	0.200	0.49	7.7	3

* Average of Four Surface Liquid Sampling Locations
NA = Not Available

Table 6.13 Sulfide Material Balance for the Settling Ponds at Mill E

Source	Test Dates	Liquid Influent, g S/s	Liquid Effluent, g S/s	Emissions, g S/s	Generation Rate, g S/s
Settling Pond No. 1	4/12-14/05	0.8	3.1	1.0	3.3
Settling Pond No. 1	3/8-9/06	41.2	63.7	2.8	25.5
Settling Pond No. 1	6/18-20/07	0.0	0.0	2.9	2.9
Settling Pond No. 2	4/13-16/05	0.2	0.4	3.4	3.6
Settling Pond No. 2	3/7-8/06	0.0	4.7	0.4	5.0
Settling Pond No. 2	6/18-20/07	3.2	27.3	1.3	25.3

Table 6.14 No. 1 Settling Pond Inlet/Outlet pH Values and Sulfide Concentrations

				Inlet		Outlet	
Date	Time	Inlet pH	Outlet pH	Sulfide Ion Detector Tube mg/L	Total Sulfide mg/L	Sulfide Ion Detector Tube mg/L	Total Sulfide mg/L
3/7/2006	11:40	6.6	8.2	ND[1]			
3/7/2006	17:15	9.1		ND[1]		14	
3/8/2006	8:45	10.3		34	28		
3/8/2006	12:38	10.8	9.1	45	28		31
3/8/2006	15:05	10.4		36	28	41	
3/9/2006	8:20	11.1		48	48		
3/9/2006	10:40	11.2	10.6	30	25		73
3/9/2006	14:32	10.8		50	35	>100	

ND[x] indicates that the analyte was not detected at a detection limit equal to x.

Table 6.15 Methane Emissions and the TOC Liquid Material Balances for the Settling Ponds at Mill E

Source	Date	TOC Inlet, g C/s	TOC Outlet, g C/s	TOC Gain, g C/s	Methane Emissions g/s
No. 1 Settling Pond	3/8-9/2006	196.3	249.5	53.1	13.1
No. 2 Settling Pond	3/7-8/2006	50.2	72.7	22.5	9.0

Table 6.16 Apparent Destruction of Sulfide in the Mill E ASB

Date	Influent*, g/s	Effluent*, g/s	Air Emissions, g/s	Apparent Destruction, %
4/18/2005	5.69	0.37	0.12	91.4
3/9/2006	69.48	0.03	0.27	99.6
6/19/2007	24.39	0.08	1.26	94.5

*total sulfide as H_2S

Table 6.17 ASB BOD and TOC Removals and Methane Emissions, Mill E

Parameter	Test Period	Liquid Balance*	Units	Methane Emissions, g/s
BOD**	1	508	g/s	7.16
BOD**	2	439	g/s	4.48
TOC	2	126	g C/s	4.48

*Inlet – outlet for the 60 day period prior to emissions testing
**From the 5-Day BOD test

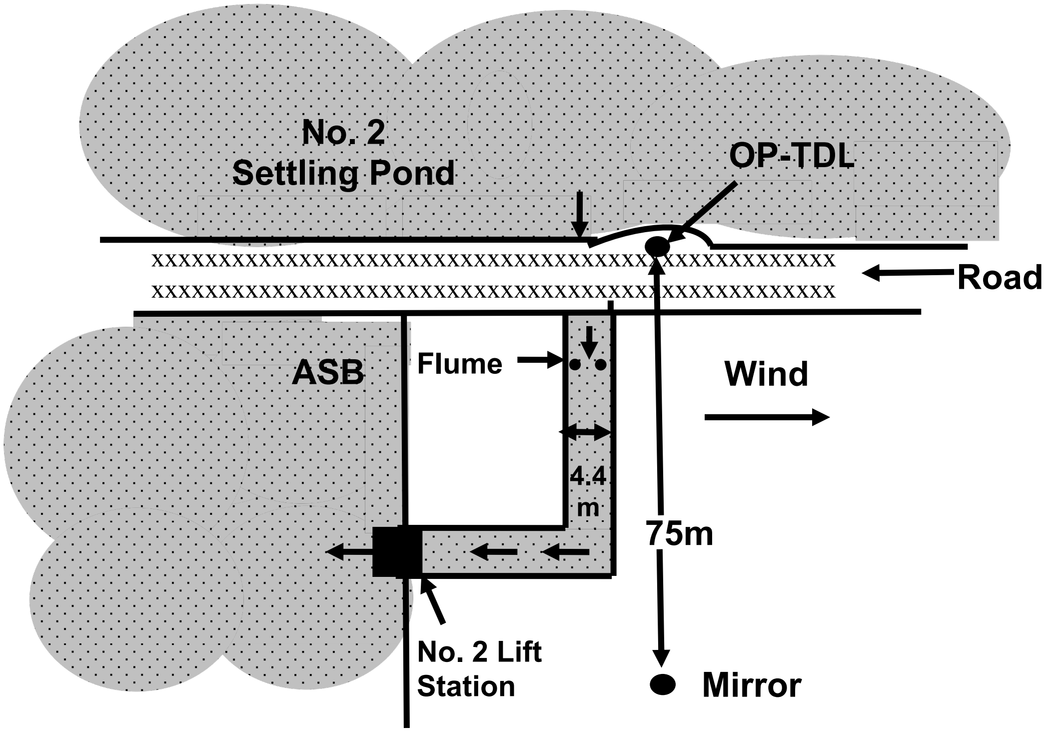


Figure 6.10 Schematic Representation of Flume Area Test

Table 6.18 Input Data for Calculation of Estimate Flume Area Emission Rates

Date	Run No.	Time Period	$C_{(Z)}$, ppmv	Z, m	Z_b, m	b	W, m	U_{10}, m/s	p
6/19/07	1	10:00-10:37	3.0	1.0	2.5 - 3.0	3.9 ± 1.8	75	2.4	0.25
6/20/07	2	10:00-11:00	1.5	1.0	2.5 - 3.0	3.9 ± 1.8	75	3.1	0.32

Table 6.19 Estimated Flume Area H_2S Emission Rates

Date	Run No.	Zb, m	H_2S Emissions, g/s b = 2.1	b = 3.9	b = 5.7
6/19/2007	1	2.5	0.77	1.09	1.83
	2	3	0.79	0.92	1.29
	Average		0.78	1.01	1.56
6/20/2007	1	2.5	0.41	0.57	0.94
	2	3	0.43	0.49	0.67
	Average		0.42	0.53	0.80
	Overall Average		0.60	0.77	1.18

7.0 SOURCE DESCRIPTION AND RESULTS OF TESTS AT MILL F

Emissions testing and associated liquid sampling was carried out at Mill F during April 28-30, 2006. During this study, emissions from the primary clarifier, several vents on the effluent transport system, and the activated sludge treatment basin were tested. This section describes the sources tested and the results of these tests.

7.1 Wastewater Treatment Plant Description, Mill F

Mill F produces approximately 280,000 tons per year of uncoated kraft bleached paper on three machines, and approximately 300,000 tons per year of bleached kraft paperboard on one machine. The pulp, which is produced on site, is approximately 55% hardwood and 45% softwood.

Figure 7.1 is a simplified schematic representation of the in-mill sewer system. The emissions from two of the manhole vents (4E and 4A) were tested. The condensate stripper feed tank overflows to the sewer upstream of the 4E manhole, and excess foul condensate is discharged to the sewer at the 4A manhole. The combined mill alkaline sewer flows to the wastewater treatment plant, where the adjacent town's municipal sewer joins the alkaline mill sewer at the low lift station. The mill's acid sewer mixes with the combined municipal and mill alkaline sewer at the primary clarifier outlet. Figure 7.2 is a schematic representation of the wastewater treatment plant, and Figure 7.3 is an aerial photograph of the mill and wastewater treatment plant. Inlet/outlet liquid sampling locations are indicated on Figure 7.2.

Mill F uses an activated sludge wastewater treatment system. Waste secondary sludge is pumped to the clarifier influent flow splitting station. There are three primary clarifiers (nos. 1, 2, and 3). The no. 1 primary clarifier is generally not used and kept in reserve as a spill basin; however, during the period of emissions testing, the no. 2 primary clarifier was shut down for maintenance, so the no. 1 primary clarifier was in service. The nos. 2 and 3 primary clarifiers are identical, with diameters of 200 ft. The no. 1 primary clarifier is 125 ft in diameter.

Recycled secondary sludge, ammonium hydroxide and phosphoric acid are mixed with the combined effluent from the primary clarifiers before the primary effluent enters secondary treatment in the activated sludge treatment reactors (ASTs). Normally, the mixing of the mill acid sewer with the alkaline primary clarifier effluent provides sufficient neutralization. However, if additional pH control is necessary, then sulfuric acid may be added to the primary effluent. Carbon dioxide may be added to the primary influent for pH control, if necessary. The rectangular aeration basin, with dimensions of 411 ft by 252 ft, is divided into four cells. Figure 7.4 is a drawing of the aeration basin on which the three surface liquid sampling locations are indicated. The two northern cells each have six surface aerators and always function as activated sludge treatment reactors. The two southern cells each have four surface aerators and can function as activated sludge treatment reactors, or aerobic digesters for waste sludge. The aerators can be run at two power levels: 125 hp or 65 hp. In the cells used as activated sludge treatment reactors, the aerators were all running at the 125 hp level during the emissions testing period. Two percent of the mixed liquor leaving the activated sludge treatment reactors is wasted and aerobically digested for several days before it is returned to the inlet of the primary clarifiers, where the wasted secondary sludge settles out with the primary sludge. During the period of emissions testing, the southeast cell was functioning as an activated sludge treatment reactor and the southwest cell was functioning as a waste sludge aerobic digester. All of the cells used as activated sludge treatment reactors operate in parallel.

There are three secondary clarifiers; however, most of the time, as was the case during the emissions test period, only two of them are used. The two normally used secondary clarifiers (nos. 4 and 5) have diameters of 200 ft. The intermittently used no. 6 secondary clarifier has a 150 ft. Oxygen is added to the secondary clarifier effluent before it is discharged to the river.

Summarized mill and WWTP process operating information is contained in Table 7.1.

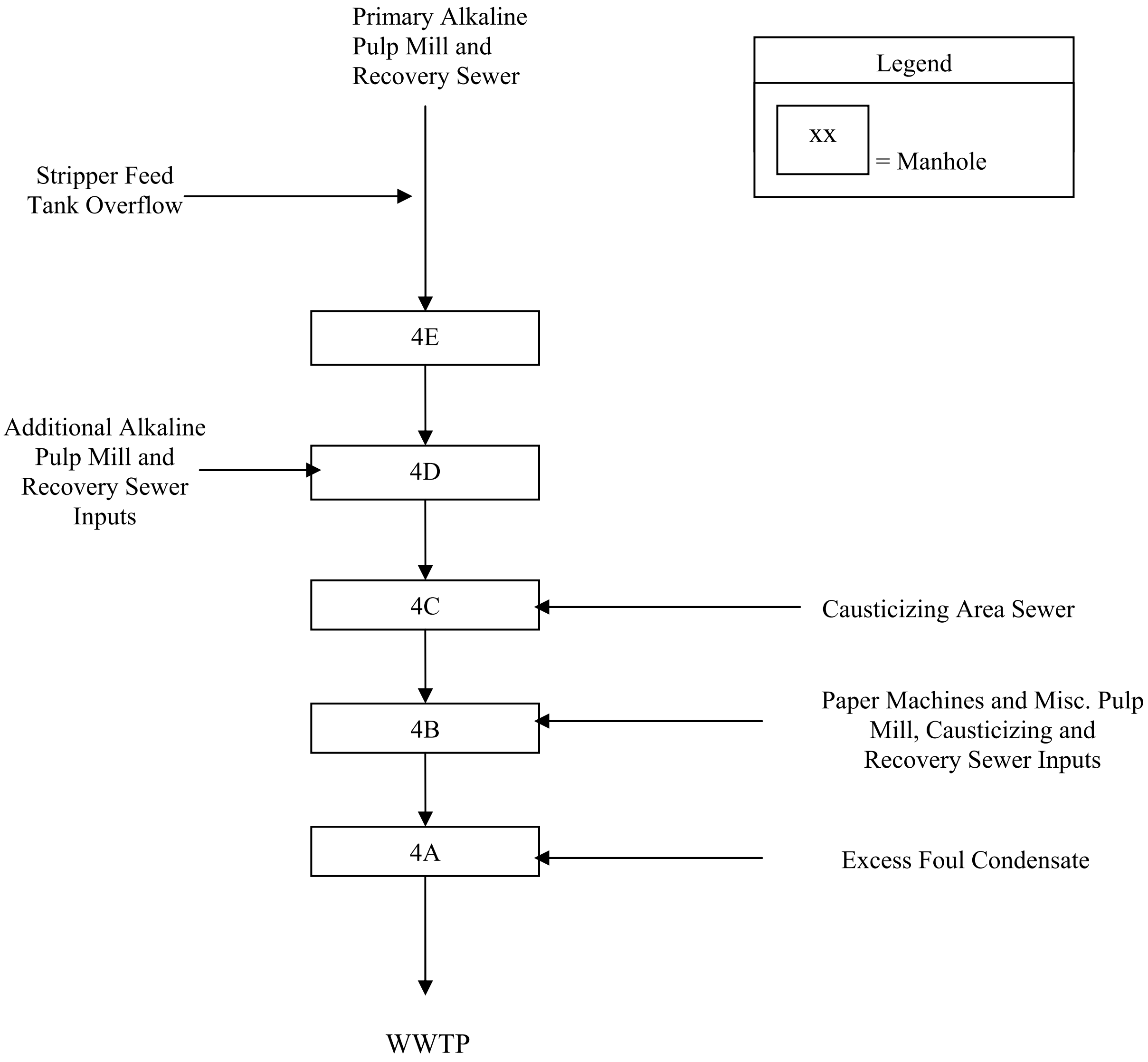


Figure 7.1 Simplified In-Mill Sewer System Schematic Diagram

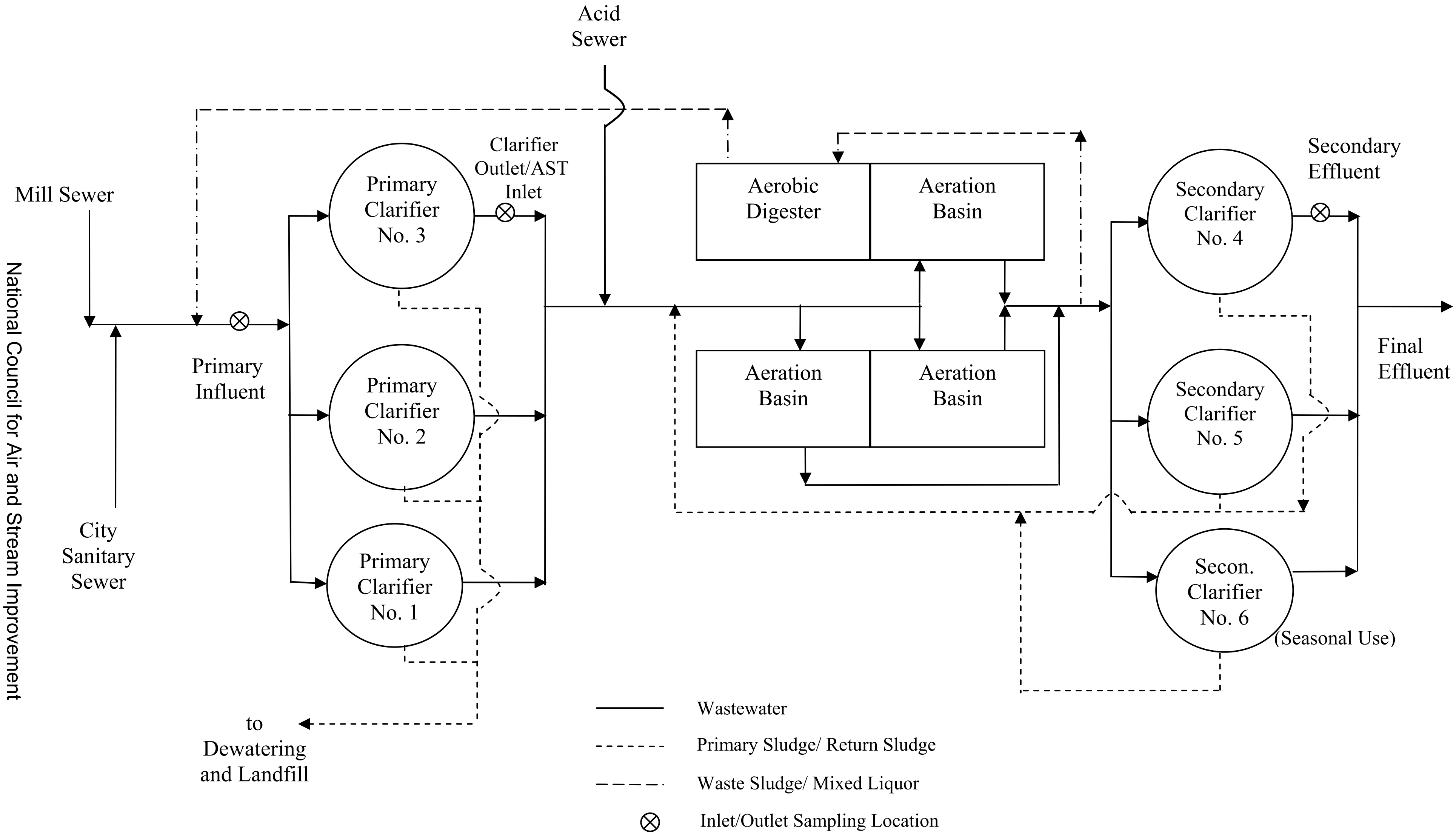


Figure 7.2 Wastewater Treatment Plant, Mill F

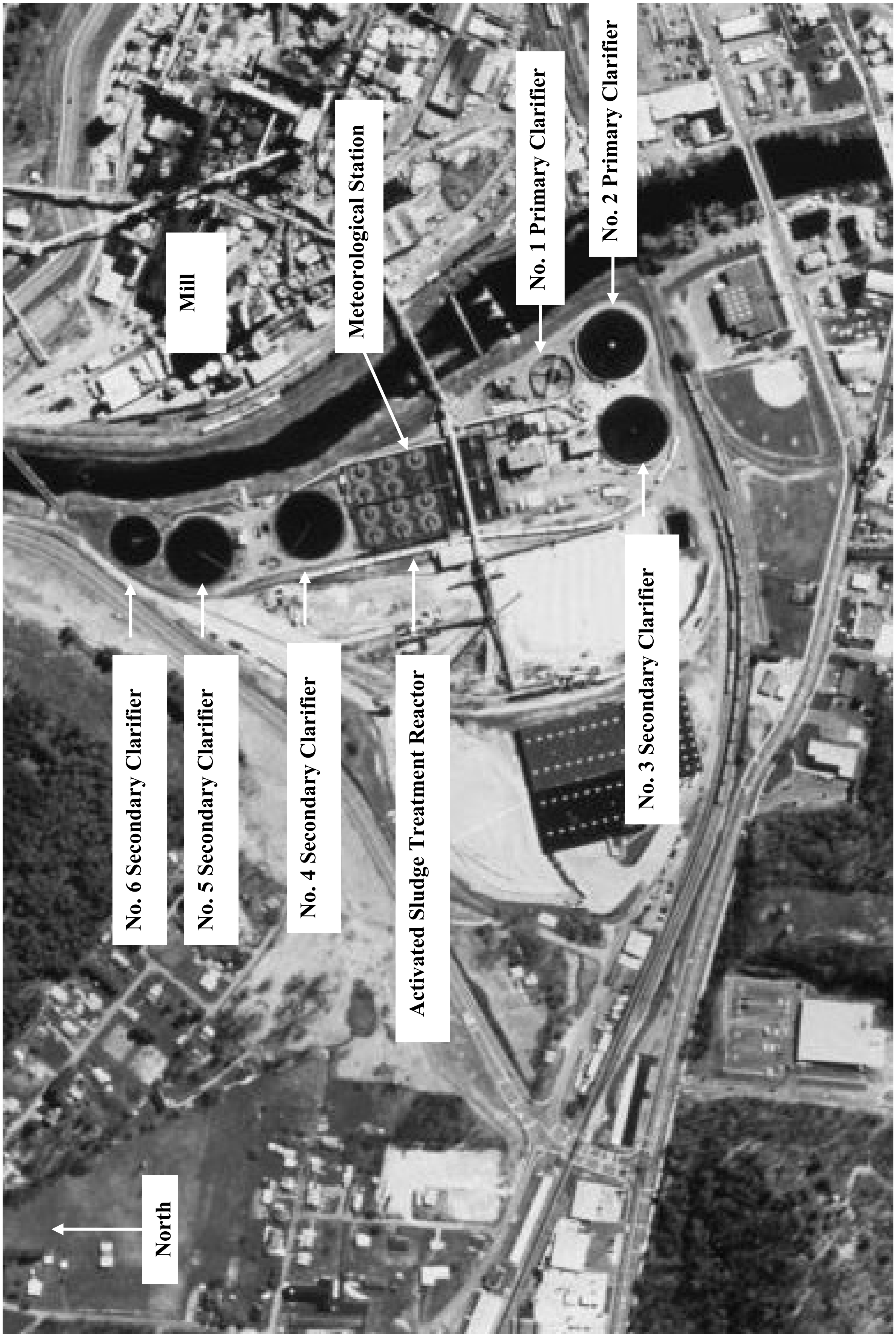


Figure 7.3 Aerial View of the Mill F WWTP

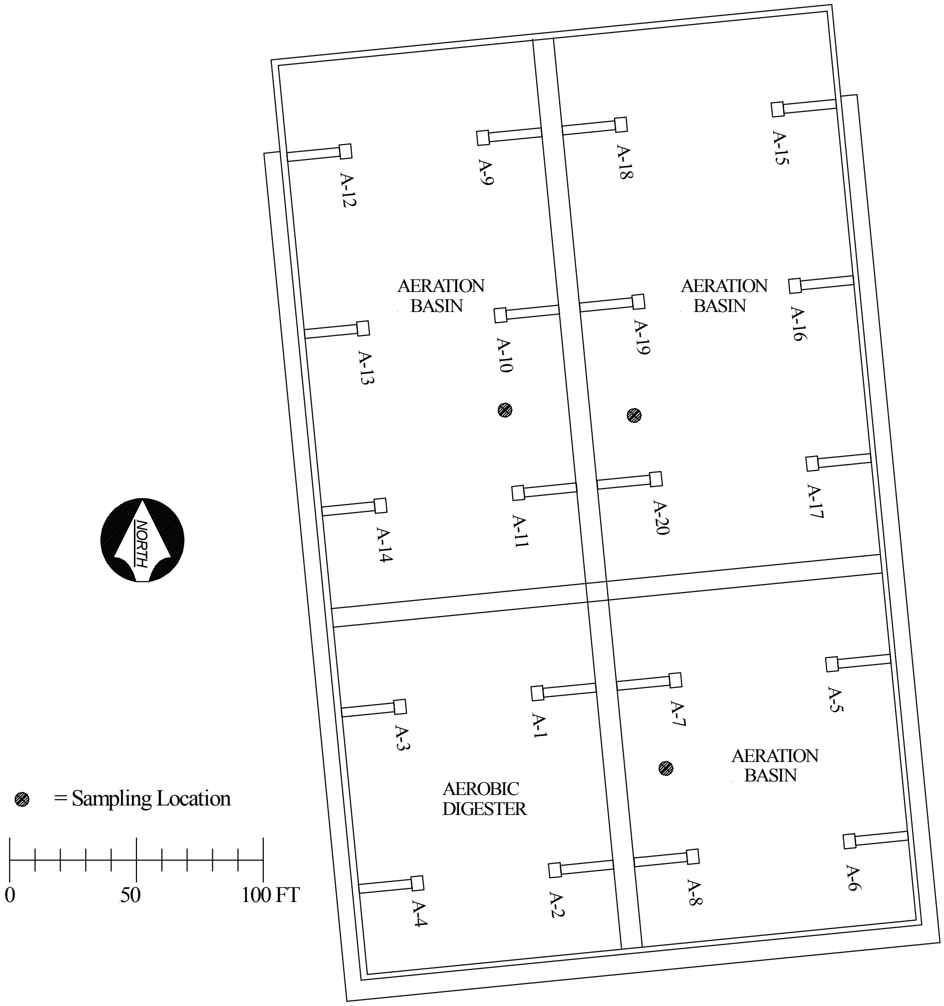


Figure 7.4 Surface Liquid Sampling Locations for the Aeration Basin at Mill F

Table 7.1 Summary of Daily Average Process Operating Parameter Information, Mill F

Process Parameter	4-29-06	4-30-06
Hardwood Pulp Prod., ADTPD	886	896
Softwood Pulp Prod., ADTPD	659	659
Condensate to 4A Sewer, gpm	15.5*	10.30*
Municipal Sewer Flow, gpm	634	-
Flow to No. 3 Primary Clarifier, MGD	22.6	-
Acid Sewer Flow, MGD	ca. 4.0	-
Acid Sewer pH	2.3	-
Secondary Effluent Flow, gpm	29.2	-
MLSS, mg/L	3540	-
Sludge Wasted, lb/day	29,500	-
Sludge Recycled, lb/day	1,548,000	-
Primary Influent BOD**, lb/day	69,000	-
Primary Effluent BOD**, lb/day	45,000	-
Secondary Effluent BOD**, lb/day	780	-
Secondary Effluent DO, mg/L	9.3	-

*The condensate flow to the 4A Sewer was highly variable. The standard deviations for both days were approximately twice the average value.

**From the 5-Day BOD test

7.2 Emissions Measurement and Liquid Sampling Results, Mill F

At Mill F emissions testing and the associated liquid sampling was conducted at the no. 3 primary clarifier and the activated sludge treatment reactor on 4/28/06 and the 4A and 4E sewer manhole vents on 4/29/06. The detailed results of this testing are available in the Mill F test report (NCASI 2008h). At each source, three sequential emissions tests were conducted. The emission rates determined from those tests are summarized in Table 7.2. Meteorological and RSC concentration data associated with those tests are summarized in Table 7.3.

As shown in Figure 7.2, process unit inlet/outlet liquid sampling was conducted at the inlet and outlet of the no. 3 primary clarifier, inlet to the activated sludge treatment Reactor (which was the same sampling location as the no. 3 primary clarifier outlet) and outlet from the no. 4 secondary clarifier. Surface liquid samples (one foot below the surface) were collected from the no. 3 primary clarifier and the activated sludge treatment reactor (AST). Figure 2.2 is a schematic diagram showing the three surface liquid sampling locations for primary clarifiers. For the no. 3 primary clarifier, physical/chemical parameter data associated with liquid sample collection were collected at two additional depths, which were one foot above the bottom and midway between the surface and bottom. The three surface liquid sampling locations for the AST are shown in Figure 7.4. The results of the liquid sample analysis are summarized in Table 7.4 and the average values of the physical/ chemical parameter data collected during this sampling are summarized in Table 7.5.

As shown in Table 7.1, for the no. 3 primary clarifier, the hydrogen sulfide emissions over three runs ranged from 0.15 g/s to 0.48 g/s with an average emission rate of 0.32 g/s. Methyl mercaptan emissions averaged 0.042 g/s and ranged from 0.035 g/s to 0.054 g/s. Dimethyl sulfide emissions averaged 0.10 g/s and ranged from 0.084 g/s to 0.13 g/s. Dimethyl disulfide emissions averaged 0.0035 g/s and ranged from 0.0022 g/s to 0.0052 g/s. The data show that the H_2S emission rate increased from 0.15 to 0.33 g/s between run nos. 1 and 2, and then increased again between run nos. 2 and 3 to 0.48 g/s, while the emissions of the three organic reduced sulfur compounds stayed essentially constant over the three run period. Table 7.6 shows that the total sulfide concentration at the clarifier outlet increased during the period of emissions testing, while the concentrations of the organic reduced sulfur compounds remained relatively consistent. The increase in the primary clarifier liquid total sulfide concentration was consistent with the increase in H_2S emissions over the test period. The methane emissions from the primary clarifier ranged from 0.09 to 0.27 g/s with an average rate of 0.17 g/s for the three runs. In Table 7.7, the methane emissions from the primary clarifier are tabulated along with the measured BOD and TOC removals across the clarifier.

For the activated sludge treatment reactor, as shown in Table 7.2, the average hydrogen sulfide emissions for three runs was 0.022 g/s and ranged from 0.021 g/s to 0.022 g/s. The methyl mercaptan emissions averaged 0.0041 g/s and ranged from 0.0036 g/s to 0.048 g/s. The dimethyl sulfide emissions averaged 0.21 g/s ranged from 0.16 g/s to 0.29 g/s. The dimethyl disulfide emissions averaged 0.0038 g/s over three runs, ranging from 0.0037 g/s to 0.0040 g/s. In Table 7.8, the liquid material balances for the four reduced sulfur compounds in the activated sludge treatment reactor are compared to the measured emissions of those four compounds. This comparison shows that most of the reduced sulfur compound loss across the activated sludge treatment reactor was not accounted-for in the measured air emissions. This indicates that all four of the reduced sulfur compounds were largely destroyed in the activated sludge treatment reactor. Based on the results from the ASBs in this study, efficient destruction of total sulfide was expected in the activated sludge treatment reactor. However, the relatively efficient destruction of the organic reduced sulfur compounds, especially DMS and DMDS, in the activated sludge treatment reactor is in contrast to the ASBs, from which most these compounds were emitted, rather than destroyed. Adsorption onto the high concentration of suspended solids followed by oxidation is certainly a plausible mechanism for destruction of the organic reduced sulfur compounds in the activated sludge treatment reactor. Recent research (Lin and Chou 2006), which shows that volatile, hydrophobic compounds tend to partition to the suspended solids in activated sludge systems, supports this hypothesis.

During the tests, the methane emissions from the activated sludge treatment reactor for the three runs ranged from 0.2 to 0.27 g/s with an average value of 0.24 g/s. For the AST, the methane emissions and the liquid material balances for BOD and TOC are summarized in Table 7.9. The BOD removal across the AST was 233 g/s, and the methane emissions were 0.24 g/s.

The flow and concentration data for the 4A and 4E sewer manhole vents are summarized in Table 7.9. Due to relatively low gaseous flow rates and concentrations at the 4A sewer manhole vent, the emissions of H_2S, MM, DMS and DMDS were determined to be very low, with average emission rates of 0.0031, 0.00032, 0.0027, and 0.0016 g/s, respectively. The gas flow rates and concentrations of the reduced sulfur gases in the 4E sewer manhole vent gases were higher, with average H_2S, MM, DMS and DMDS emission rates of 0.11, 0.22, 0.39 and 0.84 g/s, respectively. Inspection of the liquid sample reduced sulfur compound concentrations in Table 7.4 shows that the liquid phase concentrations were higher at the 4A manhole than at the 4E manhole, which is opposite of the trend seen for the emissions. The 4E manhole is vented via an induced draft fan, which can vent gas from a large area of the in-mill sewer system, including areas downstream from the 4A manhole. The 4A manhole is simply open to the atmosphere and vented only by natural convection. The results from testing these manhole vents indicate that caution should be used if any attempt is made to estimate sewer vent emissions from liquid phase data.

Table 7.2 Summary of Emission Rates

Source	Run No.	Emissions, g/s				
		H_2S	MM	DMS	DMDS	CH_4
PC	1	1.47E-01	5.44E-02	8.40E-02	3.07E-03	8.67E-02
	2	3.26E-01	3.70E-02	1.33E-01	5.18E-03	1.55E-01
	3	4.81E-01	3.46E-02	9.48E-02	2.21E-03	2.65E-01
	Average	3.18E-01	4.20E-02	1.04E-01	3.49E-03	1.69E-01
AST	1	2.19E-02	4.81E-03	2.90E-01	3.73E-03	2.70E-01
	2	2.12E-02	3.96E-03	1.60E-01	3.96E-03	2.42E-01
	3	2.17E-02	3.63E-03	1.78E-01	3.80E-03	2.04E-01
	Average	2.16E-02	4.13E-03	2.09E-01	3.83E-03	2.39E-01
4A	1	5.43E-03	4.77E-04	4.54E-03	1.17E-03	NA
	2	1.21E-03	5.89E-05	8.97E-04	1.81E-03	NA
	3	2.72E-03	4.23E-04	2.71E-03	1.78E-03	NA
	Average	3.12E-03	3.20E-04	2.72E-03	1.59E-03	NA
4E	1	1.18E-01	2.98E-01	3.63E-01	1.12E+00	NA
	2	1.44E-01	2.21E-01	4.16E-01	7.92E-01	NA
	3	5.85E-02	1.44E-01	4.01E-01	6.02E-01	NA
	Average	1.06E-01	2.21E-01	3.93E-01	8.39E-01	NA

NA = Not Available

Table 7.3 Meteorological and Concentration Summary Data for Emission Tests, Mill F

Source	Run No.	Horizontal Wind Direction*, degrees	Horizontal Wind Velocity*, m/s	P-G Stability Class*	Integrated Downwind Ground-Level Concentration**, ppbv			
					H_2S	MM	DMS	DMDS
PC	1	119	3.80	C	423.10	110.94	132.61	3.19
	2	117	4.90	C	563.46	45.32	126.12	3.24
	3	112	4.98	C	797.73	40.69	86.39	1.33
AST	1	116	4.53	C	6.42	1.00	46.66	0.39
	2	117	3.76	C	7.26	0.96	30.10	0.49
	3	119	3.89	B-C	8.60	1.02	38.87	0.55

*Determined from the anemometer at 10 meter height.
**Determined via the procedures outlined in Section 2.3.3.

Table 7.4 Average Liquid Sample Concentrations, Mill F

	Sulfide Ion, mg/L	Total Sulfide, µg S/L	MM, µg S/L	DMS, µg S/L	DMDS, µg S/L	DMTS, µg S/L	Sulfate, mg S/L	Thio-Sulfate, mg S/L	TOC, mg C/L
Primary Influent	17	11346	83.8	618	256	51.7	140.0	7.7	155
No. 3 Primary Clarifier*	15	10357	429	503	ND[11.0]	ND[10.9]	157.7	7.5	NA
PC Outlet / AST Inlet	9	6846	112	539	50.4	56.4	93.8	8.0	123
AST Basin*	NA	827	ND[9.8]	ND[10.5]	ND[11.0]	ND[10.9]	116.3	ND[1.4]	NA
No. 4 Sec. Clarifier Outlet	ND[0.5]	19.0	ND[9.8]	ND[10.5]	ND[11.0]	14.5	103.0	ND[1.4]	34
4E Sewer	ND[0.5]	96.6	14.8	ND[10.5]	ND[11.0]	ND[10.9]	19.1	ND[1.4]	NA
4A Sewer	> 33	89700	96.9	111	54.2	22.0	62.1	9.0	NA

NA = Not Available

ND[xxx] = non-detect with xxx equal to one-half of the lowest calibration limit

*Average of three surface liquid sampling locations.

Table 7.5 Average Physical/Chemical Parameter Measurement Data Associated with Liquid Sample Collection, Mill F

	Depth, Ft.	Temp., °C	Specific Conductance, mS/cm	DO, mg/L	pH
Primary Influent	1	40.9	1.902	1.12	9.8
No. 3 Primary Clarifier	1	39.5	1.709	0.20	9.3
No. 3 Primary Clarifier	8 - 9	40.0	2.254	0.14	9.5
No. 3 Primary Clarifier	15 - 17	40.3	2.537	0.12	9.4
PC Outlet / AST Inlet	1	38.5	1.458	1.19	9.2
AST Basin	1	35.0	1.488	1.70	7.7
No. 4 Sec. Clarifier Outlet	1	34.9	1.397	2.44	7.5
4E Sewer	NA	34.3	0.864	3.91	9.3
4A Sewer	NA	38.3	2.877	0.23	10.9

Table 7.6 No. 3 Primary Clarifier Outlet Concentrations and Emissions Data, Mill F

	Outlet Concentration, µg S/L				Emissions, g/s			
Time	Total Sulfide	MM	DMS	DMDS	H_2S	MM	DMS	DMDS
8:30	6760	90	594	50				
9:46					0.15	0.05	0.08	0.003
10:44					0.33	0.04	0.13	0.005
11:00	10700	105	514	57				
11:47					0.48	0.04	0.09	0.002

Table 7.7 Methane Emissions and the BOD and TOC Liquid Material Balances for the Primary Clarifier at Mill F

Date	Parameter	Inlet, g/s	Outlet, g/s	Removal, g/s	Methane Emissions, g/s
4/29/2006	BOD	362.6	236.5	126.1	0.17
4/29/2006	TOC	157.7	121.0	36.7	0.17

Table 7.8 Apparent Destruction of RSC Compounds in the Activated Sludge Treatment Reactor

Compound	Inlet, g/s	Outlet, g/s	Emissions g/s	Apparent Amount of Compound Destroyed %
H_2S	10.33*	1.13*	0.022	88.9
MM	0.24	0.02	0.004	90.6
DMS	1.13	0.03	0.209	79.1
DMDS	0.16	0.04	0.004	71.1

ND[xx.xx] = Not detected, with xx.xx equal to one-half of the method quantitation limit.
*total sulfide as H_2S

Table 7.9 Activated Sludge Treatment Reactor BOD and TOC Liquid Material Balance and Methane Emissions, Mill F

Parameter	Liquid Balance*	Units	Methane Emissions, g/s
TOC	110	g C/s	0.24
BOD**	233	g/s	0.24

*Inlet – Outlet
**From the 5-Day BOD test

Table 7.10 Flow and Concentration Summary for the 4A and 4E Manhole Vents

Source	Run No.	Temp., °F	Moisture, %	Flow ACFM	Flow DSCFM	Vent Concentration, ppbv H_2S	MM	DMS	DMDS
4A	1	56.8	1.7	1686	1561	86.6	5.4	39.7	6.7
	2	57.0	1.6	1805	1673	18.0	0.6	7.3	9.8
	3	61.3	1.7	1776	1631	41.5	4.6	22.7	9.8
	Avg.	58.4	1.7	1756	1622	48.7	3.5	23.3	8.8
4E	1	107.8	8.4	7290	5709	513.5	918.7	868.9	1772.7
	2	107.8	8.4	7290	5709	625.5	683.3	995.1	1249.8
	3	107.8	8.4	7290	5709	255.0	445.7	958.9	949.0
	Avg.	107.8	8.4	7290	5709	569.5	682.6	941.0	1323.9

8.0 SOURCE DESCRIPTION AND RESULTS OF TESTS AT MILL T

An intensive screening study was conducted at Mill T December 5-8, 2005. Although emissions measurement testing and associated liquid sampling was not conducted at Mill T in the same manner as at the other mills in this study, the extensive data collected during the screening study made it possible to develop an understanding of the emissions from the WWTP, estimate the magnitude of those emissions, and relate the variations in the emissions to variations in process operation. This section describes the source, the tests carried out, and the results of the study.

8.1 Wastewater Treatment Plant Description, Mill T

Mill T produces approximately 805,000 tons per year of bleached kraft paperboard from pulp produced entirely on site. Figures 8.1 and 8.2 are a schematic representation and a scale drawing of the Mill T WWTP, respectively. The mill alkaline sewer, with an average flow rate of approximately 37.5 MGD, flows through a 230 ft. diameter primary clarifier, with an approximate volume of 3.7 million gallons. The retention time in the primary clarifier is approximately 2 to 3 hours. At the time of the screening study, the primary clarifier weir was completely submerged and not visible. The mill acid sewer mixes with the primary clarifier effluent. The combined mill sewer, with an average flow rate of approximately 50 MGD, then flows to the 3.5-acre equalization basin, where much of the remainder of the suspended solids from the mill alkaline sewer settles out of the effluent. In addition, when intermittent problems occur with the primary sludge press, the primary sludge recovered from the primary clarifier is sent directly to the equalization basin. At the time of the screening study, solids accumulation was very visible in the equalization basin, and vigorous bubbling indicated that significant anaerobic activity was occurring. Occasionally, the equalization basin is dredged, and the dredged sludge is placed in the 46-acre sludge pond. At the time of the screening study, the sludge pond was essentially dry. From the equalization basin, the effluent flows through the no. 1 ASB canal to the 41-acre no. 1 ASB, which has an estimated retention time of approximately 1.5 days and 2220 HP of surface aeration. Figure 8.3 is a scale drawing of the no. 1 ASB, and Figure 8.4 is a scale drawing of the no. 1 ASB Canal. Although there are four openings from the no. 1 ASB Canal into the no. 1 ASB, most of the wastewater enters the no. 1 ASB through the northernmost opening.

From the no. 1 ASB, the effluent flows to the 72-acre no. 2 ASB, which has an estimated retention time of approximately 2.5 days and 2295 HP of surface aeration. Hard-piped condensates, with a flow rate of approximately 3 MGD are introduced to the no. 2 ASB at multiple locations near the inlet to the no. 2 ASB. The normal BOD load to the WWTP, including the hard-piped condensates, is in the range of 80,000 to 125,000 pounds per day.

Effluent from the no. 2 ASB is transported via a long canal to the 122-acre no. 3 ASB, which has an estimated retention time of approximately 4.5 days and 1050 HP of surface aeration. The effluent from the no. 3 ASB flows directly into a series of two retention ponds (nos. 1 and 2). These two retention ponds have areas of approximately 63 and 189 acres, respectively, and a combined retention time of 5 days.

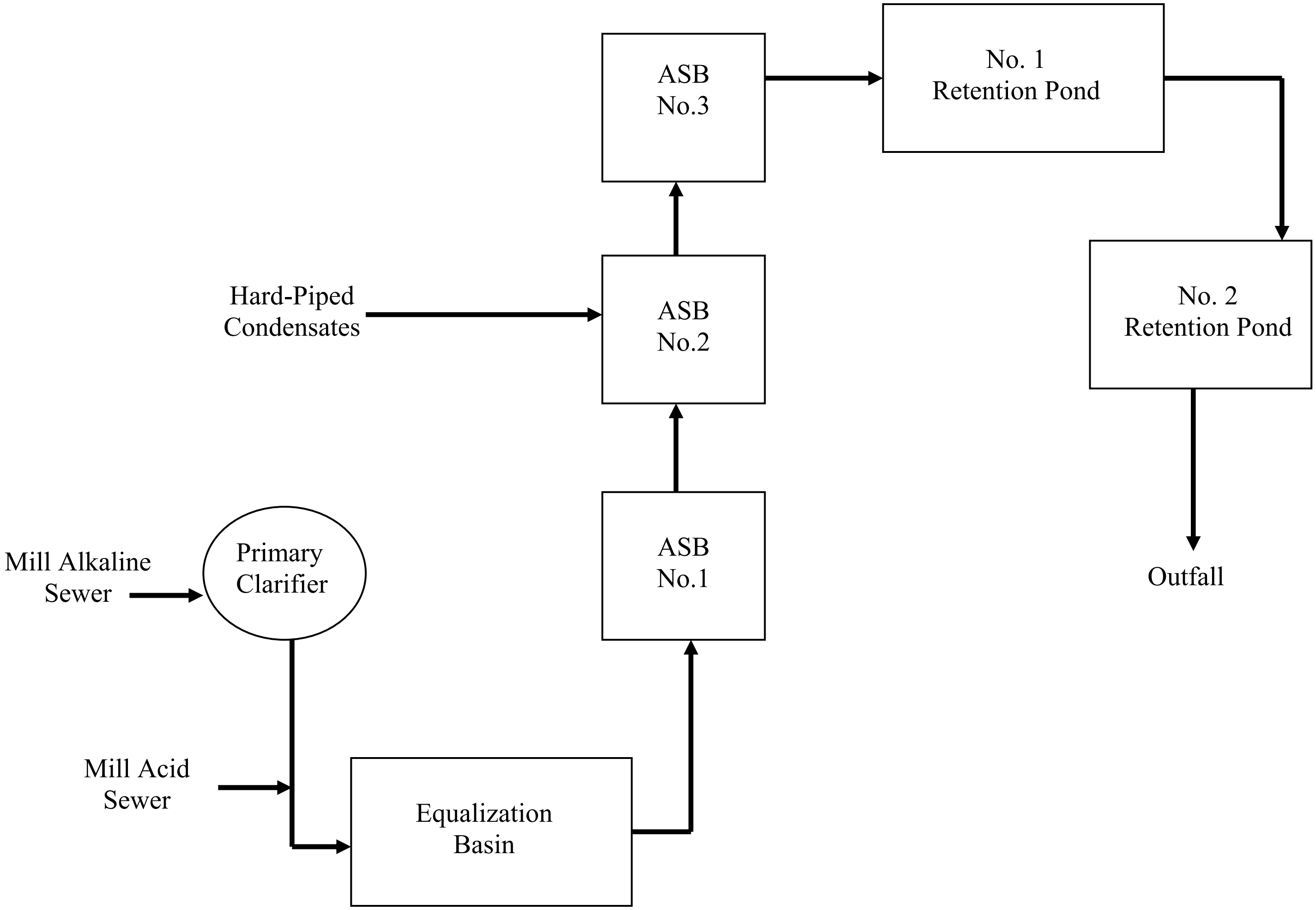


Figure 8.1 Schematic Diagram for the Mill T WWTP

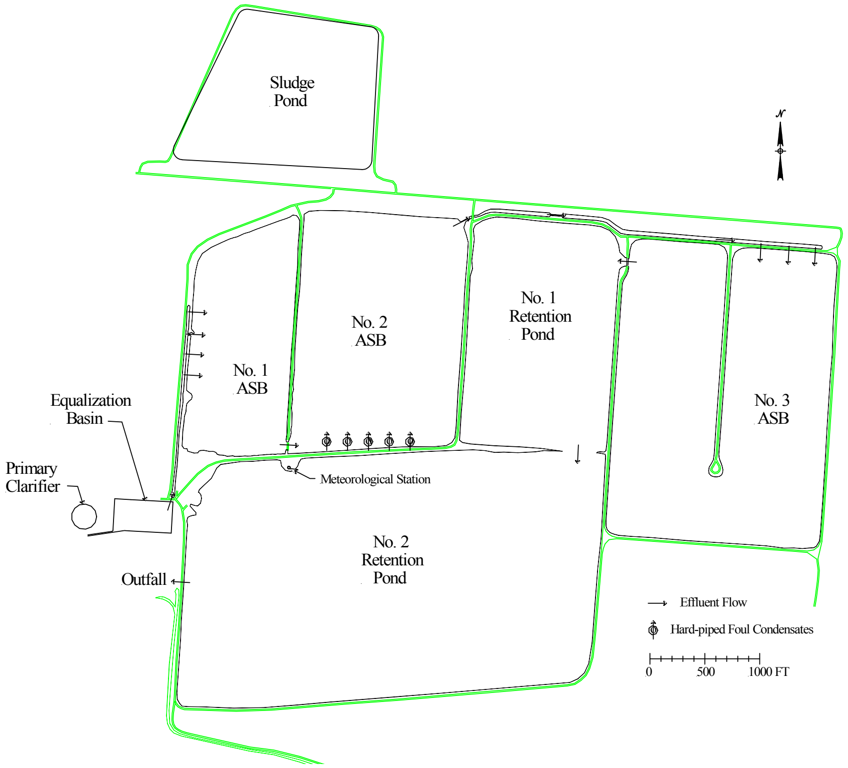


Figure 8.2 Scale Drawing of the Mill T WWTP

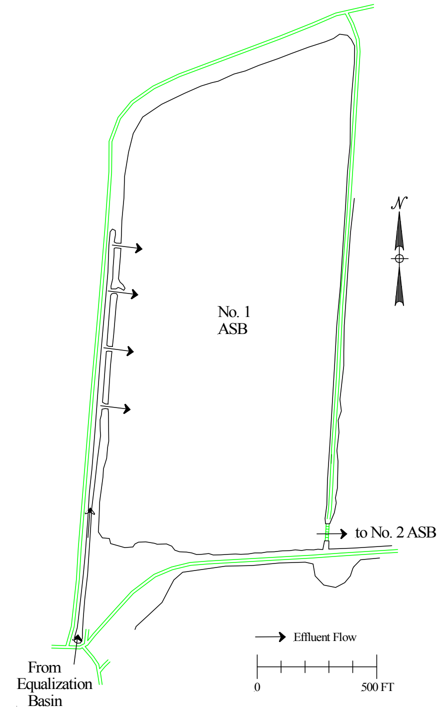


Figure 8.3 Scale Drawing of the Mill T No. 1 ASB

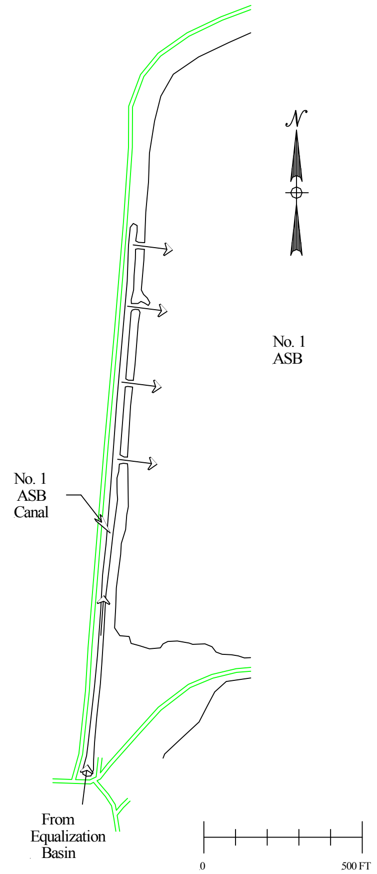


Figure 8.4 Scale Drawing of the Mill T No. 1 ASB Canal

8.2 Screening Study Results, Mill T

The Jerome H_2S analyzer screening study results summarized in Table 8.1 indicate that the nos. 1 and 2 ASBs and the equalization basin were significant sources of RSC emissions. The results indicate that the primary clarifier and no. 2 retention pond also had RSC emissions, but the downwind concentrations were lower than for the former three sources. The no. 3 ASB, no. 1 retention pond and sludge pond did not have significant RSC emissions.

Canister samples were collected downwind of the nos. 1 and 2 ASBs and the equalization basin for speciated RSC analysis. The results from the analysis of those canister samples are summarized in Table 8.1. At the equalization basin and the no. 1 ASB, the organic reduced sulfur compounds are present, but the majority of the RSC emissions were hydrogen sulfide. However, at the no. 2 ASB the organic reduced sulfur compounds comprised most of the RSC emissions. These results are consistent with WWTP operation, which included significant anaerobic activity in the equalization basin (just upstream of the no. 1 ASB) and the introduction of hard-piped condensates from the kraft pulping process to the no. 2 ASB.

Table 8.1 Jerome Analyzer Upwind/Downwind Screening Study Results, Mill T

					Avg. Meteorological Cond.*			Average Conc., ppbv	
Source	Run No.	Date	Start Time	Stop Time	Wind Direction, degrees	Wind Speed, m/s	Atmospheric Stability Class (P-G)	Upwind	Downwind
No. 1 ASB	1	12/5/2005	16:20	16:44	357	4.9	E	5	204
	2	12/5/2005	16:50	16:51	358	5.2	E-F	NA	NA
	3	12/6/2005	13:03	13:42	99	2.0	A	15	287
	4	12/6/2005	15:30	15:45	144	3.0	A	NA	1610
	5	12/7/2005	9:24	10:23	57	3.7	D	58	453
	6	12/8/2005	9:39	10:23	33	6.6	C	2	37
No. 1 ASB Canal	1	12/7/2005	9:24	10:23	57	3.7	D	478	429
No. 2 ASB	1	12/5/2005	16:20	16:44	357	4.9	E	NA	NA
	2	12/5/2005	16:50	16:51	358	5.2	E-F	NA	327
	3	12/6/2005	13:03	13:42	99	2.0	A	37	15
	4	12/6/2005	15:30	15:45	144	3.0	A	NA	187
	5	12/7/2005	9:24	10:23	57	3.7	D	5	58
	6	12/8/2005	9:39	10:23	33	6.6	C	2	134
Equalization Basin	1	12/5/2005	15:46	16:06	1	6.2	E	390	232
	2	12/6/2005	11:03	11:19	77	5.1	E	35	295
Primary Clarifier	1	12/8/2005	10:40	10:50	335	7.3	D	10	23
No. 3 ASB	1	12/6/2005	9:23	10:06	98	3.4	D-E	1	4
	2	12/7/2005	11:16	11:59	45	3.9	E	7	3
No. 1 Retention Pond	1	12/6/2005	10:10	10:40	103	3.3	D-E	NA	7
	2	12/7/2005	11:16	11:59	45	3.9	E	7	4

(Continued on next page. See notes at end of table.)

Table 8.1 Continued

					Avg. Meteorological Cond.*			Average Conc., ppbv	
Source	Run No.	Date	Start Time	Stop Time	Wind Direction, degrees	Wind Speed, m/s	Atmospheric Stability Class (P-G)	Upwind	Downwind
No. 2 Retention Pond	1	12/6/2005	10:10	10:40	103	3.3	D-E	NA	15
	2	12/7/2005	13:32	13:55	74	5.6	F	3	27
Sludge Pond	1	12/7/2005	14:21	14:42	68	5.3	F	3	5

NA = Not Available

*Determined from the anemometer at 10 meter height.

Table 8.2 Canister Downwind Speciated Screening Study Results, Mill T

					Avg. Meteorological Cond.*			Average Downwind Conc., ppbv			
Source	Run No.	Date	Start Time	Stop Time	Wind Direction, degrees	Wind Speed, m/s	Atmospheric Stability Class (P-G)	H_2S	MeSH	DMS	DMDS
ASB No. 1	1	12/5/2005	16:04	16:51	13	5.2	E	126	17	10	4
	4	12/6/2005	12:56	13:44	98	2.1	C	438	28	12	7
	5	12/6/2005	13:57	14:51	146	3.0	B	613	29	10	3
	6	12/6/2005	15:03	15:48	146	3.2	B	358	120	19	6
	7	12/7/2005	9:14	10:03	54	3.9	D	420	46	20	7
	8	12/7/2005	10:07	10:53	57	4.6	D-E	647	62	21	7
	9	12/7/2005	11:05	11:58	46	4.0	E	553	51	17	2
	10	12/7/2005	14:23	15:08	68	5.1	E-F	1103	103	39	12
	11	12/8/2005	9:22	10:10	334	6.7	C	20	ND[2]	17	ND[1]
	12	12/8/2005	10:12	10:59	332	7.0	C	19	ND[2]	16	ND[1]
ASB No. 2	1	12/5/2005	16:04	16:51	13	5.2	E	89	153	147	39
	2	12/6/2005	9:01	9:46	95	3.4	D	25	58	41	49
	3	12/6/2005	10:15	11:02	92	3.8	A	38	48	23	60
	4	12/6/2005	12:56	13:44	98	2.1	C	74	44	18	24
	5	12/6/2005	13:57	14:51	146	3.0	B	148	50	16	15
	7	12/7/2005	9:14	10:03	54	3.9	D	16	20	10	26
	8	12/7/2005	10:07	10:53	57	4.6	D-E	7	18	11	33
	9	12/7/2005	11:05	11:58	46	4.0	E	37	59	15	61
	11	12/8/2005	9:22	10:10	334	6.7	C	15	55	42	37
	12	12/8/2005	10:12	10:59	332	7.0	C	17	58	74	37
Equalization Basin	1	12/7/2005	14:07	14:52	72	4.8	E-F	602	19	10	5

ND[x] = Not detected at a detection limit of x.
*Determined from the anemometer at 10 meter height.

8.3 Results of Emission Rate Estimations and Discussion, Mill T

Emissions rate measurements using the spatial ambient air sampling technique were not conducted at Mill T; however, the extensive amount of screening study data collected combined with the experience and emissions rate data collected at other mills allowed the development of a procedure by which emission rates for several Mill T WWTP sources could be estimated. The sources of most interest for emission rate estimation were the equalization basin, no. 1 ASB and no. 2 retention pond. The no. 1 ASB was of interest because the ground-level concentration data indicated much higher emissions than were observed at any of the other ASBs tested in this study. The no. 2 retention pond was also of special interest because the ground-level concentration data indicated that this source may have significant emissions, whereas essentially all of the other data generated in this study for post-aeration retention ponds indicated insignificant emissions.

The information required to calculate a source emission rate from the spatial ambient air sampling technique includes meteorological data, geographical data, horizontally integrated ground-level concentrations and horizontally integrated vertical concentration profile data. From the Mill T screening study, complete meteorological and geographical data sets were available; however, horizontally integrated ground-level concentrations and horizontally integrated vertical concentration profile data were not available. An estimation procedure used for the vertical concentration profile under relatively stable atmospheric conditions (C through E P-G atmospheric stability classes) is described in Section 6.3. At Mill T emissions were only estimated from measurements made within this stability class range so that the same vertical concentration profile estimation could be applied. The following discussion describes how the other missing component (horizontally integrated ground level concentration) was estimated, from site-specific data, so that emission rates could be estimated.

Although horizontally integrated ground-level concentration data were not directly available at Mill T, Jerome analyzer data were available at three downwind locations for most of the screening study test runs, as detailed in the mill-specific report (NCASI 2008i). For estimating purposes, the average Jerome responses for those three locations, which are shown in Table 8.1, were used as an estimate of the horizontally integrated ground-level downwind concentration. The Jerome analyzer does not yield compound-specific data, i.e., it responds to all reduced sulfur compounds to varying degrees; however, an extensive amount of speciated reduced sulfur compound data for Mill T were available from the downwind canister samples. Each canister sample was collected over a 30 minute period at one of the multiple canister sampling locations. The results of the canister sampling, as summarized in Table 8.2, and the details of each test are described in the mill-specific report (NCASI 2008i). Additionally, the Jerome analyzer response factors for the four major reduced sulfur compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) were measured at the NCASI Southern Regional Center Laboratory. Therefore, the downwind speciated compound concentrations were estimated from 1) the Jerome analyzer responses, 2) average ratios of the four reduced sulfur compound concentrations, and 3) Jerome relative response factors for each of those compounds.

For the no. 1 ASB, Table 8.3 shows the average theoretical speciated Jerome analyzer results, which were calculated from the downwind canister analysis results and Jerome response factors of 1.03, 0.46, 0.15 and 0.41 for hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, respectively. To obtain these estimates, for each of the 12 samples, the canister analysis concentrations were multiplied by the Jerome response factors to yield the canister concentrations adjusted for Jerome response. Then, the Jerome response-adjusted canister concentrations were totaled, and the percentage of the total response was calculated for each compound to yield the theoretical Jerome responses. For the 12 samples, the percentage of the theoretical total response for each compound was averaged. This yielded source-specific factors that could be applied to the Jerome measurements to estimate the concentrations of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The values of these source-specific Jerome response factors were 93%, 4%, 3% and 0%, respectively.

As shown in Table 8.4, the source-specific Jerome response factors were applied to the results of each of the six Jerome analyzer screening test runs at the no. 1 ASB and the one test run at the equalization basin to calculate estimated average downwind concentrations for each compound. The emissions were also estimated for the no. 2 retention pond. Definitive canister data were not available for the no. 2 retention pond; therefore, since all of the reduced sulfur compound emissions from this pond would be expected to be due to anaerobic generation, 100% of the Jerome analyzer response was attributed to H_2S. The emissions from the no. 3 ASB and the no. 1 retention pond were insignificant. Therefore, the wastewater must have gone anoxic again at some point in the no. 2 retention pond to generate sulfide which was then emitted as H_2S.

Figure 8.5 shows the estimated H_2S emission rates for Jerome screening study run nos. 1, 5, and 6 at the no. 1 ASB. Also included on Figure 8.5 are the estimated H_2S emission rates for run nos. 1 and 2 at the no. 2 retention pond, and run no. 2 on the equalization basin. Emission rates were not estimated for the other test runs for one or more of the following reasons: 1) unstable atmospheric conditions (P-G Stability Classes A and B), 2) insufficient horizontal ground-level characterization of the downwind plume, and/or 3) interference from upwind emission sources. The error bars indicate the range of the estimated emission rates associated with one standard deviation of the vertical concentration profile exponent (b). The numerical values of the data shown in Figure 8.5 are summarized in Table 8.5. The results for the no. 2 retention pond indicated that the H_2S emissions were in the range of about 1 to 1.5 grams per second. Since there were virtually no H_2S emissions from the no. 3 ASB and the no. 1 retention pond, which were the two sources immediately upstream from the no. 2 retention pond, the most plausible source of the H_2S emissions from the no. 2 retention pond was the development of anaerobic conditions in the pond, which led to generation of sulfide and H_2S emissions. The results for the equalization basin indicated that the emissions were in the range of 0.2 g/s to 0.4 g/s. The results for the no. 1 ASB indicate that the emissions for runs nos. 1, 5, and 6 were in the range of about 2, 8, and 0.5 grams per second, respectively. Each of these test runs on the no. 1 ASB were conducted on different days, so the WWTP operating parameters for each day were investigated for differences that may have been responsible for this wide variation in H_2S emission rate.

At the no. 1 ASB, run nos. 1, 5, and 6 were conducted on December 5, 7, and 8, respectively. In Figure 8.6, the daily total organic carbon (TOC) loading and pH are plotted for the no. 1 ASB for the period of December 1-10. The pH value is a daily composite collected at the ASB inlet. The plots show that the TOC loading increased greatly on December 5 (from midnight December 4 to midnight December 5). This spike in TOC loading was enough to temporarily overload the no. 1 ASB. The TOC loading decreased on December 6, 7, and 8 to the point that on December 8 it was back to level it was before the spike occurred. The no. 1 ASB pH was also quite variable during this period. On December 4 and 5, the pH was close to 10, but on December 6 it dropped to about pH 7. On December 7, the pH rose to about 8, and then on December 8 it was back up to about pH 10.

The variable TOC loading and pH appear to be related to the variable H_2S emission rates observed at the no. 1 ASB on December 5, 7, and 8. With the TOC influent spike just beginning on December 5, and the high pH in the basin, low to moderate H_2S emissions were observed. On December 6, near the peak of the TOC spike with low influent pH, although it was not possible to quantitatively estimate the H_2S emission rate, screening data indicated that it was very high. On December 7, with the basin influent just starting to come off of the TOC spike and low pH, high H_2S emissions were observed. On December 8, with the TOC loading back to a normal level and high pH, low H_2S emissions were observed.

Table 8.3 Calculation of Theoretical Jerome Analyzer Response Distribution for the No. 1 ASB, Mill T

Source	Run. No.	Downwind Canister Conc., ppbv				Canister Concentration Adjusted for Jerome Response Factor, ppbv					Theoretical Jerome Response, % of total			
		H_2S	MM	DMS	DMDS	H_2S	MM	DMS	DMDS	Total	H_2S	MM	DMS	DMDS
No. 1 ASB	1	126	17	10	4	130	8	2	2	141	92	6	1	1
	4	438	28	12	7	451	13	2	3	469	96	3	0	1
	5	613	29	10	3	631	13	2	1	647	98	2	0	0
	6	358	120	19	6	369	55	3	2	429	86	13	1	1
	7	420	46	20	7	433	21	3	3	460	94	5	1	1
	8	647	62	21	7	666	29	3	3	701	95	4	0	0
	9	553	51	17	2	570	23	3	1	596	96	4	0	0
	10	1103	103	39	12	1136	47	6	5	1194	95	4	0	0
	11	20	0	17	0	21	0	3	0	23	89	0	11	0
	12	19	0	16	0	20	0	2	0	22	89	0	11	0
	Average										93	4	3	0
Equalization Basin	1	602	19	10	5	620	9	2	2	632	98	1	0	0

Table 8.4 Estimated Average Compound-Specific Concentrations for the Jerome Analyzer Screening Study Tests, Mill T

Source	Run No.	Average Downwind Jerome Conc., ppbv	Estimated Average Downwind Conc., ppbv			
			H_2S	MM	DMS	DMDS
No. 1 ASB	1	204	190	8	5	1
	2	NA	NA	NA	NA	NA
	3	287	267	11	7	1
	4	1610	1497	64	42	7
	5	453	421	18	12	2
	6	37	34	1	1	0
Equalization Basin	1	232	228	3	1	1
	2	295	289	4	1	1

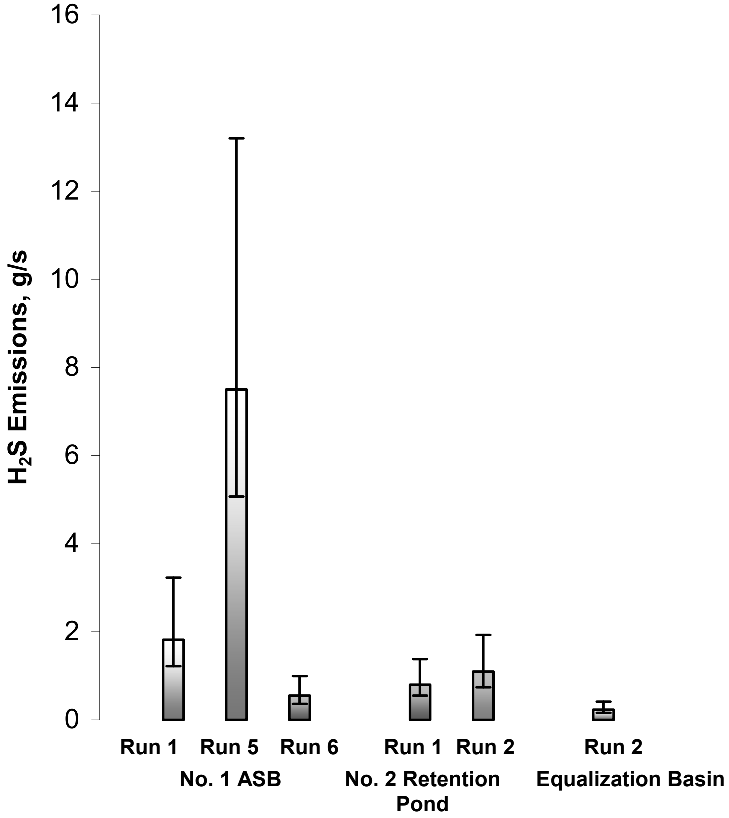
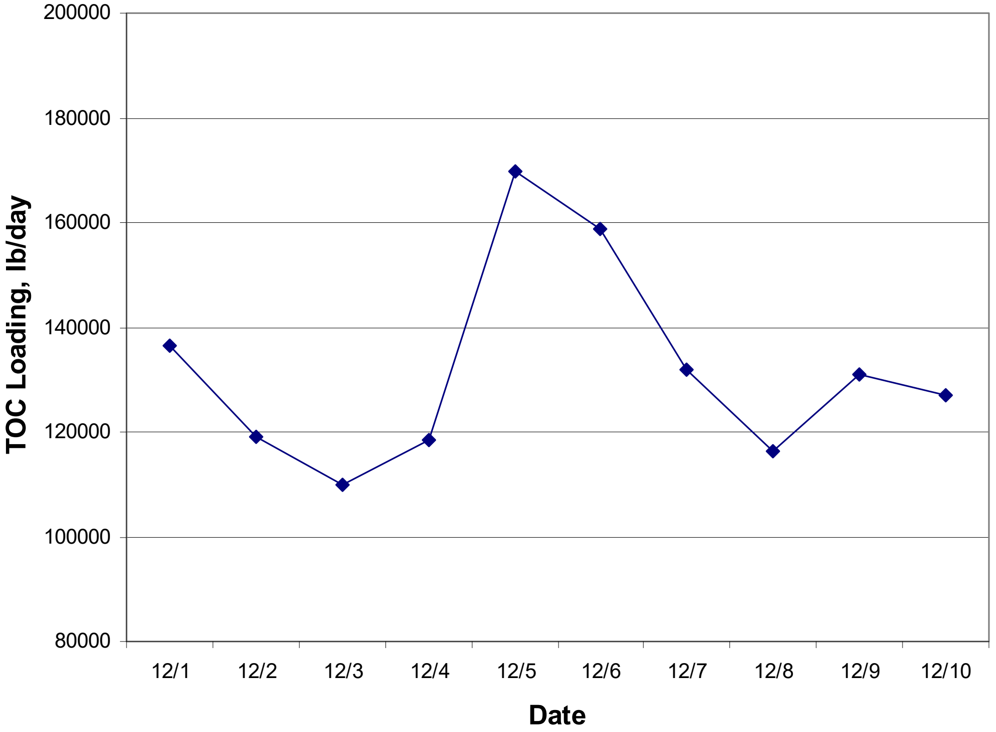


Figure 8.5 Estimated H_2S Emission Rates, Mill T

Table 8.5 Estimated H_2S Emission Rates, Mill T

Source	Run No.	H_2S Emission Rate, g/s Minimum (b = 5.7)	Average (b = 3.9)	Maximum (b = 2.1)
No. 1 ASB	1	1.22	1.82	3.23
	5	5.07	7.50	13.20
	6	0.37	0.55	1.00
No. 2 Retention Pond	1	0.55	0.80	1.38
	2	0.74	1.10	1.93
Equalization Basin	1	0.16	0.24	0.42



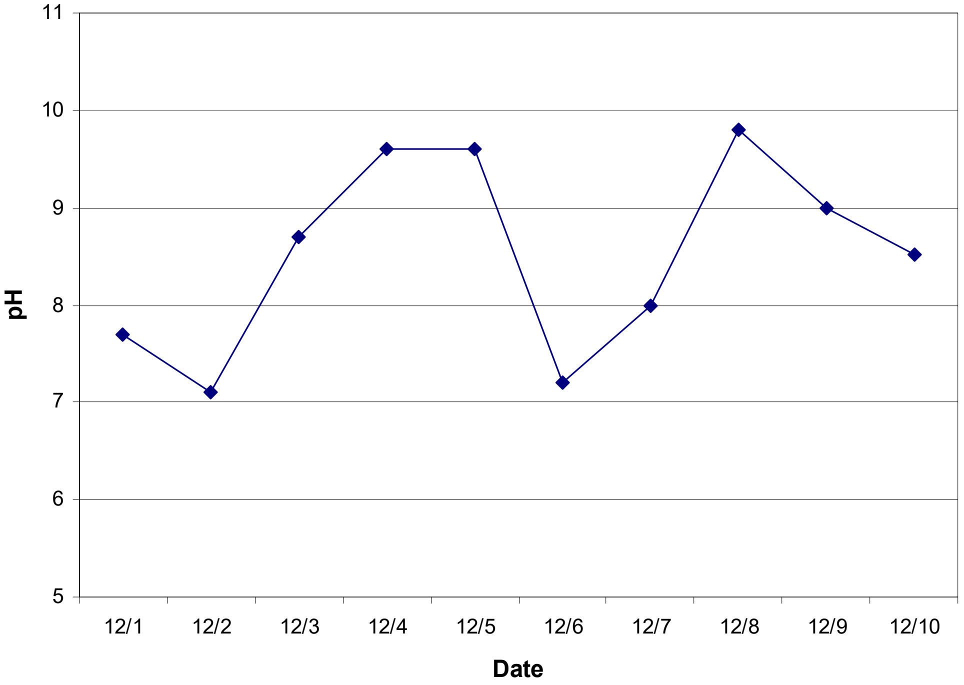


Figure 8.6 No. 1 ASB TOC Loading and pH

9.0 SUMMARY OF RESULTS BY UNIT OPERATION

The wastewater treatment systems at kraft pulp mills consist of a series of unit operations including settling basins, primary clarifiers, aerated basins, and post-aeration quiescent ponds. Some mills also use emergency ponds to store strong waste to prevent peak loads to the treatment basin. During this study, various components of wastewater treatment and transport systems at six different kraft mills were tested for their reduced sulfur and methane emissions. In addition to the air emission testing, extensive effluent sampling and analysis were carried out. This section summarizes the results of all these studies and discusses their findings.

9.1 Pre-Aeration Basin Emissions

9.1.1 *Pre-Aeration Basin Reduced Sulfur Compound Emissions*

During this study tests were performed at four pre-aeration basins including two primary settling ponds, a strong waste spill pond, and a post-primary clarifier settling/equalization basin. The reduced sulfur compound emission rates for the four pre-aeration basins are summarized in Table 9.1. The process and meteorological data collected during these studies are summarized in Table 9.2.

As described earlier, at Mill B, the primary clarifier influent, with a flow rate of approximately 15 MGD, is diverted to the spill pond whenever the wastewater conductivity exceeds a set threshold. When the mill operation returns to normal, the spill pond contents are pumped back to inlet of the primary clarifier at a flow rate of approximately 2 MGD. Wastewater flows into and out of the spill pond at approximately the same location. Tests were conducted at the spill pond during two periods. The average H_2S emissions from the spill pond were 2.7 g/s and 5.9 g/s from the first and second test periods, respectively, with an average wind speed at 10 meters elevation of 2.7 m/s for the first test period and 5.0 m/s for the second. Higher wind speeds would be expected to result in higher emissions (USEPA 1994). Because of the way the spill pond is used, it is not possible to determine how much of the H_2S emissions were due to liquid sulfide input with the wastewater versus anaerobic generation. The data in Table 9.1 also show that, except for methyl mercaptan which had an emission rate of 0.013 g/s during the second test period, all of the organic reduced sulfur compound emission rates were non-detect. It should be noted that the detection limits for methyl mercaptan in the 2005 tests were higher than the levels at which it was detected in the 2006 study. Thus, methyl mercaptan could have been present in the 2005 tests at levels measured in the 2006 tests.

The two primary settling ponds tested during the study are located at Mill E where they are used in lieu of a primary clarifier. During the first two test periods, the no. 1 settling pond handled the main mill sewer from power and recovery, papermaking and the bleach plants, whereas the no. 2 settling pond handled the fiberline sewer and the effluent from primary sludge dewatering. Additionally, during the first test period, the no. 2 settling pond also handled the effluent from an OCC recycling facility, which was shut down prior to the second test period. During the third test period, all of the mill effluent was flowing through the no. 2 settling pond, and the no. 1 settling pond had been stagnant for several months. For the no. 1 settling pond, with non-stagnant conditions the average H_2S emission rates for the first and second test periods were 1.0 and 3.0 g/s, respectively. For the no. 2 settling pond, the average H_2S emission rates for the first, second, and third test periods were 3.4, 0.4, and 1.4 g/s, respectively. At both settling ponds, the higher emissions occurred with higher wind velocities.

As the wastewater flowed through these ponds on its way to secondary treatment, there was significant sulfide generation as a result of anaerobic activity. For the no. 1 settling pond, sulfide generation rates of 3 g/s, 26 g/s, and 3 g/s were calculated for the first, second, and third test periods, respectively. Although the reason for the higher sulfide generation rate during the second test period are unclear, two differences between the test periods that may have been related to differing sulfide generation rates were 1) sludge accumulation that occurred between the first and second test periods, and 2) the higher in-basin pH during the second test period. The lack of a straightforward explanation for this situation is understandable in light of the complexity known to exist around the chemical and biological-assisted transformations of sulfide (e.g., Chen and Morris 1972; Kontronarou and Hoffman 1991; Madigan, Martinko, and Parker 1997; Buisman et al. 1990; Nielsen, Vollertsen, and Hvitved-Jacobsen 2006). The high in-basin sulfur concentrations and apparently high sulfide generation rate during the second test period imply that the emission rate could have been much higher if the pH had been at a more normal level (approximately neutral). During the third test period in June 2007, there had been no input of sulfur to the no. 1 settling pond for almost five months; therefore, the in-basin sulfide generation must have resulted from anaerobic reduction of sulfate and/or elemental sulfur associated with the water and/or sludge stored in the pond. Oxidized sulfur may have still been present in the pond at the time of sampling because the lower temperature of the stagnant pond in the preceeding winter and spring months, would have inhibited anaerobic activity.

For the no. 2 settling pond, the observed sulfide generation rates are easier to explain. At the no. 2 settling pond, similar sulfide generation rates of 3.6 g/s and 5.0 g/s were calculated for the first and second test periods, with similar in-basin temperatures (19°C) in the no. 2 settling pond, and main mill sewer flowing through the no. 1 settling pond. However, during the third test period, with the main mill sewer flowing through the no. 2 settling pond, the sulfide generation rate was 25 g/s. The increase in sulfide generation was likely due to the increase in in-basin temperature to 44°C and the BOD input associated with the main mill sewer flow. The partial covering of dried fibrous material would have also contributed to higher in-basin temperature.

At Mill T, the post-primary clarifier equalization basin, from an estimation based on the screening study results, had an H_2S emission rate of 0.24 g/s. Although no methane measurements were made for this basin, it had very vigorous bubbling, implying significant anaerobic activity. The relatively low H_2S emissions from this basin are most likely related its modest surface area of 3.5 acres. The estimated organic reduced sulfur compound emissions from this basin were 0.006 g/s, 0.002 g/s, and 0.003 g/s for methyl mercaptan, dimethyl sulfide and dimethyl disulfide, respectively.

As discussed above, at the three basins where the H_2S emissions were measured during multiple test periods (spill pond and nos. 1 and 2 settling ponds), there were large differences between the emission rates measured at different times. Examination of the process operating data, liquid sampling data, and meteorological data indicated that the factor most likely to be related to the differing emission rates was horizontal wind velocity. Models developed by EPA suggest that liquid phase mass transfer rates for volatile organics from large, shallow quiescent basins are expected to increase exponentially with wind velocity as the wind velocity increases above 3.25 m/s (USEPA 1994). Additionally, H_2S emissions from quiescent basins are expected to be directly proportional to surface area. Although normalization for surface area will not aid in understanding differences in measured emission rates for the same basin, it facilitates comparison of emission rates for different basins. The emission rates were normalized to a per acre basis and a wind velocity of less than 3.25 meters per second, with the results tabulated in Table 9.2 and shown graphically in Figure 9.1. In Figure 9.1, the emission rates are shaded differently for essentially stagnant basins versus those with significant effluent flow.

Figure 9.1 shows the wind velocity adjustment brought the average H_2S emissions for multiple test periods much closer to the same level when the basins were tested with similar flow conditions, i.e., stagnant or flow-through. Normalization for surface area and wind velocity brought the emissions from all of the tests at basins with flow-through conditions into a similar range of 0.01 to 0.04 gram per second per acre, whereas the normalization brought emissions from all of the tests at basins with stagnant conditions into a narrow range of 0.12 to 0.15 gram per second per acre. The higher H_2S emissions from basins in essentially stagnant conditions may be largely explained by the fact that the only removal mechanism for the sulfide generated via anaerobic biological activity in the stagnant ponds is volatilization to the atmosphere as H_2S. This is in contrast to the ponds with significant flow, where in-basin-generated sulfide leaves the basin with the exit stream, as well as through volatilization to the atmosphere.

Regarding the no. 1 settling basin in the flow-through configuration, it is interesting to note that pH apparently did not influence the H_2S emissions to the extent expected based on the H_2S dissociation equilibrium in water. Based on that equilibrium, the concentration of undissociated H_2S would have been about 20 times higher in the basin during test 1 than during test 2; however, the emissions after normalization for wind velocity were about the same for both tests.

At all of the mills in this study, kraft process foul condensate handling practices limited the amount of organic reduced sulfur compounds (ORSCs) associated with influent to the pre-aeration basins, which resulted in very low to non-detect emissions of those compounds from the pre-aeration basins.

9.1.2 *Pre-Aeration Basin Methane Emissions*

The results of methane emission tests at the Mill B spill pond and the two settling basins at Mill E are summarized in Table 9.3. These results show that at Mill B, the methane emission rates from the spill pond were 2.7 g/s and 0.4 g/s for the first and second test periods, respectively, suggesting lower anaerobic activity during the second test period. Shortly before the second test period, sludge accumulation near the inlet/outlet area had been dredged, which could also have resulted in less anaerobic activity and lower methane emissions. Also, as shown in Table 9.2, the liquid temperature was 10°C colder during the second test period, which could have contributed to lower methane generation.

The data for Mill E in Table 9.3 show that there was significant methane generation in the two settling ponds during the first and second test periods, with emission rates, ranging from 9 g/s to 32 g/s. Methane emissions were not measured during the third test period.

In Table 9.4, the TOC contents of the influent and outflow from the no. 1 and no. 2 settling ponds are presented along with the measured TOC gains across those ponds. The increase in the amounts of TOC as the wastewater flows through the ponds may be due to 1) the formation of water soluble carbon-containing compounds from biological degradation of the settled primary sludge, and/or 2) fixation of atmospheric carbon dioxide via photosynthetic or other biological means in these large, shallow basins.

Table 9.1 Pre-Aeration Basin Reduced Sulfur Compound Emission Rates

Mill	Source	Test Period	Emissions, g/s			
			H_2S	MM	DMS	DMDS
B	Spill Pond	1	2.7E+00	[2.3E-02]	[2.2E-02]	[2.3E-02]
		2	5.9E+00	1.3E-02	[1.6E-02]	[6.0E-03]
E	No. 1 Settling Pond	1	1.01E-01	[4.49E-02]	[4.30E-02]	7.6E-02
		2	3.0E+00	[1.4E-01]	[1.6E-01]	[6.9E-02]
		3*	3.1E+00	NA	NA	NA
E	No. 2 Settling Pond	1	3.4E+00	[1.0E-01]	1.1E-01	[1.0E-01]
		2	3.7E-01	[3.5E-02]	[3.8E-02]	[1.5E-02]
		3*	1.4E+00	NA	NA	NA
T	Equalization Basin	1*	2.4E-01	5.6E-03	1.5E-03	3.4E-03

*Emission rates for these test periods were estimated from ground-level concentration data and concurrent site-specific meteorological data
ND[xxxx] = the estimated maximum emission rate calculated from non-detect ambient air concentration data using the procedures outlined in Section 2.3.3.
NA = Not Available

Table 9.2 Summary Information Relative to Pre-Aeration Basin Emission Measurements

Mill	Source	Test Period	Area, Acres	Influent Flow, MGD	In-Basin Average			Average Wind Velocity, m/s	Sulfide Generation Rate, g S/s	H_2S Emissions g/(s x acre)	H_2S Emissions g/(s x acre)*
					Temp., °C	Liquid Total Sulfide Conc., μg/L	pH				
B	Spill Pond	1	19.6	NA	31.9	23925	8.0	2.7	NA	1.3E-01	1.3E-01
		2	-	NA	21.9	29025	8.8	5.0	NA	3.0E-01	1.2E-01
E	No. 1 Settling Pond	1	21.1	33	41.2	2003	7.0	5.1	3.3	4.8E-02	1.8E-02
		2	-	28	39.4	57417	10.4	7.2	25.5	1.4E-01	2.8E-02
		3	-	0	NA	NA	NA	3.3	2.9	1.5E-01	1.5E-01
E	No. 2 Settling Pond	1	32.0	9	18.2	5319	6.9	8.3	3.6	9.0E-02	1.4E-02
		2	-	9	19.4	11596	6.7	3.3	5.0	1.2E-02	1.2E-02
		3	-	38	43.8	6572	6.7	2.8	25.3	4.4E-02	4.4E-02
T	Equalization Basin	1	3.5	48	NA	NA	7.2	5.1	NA	6.9E-02	2.6E-02

NA = Not Available

*Normalized to the H_2S emission rate expected for wind velocities ≤ 3.25 m/s at 10 meters elevation

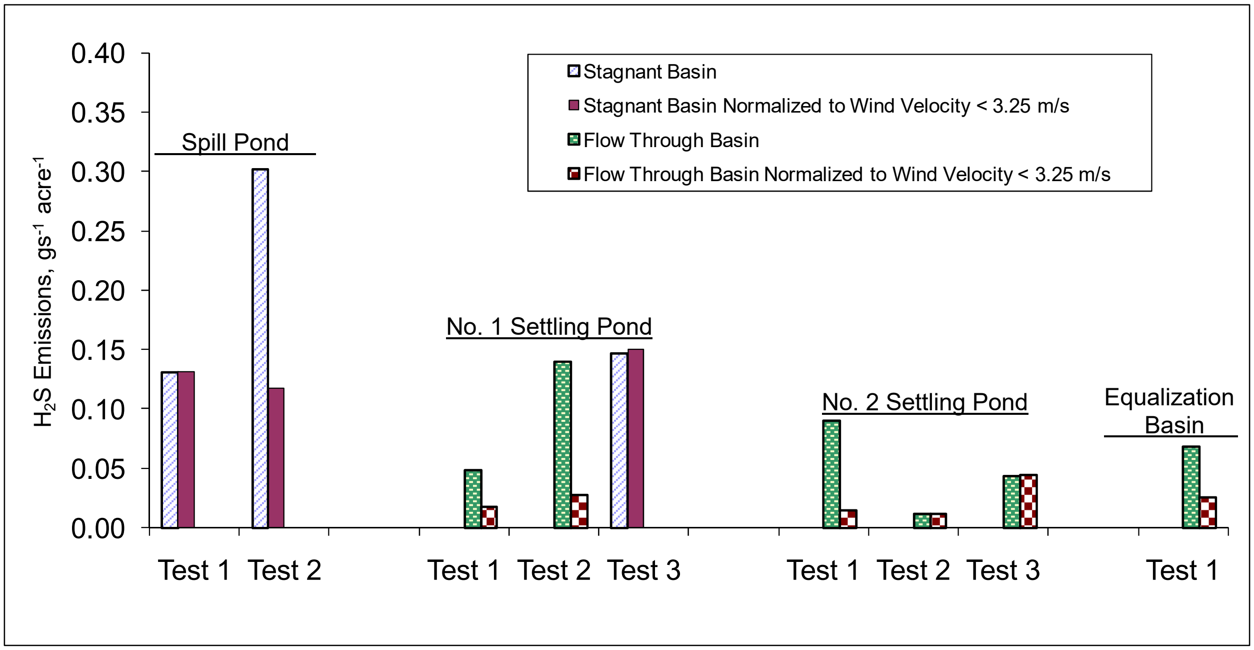


Figure 9.1 Normalization of Pre-Aeration Basin H_2S Emissions for Wind Velocity and Surface Area

Table 9.3 Pre-Aeration Basin Methane Emission Rates

		CH_4 Emissions, g/s	
Mill	Source	Test Period 1	Test Period 2
B	Spill Pond	2.7E+00	3.7E-01
E	No. 1 Settling Pond	1.4E+01	1.3E+01
E	No. 2 Settling Pond	3.2E+01	9.0E+00

Table 9.4 TOC Liquid Material Balances for the Pre-Aeration Basin Tests

Source	Date	Inlet, g C/s	Outlet, g C/s	Gain*, g C/s
No. 1 Settling Pond	3/8-9/2006	196.3	249.5	53.1
No. 2 Settling Pond	3/7-8/2006	50.2	72.7	22.5

* indicates gain in the liquid TOC between the inlet and outlet

9.2 Primary Clarifier Emissions

9.2.1 *Primary Clarifier Reduced Sulfur Compound Emissions*

The reduced sulfur compound rates for the four primary clarifiers tested in this study are summarized in Tables 9.5 and 9.6. For Mill B, the results from the two test periods are presented separately. In Table 9.5, the emissions are reported in units of grams per second, whereas in Table 9.6, the emissions are reported in units of grams per second per acre of surface area. The average H_2S emissions were generally relatively small and ranged from 0.014 g/s to 0.32 g/s. The emissions of the three organic reduced sulfur compounds (methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) were generally low to non-detect. Methyl mercaptan emissions ranged from non-detect to 0.042 g/s. Dimethyl sulfide emissions ranged from non-detect to 0.10 g/s. Dimethyl disulfide emissions ranged from non-detect to 0.11 g/s. Summary information useful for understanding the primary clarifier emissions is included in Table 9.7. Wind speeds did not vary much between the different clarifiers and test periods.

Factors that may be related to the reduced sulfur compound emissions from primary clarifiers were investigated. The liquid concentrations in the influent were expected to be important; however, it should be noted that differences in clarifier design and operating variables may also play significant roles in determining the emission rates. For example, inspection of the vertical ambient air concentration profile data in the mill-specific reports (NCASI 2008a, b, c, d, and g) shows very steep drops in concentrations between the ground-level (clarifier surface) and the low-level (next highest) sampling elevations. This indicates an area of relatively high emissions near the sample path, which for primary clarifiers is the weir. This suggests that differences in weir design, such as the height of the liquid drop, may significantly affect primary clarifier emissions.

Since most of the emissions were apparently from the weirs, the reduced sulfur compound emissions from the different clarifiers were compared as functions of average surface liquid concentrations and weir lengths. Those comparisons are made for H_2S, MM, DMS and DMDS in Figures 9.2 through 9.5, where the emissions in units of grams per second per 100 ft of weir length are plotted versus the average surface liquid concentration. For H_2S, the liquid “free” H_2S concentrations were calculated from the liquid total sulfide concentrations and pH values, as shown in Table 9.2.3. Since methyl mercaptan is also a weak acid, a similar procedure was used to calculate the liquid “free” methyl mercaptan concentrations. Below detection limit values, for both the average surface liquid concentrations and emissions, were plotted at one-half of the detection limits. These plots suggest relationships between influent concentrations and emissions. Additionally, the Mill F data (Section 7.2) show H_2S emissions increasing over three consecutive test runs as the liquid total sulfide concentration increased.

It is interesting to note that the slopes from linear regressions of the MM, DMS and DMDS data (Figures 9.2 through 9.5), are of approximately equal magnitude (2.0E-07, 3.3E-07, and 3.6E-07). This would be expected for these three organic reduced sulfur compounds which have relatively similar characteristics with respect to their volatility in dilute aqueous solutions, whereas the H_2S data (Figure 9.2), have a much steeper slope (2.0E-05), which would be expected for this extremely volatile compound.

9.2.2 *Primary Clarifier Methane Emissions*

As shown in Table 9.8, the primary clarifier methane emissions measured during this study ranged from 0.017 g/s to 0.17 g/s. The table also includes information on inlet and outlet BODs and TOCs and their removal or gain across the primary clarifiers. The apparent inconsistency between the BOD removal in comparison to the TOC gain across the clarifier at Mill B may be related to differences between the two methods in the way the solid material, which is removed during clarification, were handled in the inlet samples. For example, fiber, which may lead to oxygen consumption during the 5-day BOD test, would not be included as part of the organic carbon-containing material in the TOC test. Also, variability between different clarifiers and test periods may be related to differences in the fractions of the total (liquid + solid) organic matter represented by the material removed during clarification.

Table 9.5 Primary Clarifier Emission Rates (gram per second)

Mill	Test Period	Emissions, g/s			
		H_2S	MM	DMS	DMDS
A	1	3.2E-02	ND[2.1E-02]	1.5E-02	6.7E-04
B	1	1.4E-02	ND[7.1E-04]	9.3E-04	ND[1.1E-03]
B	2	6.0E-02	ND[2.4E-04]	ND[6.5E-04]	3.5E-04
D	1	4.9E-02	2.0E-02	9.5E-03	1.1E-01
F	1	3.2E-01	4.2E-02	1.0E-01	3.5E-03

ND[xxxx] = the estimated maximum emission rate calculated from non-detect ambient air concentration data using the procedures outlined in Section 2.3.3.

Table 9.6 Primary Clarifier Emission Rates (gram per second per acre)

Mill	Test Period	H_2S	Emissions, g/(sec x acre)* MM	DMS	DMDS
A	1	1.6E-02	[1.1E-02]	7.7E-03	3.4E-04
B	1	2.0E-02	[9.9E-04]	1.3E-03	[1.5E-03]
B	2	8.3E-02	[3.3E-04]	[9.0E-04]	4.9E-04
D	1	4.3E-02	1.8E-02	8.4E-03	9.8E-02
F	1	4.4E-01	5.8E-02	1.4E-01	4.9E-03

*Although release rates are expressed in terms of per acre, existing information is insufficient to demonstrate that this is the most appropriate approach for expressing release rates.

Table 9.7 Summary Information Relative to Primary Clarifier Emission Measurements

Mill	Test Period	Diameter, Ft	Influent Flow, MGD	Average Wind Velocity, m/s	Liquid Total Sulfide Conc., µg S/L	Liquid MM Conc., µg/L	pH	Liquid Concentrations, µg/L			
								H_2S	MM**	DMS	DMDS
A	1	330	16.1	4.0	NA	NA	11.5	NA	NA	NA	NA
B	1	200	14.3	2.4	699	NA	9.1	5.85	NA	38.0	ND[1.6E+01
B	2	200	13.5	3.6	8152	NA	10.1	6.87	NA	ND[2.0E+01]	29.2
D	1	250	9.8	3.5	1349	176	9.0	14.2	167	94.4	786
F	1	200	22.6	4.6	10357	644	9.3	51.6	585	975	ND[1.6E+01]

*Calculated from H_2S pka of 7.0 (Rydholm 1967).

** Calculated from CH_3SH pka of 10.3 (Lide 1993)

ND[xxxx] = non-detect with xxxx equal to one-half of the lowest calibration limit.

NA = Not Available

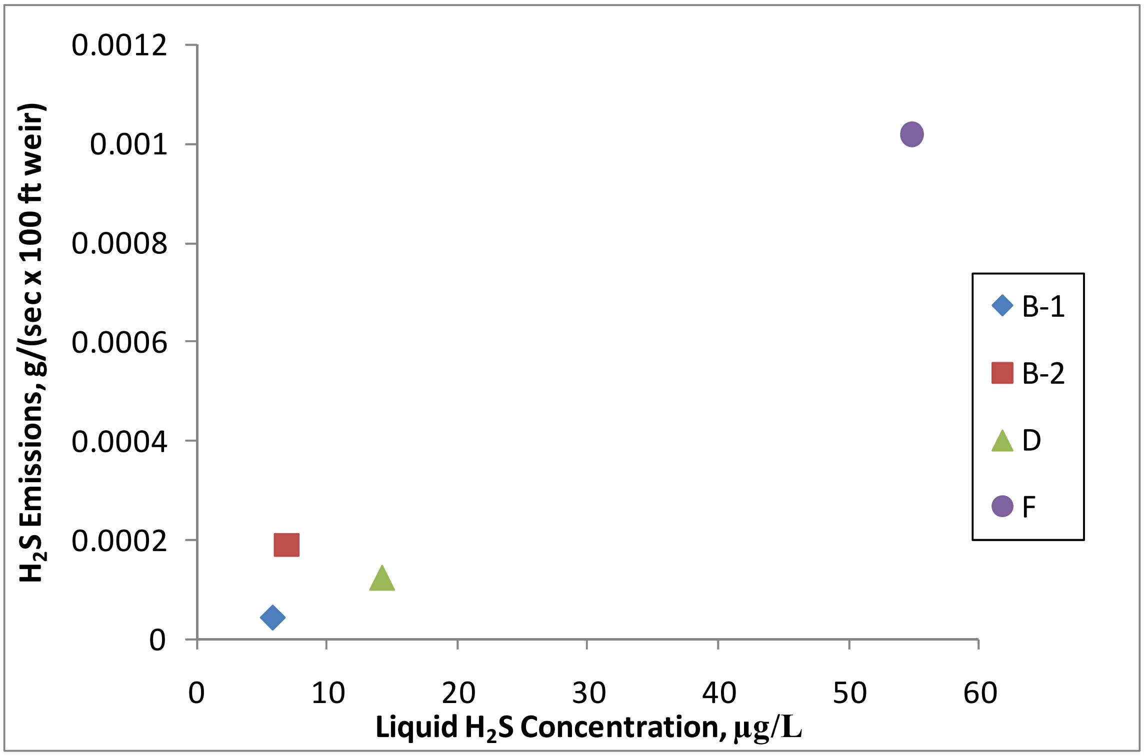


Figure 9.2 Primary Clarifier H_2S Emissions Versus the Surface Liquid H_2S Concentration

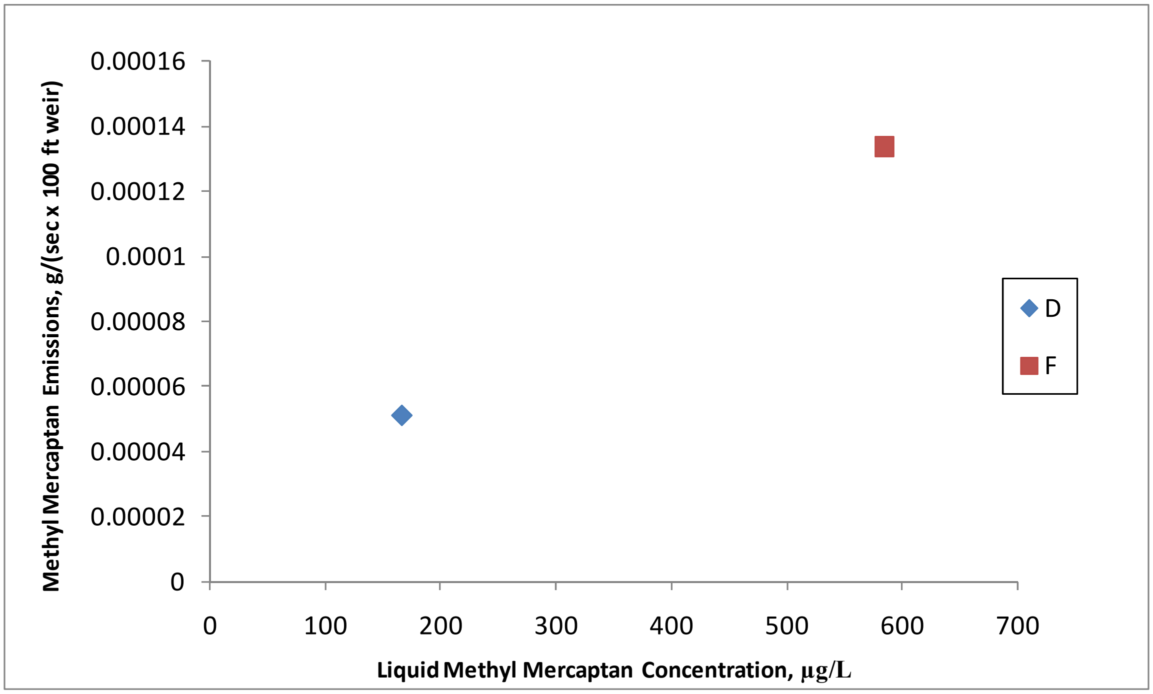


Figure 9.3 Primary Clarifier Emissions Versus the Surface Liquid Concentration for Methyl Mercaptan

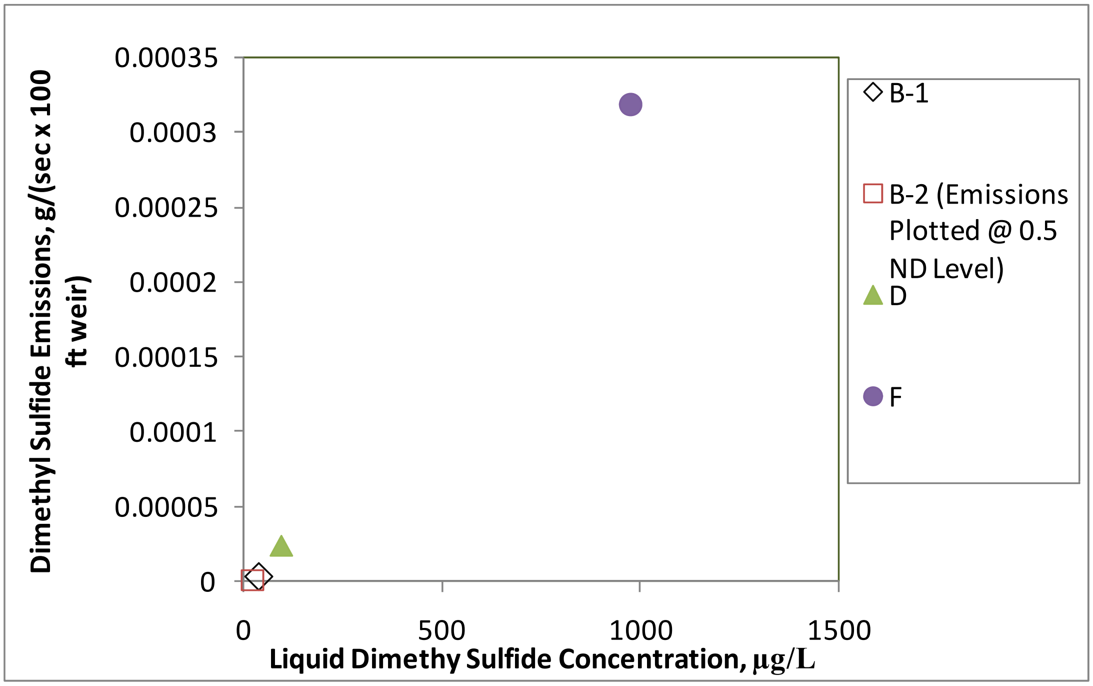


Figure 9.4 Primary Clarifier Emissions Versus the Surface Liquid Concentration for Dimethyl Sulfide

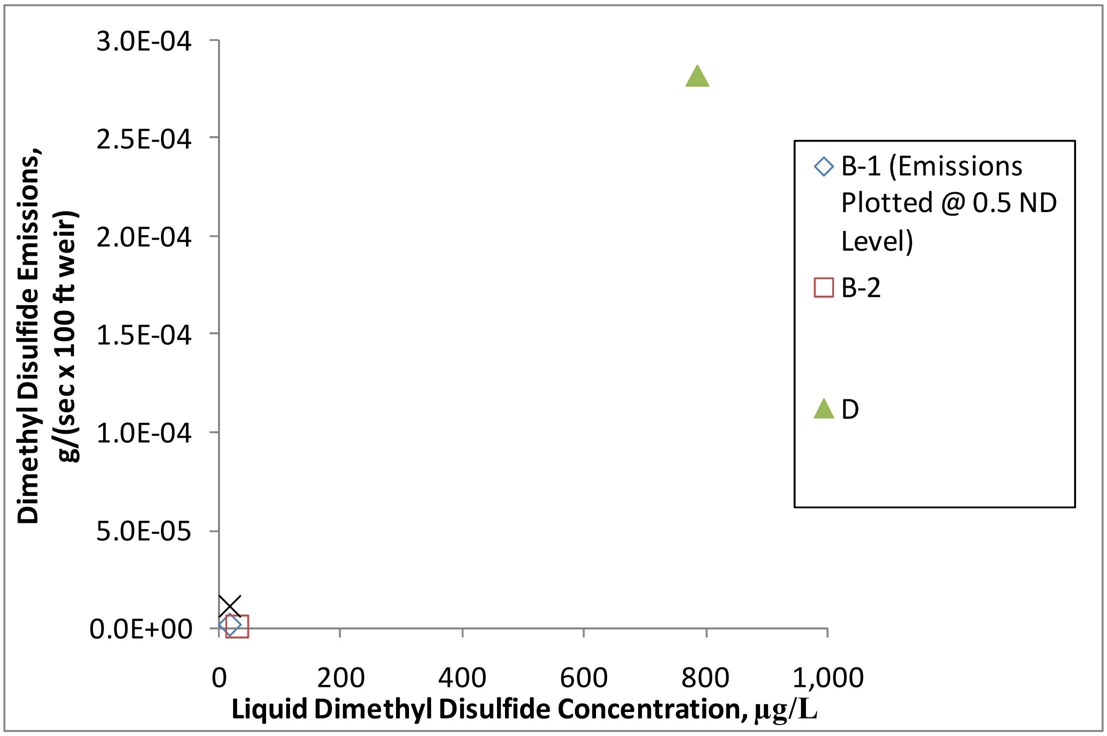


Figure 9.5 Primary Clarifier Emissions Versus the Surface Liquid Concentration for Dimethyl Disulfide

Table 9.8 Methane Emissions and Inlet and Outlet BODs and TOCs for Primary Clarifiers

Mill	Test Period	Methane Emissions, g/s	Parameter	Inlet, g/s	Outlet, g/s	Removal or (Gain), g/s
B	1	1.72E-02	BOD	142.1	68.1	74.0
B	1	1.72E-02	TOC	68.5	78.0	(9.5)
B	2	1.80E-02	TOC	274.2	185.3	88.9
D	1	1.16E-01	TOC	106.6	95.7	11.0
F	1	1.69E-01	BOD	362.6	236.5	126.1
F	1	1.69E-01	TOC	157.7	121.0	36.7

(xx) indicates gain in the liquid parameter between the inlet and outlet
[xxxx] indicates the methane emissions as a fraction of the gain in the liquid parameter between the inlet and outlet

9.3 Aerated Basin Emissions

9.3.1 *Aerated Basin Reduced Sulfur Compound Emissions*

The reduced sulfur compound and methane emission rates for the five aerated stabilization basins and one activated sludge treatment reactor tested in this study are summarized in Table 9.9. The H_2S emission rates ranged from 0.1 g/s to approximately 8 g/s. The destruction and/or generation rates for the reduced sulfur compounds in the aerated basins tested in this study are summarized in Table 9.10. At three of the four ASBs, for which simultaneous air emission and liquid concentration data were available (Mills A, B, and E), over 90% of the total sulfide entering the ASB with the wastewater was apparently destroyed via biological and/or chemical oxidation, rather than emitted to the atmosphere. The fate of the majority of the sulfide entering those ASBs with the wastewater was apparently in-basin chemical and/or biologically assisted oxidation to sulfate, elemental sulfur, or intermediate sulfur species. Although there is not much information available specifically for kraft pulp and paper mill wastewaters, there are numerous literature references supporting the oxidation of sulfide in other aqueous matrices (e.g., Kontronarou and Hoffman 1991; Madigan, Martinko, and Parker 1997; Buisman et al. 1990; Nielsen, Vollertsen, and Hvitved-Jacobsen 2006). In general, biological oxidation is thought to be more rapid than chemical oxidation; however, metals and organic compounds present in kraft pulp and paper mill wastewaters have been shown to catalyze chemical oxidation (Kontronarou and Hoffman, 1991; Chen and Morris 1972).

The data gathered in this study show H_2S emissions from aerated stabilization basins are related to sulfide loading, in-basin pH and dissolved oxygen. The data from the Mill E ASB indicate that maintaining sufficiently high in-basin dissolved oxygen levels resulted in efficient sulfide removal, by means other than emissions to the atmosphere, even when the sulfide loading increased 12-fold.

At Mill D, the H_2S emissions of 0.6 g/s were approximately two times greater than what would be expected based on the liquid material balance, showing a small amount of H_2S generation in the ASB. The ASB was operated with just enough aeration to effect adequate BOD removal. The data from the no. 1 ASB at Mill D indicate that operation with minimal aeration (DO levels of 0.2 or less throughout the ASB) resulted in H_2S emissions that were higher than the sulfide input. Apparently, in some areas within the basin, sulfide was being anaerobically generated and released to the atmosphere as H_2S faster than it was being oxidized in the water column. At the Mill D ASB, the in-basin pH levels were also slightly acidic, which would have facilitated the release of sulfide as H_2S from the water surface.

At Mill T, the no. 1 ASB H_2S emissions increased from about 1.5 g/s to about 8 g/s and then went back down to about 0.5 g/s over a four-day period apparently because of operational variability in the mill which resulted in a spike in the COD loading simultaneous with a steep dip in the pH. Continuous high sulfide input is expected (no sulfide measurements were taken) at this ASB because of an upstream 3.5-acre pond with vigorous anaerobic activity. Therefore, the indications are that the spike in COD loading caused the in-basin dissolved oxygen levels to drop, which allowed a large portion of the sulfide input to be released as H_2S, rather than be destroyed via oxidation, and the steep drop in pH exacerbated the problem. Additionally, the drop in dissolved oxygen levels could have resulted in some anaerobic generation of sulfide in the ASB.

Thus, the conclusions drawn from this study relative to factors that affect H_2S emissions from ASBs are as follows. Minimal aeration in ASBs may result in relatively high H_2S emissions, especially with high sulfide input, and lower in-basin pH levels will exacerbate the problem. However, with neutral or higher pH and adequate aeration, relatively low H_2S emissions can be expected from ASBs, regardless of the sulfide input. Low in-basin pH levels may result in high emissions with high sulfide input, even with adequate aeration, although this situation was not encountered during this study.

The emissions of organic reduced sulfur compounds (methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) from aerated stabilization basins were primarily related to condensate handling practices, and secondarily related to ASB operation. As shown in Tables 9.9 and 9.10, at Mill A, where all of the foul condensates are hard-piped to the ASB, the liquid input and emissions of the ORSCs were both relatively high. At Mill B, where only a portion of the foul condensates are hard-piped to the ASB and the remainder are steam stripped, the input and emissions of the ORSCs were lower than at Mill A; however, the fate of the ORSCs entering these well aerated ASBs was similar at both mills. The material balance data indicate that most of the DMS entering the basins with the wastewater was stripped from the liquid and released to the atmosphere. The data from Mill D indicate another relatively minor potential source of ORSCs from minimally aerated ASBs. At this ASB, the emissions of all three ORSCs, although relatively small, were still higher than what could be explained from the liquid material balance. Additionally, the in-basin liquid concentration data indicated generation of minor amounts of ORSCs. Other studies have shown that all three of the organic reduced sulfur compounds (methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) can be generated in settled anaerobic sludge/soil layers (Devai and DeLaune 1995; Higgins et al 2002).

The situation is more complicated for methyl mercaptan and dimethyl disulfide. Methyl mercaptan is easily oxidized to dimethyl disulfide. Liquid material balance data in conjunction with emissions data indicated that a significant fraction of the methyl mercaptan entering the ASBs with the influent was destroyed, and that a significant amount of dimethyl disulfide was generated. This is consistent with liquid phase oxidation of methyl mercaptan to dimethyl disulfide. When the combined emissions of methyl mercaptan and dimethyl disulfide as sulfur were compared to the combined liquid material balance data for the two compounds as sulfur, it was found that most of the methyl mercaptan was oxidized to dimethyl disulfide in the liquid phase, and most of remaining methyl mercaptan along with most of the inputted and generated dimethyl disulfide was stripped to the atmosphere.

For the one activated sludge treatment reactor tested in this study, the situation relative to H_2S destruction was similar to the well aerated ASBs; however, in contrast to the ASBs, it also accomplished relatively efficient destruction of the ORSCs. This may be due to the very high suspended solids concentration, to which the ORSC compounds may have been adsorbed and subsequently biologically degraded.

9.3.2 *Aerated Basin Methane Emissions*

Table 9.11 shows the results of CH_4 emission measurements along with TOC and BOD reduction data for three aerated stabilization basins and one activated sludge treatment basin. The results show that methane emissions from the ASBs ranged from 1.9 to 5.8 g/s. The methane emission rate from the activated sludge treatment basin was 0.2 g/s.

In Table 9.11, TOC reduction across the basins was calculated from liquid inlet and outlet samples collected during the emissions testing period. BOD reduction for the ASBs was calculated from the average of the 60-day period prior to emissions testing because methane emissions are expected to originate from the settled sludge layer. At the AST, BOD reduction was calculated for the period of emissions testing since ASTs do not have a settled sludge layer. The data show TOC reduction ranging from 94 to 110 g C/s and BOD reductions ranging from 124 to 419 g/s.

Table 9.9 Aerated Stabilization Basin and Activated Sludge Treatment Reactor Emission Rates

Mill	Type of Secondary Treatment	Foul Condensate Handling	Average Emissions, g/s				
			H_2S	MM	DMS	DMDS	CH_4
A	ASB	Hard Pipe	0.4	0.9	3.1	5.5	4
B	ASB	Hard Pipe*	0.3	0.9	0.2	0.7	NA
D	ASB	Steam Stripper	0.6	0.4	0.2	0.3	2
E	ASB	Steam Stripper	0.1 - 1.3***	ND[0.05]	ND[0.05]	ND[0.03]	6
T	ASB	Hard Pipe**	0.5 – 8****	NA	NA	NA	NA
F	AST	Steam Stripper	0.02	0.004	0.2	0.004	0.2

* In addition to the hard pipe, Mill B also has a steam stripper which handles a portion of the foul condensates.

** Condensates are hard-piped to the No. 2 ASB; emission rates are reported for the No. 1 ASB.

NA = Not Available

ND[xxxx] = the estimated maximum emission rate calculated from non-detect ambient air concentration data using the procedures outlined in Section 2.3.3.

***The emissions data includes measured emission rates and emission rates estimated from ground-level concentration data and concurrent site-specific meteorological data

****Estimated from ground-level concentration data and concurrent site-specific meteorological data.

Table 9.10 Apparent Destruction and (Generation) of RSCs in ASBs and ASTs

Mill	Type of Secondary Treatment	Test Period	Total Sulfide Input, g/s	Destruction or (Generation)*, %				
				H_2S	DMS	MM	DMDS	MM + DMDS (as S)
A	ASB	1	5.1	93	44	91	(75)	44
B	ASB	1	4.8	94	15	60	(320)	35
D	ASB	1	0.28	(184)	(363)	(221)	(42)	(109)
E	ASB	1	5.7	91.4	NA	NA	NA	NA
		2	69.5	99.6	NA	NA	NA	NA
		3	24.4	94.5	NA	NA	NA	NA
F	AST	1	11.9	89	79	91	71	88

* Destruction and (Generation) given as the percentage of the liquid input.
NA = Not Available

Table 9.11 Methane Emissions and TOC and BOD Removals from Aerated Basins

Mill	Type of Secondary Treatment	Methane Emissions, g/s	TOC Reduction, g C/s	BOD Reduction, g/s
A	ASB	3.9	NA	419
D	ASB	1.9	94	124
E	ASB	5.8	126	474
F	AST	0.2	110	233

9.4 Post-Aeration Basin Emissions

9.4.1 *Post-Aeration Basin Reduced Sulfur Compound Emission*

The results from the reduced sulfur compound emissions testing of post-aeration basins at four mills are summarized in Table 9.12. Two of these were aerated basins that followed one or more aerated basins. Screening studies were conducted at all eleven basins. The screening study results indicated that the reduced sulfur compound emissions were minimal at all but two of those basins. The specific situations relative to those two basins are discussed below.

The screening study results from Mill B indicated significant emissions from the no. 1 retention pond, which immediately follows the ASB. During the screening study, accumulated sludge was visible throughout most of the 62-acre pond. Because of the high level of sludge accumulation in the no. 1 retention pond, the liquid level had to be raised to allow the use of a boat for liquid sample collection. Therefore, the liquid level was raised during the approximately 10-day period between the initial screening study and the start of the full emissions measurement and liquid sample collection study. Additional screening study work during the full emissions measurement study, and the results of the full emissions measurement study, indicated lower H_2S emissions (0.04 g/s) than what were expected based on the initial screening study results. The increase in the liquid level may have resulted in lower than expected H_2S emissions, but other factors cannot be ruled out.

At Mill T, the screening study results indicated significant emissions from the no. 2 retention pond. An H_2S emission rate of 1.0 g/s was estimated from the ground-level concentrations, as described in Section 8.2. At Mill T there are three aerated basins in series, which are followed by two retention ponds in series. There were significant H_2S emissions from the no. 1 ASB. The no. 2 ASB also had significant H_2S emissions due to the presence of kraft process condensates which were hard-piped directly to the no. 2 ASB. The emissions from the no. 3 ASB and the no. 1 retention pond were insignificant. Therefore, the wastewater must have gone anoxic again at some point in the no. 2 retention pond to generate sulfide which was then emitted as H_2S.

At all 11 post-aeration basins, the emissions of the organic reduced sulfur compounds were either non-detect or not significant.

9.4.2 *Post-Aeration Basin Methane Emissions*

Methane emissions were only measured at the Mill B no. 1 retention pond. The results of the methane emission tests as well as basin inlet and outlet TOC data are summarized in Table 9.13. The data show that there was an increase in TOC across the pond. This increase may be due to 1) the formation of water soluble carbon-containing compounds from biological degradation of the settled secondary sludge, and/or 2) fixation of atmospheric carbon dioxide via photosynthetic or other biological means in this large, shallow basin.

Table 9.12 Post-Aeration Basin Emission Rates

Mill	Source	Area, acres	Aeration	Emissions, g/s			
				H_2S	MM	DMS	DMDS
B	No. 1 Retention Pond	62	NO	0.04	[0.03]	[0.03]	[0.03]
	No. 2 Retention Pond	128**	NO	NS	NS	NS	NS
	No. 3 Retention Pond	-	NO	NS	NS	NS	NS
	No. 4 Retention Pond	97	NO	NS	NS	NS	NS
D	No. 2 ASB	41	YES	NS	NS	NS	NS
	Retention Pond	81	NO	NS	NS	NS	NS
E	No. 1 Retention Pond	36	NO	NS	NS	NS	NS
	No. 2 Retention Pond	282	NO	NS	NS	NS	NS
T	No. 3 ASB	120	YES	NS	NS	NS	NS
	No. 1 Retention Pond	63	NO	NS	NS	NS	NS
	No. 2 Retention Pond	189	NO	0.95*	NS	NS	NS

NA = Not Available
NS = Not Significant based on screening study results
* Estimated from screening study data
ND[xxxx] = the estimated maximum emission rate calculated from non-detect ambient air concentration data using the procedures outlined in Section 2.3.3.
** Combined area for Nos. 2 and 3 Retention Ponds

Table 9.13 Methane Emissions and Liquid TOC Data for Mill B No. 1 Retention Pond

Source	TOC, g C/s			Methane Emissions, g/s
	Inlet	Outlet	Gain	
No. 1 Ret. Pond	49.0	52.5	3.5	2.0

9.5 Emissions from Miscellaneous Sewer and Effluent Transport Sources

During the course of this study, several miscellaneous sewer and effluent transport sources were tested. The reduced sulfur compound emissions from those sources are summarized in Table 9.14. At Mill F, two sewer manhole vents (4E and 4A) were tested. The 4E manhole vent, which is located in the mill and vents the headspace from much of the in-mill sewer system via suction from an induced-draft fan, had relatively high reduced sulfur compound emissions. The 4A manhole is passively vented and located at the point where the alkaline sewer leaves the mill to be transported via pipeline to the WWTP. Relatively low emissions of reduced sulfur compounds were observed here even though concentrations of reduced sulfur compounds were much higher in the liquid flowing through the 4A manhole than through the 4E manhole. The relatively high emissions from the 4E manhole were thus apparently due to the induced-draft fan venting of large sections of the in-mill sewer system.

At Mill D, the acid sewer vent is located above the area where the acid sewer transitions from a closed pipe leaving the mill to an open ditch entering the WWTP. This vent had low emissions of reduced sulfur compounds, similar to the passive 4A manhole vent at Mill F.

At Mill E, an open channel containing a Parshall flume transports the effluent from the primary settling ponds to the ASB. During Phase I and II, screening studies showed that reduced sulfur compound concentrations near the canal and flume area were minimal. However, during the Phase III test period, the H_2S emission rate was estimated at 0.8 g/s based on ground-level H_2S concentrations and meteorological data. Changes in WWTP operation which resulted in higher liquid total sulfide concentration and higher temperatures in the effluent during Phase III could explain the change from insignificant H_2S emissions during Phase I and II.

The test data gathered in this study showed miscellaneous sewer and effluent transport sources at kraft mills can sometimes emit non-trivial amounts of reduced sulfur compounds. In particular, in-mill fan-assisted sewer vents, and areas of turbulence in open sewers, such as those caused by a Parshall flume, were found to be significant sources.

Table 9.14 Emissions from Miscellaneous Sewer and Effluent Transport Sources

Mill	Source		Emissions, g/s H_2S	MM	DMS	DMDS
F	4E Manhole Vent		1.1E-01	2.2E-01	3.9E-01	8.4E-01
F	4A Manhole Vent		3.1E-03	3.2E-04	2.7E-03	1.6E-03
D	Acid Sewer Vent		1.7E-04	3.0E-05	1.5E-06	6.4E-05
E	Parshall Flume and Open Channel	Phase I	NS	NS	NS	NS
		Phase II	NS	NS	NS	NS
		Phase III	7.7E-01	NS	NS	NS

NS = not significant

10.0 SUMMARY OF RESULTS BY COMPOUND TYPE

When initially conceived, this investigation of wastewater treatment plant emissions was focused on the reduced sulfur compounds - hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide – because of their community odor impacts. Methane was later added due to the need to better understand its significance as a greenhouse gas associated with the carbon footprint of the pulp and paper industry. The overall objectives of the investigation were to determine emission rates of these compounds from actual wastewater treatment plants and to identify the key factors affecting the emission rates. To meet the objectives, extensive field measurements were made at six kraft mill wastewater treatment plants with varying configurations.

In Section 9, study results were summarized according to the type of unit process. In this section, the overall results are discussed by compound.

10.1 Hydrogen Sulfide

For the mills with well aerated secondary treatment, the major sources of hydrogen sulfide emissions were generally pre-aeration anoxic basins such as primary sludge settling ponds and spill ponds. Hydrogen sulfide may enter these basins with the wastewater and/or be anaerobically generated in them. The fraction of the hydrogen sulfide emitted from those basins to the atmosphere versus the amount transferred with the liquid effluent to the next treatment unit depends on meteorological conditions (primarily wind speed) and in-basin liquid conditions such as pH and temperature. Hydrogen sulfide emissions increase with wind speed and liquid temperature, and decrease with increasing pH.

Although primary clarifiers are pre-aeration anoxic basins, mass emissions of hydrogen sulfide were small by comparison to settling and spill ponds due to smaller surface areas. However, relatively high hydrogen sulfide concentrations were sometimes observed in the ambient air immediately downwind from primary clarifiers. Material balance calculations indicated approximately 30% of the total sulfide entering the primary clarifiers with the wastewater was removed, presumably with the settled primary sludge.

For well aerated stabilization basins and the activated sludge treatment reactor, hydrogen sulfide emissions were low, and 89% to 99.6% of the sulfide entering the basins with the wastewater was destroyed, presumably via biological and/or chemical oxidation. However, where aeration was marginal or low relative to the BOD loading, significant hydrogen sulfide emissions occurred due to sulfide entering the basin with the wastewater and/or in-basin anaerobically generated sulfide.

Hydrogen sulfide emissions were generally not significant from post-aeration retention ponds probably owing to a lack of organic substrate sufficient to support robust anaerobic activity.

The few measurements made on miscellaneous sewer vents and effluent transport channels showed some of these sources have non-negligible H_2S releases. Releases depended on air flows and effluent physical and chemical characteristics.

10.2 Organic Reduced Sulfur Compounds

Emissions of methyl mercaptan, dimethyl sulfide and dimethyl disulfide were largely a function of condensate collection and stripping practices and type of secondary treatment. Hard-piping of condensates to aerated stabilization basins resulted in significant organic reduced sulfur compound emissions. Most of the dimethyl sulfide (55% to 85%) hard-piped to those aerated stabilization basins was stripped and emitted to the atmosphere.

With respect to methyl mercaptan, it can be readily oxidized to dimethyl disulfide. Material balance calculations suggest this occurred in the aerated stabilization basins. Sixty to 90% of the methyl mercaptan entering these aerated stabilization basins was destroyed, while the amount of dimethyl disulfide increased by 75% to 320% relative to the liquid input of dimethyl disulfide. When methyl mercaptan and dimethyl disulfide were considered together (as sulfur), material balance calculations showed that 55% to 65% of the total was released to the atmosphere, mostly as dimethyl disulfide. The remaining 35% to 45% of the sum was apparently destroyed in the ASBs.

The one activated sludge treatment reactor tested in this study did not have condensates hard-piped to it, but the influent contained a fair amount of organic reduced sulfur compounds. Similar to the aerated stabilization basins, material balance calculations indicated the activated sludge treatment reactor efficiently destroyed the sulfide entering with the wastewater. In contrast to the aerated stabilization basins, the reactor provided relatively efficient destruction of organic reduced sulfur compounds, with 79% destruction of dimethyl sulfide, 91% destruction of methyl mercaptan, and 71% destruction of dimethyl disulfide.

For the two aerated stabilization basins tested in this study which did not have hard-piped condensates, the well aerated one had insignificant to non-detect organic reduced sulfur compound emissions, whereas the minimally aerated one had relatively low, but detectable organic reduced sulfur compound emissions. At the minimally aerated stabilization basin, the material balance and in-basin liquid sample data indicated generation of small amounts of these compounds which were 42% to 363% of the small amount entering the basin with the wastewater. However, the emission rates of these compounds were in the range of 0.4 g/s to 0.6 g/s, and from a practical standpoint this phenomenon is of marginal significance.

Primary clarifiers, pre-aeration basins, post-aeration basins, and sewer vents without fans were not significant sources of organic reduced sulfur emissions. The single sewer vent with a fan did have considerable organic reduced sulfur compound emissions.

10.3 Methane

Methane emissions from the WWTP components tested in this study varied widely. At the un-aerated basins (which included pre-aeration primary settling basins, primary clarifiers, a strong waste spill pond, and a post-aeration retention pond) methane emission rates ranged from 0.02 to 32 g/s. The two pre-aeration settling basins had the highest methane emission rates, which varied from 9 to 32 g/s. At the strong waste spill pond, methane emissions ranged from 0.4 to 3 g/s. Methane emissions from the post-aeration retention pond were 2 g/s. At the primary clarifiers, methane emission rates ranged from 0.02 to 0.2 g/s. For the aerated stabilization basins, average methane emission rates ranged from 1.9 to 5.8 g/s, whereas the one activated sludge treatment reactor tested in this study had a lower methane emission rate of 0.2 g/s.

11.0 RECOMMENDATIONS FOR FUTURE WORK

The recommendations for future work relative to reduced sulfur compound and methane emissions from kraft mill wastewater treatment plants fit into four categories: 1) improvement of reduced sulfur compound measurement methods, 2) development of emission factors, 3) evaluation of emission reduction strategies, and 4) development of predictive models for emission rate estimation.

The two major areas of potential future work relative to reduced sulfur compound measurement methods are methods for measurement of "free" sulfide in kraft mill wastewater, and methods for measurement of reduced sulfur compounds in ambient air. In this study, the method used for determining "total" sulfide in wastewater (NCASI Method RSC-02.02) measures the total amount of sulfide in a sample volatile at pH 2.5. It is believed that this includes all freely dissolved sulfide, plus sulfide weakly associated with dissolved organic matter or certain transition metals, which may not be "free" for potential release as H_2S. Measurement of the "free" fraction of the "total" sulfide has proved to be a thorny issue, yet it is an important distinction that still needs to be resolved for development of models to predict H_2S emissions from wastewater concentration values. The method used in this study for determination of speciated reduced sulfur compound concentrations in ambient air started with canister sample collection, which was followed by cryogenic pre-concentration of the canister contents and GC-PFPD analysis. This ultimately proved to be an effective method; however, it was also very laborious, exacting and time consuming. Less labor-intensive methods are needed for both investigative and continuous monitoring purposes. These methods must be proven to yield accurate, precise values at low ppbv levels. Several easier, simpler methodologies already exist for H_2S and TRS; however, especially for H_2S determination in the vicinity of kraft mills, the accuracy, precision, and overall reliability of these methods have not, in general, been adequately demonstrated. For determination of organic reduced sulfur compound concentrations in ambient air, at present the only available method is gas chromatographic analysis.

During the course of this study, multiple pre-aeration basins, primary clarifiers and aerated stabilization basins were tested; however, full sets of emission rate values were only developed for one activated sludge treatment reactor and one post-aeration basin. Relatively low reduced sulfur compound and methane emissions were found at the activated sludge treatment reactor. The low reduced sulfur compound emissions were apparently largely due to relatively efficient biological oxidation (71% to 91%) of those compounds which entered the basin with the influent. Other activated sludge treatment reactors should be tested to determine whether or not these results are typical. Of the eleven post-aeration retention ponds for which screening results were available from this study, only one was tested for methane emissions. The methane emissions from this retention pond were significant relative to the other sources in this study; therefore, methane emissions should be tested from additional post-aeration ponds to develop better emission factors. From the screening study results, the post-aeration basin emissions of organic reduced sulfur compound emissions were insignificant; however, at two basins apparently significant levels of H_2S emissions were measured. The H_2S emission rates, on a per acre basis for these two basins were much less than pre-aeration basins and primary clarifiers. Therefore, additional H_2S emission measurements may not be needed for post-aeration basins; however, development of an understanding of the factors that could result in elevated H_2S emissions from post-aeration basins may be needed.

Strategies for minimizing H_2S emissions from pre-aeration basins, primary clarifiers and aerated stabilization basins are needed. The most promising technique for pre-aeration basins and primary clarifiers is oxygen addition to influents. A co-benefit of this strategy may be reduced methane emissions due to avoidance of anoxic conditions, which may reduce anaerobic biological activity. Currently, there is very little information available about the application and optimization of this technique; therefore, a project aimed at testing, evaluating, and optimizing oxygen addition to influents could help address this information need. In aerated stabilization basins, oxygen is already being transferred to the wastewater at high rates; however, current operating practices are aimed at meeting the required BOD removal. The data from this study indicate optimization of ASB operation to meet required BOD removal with minimal energy input may not be compatible with minimizing H_2S emissions. Therefore, additional work needs to be done to determine the most efficient means for operating ASBs to accomplish required BOD removal, while maintaining minimal H_2S emissions.

Finally, the data from this study and related investigations should be used to develop mechanistic and/or semi-empirical models for estimation of emissions from liquid sample analyses, WWTP configuration and operating data, and meteorological data. Due to the expense and difficulty involved, routine determination of emission rates via spatial ambient air testing is not practical.

REFERENCES

American Public Health Association (APHA). 1998. *Standard Methods for the Examination of Water and Wastewater,* 20th ed. Washington, D.C.: American Public Health Association.

Buisman, C., Jespeert, P., Janssen, A., and Lettinga, G. 1990. Kinetics of chemical and biological sulphide oxidation in aqueous solutions. *Water Research* 24(5):667-671.

Chen, K.Y. and Morris, J.C. 1972. Oxidation of sulfide by O_2: Catalysis and inhibition. *Journal of the Sanitary Engineering Division* 98(1):215-227.

Devai I. and DeLaune, R.D. 1995. Formation of volatile sulfur compounds in salt marsh sediment as influenced by soil redox condition. *Organic Geochemistry* 23(4):283-287.

Ehhalt, D.H. and Heidt, L.E. 1973. Vertical profiles of CH_4 in the troposphere and stratosphere. *Journal of Geophysical Research* 78(24):5265-5271.

Esplin, G.J. 1988. Boundary layer emission monitoring. *Journal of Air Pollution Control Association* 38(9): 1158-1161.

———. 1989. Total reduced sulfur (TRS) emissions from effluent lagoons. *Pulp and Paper Canada* 90(10): 105-107.

Gifford, F.A. 1976. Turbulent diffusion typing schemes. A review. *Nuclear Safety* 17(1):68-85.

Higgins, M.J., Yarosz, D.P., Chen, Y-C., Murthy, S.N., Mass, N.A., and Cooney, J.R. 2002. Mechanisms of volatile sulfur compound and odor production in digested biosolids. Presented at 2003 Residuals and Biosolids conference, Baltimore, MD.

Horst, T.W. and Slinn, W.G.N. 1984. Estimates for pollution profiles above finite area-sources. *Atmospheric Environment* 18(7):1339-1346.

Irwin, J.S. 1983. Estimating plume dispersion – A comparison of several sigma schemes. *Journal of Applied Meteorology.* 22:92-114.

Kotronarou, A. and Hoffmann, M.R. 1991. Catalytic autoxidation of hydrogen sulfide in wastewater. *Environmental Science & Technology* 25(6):1153-1160.

Kunkel, B.A. 1985. *Development of an atmospheric diffusion model for toxic chemical releases*. NTIS: AD/A169-135. Air Force Geophysics Laboratory, Hanscom AFB.

Lide, D.R. 1993. *Handbook of chemistry and physics*, 74th ed. Boca Raton, FL: CRC Press.

Lin, J-H. and Chou, M-S. 2006. Partition of volatile organic compounds in activated sludge and wastewater. *Journal of the Air and Waste Management Association* 56:1083-1090.

Liss, P. S. and Slater, P. G. 1974. Flux of gases across the air-sea interface. *Nature* 247: 181-184.

Madigan, M.T., Martinko, J.M. and Parker, J. 1997. *Brock biology of microorganisms,* 8th ed. Saddle River, NJ: Prentice Hall.

Morrison, R.H. and Boyd, R.N. 1973. *Organic chemistry,* 3rd ed. p. 1173. Boston, MA: Allyn and Bacon, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI). 2005a. *Methods manual – Reduced sulfur compounds by direct injection GC/PFPD*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

———. 2005b. *Evaluation of sulfide ion detector tubes for determining sulfide concentrations in pulp and paper mill wastewaters.* Special Report No. 05-01. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

———. 2008a. Emissions of Reduced Sulfur Compounds from the Mill A Wastewater Treatment Plant. Final Draft. http://www.ncasi.org/support/downloads/Detail.aspx?id=45

———. 2008b. Emissions of Reduced Sulfur Compounds and Methane from the Mill B Wastewater Treatment Plant Phase I Testing. Final Draft. http://www.ncasi.org/support/downloads/Detail.aspx?id=45

———. 2008c. Emissions of Reduced Sulfur Compounds and Methane from the Mill B Wastewater Treatment Plant Phase II Testing. Final Draft. http://www.ncasi.org/support/downloads/Detail.aspx?id=45

———.2008d. Emissions of Reduced Sulfur Compounds and Methane from the Mill D Wastewater Treatment Plant. Final Draft. http://www.ncasi.org/support/downloads/Detail.aspx?id=45

———. 2008e. Emissions of Reduced Sulfur Compounds and Methane from the Mill E Wastewater Treatment Plant Phase I Testing. Final Draft. http://www.ncasi.org/support/downloads/Detail.aspx?id=45

———. 2008f. Emissions of Reduced Sulfur Compounds and Methane from the Mill E Wastewater Treatment Plant Phase II Testing. Final Draft. http://www.ncasi.org/support/downloads/Detail.aspx?id=45

———. 2008g. Emissions of Reduced Sulfur Compounds from Wastewater Treatment Plant at Mill E: Phase III Testing. Final Draft. http://www.ncasi.org/support/downloads/Detail.aspx?id=45

———. 2008h. Emissions of reduced sulfur compounds and methane from the mill F wastewater treatment plant. Final Draft. http://www.ncasi.org/support/downloads/Detail.aspx?id=45

———. 2008i. Screening Study of Reduced Sulfur Compound Emissions from the Wastewater Treatment Plant at Mill T. Final Draft. http://www.ncasi.org/support/downloads/Detail.aspx?id=45

———. Forthcoming. *Spatial ambient air sampling and analysis methods for quantifying reduced sulfur compound and methane emissions from kraft mill wastewater treatment plants*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Nielsen, A.H., Vollertsen, J., and Hvitved-Jacobsen, T. 2006. Kinetics and stoichiometry of aerobic sulfide oxidation in wastewater from sewers—Effects of pH and temperature. *Water Environment Research* 78(3):275-283.

Rydholm, S.A. 1967. *Pulping processes*, p. 584. New York: Inter-Science Publishers.

Sugawara, S., Nakazawa, T., Shirakawa, Y., Kawamura, K., Aoki, S., Machida, T., and Honda, H. 1997. Vertical profile of the carbon isotopic ratio of stratospheric methane over Japan. *Geophysical Research Letters* 24(23):2989-2992.

Treybal, R. E. 1980. *Mass-transfer operations*, 3rd ed. New York: McGraw Hill.

Turner, D.B. 1994. *Workbook of atmospheric dispersion estimates: An Introduction to dispersion modeling*. Boca Raton, FL: CRC Press.

United States Environmental Protection Agency (USEPA). 1994. Air Emissions Models for Waste and Wastewater. Contract No. 68D10118. Research Triangle Park, NC: United States Environmental Protection Agency, Office of Air Quality Planning and Standards.

———. 2000. *Meteorological monitoring guidance for regulatory modeling applications*. EPA-454/R-99-005. Research Triangle Park, NC: United States Environmental Protection Agency, Office of Air Quality Planning and Standards.

———. 2008. *Assessment of minimum detection limits for hydrogen sulfide tunable diode laser open path monitor and estimated hydrogen sulfide emissions from a pulp and paper mill*. Draft Final Report. Contract No. EP-C-04-023, Project No. RN990233.0062.

Walter, B.P., Heimann, M., and Matthews, E. 2001. Modeling modern methane emissions from natural wetlands - 1. Model description and results. *Journal of Geophysical Research* 106(D24):34,189-34,206.

APPENDIX G – NCASI TB NO. 957, SPATIAL AMBIENT AIR SAMPLING AND ANALYSIS METHODS FOR QUANTIFYING REDUCED SULFUR COMPOUND AND METHANE EMISSIONS FROM KRAFT MILL WASTEWATER TREATMENT PLANTS

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SPATIAL AMBIENT AIR SAMPLING AND ANALYSIS METHODS FOR QUANTIFYING REDUCED SULFUR COMPOUND AND METHANE EMISSIONS FROM KRAFT MILL WASTEWATER TREATMENT PLANTS

TECHNICAL BULLETIN NO. 957
NOVEMBER 2008

by
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Acknowledgments

The authors would like to acknowledge the other NCASI employees who contributed to this effort, and without whose help this research would not have been possible. At the NCASI Southern Regional Center, those employees include Ann Crapo, Derek Sain, Jeff Drese, Lee Carlson, Bill Rice, Ben Fair, Raulie Raulerson, Ganka Slavova, Tracy Stubbs, Vickie Tatum, Vipin Varma, Karen Mentz and Susan Kirkland. At the NCASI West Coast Regional Center, those employees include Diana Cook and Dean Hoy.

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National Council for Air and Stream Improvement, Inc. (NCASI). 2008. *Spatial ambient air sampling and analysis methods for quantifying reduced sulfur compound and methane emissions from kraft mill wastewater treatment plants*. Technical Bulletin No. 957. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.

PRESIDENT'S NOTE

Determining reduced sulfur compound (RSC) emissions from kraft mill wastewater treatment plants (WWTPs) represents a significant challenge. Because reduced sulfur compounds can be both formed and destroyed in the wastewater, it is not possible to estimate emissions from liquid material balance calculations, especially for hydrogen sulfide (H_2S). Therefore, quantifying emissions from the various components of a wastewater treatment plant requires direct measurement of the emissions flux.

The most common approach to quantify emissions from heterogeneous ground level area emission sources, such as aeration basins, involves use of a spatial ambient air sampling method known as the transect technique. In typical applications of the transect technique, an array of masts or towers is constructed in an area expected to be downwind of the emissions source. The masts or towers are used to facilitate sampling of ambient concentrations at multiple horizontal and vertical locations. The concentration data are then used in conjunction with geographical information and meteorological data to determine emissions flux. Using masts or towers is not a viable option for kraft mill WWTP plants, given they have several components such as clarifiers, aerated basins, and settling basins, some of which may have large surface areas. Thus, NCASI opted to use a variation of the transect technique described by Esplin in his study of total reduced sulfur emissions from wastewater operations at three British Columbia kraft mills. Esplin's approach used a helium-filled balloon tethered to mobile cart to hoist sampling lines to multiple elevations downwind of the sources being tested. His technique provided a relatively simple and versatile method for determining emissions flux in the complex situations encountered at kraft mill WWTPs.

Measurement of RSC concentrations in ambient air is complicated by their extreme reactivity, especially for H_2S. The relatively small RSC emissions from many components of kraft mill WWTPs result in quite low ambient downwind concentrations, necessitating use of methods with detection limits in the range of 1 to 2 ppbv. NCASI performed extensive method development and evaluation work to meet this need.

The outcome was a canister sampling method with subsequent off-site analysis via cryogenic pre-concentration followed by gas chromatographic analysis with pulsed-flame photometric detection. Although complicated, the method will produce reliable results when carefully conducted by an experienced analyst. This method was successfully used in the NCASI study of RSC emissions from kraft mill WWTPs, as reported in NCASI Technical Bulletin No. 956. However, simpler methods are desirable and are currently being investigated.

This technical bulletin provides detailed descriptions of the spatial ambient air sampling technique, emission rate calculation procedures, and the laboratory analysis methods. It also provides an extensive evaluation of the accuracy and precision of those methods using data obtained over the course of the NCASI study summarized in NCASI Technical Bulletin No. 956.

Ron Yeske

Ronald A. Yeske

November 2008

MOT DU PRÉSIDENT

La quantification des émissions de composés de soufre réduit (CSR) provenant des systèmes de traitement des effluents (STE) représente un défi important. Puisque les composés de soufre réduit peuvent être formés et détruits dans les eaux usées, il n'est pas possible d'en estimer les émissions à l'aide de calculs de bilan massique sur les effluents, plus particulièrement en ce qui concerne le sulfure d'hydrogène (H_2S). Ainsi, la quantification des émissions des différentes sections d'un système de traitement des effluents nécessite des mesures directes du flux des émissions.

L'approche de mesure la plus commune pour la quantification de sources d'émissions hétérogènes au niveau du sol comme les étangs aérés, requiert l'utilisation d'une méthode d'échantillonnage spatial d'air ambiant connue sous l'appellation : technique des transects. Pour les applications typiques de la technique des transects, une matrice de mâts ou de tours est installée à un endroit situé en aval des vents dominants par rapport à la source d'émissions. Les mâts ou les tours sont utilisés afin de faciliter l'échantillonnage des concentrations ambiantes en plusieurs points sur des axes verticaux et horizontaux. Les données de concentrations sont ensuite utilisées en conjonction avec des informations géographiques et des données météorologiques pour déterminer les flux d'émissions. L'utilisation de mâts ou de tours n'est pas une option envisageable pour les STE des fabriques de pâte kraft car ceux-ci sont composés de plusieurs unités telles que des clarificateurs, étangs aérés et bassins de sédimentation dont certains se caractérisent par des surfaces considérables. Ainsi, NCASI a choisi d'utiliser une variante de la technique des transects décrite par Esplin dans son étude des émissions de soufres réduits totaux provenant de systèmes de traitement des effluents de trois fabriques de pâte kraft situées en Colombie-Britannique. L'approche d'Esplin consistait à utiliser un ballon gonflé à l'hélium attaché à un chariot mobile pour lever des tubes d'échantillonnage à des élévations diverses dans le sens du vent par rapport à la source échantillonnée. La technique d'Esplin procurait une méthode relativement simple et versatile pour déterminer le flux d'émissions pour les situations complexes comme celles rencontrées aux STE de fabriques de pâte kraft.

Les mesures de concentrations de CSR dans l'air ambiant sont compliquées par leur réactivité extrême, en particulier pour le H_2S. Les émissions relativement faibles de CSR provenant de plusieurs composantes de STE de fabriques de pâte kraft résultent en des concentrations en aval très basses, ce qui requiert des méthodes ayant des limites de détection de l'ordre de 1 à 2 ppbv. NCASI a effectué un travail exhaustif de développement et d'évaluation de méthodes afin de répondre à ce besoin.

Les résultats de cette étude démontrent qu'il est nécessaire d'utiliser une méthode d'échantillonnage comprenant une bonbonne (*canister*) suivie d'une analyse en laboratoire impliquant une pré-concentration cryogénique complétée par une analyse par chromatographie en phase gazeuse avec détection photométrique à flamme pulsée. Quoiqu'elle soit compliquée, cette méthode procure des résultats fiables lorsqu'elle est soigneusement exécutée par du personnel expérimenté. NCASI a utilisé cette méthode avec succès dans le cadre de son étude de détermination des émissions de CSR de STE de fabriques de pâte kraft (voir à cet effet le bulletin technique n^{o} 956 de NCASI). Cependant, des méthodes plus simples sont préférables et sont présentement en cours d'étude.

Ce bulletin technique présente des descriptions détaillées de la technique spatiale d'échantillonnage d'air ambiant, des procédures de calculs de taux d'émissions et des méthodes d'analyses en laboratoire. Il présente en outre une évaluation exhaustive de l'exactitude et de la précision de ces méthodes en utilisant les données obtenues lors d'une étude de NCASI résumée dans le bulletin technique n^{o} 956 de NCASI.

Ron Yeske

Ronald A. Yeske

Novembre 2008

SPATIAL AMBIENT AIR SAMPLING AND ANALYSIS METHODS FOR QUANTIFYING REDUCED SULFUR COMPOUND AND METHANE EMISSIONS FROM KRAFT MILL WASTEWATER TREATMENT PLANTS

TECHNICAL BULLETIN NO. 957
NOVEMBER 2008

ABSTRACT

Sampling and analytical methods to measure ambient air concentrations of hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide in the vicinity of kraft mill wastewater treatment plants were developed and evaluated. Satisfactory results were obtained by drawing ambient air through a permeation dryer into a stainless steel canister with inert internal coating and then pressurizing the canister with nitrogen. Analysis of the canisters for the reduced sulfur compounds involved cryogenic pre-concentration of the sample gas followed by gas chromatography with a pulsed flame photometric detector. Detection limits for this methodology were on the order of 1 to 5 ppbv for the four compounds. To determine reduced sulfur compound emission rates from the different components of wastewater treatment systems, a spatial ambient air sampling technique developed by Esplin was employed. This technique required horizontally-integrated ambient concentration measurements at three to four elevations downwind of the area source and on-site meteorological data. By assuming Gaussian plume dispersion and a power law vertical concentration profile, emission rates were calculated from these data. Although it was not possible to specifically determine the overall uncertainty in the calculated emission rates, the average percent relative standard deviation for emission rates determined from runs on the same source made on the same day ranged from 20 to 50 percent.

KEYWORDS

ambient air, analysis, dimethyl disulfide, dimethyl sulfide, emissions, hydrogen sulfide, kraft pulp mill, methane, methyl mercaptan, reduced sulfur compounds, sampling, wastewater treatment plant

RELATED NCASI PUBLICATIONS

Technical Bulletin No. 956 (September 2008). *Emissions of reduced sulfur compounds and methane from kraft mill wastewater treatment plants.*

MÉTHODES D'ANALYSE ET D'ÉCHANTILLONNAGE SPATIAL D'AIR AMBIANT POUR LA QUANTIFICATION DES ÉMISSIONS DE COMPOSÉS DE SOUFRE RÉDUIT ET DE MÉTHANE DES SYSTÈMES DE TRAITEMENT DES EFFLUENTS DE FABRIQUES KRAFT

BULLETIN TECHNIQUE N^{O} 957
NOVEMBRE 2008

RÉSUMÉ

NCASI a développé et évalué des méthodes d'échantillonnage et d'analyse permettant de mesurer les concentrations dans l'air ambiant de sulfure d'hydrogène, méthylmercaptan, sulfure de diméthyle et disulfure de diméthyle aux environs de systèmes de traitement des effluents de fabriques de pâte kraft.

Des résultats acceptables ont été obtenus lorsque les échantillons d'air ambiant, préalablement séchés sur un tube de perméation, ont été prélevés dans une bonbonne (*canister*) en acier inoxydable dont les parois étaient couvertes d'un enduit inerte. La bonbonne a ensuite été pressurisée à l'azote. L'analyse des bonbonnes pour les composés de soufres réduits requiert une pré-concentration cryogénique suivie d'une analyse par chromatographie en phase gazeuse avec détection photométrique à flamme pulsée. Les limites de détection de cette méthodologie sont de l'ordre de 1 à 5 ppbv pour les quatre composés. NCASI a utilisé une technique d'échantillonnage spatial de l'air ambiant, développée par Esplin, pour déterminer les taux d'émission de composés de soufre réduit provenant des différentes composantes des systèmes de traitement des effluents. Cette technique nécessite des mesures de concentrations dans l'air ambiant, intégrées à l'horizontale, à trois ou quatre élévations en aval de la source diffuse ainsi que des données météorologiques sur le site. Les auteurs ont calculé les taux d'émission en appliquant une dispersion des émissions selon un modèle Gaussien et un profil vertical de concentrations selon la loi de puissance. Malgré qu'il n'ait pas été possible de déterminer spécifiquement l'incertitude globale des taux d'émissions calculés, le pourcentage moyen de l'écart-type relatif des taux d'émissions déterminés à partir d'essais effectués sur une même source durant la même journée variait entre 20 et 50 pourcent.

MOTS CLÉS

air ambiant, analyse, composés de soufre réduit, disulfure de diméthyle, échantillonnage, émissions, fabrique kraft, fabrique de pâte kraft, méthane, méthylmercaptan, sulfure de diméthyle, sulfure d'hydrogène, système de traitement des effluents

AUTRES PUBLICATIONS DE NCASI DANS CE DOMAINE

Bulletin technique n^{o} 956 (septembre 2008). *Emissions of reduced sulfur compounds and methane from kraft mill wastewater treatment plants.*

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SPATIAL AMBIENT AIR SAMPLING AND ANALYSIS METHODS FOR QUANTIFYING REDUCED SULFUR COMPOUND AND METHANE EMISSIONS FROM KRAFT MILL WASTEWATER TREATMENT PLANTS

1.0 INTRODUCTION

Between 2004 and 2007, NCASI carried out a study of reduced sulfur compound (RSC) and methane emissions from kraft pulp and paper mill wastewater treatment plants. The study encompassed measurement of ambient concentrations of these compounds at numerous ground level and elevated downwind locations, collection of meteorological data, and calculation of emission rates using these data. In addition, extensive liquid sampling and analyses were conducted to aid in the interpretation of the computed emission rates. NCASI Technical Bulletin No. 956, *Emissions of Reduced Sulfur Compounds and Methane from Kraft Mill Wastewater Treatment Plants*, summarizes the study results with only brief descriptions of the various measurement methods, sampling protocols, and calculation procedures.

The purpose of this report is to provide more detailed documentation of the methods, protocols, and procedures employed in the investigation. This report also includes quality assurance information and an assessment of uncertainties.

2.0 SPATIAL AMBIENT AIR SAMPLING METHOD

Esplin (1988, 1989) developed and used a spatial ambient air sampling method, which he called "Boundary Layer Emission Monitoring," to measure total reduced sulfur compound (TRS) emissions flux from three WWTP basins at kraft mills in British Columbia. He did this by measuring wind velocities and concentration values over the area of the downwind dispersion plume. This method involved 1) crosswind-integrated downwind sampling at multiple elevations using a mobile cart and helium-filled balloon to hoist sample lines to multiple elevations, 2) sample conditioning with a permeation dryer, 3) collection of samples in Tedlar bags, and 4) on-site analysis for total reduced sulfur (TRS). For the purposes of the NCASI study, Esplin's method was modified to allow off-site speciated analysis of reduced sulfur compound and methane emissions. The four reduced sulfur compounds quantified in this study were hydrogen sulfide (H_2S), methyl mercaptan (MeSH or MM), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS).

The procedure for spatial ambient air sampling used in the NCASI study was a variation of the transect technique, but instead of employing a permanent or semi-permanent array of masts downwind of a source to collect samples at multiple vertical and horizontal locations, a mobile cart with sample lines set at multiple elevations was used to traverse the dispersion plume and collect integrated samples. Thus, horizontally integrated samples were collected at multiple elevations, which allowed determination of the emissions flux. As shown in Figure 2.1, a Tethersonde helium-filled balloon (Vaisala TTB327), which was tethered to the sample cart, was used to raise the sample lines to the desired elevations. This balloon was 14 feet long by 6.5 feet in diameter and was aerodynamically shaped to fly essentially directly over the cart.

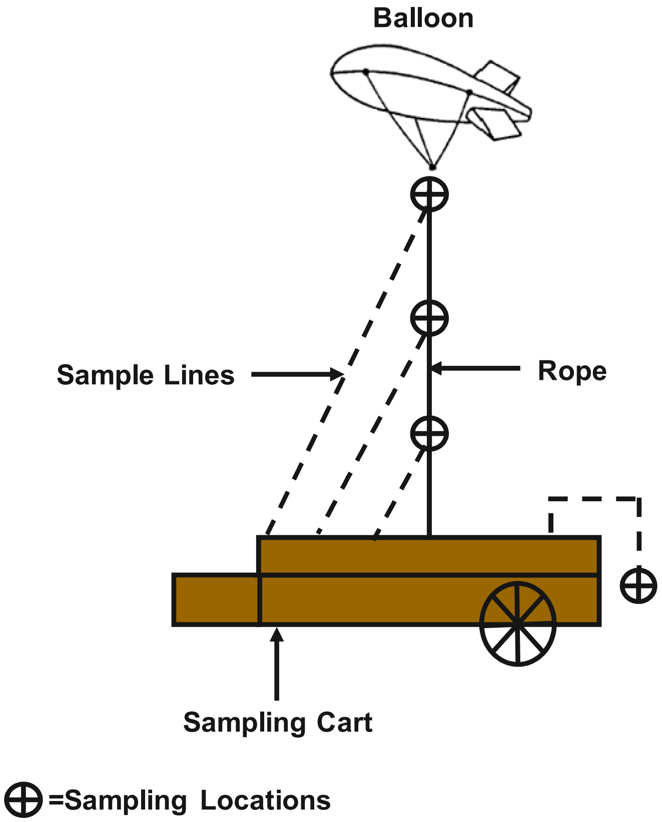


Figure 2.1. Downwind Ambient Air Mobile Sampling System

The application of Esplin's spatial ambient air sampling technique to this study involved moving the sample cart along the downwind sample path and collecting downwind composite crosswind samples at each of four elevations as illustrated in Figure 2.2. The sample path was generally a road around the perimeter of the basin. The crosswind emission flux profile was integrated by partially filling canisters at equally spaced sampling locations along the downwind sample path. Flow controllers were used to fill the canisters at a constant rate, so the amount of sample collected at each location was controlled by the amount of time the canister valves were opened at each location. The sampling time at each location was proportional to the sine of the angle (θ) between the wind direction and the sample path. The total sample collection time was set to 45 minutes. When the time required to move between the sampling stations was included, the total time elapsed during sample collection was typically in the range of 50 to 60 minutes. Generally, approximately 10 downwind sample collection locations were used, and the sample collection times at each location ranged from approximately 1 to 6 minutes, depending on the sine of the angle (θ) between the wind direction and sample path at each location.

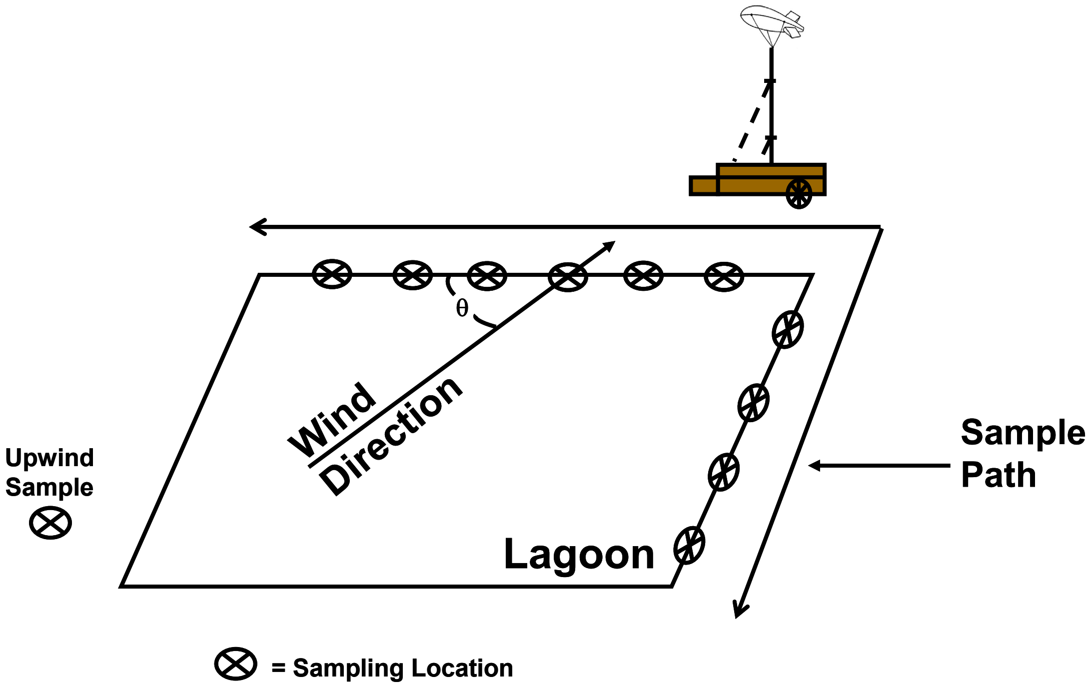


Figure 2.2. Ambient Air Sampling Scheme

2.1 Sampling System

Figure 2.3 is a schematic representation of one of the ambient air sampling systems used on the mobile cart. Each sampling system consisted of a clean, evacuated six-liter canister (Entech 29-10622), a mass flow controller (Entech CS1200), a sample pump (KNF Neuberger diaphragm pump Model N86KTDC 12 volt DC), a permation dryer (Perma Pure MD-Series gas dryer with Nafion polymer membrane), and a black rubber-coated 1/8” outer diameter Teflon sample line. The Teflon head pump continuously pulled the sample through the sample line. When the valve on the evacuated canister was open, a portion of the gas exiting the pump was pulled through a permeation dryer and then through a flow controller before entering the canister. The cart used for collecting the downwind horizontally-integrated samples at four elevations has four sampling systems – one for each elevation. In addition, the ground-level sampling system was configured to provide the capability of acquiring a field duplicate sample. The lowest elevation was essentially ground level, and the highest elevation used in this study was 55 meters, although the system was designed for sampling up to 91 meters. The apparatus for collecting the upwind or background sample contained only one sampling system which was similar to the downwind systems, except that it did not use a sample pump. The sample pumps were required for the downwind sampling systems to continuously sweep the long sample lines with relatively high flows of ambient air. The upwind system’s sample line was only a few feet long whereas even the ground-level sampling line on the downwind system was 15 feet long. The ground-level sample line was that long because in some situations it was attached to the balloon tether line to hoist it to the top of elevated sources, such as primary clarifiers, which were not at the ground-level. For both the upwind and downwind sampling systems, appropriately-sized 12-volt lead-acid batteries were used to power the pumps.

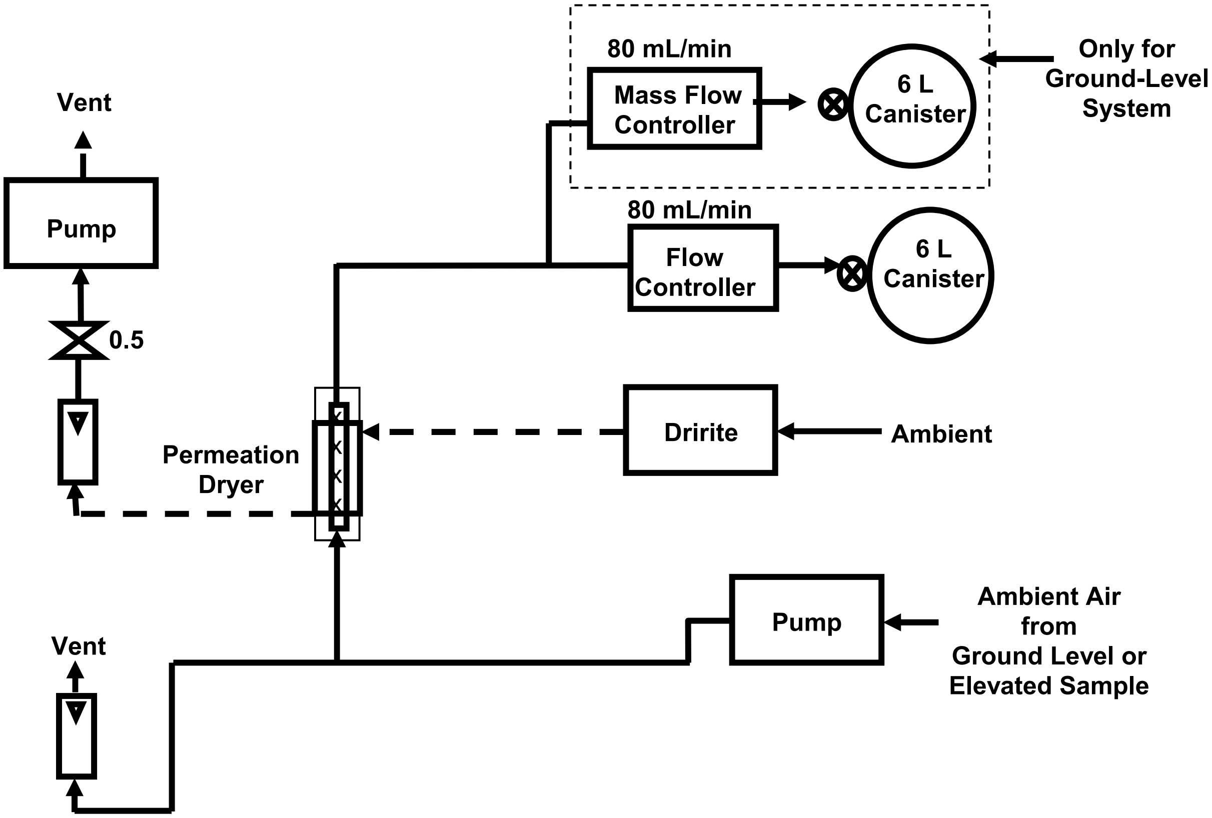


Figure 2.3 Ambient Air Sampling System

To avoid degradation of the reduced sulfur compounds, the stainless steel canisters were coated with a special sulfur-inert coating (Silonite™). All metal components in the sampling and analytical systems that came in contact with the sample had to have this coating. As shown in Figure 2.3, the sample had to be conditioned before collection in the canister by first passing it through a permeation dryer. Additionally, immediately following sample collection the canister contents had to be diluted with nitrogen. This was done by pressurizing the canister with nitrogen to achieve a dilution ratio of approximately 3.75. The canister samples were shipped via overnight courier to the laboratory where they were analyzed via gas chromatography with pulsed flame photometric detection and cryogenic pre-concentration. With very careful analysis and attention to detail, this method yielded accurate and precise results, with ambient air detection limits in the range of 1-2 parts per billion (ppb) for hydrogen sulfide, dimethyl disulfide, methyl mercaptan and dimethyl sulfide. Methane was determined via gas chromatography with flame ionization detection. Since significant background ambient air methane concentrations were always present, having a low detection limit for methane was not necessary. However, good analytical precision was required to accurately determine the often relatively small differences between the upwind and downwind concentrations.

2.2 Meteorological Data

The meteorological parameters were wind speed, wind direction, temperature, and barometric pressure. Two R.M. Young model 81000V sonic anemometers were sited at 10 meters and 2 meters above ground level in the vicinity of the WWTP. Data from the two sonic anemometers were collected on a field portable computer to provide the meteorological record for the sample test runs.

All testing was conducted during daylight hours when unstable atmospheric conditions tend to prevail. Atmospheric mixing during moderately unstable atmospheric conditions is sufficient to outweigh local terrain effects (Irwin 1983). Thus, EPA Meteorological Monitoring Guidance for Regulatory Modeling Applications (USEPA 2000) siting criteria for wind speed and wind direction in simple terrain were followed. Deviations from the criteria were documented in the sonic anemometer logbook for each site where site limitations did not permit the full criteria to be attained. Specifically, meteorological instruments were to be sited at 10 meters above ground level in level open terrain, and at a distance from any obstructions of at least 10 times the height of said obstruction, whenever possible. Siting an additional anemometer at a height of 2 meters above ground level permitted a representation of the vertical profile of horizontal wind speed to be obtained.

Ambient temperature was measured at 2 meters above ground level with a shielded thermocouple in accordance with World Meteorological Organization (WMO) standards (USEPA 2000). Barometric pressure was measured once per test run with a digital manometer.

The meteorological data were recorded as five-second averages. This rate was selected so that a minimum of 360 evenly spaced data values were obtained over a sample run. The estimate of the standard deviation thus derived was expected to be within 5-10% of the true value (Hoffnagle et al. 1981).

Accuracy, resolution, and threshold values for the study instruments are shown in Table 2.1. Assurance of parameter accuracy was determined through periodic calibration and system audits of the meteorological equipment.

Table 2.1 Accuracy, Resolution and Threshold for Study Meteorological Instruments

Instrument	Meteorological Parameter	Accuracy	Measurement Resolution	Threshold
Sonic Anemometer	Wind Speed	± 0.05 m/s	0.01 m/s	0.01 m/s
	Wind Direction	± 2^{o}	0.1^{o}	NA
Shielded Thermocouple	Ambient Temperature	0.5^{o}F	0.1^{o}F	NA
Digital Manometer	Barometric Pressure	± 0.05% FS (FS = 2000 mm Hg)	0.1 mm Hg	NA

Calibration of meteorological equipment by the manufacturer was completed prior to use. Audits were performed prior to field deployment of the equipment, and only units that passed the audits were installed. Any "fail" units were returned to the manufacturer for recalibration. Audits were performed by comparing the output from two sonic anemometers when they were placed adjacent to each other on a line perpendicular to the wind direction.

2.3 Field Sampling Procedures

Prior to any sample collection, the perimeter of the area source to be tested was measured, and equidistant sampling locations were flagged and uniquely identified, on both a scale site map and around the source perimeter. For accessibility, the sample path typically followed the source service road. Spacing between sampling points was determined such that typically 10 to 12 sampling points were used for any given wind direction. The minimum number of sampling points was five.

A subjective evaluation of the anemometer wind direction and wind speed record was made prior to initiating sample collection. When it appeared that steady state conditions would continue for the next hour, the sample path and sampling locations were determined and the sampling times and sample line heights were calculated.

Based on the stable average wind direction, the downwind distance to the sample path from the leading edge of the area source was calculated and the approximate stability class was estimated based on Turner's Key to Pasquill-Gifford (P-G) Stability Categories (Turner 1994), shown in Table 2.2, which relates P-G stability class to surface wind speed and incoming solar radiation. In Table 2.2, night refers to the period from one hour before sunset to one hour after sunrise. Sampling was only conducted during daylight hours. According to Turner's Key, the neutral class D should be assumed for overcast conditions during day or night, regardless of wind speed. "Strong" incoming solar radiation corresponds to a solar altitude greater than 60 degrees with clear skies. "Slight" incoming solar radiation corresponds to a solar altitude from 15° to 35° with clear skies. Cloudiness will decrease incoming solar radiation and should be considered along with solar altitude in determining solar radiation. Incoming radiation that would be strong with clear skies can be expected to be reduced to moderate with broken (5/8 to 7/8 cloud cover) middle clouds, and to slight with broken low clouds. Before leaving to test a facility, the solar altitude angles for the test dates were printed from the "Sun or Moon Altitude/Azimuth Table for One Day," which is published by the U.S. Naval Observatory, Astronomical Application Department (http://aa.usno.navy.mil/data/docs/AltAz.php.

Table 2.2 Key to Pasquill Stability Categories (Turner 1994)

Surface Wind Speed (@10 m) (m/s)	Day			Night	
	Incoming Solar Radiation				
	Strong	Moderate	Slight	Thinly Overcast or >4/8 Low Cloud	<3/8 Cloud
<2	A	A – B	B	--	--
2 – 3	A – B	B	C	E	F
3 – 5	B	B – C	D	D	E
5 – 6	C	C – D	D	D	D
>6	C	D	D	D	D

With these two parameters (downwind distance and P-G stability class), the plume vertical dispersion coefficient, σ_z may be estimated from the Pasquill-Gifford curves (Turner 1994). In this study, σ_z was calculated from the equations, which correspond to the Pasquill-Gifford curves, shown in Table 2.3. Based on a Gaussian distribution, the maximum plume vertical dispersion height as it crossed the sample path (Z_b) was then estimated as 2.15 σ_z. Sample line heights were calculated and adjusted to 0% Z_b (actually 0.5 meters) and three higher elevations within Z_b.

Sampling times at each location were calculated to be proportional to the sine of the angle (θ) between the wind direction and the sample path. Table 2.4 contains sin θ values for 5° increments of θ from 0° to 90°. If the sample path was straight, then all sampling points would have had equal sampling times. If the sample path was curved or angular, then the sampling times would have varied between sampling points. The total sample collection time, with a flow rate to each canister of 80 mL/min, was 45 minutes. Including the time required to move the sampling cart between sampling locations, this resulted in a total sample collection period of approximately 50 to 60 minutes. The minimum sample time was 30 minutes and the minimum sample volume was 2 liters. The canister sample flow controller flow rates were checked and set before and after each sampling trip.

Table 2.3 Equations for Calculating Pasquill-Gifford Vertical Dispersion Parameter; $\sigma_Z = a\,x^b$ where x is in km

Stability	Distance (km)	A	b	σ_Z at Upper Boundary
A	>3.11			5000
	0.5 - 3.11	453.85	2.1166	
	0.4 - 0.5	346.75	1.7283	104.7
	0.3 - 0.4	258.89	1.4094	71.2
	0.25 - 0.3	217.41	1.2644	47.4
	0.2 - 0.25	179.52	1.1262	37.7
	0.15 - 0.2	170.22	1.0932	29.3
	0.1 - 0.15	158.08	1.0542	21.4
	<0.1	122.8	0.9447	14.0
B	>35			5000
	0.4 - 35	109.30	1.0971	
	0.2 - 0.4	98.483	0.98332	40.0
	<0.2	90.673	0.93198	20.2
C	all x	61.141	0.91465	
D	>30	44.053	0.51179	
	10 - 30	36.650	0.56589	251.2
	3 - 10	33.504	0.60486	134.9
	1 - 3	32.093	0.64403	65.1
	0.3 - 1	32.093	0.81066	32.1
	<0.3	34.459	0.86974	12.1

(Continued on next page)

Table 2.3 Continued

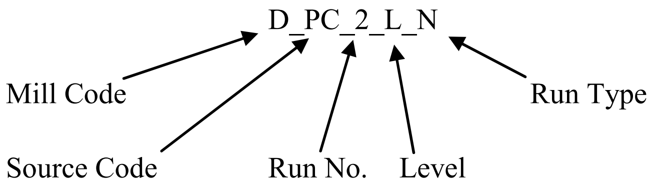
Stability	Distance (km)	A	b	σ_Z at Upper Boundary
E	>40	47.618	0.29592	
	20 - 40	35.420	0.37615	141.9
	10 - 20	26.970	0.46713	109.3
	4 - 10	24.703	0.50527	79.1
	2 - 4	22.534	0.57154	49.8
	1 - 2	21.628	0.63077	33.5
	0.3 - 1	21.628	0.75660	21.6
	0.1 - 0.3	23.331	0.81956	8.7
	<0.1	24.260	0.83660	3.5
F	>60	34.219	0.21716	
	30 - 60	27.074	0.27436	83.3
	15 - 30	22.651	0.32681	68.8
	7 - 15	17.836	0.4150	54.9
	3 - 7	16.187	0.4649	40.0
	2 - 3	14.823	0.54503	27.0
	1 - 2	13.953	0.63227	21.6
	0.7 - 1	13.953	0.68465	14.0
	0.2 - 0.7	14.457	0.78407	10.9
	<0.2	15.209	0.81558	4.1

Table 2.4 θ vs. Sin θ

θ	Sin θ
5	0.09
10	0.17
15	0.26
20	0.34
25	0.42
30	0.50
35	0.57
40	0.64
45	0.71
50	0.77
55	0.82
60	0.87
65	0.91
70	0.94
75	0.97
80	0.98
85	1.00
90	1.00

Before the start of each run, the initial pressure of each canister was checked and recorded. The initial canister pressure had to be less than one inch Hg. Each sampling system was then leak checked through the flow controller and canister. Each canister was assigned a unique sample ID which identified the mill, the source, the run number, the sampling line level (ground, low, mid, or high), and the canister run type (normal, duplicate, spike, or field blank). This code was recorded on the canister and on the field data sheet. Additionally, ambient air was pulled through the sampling systems for at least five minutes at a minimum flow rate of 200 mL/min before starting the test run. Figure 2.4 illustrates the sample code scheme for the canister-contained ambient air samples.

Air Samples



Source Codes	Level	Type
PC = Primary Clarifier	B = Background Level	N = Normal
AP = A Pond	G = Ground Level	D = Duplicate/Spike
XX = Combined WWTP	L = Low Elevation	B = Blank
	M = Middle Elevation	
	H = High Elevation	

Figure 2.4 Sample Code Scheme for Canister-Contained Ambient Air Samples

Once initial data were recorded, leak checks were performed, the sample lines were purged, attached to the balloon tether line and raised to their respective heights, sampling was begun. The canister valves were opened for the prescribed sampling time, and canister pressure and critical orifice flow were recorded on the field data sheet. At the end of the prescribed sampling time, the valves were closed and the field cart was moved to the next sampling station along the sample path, where the valves were reopened for a prescribed sampling time, and canister pressure and critical orifice flow were recorded. This process was repeated until sampling had been completed at all of the stations along the specified sample path.

When the sampling was completed, the canister valves were closed and the canisters were removed from the cart. Final pressures were checked and recorded. To enhance sample storage stability, the canisters were pressurized with nitrogen gas to yield a canister dilution factor of approximately 3.75; e.g., if the post-sample pressure was 18 in. Hg, then the canister would have been pressurized with nitrogen to a final pressure of 67.5 in. Hg. The ambient air samples were then shipped via overnight courier to the NCASI Southern Regional Center laboratory where they were analyzed via the method described in Section 3.

The upwind sampling system consisted of a single canister, a flow controller, and a permeation dryer with its associated system to supply dry air to the dryer. This portable system was placed at a point upwind of, and adjacent to, the area source under test. One ground-level sample was collected for each run. The sampling flow rate for the upwind system was set to 60 mL/min. A schematic representation of this equipment is shown in Figure 2.5.

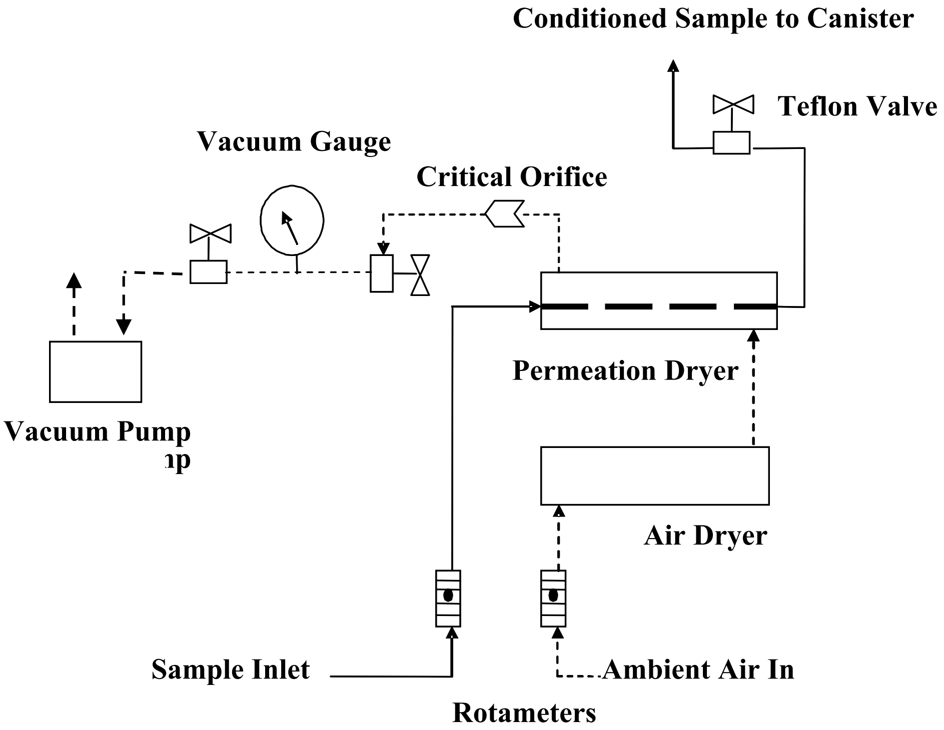


Figure 2.5 Pneumatic Diagram for the Upwind Sampling System

Before the start of each run, the initial pressure of the canister was checked and recorded. The sampling system was then leak checked through the flow controller and canister. The canister was assigned a unique sample ID which identified the mill, the source, the run number, the sampling level (background), and the canister run type (normal). This code was recorded on the canister and on the field data sheet.

At the end of the sampling run, the canister valve was closed, the final pressure was checked and recorded, and the canister was pressurized with nitrogen gas to yield a canister dilution factor of approximately 3.75. The ambient air samples were shipped via overnight courier to the NCASI Southern Regional Center laboratory where they were analyzed via the method described in Section 3.

As a general guideline for wind stability, the average wind direction for the second half of the test run should have been within ±20° of the average wind direction for the first half of the test run. And the average wind speed for the second half of the test run should have been within ±40% of the wind speed for the first half of the test run.

2.4 Calculation of Emission Rates

Emission rates were determined according to the approach described by Esplin (1988). Concentration and wind direction and speed measurements are used to estimate the spatial distribution of flux of a gas, e.g., H_2S, passing through an imaginary vertical plane downwind of an area source such as a wastewater basin. By integrating over the entire area of the vertical plane, the total amount of the gaseous compound passing through the plane can be computed. This amount is assumed to be equal to the amount of the gas emitted per unit time from the surfaceof the basin.

The horizontal path and heights for the concentration measurements must be selected before each sampling run so that essentially all of the gaseous releases from the basin surface will pass through the downwind plane of sampling locations. Due to the unique circumstances surrounding each test, it was not possible to establish an objective set of criteria for acceptable lateral plume coverage; however, each test was evaluated for the reasonableness of the plume coverage and the calculated emission rate. The details surrounding each test can be found in the individual mill test reports (NCASI 2008a-i). Gaussian dispersion of the released gases is assumed, implying the gas plume expands vertically and horizontally due to atmospheric turbulence as it travels downwind. The amount of expansion depends on the degree of turbulence, with more turbulent (unstable) conditions resulting in greater expansion. Thus, the height and width of the vertical plane for concentration measurements will increase with downwind distance and with increasing instability.

In order to perform the flux integration calculation over the vertical plane, several assumptions are made.

1. Wind direction is uniform within the plane.
2. Wind speed at a given height is horizontally uniform across the plane.
3. The vertical profile of wind speed u can be described by a power law function, $u(z)=u_r(z/z_r)^p$, where z is height above ground, z_r is the height above ground of the wind speed measurement u_r, and p is a stability-dependent parameter.
4. The vertical profile of the horizontally averaged concentration c(z) is of the following power law form, $c(z)=C_o(1-z/Z_b)^b$, where z is the height above ground, C_o is the concentration at z=0, b is an empirical constant, and Z_b is the boundary layer height, i.e., $c(Z_b)=0$.
5. Emission rates, winds, and atmospheric stability are constant over the duration of a sampling run.

2.4.1 *Emission Rate Calculation Equation*

Emission rates were calculated using the following equation.

$$E = C_o W U_{10} \int_0^{Z_b} \left(\frac{Z}{10}\right)^p \left(1-\frac{Z}{Z_b}\right)^b dz$$

where

E = emission rate, g/s
C_o = horizontally averaged ground-level (Z=0) compound concentration, g/m^3
W = crosswind length of the sample path, m

U_{10} = average wind velocity at 10 meters, m/s
Z_b = pollutant boundary layer height, m
p = wind profile exponent whose value is a function of atmospheric turbulence
b = concentration profile exponent

To compute E, values for C_o, p, Z_b, and b must first be calculated. W and U_{10} are measured. Then the integral was numerically evaluated using 0.1 meter increments for Z. The following sections describe the procedures used in the calculations.

2.4.2 *Determination of Atmospheric Stability Class and Z_b*

The pollutant boundary layer height Z_b is a function of atmospheric stability and downwind distance from the emission source. Atmospheric stability is typically characterized in terms of a stability class, which is estimated from meteorological parameters. There are several different approaches for determining the stability class.

In this study, an estimate of the stability class was made prior to each sampling run following the approach outlined by Turner (Turner 1994) which assigns a Pasquill-Gifford stability category (A, B, C, D, E, or F) based on wind speed at 10 meters, incoming solar radiation, and cloud cover. σ_z, the standard deviation of the Gaussian concentration distribution in the vertical direction, was then calculated with a formula, $\sigma_z = ax^d$, where x is the downwind distance from the upwind edge of the basin to be sampled to the sampling path for the cart and balloon apparatus, and a and d are stability dependent parameters. As recommended by Esplin (1988), Z_b was assumed to be $2.15\sigma_z$. This value of Z_b was used to set the heights for the concentration measurements.

After the sampling run, two other approaches using wind data collected during the sampling run were used to recalculate the stability class, σ_z, and Z_b. The fluctuations in the horizontal wind direction (azimuth angle), vertical wind direction (elevation angle), and vertical velocity measured by the sonic anemometer at the 10 meter height were used to compute σ_A, σ_E, and σ_w, respectively. The relationship between Pasquill-Gifford stability class and the standard deviation of the azimuth and elevation angles over a 60 minute averaging period is shown in Table 2.5 (Gifford 1976; Kunkel 1985). When the sampling period was different from 60 minutes, the σ_A value was adjusted to a 60 minute mean σ_A value with the following equation (Kunkel 1985): $(\sigma_A)_{60} = (\sigma_A)_t\,(60/t)^{0.2}$, where t is in minutes. A minimum of 360 values obtained during the averaging period should be used for calculating the standard deviations (USEPA 2000).

Table 2.5 Relationship Between Pasquill-Gifford (P-G) Stability Class and the Standard Deviation of the Azimuth and Elevation Angles (σ_A and σ_E) of the Horizontal and Vertical Wind Components

Stability Description	P-G Stability Class	σ_A, deg.	σ_E, deg.
Very unstable	A	25	10
Moderately unstable	B	20	–
Slightly unstable	C	15	–
Neutral	D	10	2 – 5
Moderately stable	E	5	–
Very stable	F	2.5	1

In the first approach, the computed σ_A values were used to determine the stability class. σ_z and Z_b were then determined with the same relationships as before, i.e. $\sigma_z = ax^d$ and $Z_b = 2.15\sigma_z$.

In the second approach, σ_Z was directly calculated from the standard deviation of the vertical component of the wind velocity (σ_w) using Irwin's model (Irwin 1983). This model relates the two parameters through the following equation.

$$\sigma_z = \sigma_w \, T \, f_z$$

where

σ_w = standard deviation of the vertical component of the wind velocity, m/s

T = travel time (seconds) = $\dfrac{x(meters)}{U_{10}(m/s)}$

$$f_z = 1.88\left(\frac{T}{100} - 0.4\right)^2 + 0.7 \quad \text{for unstable conditions, and}$$

$$= \frac{1}{1 + 0.9(T/50)^{0.5}} \quad \text{for stable conditions.}$$

If measurements of σ_w are not available, it can be approximated from σ_E and $\bar{U}_{10}$ by using the following equation (USEPA 2000).

$$\sigma_w = \sigma_E \cdot \overline{U_{10}}$$

where

σ_E = standard deviation of the elevation angle, radians

$\bar{U}_{10}$ = average 10-meter wind velocity, m/s

Again, Z_b was assumed to be $2.15\sigma_z$.

Normally the value of σ_z calculated from σ_w was used to determine Z_b. However, this method can yield unrealistically large values for σ_z when wind speeds are low. Thus, if σ_Z calculated from σ_w was approximately two or more times the value of σ_Z based on σ_A, then other factors were evaluated to determine which value of σ_z should be used for calculating Z_b. First, the meteorological conditions and associated atmospheric stability were examined before, during, and after the sampling run to determine if there were any trends, and if so, whether the trend in vertical stability was better represented by σ_z based on the σ_A or σ_w method. Second, emission fluxes were calculated using values of σ_z determined from both the σ_A and σ_w methods, and the resulting flux profiles were examined to determine which Z_b value appeared to give the most reasonable profile. If the trends and flux profiles both suggested σ_z calculated from the σ_A method resulted in the best fit to the observations, then the σ_z value based on the σ_A method was used to calculate Z_b. Otherwise, σ_z and Z_b were based on the σ_w method.

2.4.3 *Calculation of the Wind Velocity Profile Exponent (p)*

The value of p was calculated from the site-specific horizontal wind velocities measured at 2 meters and at 10 meters using the following equation.

$$p = \frac{\ln(U_{10}) - \ln(U_2)}{\ln(10) - \ln(2)}$$

On rare occasions, the mean wind speed at 2 meters slightly exceeded that at 10 meters. In that circumstance, p was set to zero. When wind speed values were not available for both levels, a default p value (USEPA 2000) based on the atmospheric stability class was assigned. The stability class was determined from σ_A. The p values are shown in Table 2.6, and represent "rural" conditions with a modest surface roughness.

Table 2.6 Wind Profile Exponent as a Function of Atmospheric Stability Class for Rural Sites

Stability Class	p
A	0.07
B	0.07
C	0.10
D	0.15
E	0.35
F	0.55

2.4.4 *Background Concentration Correction*

Normally, the measured background RSC concentrations were subtracted from the downwind sample concentrations only if they were considered to represent relatively three-dimensionally homogeneous background concentrations. If the results of screening studies indicated that a three-dimensionally non-homogeneous background concentration profile existed in a given situation, then emission testing was only done in that situation if the relative concentration levels, considering dispersion conditions, indicated that ignoring the background would not significantly bias the calculated emission fluxes. When a correction for upwind background concentration was to be applied to the downwind canister RSC concentrations, then the pre-dilution concentration of the background canister was subtracted from the pre-dilution concentrations in the canisters collected downwind from the source at multiple elevations. After the downwind sample RSC concentrations had been corrected for the background concentration, or the decision was made not to correct for background concentration, the resulting concentration values were considered the downwind ambient air concentrations due to source emissions.

For methane, all downwind concentrations were corrected for background concentrations because background methane concentrations were always a significant portion of the downwind concentrations. Background methane concentrations, in the absence of any nearby upwind sources, were assumed to be spatially uniform. Data in the literature indicate that this is a reasonable assumption. A study of the vertical distribution of ambient air methane concentrations in the lower troposphere showed no significant variation (Sugawara et al. 1997). Interference from nearby upwind sources was not expected to be a significant problem in the study reported herein, because methane emissions quantitation was only performed when the sources could be tested without interference from upwind anthropogenic methane emission sources. Additionally, given the distance of the tested sources to natural methane emissions from upwind wetlands, and the maximum estimated emissions from natural wetlands (Ehhalt and Heidt 1973; Walter, Heimann, and Matthews 2001), methane emissions from natural sources would not be expected to significantly affect the measured downwind methane vertical concentration profiles.

2.4.5 *Calculation of C_0 and b*

The balloon sampling system provided horizontally averaged ambient concentrations for each of the four reduced sulfur compounds and methane at three or four heights. The vertical concentration distribution was assumed to be of the form

$$C(z) = C_o\left(1 - \frac{Z}{Z_b}\right)^b$$

In order to solve for b and C_0, the natural logarithm was taken of both sides of the equation to yield

$$\ln[C(z)] = \ln C_o + b\ln\left[1 - \frac{Z}{Z_b}\right]$$

As this equation represents a straight line in log-log space, linear regression can be used to obtain values for the slope b and intercept ln C_0, provided that values of C are available for at least three heights. However, there were many sampling runs where less than three concentrations were above method detection limits, especially for the reduced sulfur compounds at the elevated sampling heights. Thus procedures had to be developed to handle these situations, as described in the following sections. These procedures were used to calculate compound-specific C_0 values, compound-specific b values and average b values. Occasionally deviations from these procedures were necessary to accommodate data sets with unusual characteristics. Any such departures have been identified in the individual mill reports (NCASI 2008a-g).

If all five compounds were released uniformly over the surface of a basin at a constant rate, then in theory the slope of the horizontally averaged vertical concentration profile (in log-log space) would be the same for all five compounds. However, it is likely the releases of each compound vary horizontally over the basin surface and vary over time. Furthermore, slopes determined from field data for individual compounds are subject to considerable uncertainties due to measurement inaccuracies, non-steady state meteorological conditions, non-uniform background concentrations, and non-Gaussian concentration distributions. Thus, the calculated slopes for the five different compounds are not expected to be in agreement with each other.

Because of the uncertainties inherent in the individual compound concentration profiles obtained through linear regression, use of the average of the b exponents determined for each of the five compounds was believed to be the most reasonable approach for calculating emissions, with some rare exceptions. If any compound lacked sufficient concentration measurements to calculate a b exponent from detectable values, it was not included in the calculation of the average b value.

Because Esplin's (1988) measurements were limited to a single parameter (TRS), only one vertical concentration profile could be computed. Also, he apparently did not encounter any TRS concentrations below his method detection limits. Procedures to handle non-detects and compute vertical profiles with less than three data points were therefore unnecessary in his study.

2.4.6 *Calculation of Compound-Specific b and C_0 for RSC Compounds*

If measured concentrations of a given compound were above the quantitation limit at three or four elevations, then all of the concentration values above the quantitation limit were used for linear regression to calculate the compound-specific b and C_0 values.

If measured concentrations of a given compound were above the quantitation limit at only two elevations, then the two quantified values and one-half of the quantitation limit at the next highest elevation were used to calculate compound-specific b and C_0 values. If the two above quantitation limit concentrations were the ground level (0.5 meters) and the high level, then the quantitated ground level (0.5 meter) and high level concentrations were used in conjunction with an assumed value of 0.001 ppbv at 95% Z_b to calculate compound-specific b and C_0 values.

Assigning a 0.001 ppbv value at 95% of Z_b was somewhat arbitrary. The assumed form of the vertical concentration profile implies $C(Z_b) = 0$. However, the b exponent is calculated by linear regression using the logarithmic form of the profile where the term $\ln(1\text{-}z/Z_b)$ becomes infinitely large as z approaches Z_b, as shown in Figure 2.6. Through trial and error, it was found that using a concentration value of 0.001 ppbv at $0.95Z_b$ appeared to give reasonable flux profiles and fit what was known about the vertical concentration profiles for the area sources and atmospheric stability conditions encountered in this study in almost all situations. Nevertheless, there were a few situations where alternative calculation procedures were necessary.

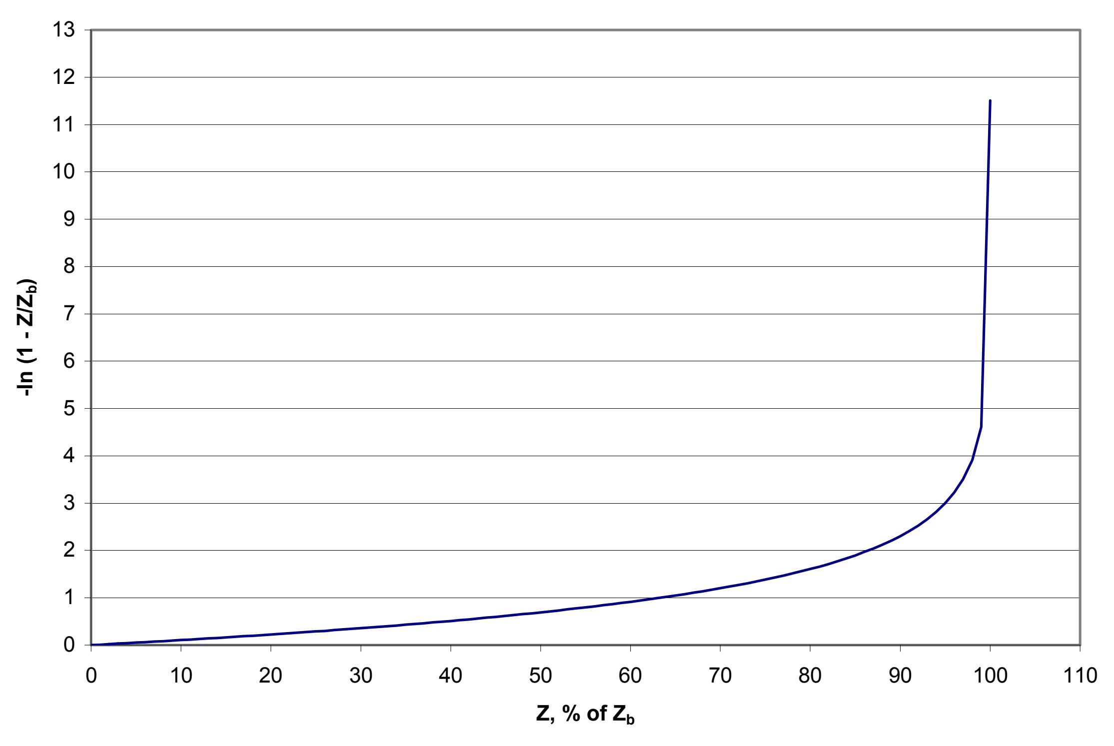


Figure 2.6 Effect of Z Approaching the Pollutant Boundary Layer Height, Z_b

When only three sampling elevations were used (mainly at the beginning of the study), and the highest elevation exceeded Z_b, then the concentrations at the lower two sampling elevations were used in conjunction with 0.001 ppbv at 95% Zb for calculation of the compound-specific b and C_0 values.

In situations where concentrations for one compound were above the quantitation limit only at the ground level, then the measured 0.5 meter concentration was used as C_0. If duplicate concentration values were available for the 0.5 meter level and both of those values were above the quantitation limit, then the average of the duplicate values were used as C_0. However, if one of those duplicate values was less than one-half the other, then the lower value was not used. Also, if the 0.5 meter level concentration was measured in duplicate, but only one of the two values was above the quantitation limit, then only the value that was above the quantitation limit was used as C_0. In the preceding cases, it was assumed that the lower duplicate values were due to the development of active sites on the interior canister surfaces. Compound-specific b values were not calculated when only the 0.5 meter concentration was above the quantitation limit unless vertical concentration profiles could not be computed for any of the other compounds, including methane. If b had to be calculated because it was not available from any of the other compounds, then one-half of the detection limit at the low level and 0.001 ppbv at 95% of Z_b were used to determine b and C_o.

If concentrations at all elevations were below the quantitation limit, then the quantitation limit was used as C_0, the emission rate was reported as ND[xxxx] and a compound-specific b was not calculated. If measured vertical concentration profile data were not available for any of the other compounds, including methane, then one-half of the detection limit at the low level and 0.001 ppbv at 95% Z_b were used to calculate b.

In all cases where a concentration value of 0.001 ppbv at 95% of Z_b was used to estimate b for a reduced sulfur compound, the resulting vertical concentration profile curve fit was visually inspected. If the fit with the known concentration data was poor, then the vertical concentration profile was refitted using the measured ground-level concentration and one-half of the quantitation limit at the low, mid and, in some cases, the high sampling elevations in the regression calculation for the determination of the b and C_o values.

2.4.7 *Calculation of b and C_0 for Methane*

If the background-corrected concentrations were above zero at three or four levels, then all of the positive values were used for linear regression to calculate b and C_0 for methane.

If the background-corrected methane concentrations were above zero at two elevations and the highest of those two elevations was less than 80% of Z_b, then all of the detect values were used in conjunction with 0.001 ppbv at 95% Z_b to calculate b and C_0.

Whenever a concentration value of 0.001 ppbv at 95% of Z_b was used to estimate b for methane, the resulting vertical concentration profile curve fit was visually inspected. If the fit with the known concentration data was poor, then a value for b was not calculated for methane, the measured ground-level concentration was used as C_o, and the average b value for the reduced sulfur compounds was used to calculate the methane emission rate.

If only the ground level (0.5 meter) background-corrected concentration was positive, then the 0.5 meter concentration was used as the C_0 value, and a compound-specific b value was not calculated.

If the ground level (0.5 meter) background-corrected concentration was negative, no values for methane were calculated and the emission rate was report as NA (not available).

2.4.8 *Calculation of Average b*

In the average b calculation, all of the compounds were included for which above quantitation limit (or for methane, above zero) concentrations were measured at a minimum of two levels.

If none of the compounds were detected at two or more levels, then the average b was computed from the compound-specific b values for those compounds detected at ground-level. Compound-specific b values less than one were not used when calculating the average.

2.4.9 *Use of Average b vs. Compound-Specific b in the Emission Rate Calculation*

The average b value was used in all emission rate calculations, unless there was evidence indicating specific source characteristics and meteorological conditions resulted in significantly different compound-specific vertical concentration profiles. Examples of this situation are the data from test run nos. 1, 7, 8, 9, 10 and 11 at the Mill D no. 1 ASB. During these test runs, a portion of the sample path passed close to the area where the acidic mill effluent was entering the basin. The acidic area near the basin inlet was relatively small, due to the buffering effect of aerobic biological activity as the mill effluent moved through the basin. The acidic conditions resulted in a relatively high hydrogen sulfide emission rate in that area; however, it had little effect on the emission rates of the organic reduced sulfur compounds or methane. Therefore, in this situation, the use of compound-specific b exponents yielded the most accurate vertical concentration profiles and emission rates.

2.5 Overall Quality Assurance Procedures for Concentration Measurements

The overall quality assurance program for the ambient concentration measurements included field duplicates, train spikes, and train blanks.

Generally, a ground-level field duplicate canister was collected for each test run. Duplicate samples were collected by simultaneously filling two canisters at the ground-level elevation.

Train spike tests were performed before each field sampling trip, and train blank tests were performed before and after each sampling trip. Train spike tests were performed by dynamically diluting a cylinder gas of H_2S in nitrogen to a concentration of approximately 50 ppbv. The test gas was sampled through the high sampling system, which had the longest sample line. A Jerome H_2S analyzer was used to test the concentration of H_2S exiting the Teflon line, which during ambient air sampling would have been connected to the canister flow controller. The average measured concentration from three readings was required to be within ±20% of the expected concentration.

Train blank tests were performed by sampling zero air through the high sampling system. A Jerome H_2S analyzer, which had been zeroed on zero air, was used to test the concentration of H_2S exiting the Teflon line, which during ambient air sampling would be connected to the canister flow controller. For an acceptable blank test, the average measured H_2S concentration level from three readings was required to be less than 5 ppbv.

3.0 A GC-PFPD METHOD FOR DETECTION OF HYDROGEN SULFIDE, METHYL MERCAPTAN, DIMETHYL SULFIDE, AND DIMETHYL DISULFIDE AT PPB LEVELS IN AMBIENT AIR

3.1 Introduction

This test method was developed to measure low parts-per-billion (ppb) to low parts-per-million (ppm) levels of the reduced sulfur gases hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide that may be present in ambient air around pulp and paper mills and wastewater treatment facilities. Low levels of these reduced sulfur gases are difficult to accurately quantify in ambient air due to their high reactivity. Sample losses occur due to adsorption to the surfaces of materials used for sample collection and analyses, as well as reactions with water and other substances present in samples of ambient air.

Ambient air samples were captured in evacuated canisters, concentrated using a cold trap procedure, and analyzed using gas chromatography (GC) and pulsed flame photometric detection (PFPD). Sample losses were minimized both by the use of 1) a permeation dryer during sample collection to minimize moisture levels in the sample gas, 2) a post-collection dilution with nitrogen, and 3) insuring that all of the sampling and analytical equipment (e.g., canisters, valves, tubing, fittings) in contact with the sample had been lined with Silonite™ (sulfur inert) coating. The importance of using Silonite™ coated equipment cannot be overemphasized, as preliminary testing with similar products yielded unacceptable sample loss, and the presence of even a single uncoated metal fitting could result in significant sample loss. Similarly, collecting samples without the use of the permeation dryer and post-collection dilution with nitrogen resulted in unacceptable levels of sample loss prior to analysis.

3.2 Applicability

This method was developed to be applicable to the determination of low levels of reduced sulfur gases in ambient air. The method as written has been optimized for four common reduced sulfur gases (hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide).

3.3 Materials and Methods

3.3.1 *Silonite™ Coating*

Any sampling or analytical equipment that would contact the sample gas was covered with an inert coating in order to prevent negatively biased results. In preliminary testing, the performance of Silonite™ coated equipment, manufactured by Entech Instruments, Inc. (Simi Valley, CA) provided an acceptably inert surface. Therefore, all canisters, valves, tubing, fittings, injection port liners, and other items used in the application of this method were purchased from the Silonite™ product line or sent to Entech Instruments, Inc. for custom coating with Silonite™.

3.3.2 *Materials*

3.3.2.1 6 L vacuum canister and inlet flow controller. This method was developed using a 6 L Silonite™ vacuum canister and CS1200 flow controller manufactured by Entech Instruments, Inc.

3.3.2.2 Canister autosampler. This method was developed using an Entech Instruments, Inc. 7016CAA Canister Autosampler.

3.3.2.3 Sample preconcentrator. This method was developed using a Model 7100A Preconcentrator (Entech Instruments, Inc.).

3.3.2.4 Gas chromatograph equipped with a pulsed flame photometric detector (PFPD). This method was developed using a Hewlett-Packard 5890 gas chromatograph (GC) equipped with an OI Analytical PFPD. Any metal components of the GC that would come into contact with the sample gas were Silonite™-coated.

3.3.2.5 Liquid nitrogen for use in preconcentrator cold trap cycle and sub-ambient GC oven.

3.3.2.6 Nitrogen gas for use in the preconcentrator in the lab and for pressurizing sample canisters following sample collection in the field.

3.3.2.7 Helium for use in the GC as a carrier gas.

3.3.2.8 Cylinder gas containing approximately 0.5 ppmv H_2S in nitrogen for canister spiking.

3.3.2.9 Permeation tube calibration system.

3.3.3 *Sample Collection*

The sample collection system is shown in Figure 3.1. Ambient air was drawn into a six-liter Silonite™ coated, evacuated canister (Entech Instruments, Inc.) at a flow rate of 60 to 80 mL/min for 45 minutes. The flow rate was controlled using a CS1200 mass flow controller (Entech Instruments, Inc.). Prior to entering the canister, air was drawn through a permeation dryer for moisture removal. Countercurrent dry air for operation of the permeation dryer was generated by passing ambient air through a Dririte column at a flow rate of 500 mL/min. After samples were collected, the canisters were pressurized with nitrogen to yield a canister dilution factor of 3.75 and final canister pressure was checked and recorded. Canisters were maintained at ambient temperatures.

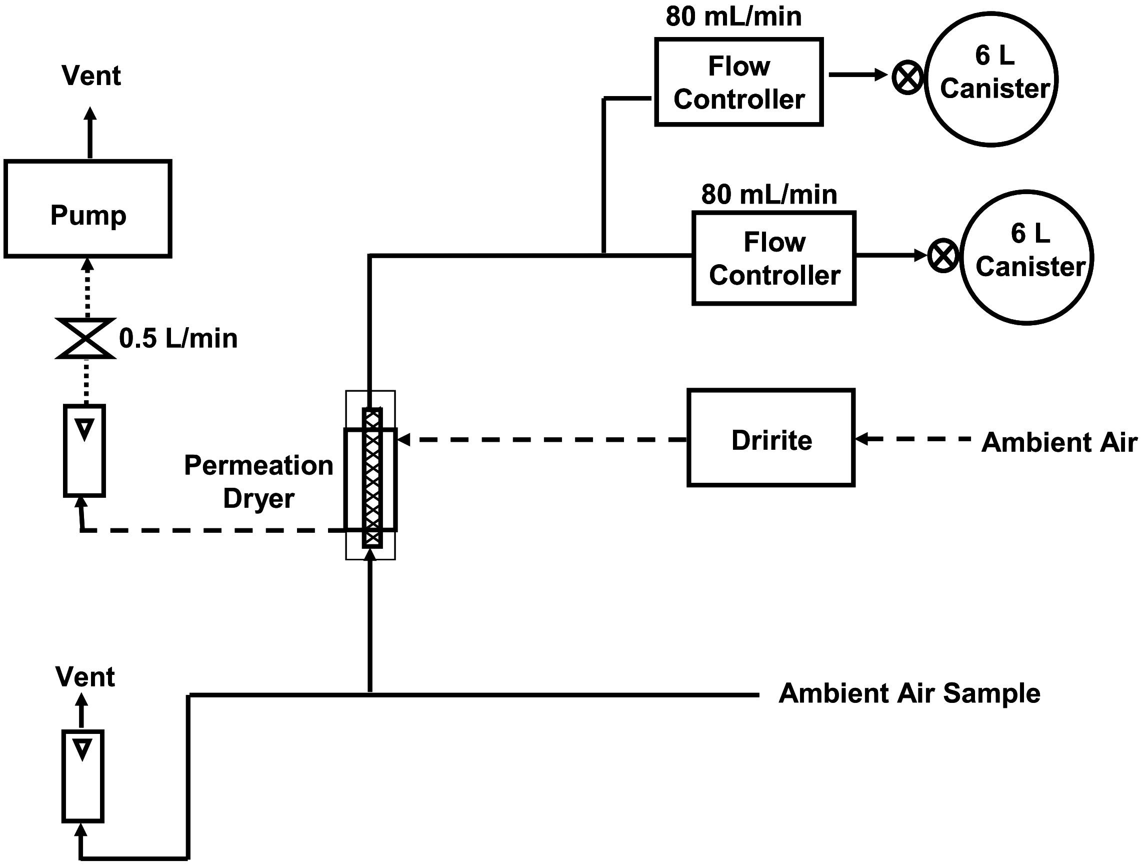


Figure 3.1 Ambient Air RSC Sampling System

3.3.4 *Sample Analysis*

3.3.4.1 ***Autosampler*** - For analysis, canisters were connected to an Entech Instruments, Inc. autosampler. The autosampler valves and transfer lines were maintained at a temperature of 80°C.

3.3.4.2 ***Preconcentrator*** - Sample gases were concentrated prior to analysis by the process of cold trap dehydration using a Model 7100A Preconcentrator (Entech Instruments, Inc.). Preconcentrator operating parameters are shown in Table 3.1. For each analysis, sample gas was drawn from the canister through the preconcentrator at a flow rate of 100 mL/min. The volume of sample used was varied between 50 and 1000 mL as appropriate for reduced sulfur gas levels in the sample gas. Module 1 of the preconcentrator was operated with an empty trap at a temperature of −20°C. Module 2 of the preconcentrator was operated with a Tenax trap at a temperature of −80°C. After the sample passed through the preconcentrator, the lines were swept for 10 seconds with nitrogen at a flow rate of 60 mL/min. When the GC was ready, the preconcentrator cooled the cryo-focusing trap to -200°C, then module 2 was heated to 180°C and the sample was desorbed for two minutes from the Tenax trap on to the cryo-focusing trap. Then the sample was immediately desorbed for two minutes from the cryo-focusing trap onto the GC column, and the sample analysis was started.

Table 3.1 Preconcentrator Operating Conditions for Canister Sample Analysis

Cryogenic Preconcentrator	
Sample Volume for Calibration:	1000 mL
Module 1 Blank Trap Temperature:	-20°C
Module 1 Desorb Temperature:	10°C
Module 2 Tenax Trap Temperature:	-80°C
Module 2 Desorb Temperature:	180°C
Module 3 Cryofocus Temperature:	-195°C
Module 3 Desorb Temperature:	180°C
Transfer Line Temperature:	100°C
Preconcentrator Valve Temperature:	100°C
Autosampler Transfer line Temperature:	80°C
Autosampler Valve Temperature:	80°C

3.3.4.3 ***Chromatography*** - A Hewlett-Packard 5890 gas chromatograph (GC) equipped with a pulsed flame photometric detector (PFPD) was used for compound separation, identification, and quantification. Gas chromatograph instrument control parameter settings are shown in Table 3.2. Compound separations were achieved on a Restek RTX-1 column (Restek, Inc., State College, PA) that was 30 m long and had a 0.32-mm interior diameter and a film thickness of 5 µm. Oven temperature was programmed as follows: -20°C for 4 minutes, ramped at 10°C/minute to 50°C, held for 3 minutes, then ramped at 70°C/minute to a final temperature of 130°C and held for 5 minutes, then ramped at 70°C/minute to a final temperature of 250°C and held for 5 minutes. The carrier gas was helium with a column flow rate of 2 mL/min. Figure 3.2 is an example chromatogram from analysis of a ground-level ambient air sample collected downwind of the aerated stabilization basin (ASB) at a kraft mill wastewater treatment plant (WWTP). Table 3.3 lists the compound identification for each of the peaks.

Table 3.2 GC Operating Conditions for Canister Sample Analysis

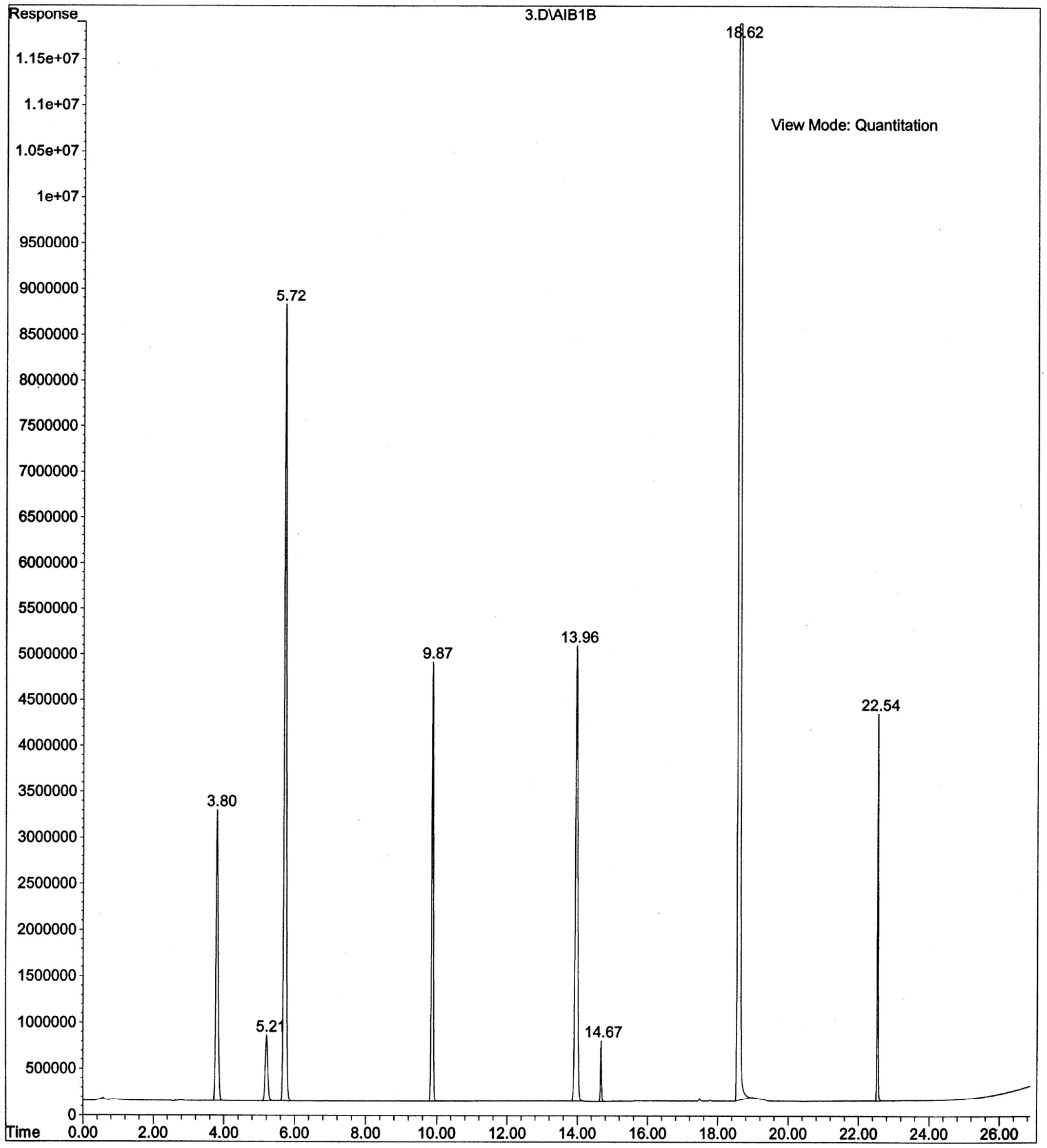
Hewlett Packard 5890 Gas Chromatograph	
Injection:	Split (1:9)
Injector Temperature:	220°C
Injection Liner Size:	2 mm id (no packing)
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 2 mL/min at room temperature, or use constant flow mode at 2 mL/min
Column:	RTX - 1, 30 m x 0.53 mm id x 5 micron fused silica capillary column
Cryogenics:	On
Temperature Program °C:	
Initial:	-20°C for 4 min
Ramp 1:	10°C/min to 50°C for 3 minutes
Ramp 2:	70°C/min to 130°C for 5 minutes
Ramp 3:	70°C/min to 250° for 5 minutes
Retention Time Order:	Hydrogen Sulfide, Methyl Mercaptan, Dimethyl Sulfide, and Dimethyl Disulfide

Table 3.3 Compound Identification for Figure 3.2

Retention Time	Compound Identification
3.80	H_2S (hydrogen sulfide)
5.21	COS (carbonyl sulfide)
5.72	SO_2 (sulfur dioxide)
9.87	MeSH (methyl mercaptan)
13.96	DMS (dimethyl sulfide)
14.67	CS_2 (carbon disulfide)
18.62	DMDS (dimethyl disulfide)
22.54	DMTS (dimethyl trisulfide)

Figure 3.2 Example Chromatogram from Analysis of a Ground-Level Ambient Air Sample Collected Downwind of the ASB at a Kraft Mill WWTP

```
File       : C:\HPCHEM\2\DATA\031405B\3.D
Operator   : jes
Acquired   : 15 Mar 20105   5:4     using AcqMethod 0PFPD1M.M
Instrument :   GC/MS Ins
Sample Name: 3
Misc Info  :
Vial Number: 35
```



3.3.4.4 Detection and Quantitation – Compound detection was accomplished with a pulsed-flame photometric detector (PFPD) manufactured by OI Analytical (Model 5380). The detector operating parameters are listed in Table 3.4.

Table 3.4 PFPD Operating Conditions for Canister Sample Analysis

Pulsed - Flame Photometric Detector	
Detector Temperature:	250°C
H_2 Flow Rate:	approx. 11 mL/min
Air Flow Rate:	approx. 20 mL/min
Makeup Gas:	None
Optical Filter:	Blue (394 nm)
Ignitor Frequency:	3.1 Hertz
Gate Time:	6-24 msec

3.3.4.5 ***Standard Curve*** - Standard curves based on five points were prepared for hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Standard gases from permeation tubes, were diluted to desired concentrations with nitrogen. For each compound, a standard curve was prepared. Table 3.5 shows the concentration ranges of the example calibration curves shown in Figures 3.3 through 3.6 for hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, respectively. Table 3.6 shows the absolute percent error (APE) for each calibration point, and the mean absolute percent error (MAPE) for each compound. Table 3.7 shows the daily recovery results for three mid-level check standards that were run each of the four days following the calibration curve preparation.

Table 3.5 Concentration Ranges for Initial PFPD Calibration Curves
(analysis sample size = 1000 mL)

	Concentration Range, ppbv	
Compound	Low	High
H_2S	1.9	12.0
MeSH	1.9	11.3
DMS	1.9	11.3
DMDS	0.7	4.0

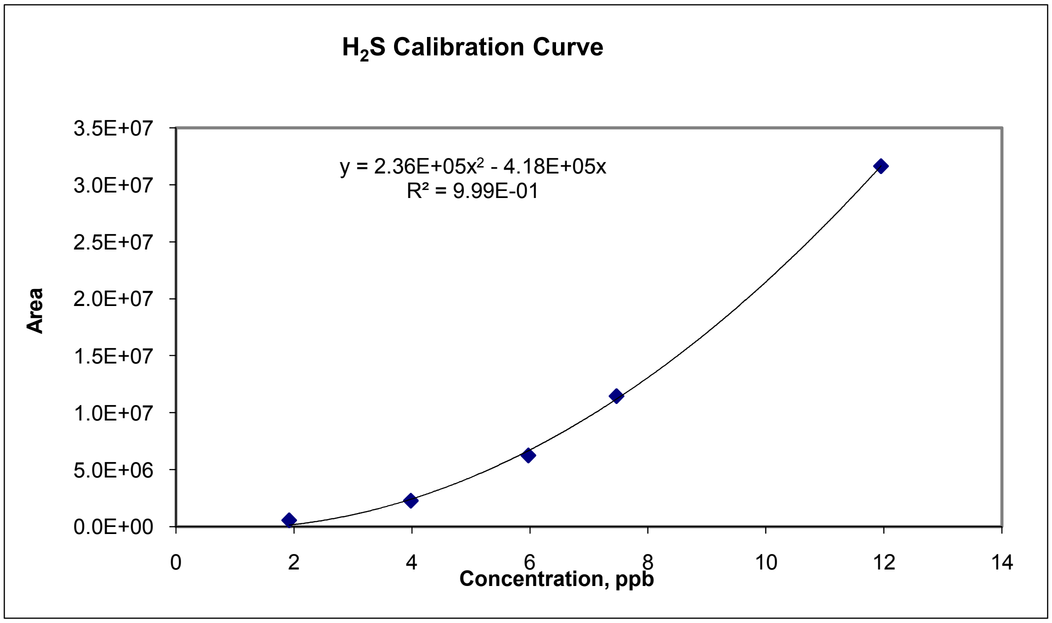


Figure 3.3 H_2S Calibration Curve (2/7/06)

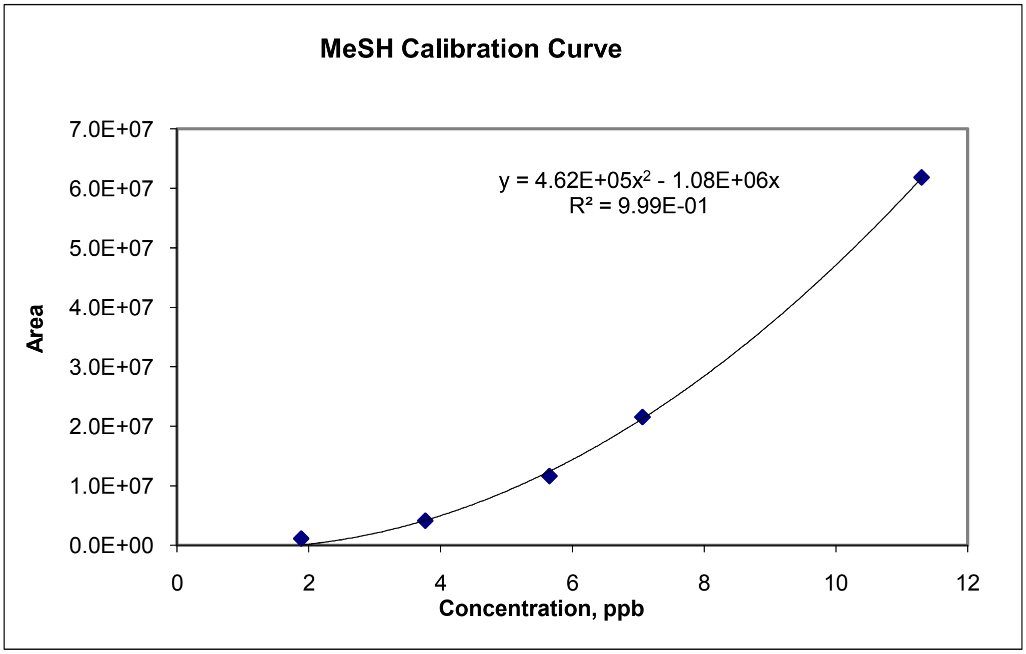


Figure 3.4 MeSH Calibration Curve (2/7/06)

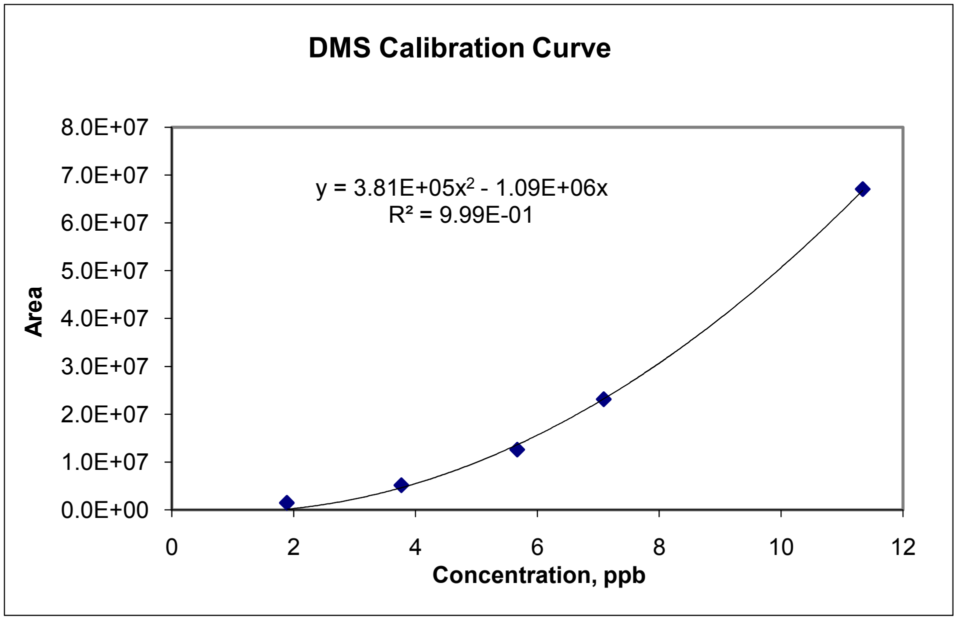


Figure 3.5 DMS Calibration Curve (2/7/06)

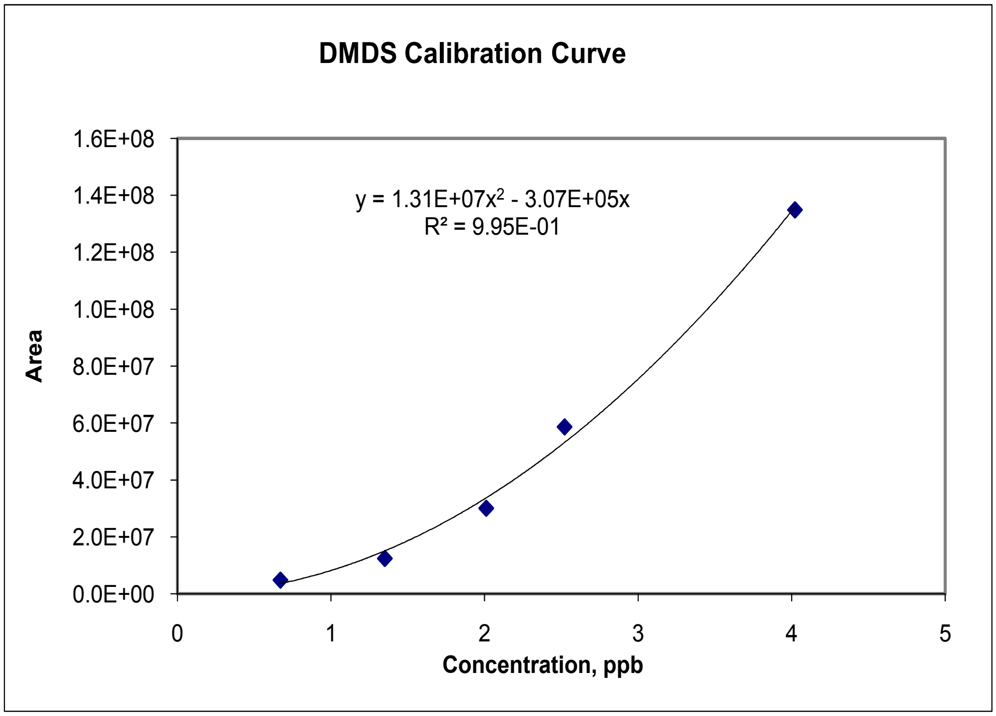


Figure 3.6 DMDS Calibration Curve (2/7/06)

Table 3.6 Calibration Curve Quality (2/7/06)

Calibration Point No.	H_2S SC, Ppbv	H_2S APE, %	MeSH SC, ppbv	MeSH APE, %	DMS SC, ppbv	DMS APE, %	DMDS SC, ppbv	DMDS APE, %
1	1.9	31.3	1.9	37.7	1.9	40.4	0.7	15.6
2	4.0	1.7	3.8	0.4	3.8	3.5	1.4	8.9
3	6.0	2.5	5.7	2.6	5.7	3.2	2.0	5.4
4	7.5	1.1	7.1	0.5	7.1	0.2	2.5	5.1
5	12.0	0.0	11.3	0.1	11.3	0.1	4.0	0.4
MAPE, %		7.3		8.3		9.5		7.1

SC = standard concentration, ppbv
APE = absolute percent error, %
MAPE = mean absolute percent error, ppbv

Table 3.7 Daily Check Standard Recoveries (2/8-11/06)

Compound	Check Standard Conc., ppbv	Check Standard Recovery, % Day 1	Day 2	Day 3	Day 4
H_2S	4.0	104.5	110.4	107.9	103.7
	6.0	100.6	109.9	98.9	104.2
	7.5	97.9	109.9	92.5	101.9
MeSH	3.8	109.8	115.1	111.1	105.1
	5.7	93.1	105.2	94.8	104.9
	7.1	95.8	101.4	87.8	99.3
DMS	3.8	107.5	111.9	104.7	102.8
	5.7	98.7	105.5	89.1	97.7
	7.1	93.2	100.6	81.6	92.2
DMDS	1.4	116.4	121.5	111.9	106.5
	2.0	109.2	112.8	95.0	117.2
	2.5	106.7	109.6	89.6	110.5

3.3.5 *Minimum Quantitation Level/MQL*

For this method, results less than the lowest calibration standard/minimum quantitation level were reported as less than the MQL.

3.3.6 *Sample Storage Time Correction Factors*

Due to the extremely reactive nature of the reduced sulfur compounds, and despite all of the precautions taken, some analyte degradation in the canisters was unavoidable. Therefore, as discussed in Section 4.2, correction factors were developed to correct for hydrogen sulfide, methyl mercaptan and dimethyl sulfide degradation over time. Correction factors were not needed for dimethyl disulfide. Starting at two days after sample collection, the analytical results were multiplied by the correction factors shown in Table 3.8. Samples were not to be stored longer than 10 days.

Table 3.8 H_2S, MM and DMS Correction Factors for Storage Time

Days Since Sample Collection	Correction Factor		
	H_2S	MM	DMS
2	1.14	1.16	1.08
3	1.21	1.24	1.12
4	1.28	1.32	1.16
5	1.35	1.40	1.20
6	1.42	1.48	1.24
7	1.49	1.56	1.28
8	1.56	1.64	1.32
9	1.63	1.72	1.36
10	1.70	1.80	1.40

3.4 Canister Analysis Quality Assurance Check Procedures

The implementation of a stringent quality control program allowed for optimum instrument performance and analytical precision in sample analysis. Imperative to the quality control of the analytical program was the verification of optimum instrument performance. Also vital to this aspect of the study was the analysis of QA/QC samples such as replicate sample analysis.

3.4.1 *General Approach*

The general approach for quality assurance was to use the calibration and certification procedures outlined in USEPA Compendium Method TO-14A (USEPA 1999).

3.4.2 *Clarification and Customization of Method TO-14A Procedures*

3.4.2.1 *Routine (Daily) Calibration*

For non-linear GC detector responses, Method TO-14A specifies an initial five-point calibration and daily three-point calibration checks, followed by a five-point recalibration, if necessary.

TO-14A does not describe a procedure for assessing the quality of the calibration curve fit for detectors with non-linear responses. Consequently, the quality of the calibration curve fit was evaluated by calculating the mean absolute percent error (MAPE) of the calibration points according to the following equation.

$$MAPE = \frac{\sum \left| \frac{C_{cal} - C}{C_{cal}} \right| * 100}{n}$$

where:

MAPE is the mean absolute percent error
C_{cal} is the concentration on the calibration standard
C is the concentration measured for the calibration level
n is the number of calibration levels

The use of MAPE for calibration curve quality assessment is described in NCASI Method RSC-02.02, Reduced Sulfur Compounds by Direct Injection GC/PFPD (NCASI 2005). The following criteria were used to determine the acceptability of a calibration curve: For a calibration curve to be valid, it must have been based on no less than five data points and the MAPE must have been less than or equal to 30%.

For daily calibration checks, three calibration standards at low, medium, and high concentrations were analyzed and, based on the instrument responses, MAPE was calculated. If the 30% MAPE requirement was not met, the instrument was recalibrated with a minimum of five points to achieve a MAPE of less than or equal to 30%.

3.4.2.2 *Canister Certification*

The canisters were certified initially and recertified after each field use. For the initial certification, cleaned, evacuated canisters were spiked from a cylinder containing approximately 500 ppbv H_2S in nitrogen. The amount of spike gas was adjusted so that the final H_2S canister concentrations would be approximately 30 ppbv after completion of the ambient air sampling and post-sampling pressurization. The canisters were then connected to the downwind sampling system for collection of outdoor ambient air at the normal sampling conditions, which included a sampling flow rate of 80 mL per minute and a sample collection time of 45 minutes. Following sample collection, the canisters were pressurized with nitrogen, as was normally done during sample collection, using a dilution factor of 3.75. The canisters were analyzed with a Jerome H_2S analyzer after 24 hours. The canister H_2S concentration had to be within ±20% of the calculated theoretical concentration. If the canister failed initial certification, it was taken out of service until the initial certification requirement could be met.

For recertification of canisters after use in the field, each canister was spiked (if necessary) with gas from a cylinder containing approximately 500 ppbv H_2S in nitrogen to yield an expected Jerome H_2S

analyzer response of approximately 30 ppbv after pressurization to 40-50 psig. The canister was analyzed with a Jerome H_2S analyzer after pressurization and then again one day later. The second concentration reading had to be within 10% of the first value. If the second reading met the 10% criterion, the canister was cleaned according to the canister cleaning protocol and then considered ready for reuse. If the change in the measured canister concentration exceeded 10%, the canister was taken out of service. The out-of-service canister would then have to undergo the initial certification tests described above prior to further use.

3.4.3 *Canister Cleaning Procedures*

Canisters were cleaned by completing 22 heated evacuation/pressurization cycles. During each 21-minute cycle, the canisters were evacuated to less than 500 millitorr, and then pressurized to between 10 and 18 psig. In the final cycle, the canisters were evacuated to <200 millitorr and sealed in the evacuated state until they were used for sampling.

4.0 ANALYTICAL METHOD DEVELOPMENT AND EVALUATION

During the analytical method development and evaluation work, and during WWTP emissions testing carried out in 2004 through 2006, some variations were used in the analytical method as it is reported in Section 3 in its final form. Those variations included minor changes in the operation of the cryogenic pre-concentration system, changes in calibration procedures, the use of a sample split at the injection port, the use of an FPD detector in place of the PFPD detector, the implementation of a canister certification program, changes in acceptable sample storage times, the use of correction factors relative to sample storage time, and the use of correction factors based on analytical recovery. In each of the individual mill test reports (NCASI 2008a-g), the analytical method is included as it was used for analysis of that sample set.

Gas chromatographic analysis with flame photometric detection is the most commonly used technique for determination of volatile reduced sulfur compounds in different matrices (Wardencki 1998). The NCASI study described herein was begun using gas chromotagraphy with flame photometric detection. However, as the study progressed it became apparent that a more sensitive detector would be helpful for low-level quantitation. For this purpose, the pulsed-flame photometric detector (PFPD) was chosen based on its sensitivity, selectivity and suitability for interfacing with the rest of the analytical system. The PFPD is one of the most sensitive and selective tools to detect sulfur-containing compounds (e.g., Cheskis, Atar, and Amirav 1993; MacTaggart et al. 1999)

Multiple studies have reported success using cryogenic pre-concentration systems for low-concentration analysis of reduced sulfur compounds in air (e.g., Winegar 2002; Catalan 2006; Inomata et. al. 1999; Wardencki 1998). Additionally, a three-stage Entech cryogenic preconcentration system, which was similar to the one used in this study, was reported to have been used successfully for analysis of pptv and ppbv levels of methyl mercaptan, dimethyl sulfide and dimethyl disulfide in human exhaled breath (Ochiai et al. 2001). This system also has the advantage that it can be interfaced with a canister autosampler.

4.1 Evaluation of the Ambient Air Sampling System

The requirements for the ambient air sampling system used in this study included accurate, precise results to low ppbv levels, off-site analysis, up to 10 days of sample storage stability, and ease of use in the field since several sampling systems would have to be operated concurrently to allow the determination of emissions flux via spatial ambient air sampling. To meet these requirements, the sampling system shown in Figure 2.3 was developed. This sampling system uses a Teflon diaphragm pump to continuously pull ambient air at relatively high rates through Teflon sample lines up to 91 meters long. An evacuated six-liter stainless steel canister is used to draw a portion of the ambient air exiting the pump through a permeation dryer, a mechanical constant-flow controller and then into the canister. All of the connecting lines are constructed of Teflon.

Reduced sulfur gases, and especially hydrogen sulfide, are very reactive; therefore, the initial method development work for this study included an investigation of various types of stainless steel canister interior coatings to determine if there was one that would allow sufficient storage stability. Since the samples would be shipped from the field to the laboratory for analysis, a minimum of several days of storage stability was required. Tedlar bags and stainless steel canisters were both considered for use as the sample containers. The advantages of Tedlar bags are that they are inexpensive and provide good short-term recovery of reduced sulfur compounds (Bontempo and Kao 2002, Lau 1989, Quang and Tang 1994, Wardencki 1998). The disadvantages of Tedlar bags are 1) the recovery of low ppbv levels of H_2S drop off significantly after several days, 2) the sampling systems necessarily tend to be more complicated than for canisters, and 3) they are not rugged containers for the sampling, shipment, storage and analysis process. The disadvantages of stainless steel canisters involve potential problems with reduced sulfur compound recovery and their relatively high expense. However, stainless steel canisters offer the advantages of ruggedness and relatively simple sampling systems.

Several studies have shown that any uncoated stainless steel in the sampling or analytical system, including SUMMA polished canisters, can result in poor recovery and poor storage stability for hydrogen sulfide (Parmer 1991; Talbert et. al. 2004; Ki-Hyun et. al. 2006; Quang and Tang 1994). Other studies of the newer "glass-lined" type of stainless steel canister indicated that that type of interior coating had promise for use with ambient air samples containing hydrogen sulfide (Shelow and Stidsen 1998; Sulyok et. al. 2001). Studies reported in the literature (Bontempo and Kao 2002; Ochiai et. al. 2001) and internal investigations indicated that the Silonite coated canisters sold by Entech Corporation were the only ones likely to meet the storage stability requirements of this study.

A report in the literature indicated that removal of moisture from ambient air samples could significantly improve sample storage stability (Devai and DeLaune 1994). Initial tests at NCASI also indicated that the storage stability requirements could only be met if most of the moisture present in ambient air samples was removed prior to collection in the canisters. Several investigations reported in the literature had suggested that ambient air could be passed through a permeation dryer to remove most of the moisture without affecting the reduced sulfur compound concentrations (Wardencki 1998; Haberhaeur-Troyer, Rosenberg, and Grasserbauer 1999).

A number of studies reported (Haberhaeur-Troyer, Rosenberg, and Grasserbauer 1999; Inomata et. al. 1999; Rodrigues, Pitombo, and Cardoso 2000; Helmig 1997) on the use of scrubbers for removal of oxidants such as sulfur dioxide, ozone and nitrogen dioxide to enhance the storage stability and analytical recovery of atmospheric trace levels of reduced sulfur species. However, the concentrations of interest relative to determining emissions from kraft mill WWTPs are in the ppbv range versus the pptv ranges of interest to those who are studying atmospheric trace levels. Therefore, for the relatively high concentrations encountered in this study, oxidant scrubbing was judged to be unnecessary.

The literature indicated that PTFE Teflon could be used to transfer ambient air samples with minimal loss of the reduced sulfur compounds (Kuster and Goldan 1987; Sulyok, Haberhauer-Troyer, and Rosenberg 2002; Ki-Hyun et. al. 2006; Winegar 2002). Additionally, it had been demonstrated in a study of regulators, for compressed gas cylinders containing low concentrations of hydrogen sulfide, that maintaining a relatively high flow rate through the sample line would tend to mitigate any potential for loss due to sorption or reactivity (Talbert et al. 2004).

To test for potential bias introduced by the permeation dryer, a test gas generation system was constructed as shown in Figure 4.1. Approximately 1 ppmv reduced sulfur compound cylinder gases were diluted with humidified air to generate a test gas stream containing hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The ability of the system shown in Figure 4.1 to generate a moist gas stream and the ability of the permeation dryer to remove that moisture were tested. A single midget impinger was used. At a barometric pressure of 762 mm Hg and temperature of 22°C, the challenge gas stream contained 72% relative humidity. The permeation dryer reduced the relative humidity to 16%.

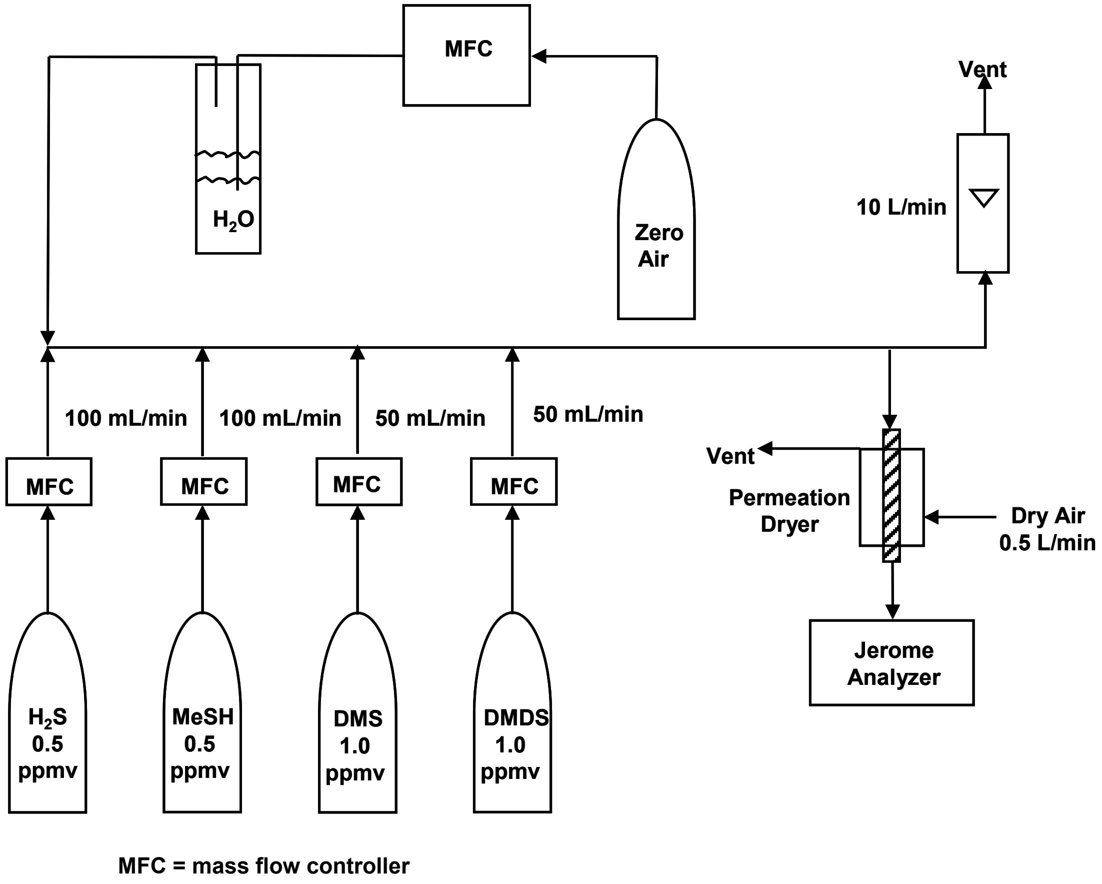


Figure 4.1 System for Evaluation of the Ambient Air Sampling and Analysis Method

A Jerome® 631-X™ H_2S analyzer (Arizona Instrument LLC) was used to test the gas coming from the test gas generation system, with and without the water-containing impinger inline, and with and without the permeation dryer inline. The Jerome analyzer is intended for H_2S analysis, but it also responds to MeSH, DMS and DMDS to varying degrees, so its response to each of the three gases was tested under the four sets of conditions. The results of those tests are shown in Table 4.1. During these tests, the ambient air temperature was 22°C. These results demonstrate quantitative passage of the analytes through the permeation dryer.

Table 4.1 Effect of Permeation Dryer on Test Gas Reduced Sulfur Compound Concentrations

		Instrument Response			
Compound	Calculated Conc., ppbv	W/O Water, W/O Dryer, ppbv	W/O Water, With Dryer, ppbv	With Water, W/O Dryer, ppbv	With Water, With Dryer, ppbv
H_2S	48	54	50	43	50
MeSH	55	30	32	22	32
DMS	181	20	18	11	19
DMDS	44	22	18	12	19

4.2 Canister Sample Storage Stability

Preliminary tests indicated reduced sulfur compound storage stability was not adequate in undiluted ambient air samples. Therefore, an experiment was conducted to determine the effect of post-sampling dilution, via canister pressurization with nitrogen, on reduced sulfur compound storage stability. It was important to dilute the sample enough to provide adequate storage stability without adding any more nitrogen than necessary because any increase in dilution is directly proportional to an increase in analyte detection limit.

This experiment was conducted to evaluate sample recovery and storage stability at three different post-sampling canister pressurization levels (40, 60, and 90 in Hg). The ambient air samples for this experiment were generated using the system shown in Figure 4.1. The post-sampling canister pressures were approximately 24 in Hg. Thus, the dilution factors were 1.7, 2.5, and 3.8, respectively. The canister samples were analyzed with a GC-FPD system with cryogenic pre-concentration. The results of this experiment are summarized in Figure 4.2. Each point on the graphs represents the average of the concentration values obtained from duplicate sample analyses. The data indicates that acceptable storage stability was achieved only at the highest dilution factor (3.8).

Following the determination to use a post-sampling canister nitrogen dilution factor of 3.8, a storage stability study was conducted to establish factors that could be used to correct for H_2S, MM, DMS and DMDS degradation between the time the samples were collected and analyzed. To accomplish this objective, several sets of triplicate canisters were collected downwind of an ASB at a kraft mill WWTP with hard piped condensates. Only one of the sets of triplicate canisters was to be analyzed, but several sets were collected so that they could be pre-analyzed to determine which set would best fit the criteria for the storage stability study. The criteria were approximately equal concentrations of all four compounds in a range that would fall approximately in the middle of the PFPD calibration curve. Prior knowledge of this ASB indicated that the H_2S concentration would likely be significantly less than that of the organic reduced sulfur compounds; therefore, the canister sets were spiked with various levels of H_2S before they were taken to field. After the canister sets had been returned from the field, the pre-analysis showed that one of the canister sets met the criteria for the stability study. That canister set was then analyzed over an 11-day period. The results of those analyses are summarized in Table 4.2. Also included in the table are the canister-specific and average correction factors required to correct each day's analysis values to the initial analysis values. The average correction factors are plotted versus storage time in Figure 4.3. Included on the plots for each compound are the equations and R^2 correlation coefficients for the linear relationships between correction factors and storage times. Table 4.3 summarizes the analytical quality control data (check standard recoveries and calibration curve MAPEs) for each storage stability study analysis day. Analytical data were not available for days 1, 6, 7, and 8 due to instrument down time.

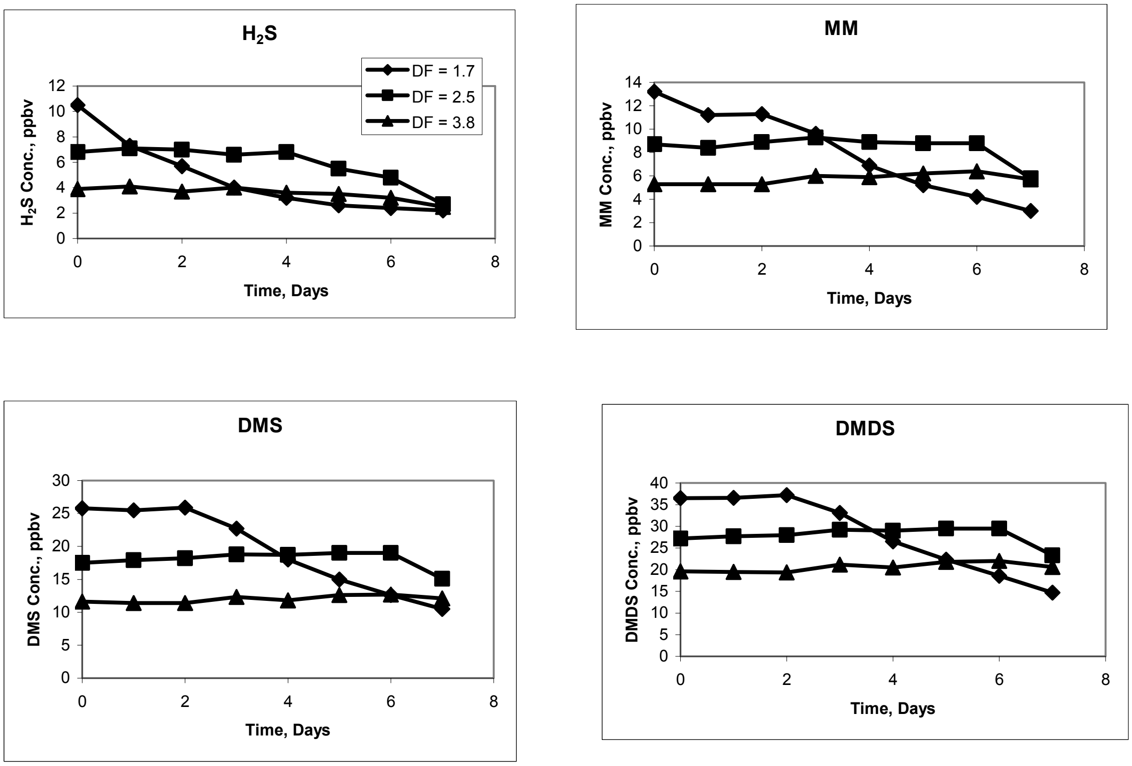


Figure 4.2 Effect of Canister Dilution Factor (DF) on Sample Storage Stability

Table 4.2 Canister Storage Stability for RSCs.

	Canister	Day 0		Day 2		Day 3		Day 4		Day 5		Day 9		Day 10	
Compound	No.	ppbv	CF	ppbv	CF	ppbv	CF	ppbv	CF	ppbv	CF	ppbv	CF	ppbv	CF
H_2S	1	5.18	1.00	5.24	0.99	4.64	1.12	4.57	1.13	3.81	1.36	2.74	1.89	3.00	1.73
	2	5.23	1.00	5.00	1.05	4.29	1.22	4.48	1.17	4.38	1.19	3.09	1.69	3.16	1.66
	3	4.71	1.00	4.44	1.06	4.12	1.14	3.87	1.22	4.21	1.12	2.87	1.64	2.63	1.79
	Avg.		1.00		1.03		1.16		1.17		1.22		1.74		1.72
MM	1	4.63	1.00	4.73	0.98	4.50	1.03	4.17	1.11	3.88	1.19	2.35	1.98	2.50	1.86
	2	4.68	1.00	4.51	1.04	4.04	1.16	4.05	1.15	4.01	1.17	2.49	1.88	2.48	1.88
	3	4.38	1.00	4.18	1.05	3.96	1.11	3.80	1.15	4.11	1.07	2.56	1.71	2.22	1.98
	Avg.		1.00		1.02		1.10		1.14		1.14		1.86		1.91
DMS	1	3.52	1.00	3.34	1.05	3.02	1.17	3.01	1.17	2.87	1.23	2.17	1.62	2.72	1.29
	2	3.55	1.00	3.24	1.10	2.98	1.19	2.96	1.20	2.99	1.19	2.29	1.55	2.63	1.35
	3	3.47	1.00	3.19	1.09	3.06	1.13	2.91	1.19	3.15	1.10	2.50	1.39	2.44	1.42
	Avg.		1.00		1.08		1.16		1.19		1.17		1.52		1.36
DMDS	1	2.53	1.00	2.71	0.93	2.33	1.09	2.53	1.00	2.66	0.95	2.41	1.05	2.80	0.90
	2	2.52	1.00	2.47	1.02	2.31	1.09	2.37	1.06	2.72	0.92	2.47	1.02	2.59	0.97
	3	2.51	1.00	2.43	1.03	2.44	1.03	2.36	1.06	2.98	0.84	2.89	0.87	2.39	1.05
	Avg.		1.00		1.00		1.07		1.04		0.91		0.98		0.98

CF = Correction Factor

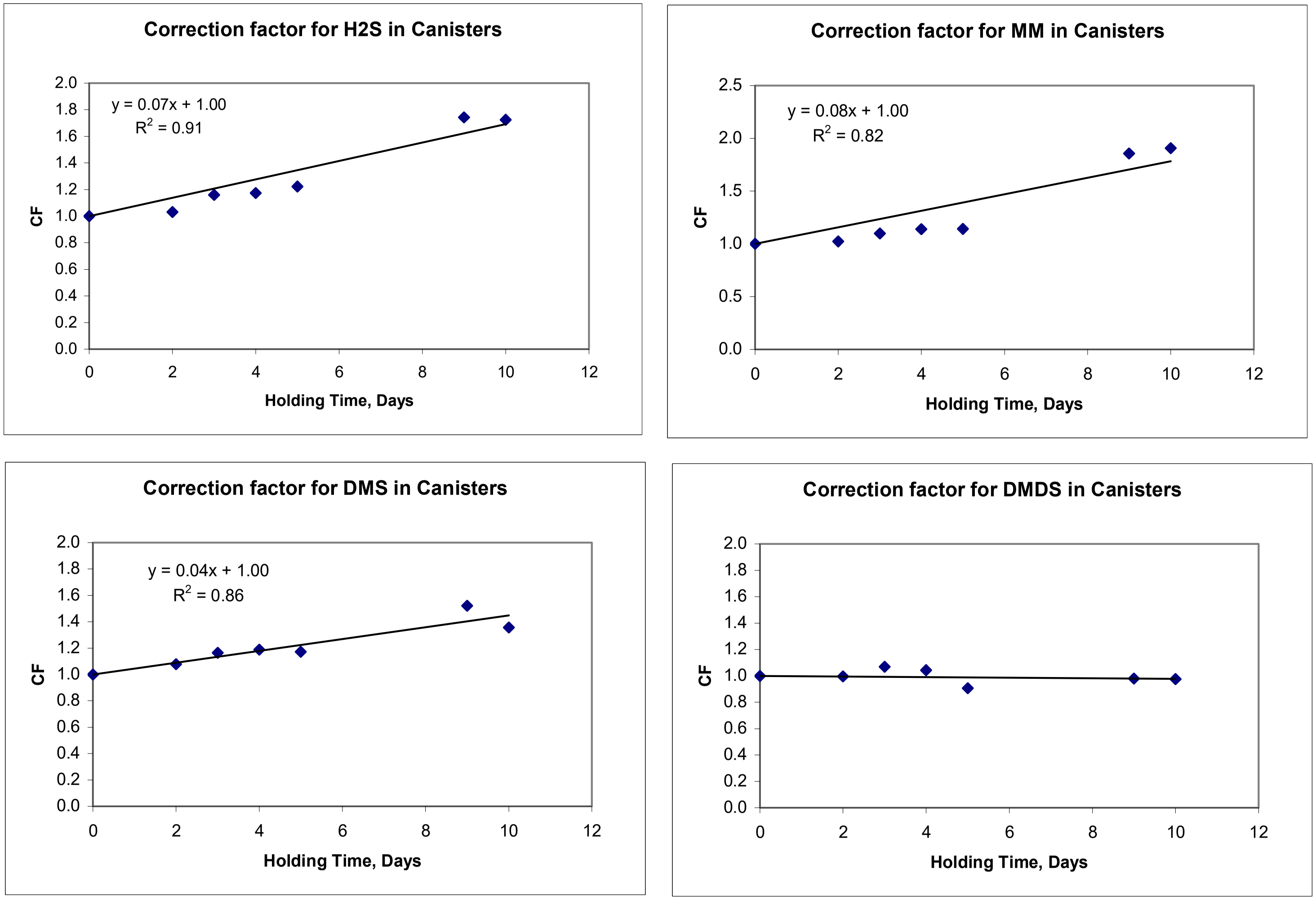


Figure 4.3 Relationships between Correction Factors and Holding Times

Table 4.3 Analytical Check Standard Data Associated with the Canister Storage Stability Study for RSCs

Daily Check Standards	Hydrogen Sulfide				Methyl Mercaptan				DMS				DMDS			
	Concentration, ppb				Concentration, ppb				Concentration, ppb				Concentration, ppb			
Date	Actual	Measured	% Rec	MAPE	Actual	Measured	% Rec	MAPE	Actual	Measured	% Rec	MAPE	Actual	Measured	% Rec	MAPE
2/16/06	3.985	4.167	104.6%	3.24%	3.767	4.259	113.1%	6.93%	3.777	3.773	99.9%	8.47%	1.341	1.581	117.9%	13.06%
	5.977	5.905	98.8%		5.651	5.958	105.4%		5.666	5.142	90.8%		2.012	2.361	117.4%	
	7.471	7.177	96.1%		7.064	6.900	97.7%		7.082	5.944	83.9%		2.515	2.614	103.9%	
2/18/06	3.985	4.228	106.1%	4.50%	3.767	4.098	108.8%	5.09%	3.777	3.456	91.5%	14.27%	1.341	1.315	98.0%	4.18%
	5.977	6.211	103.9%		5.651	5.797	102.6%		5.666	4.707	83.1%		2.012	1.922	95.6%	
	7.471	7.732	103.5%		7.064	7.340	103.9%		7.082	5.851	82.6%		2.515	2.669	106.1%	
2/19/06	3.985	3.825	96.0%	7.82%	3.767	4.005	106.3%	6.84%	3.777	3.259	86.3%	21.58%	1.341	1.417	105.7%	4.60%
	5.977	5.448	91.2%		5.651	5.432	96.1%		5.666	4.403	77.7%		2.012	2.062	102.5%	
	7.471	6.679	89.4%		7.064	6.335	89.7%		7.082	5.048	71.3%		2.515	2.374	94.4%	
2/20/06	3.985	3.647	91.5%	13.85%	3.767	3.754	99.7%	3.30%	3.777	3.085	81.7%	24.93%	1.341	1.198	89.3%	9.80%
	5.977	5.173	86.6%		5.651	5.422	96.0%		5.666	4.169	73.6%		2.012	2.059	102.4%	
	7.471	6.006	80.4%		7.064	6.676	94.5%		7.082	4.956	70.0%		2.515	2.926	116.3%	
2/21/06	3.985	3.348	84.0%	18.21%	3.767	3.720	98.7%	6.64%	3.777	2.989	79.1%	27.43%	1.341	1.313	97.9%	5.08%
	5.977	4.874	81.5%		5.651	5.123	90.7%		5.666	3.955	69.8%		2.012	2.090	103.9%	
	7.471	5.964	79.8%		7.064	6.404	90.7%		7.082	4.869	68.8%		2.515	2.748	109.3%	
2/24/06	3.985	3.624	91.0%	3.88%	3.767	3.101	82.3%	9.40%	3.777	3.145	83.3%	7.85%	1.341	0.900	67.1%	19.02%
	5.977	5.840	97.7%		5.651	5.377	95.2%		5.666	5.393	95.2%		2.012	1.814	90.1%	
	7.471	7.448	99.7%		7.064	7.465	105.7%		7.082	7.222	102.0%		2.515	2.876	114.4%	
2/25/06	3.985	3.947	99.1%	1.66%	3.767	3.186	84.6%	7.92%	3.777	3.163	83.7%	6.98%	1.341	0.928	69.2%	14.79%
	5.977	6.200	103.7%		5.651	5.977	105.8%		5.666	5.749	101.5%		2.012	2.243	111.5%	
	7.471	7.493	100.3%		7.064	7.246	102.6%		7.082	6.854	96.8%		2.515	2.462	97.9%	
2/26/06	3.985	3.698	92.8%	4.47%	3.767	2.887	76.6%	12.53%	3.777	3.181	84.2%	9.03%	1.341	0.786	58.6%	22.85%
	5.977	5.941	99.4%		5.651	5.157	91.3%		5.666	5.331	94.1%		2.012	1.629	80.9%	
	7.471	7.053	94.4%		7.064	6.676	94.5%		7.082	6.700	94.6%		2.515	2.312	91.9%	

4.3 Analytical Precision

Table 4.4 summarizes the results from five replicate analyses of an ambient air sample collected downwind of the primary clarifier at a kraft mill WWTP, and 10 replicate analyses of a canister containing approximately 40 ppbv of H_2S in nitrogen. The average concentrations of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide in the ambient air sample were 28.4, 69.6, 29.9, and 77.2 ppbv, respectively. The relative standard deviations from the five analyses for those compounds were: 4.3, 2.8, 2.4, and 0.5 %, respectively. For the approximately 40 ppbv canister containing hydrogen sulfide in nitrogen, the average measured concentration was 41.0 ppbv, and the relative standard deviation of the ten analyses was 6.6 %.

Table 4.4 Analytical Precision Data for Analysis of the RSC Gas Analysis Method With the PFPD. (Analysis conditions: 50 mL Analytical Volume)

	Concentration, ppbv				
Analysis	WWTP Ambient Air				Diluted Cylinder Gas
No.	H_2S	MeSH	DMS	DMDS	H_2S
1	29.46	72.36	31.16	77.82	38.82
2	27.16	67.48	29.96	77.32	37.24
3	27.34	68.26	29.70	77.32	37.24
4	28.34	69.14	29.48	76.92	40.70
5	29.90	70.52	29.32	76.84	40.70
6					42.98
7					42.44
8					42.60
9					43.20
10					45.32
Average	28.44	69.55	29.92	77.24	41.04
Std. Dev.	1.23	1.93	0.73	0.39	2.72
Rel. Std. Dev., %	4.32	2.78	2.44	0.51	6.62

4.4 Analytical Accuracy

Table 4.5 summarizes the results from the analyses of hydrogen sulfide check standards with known concentrations of approximately 10 ppbv and 50 ppbv. For the approximately 10 ppbv check standards, five replicate canisters were analyzed with a concentration volume of 100 mL and five replicate canisters were analyzed with a concentration volume of 1000 mL. For the approximately 50 ppbv check standards, five replicate canisters were analyzed with a concentration volume of 100 mL.

Table 4.5 H_2S Check Standard Results for Evaluation of the Gas Analysis Method Using the PFPD

Approximate Concentration, ppbv	Analytical Volume, mL	Canister	Actual Concentration, ppbv	Measured Concentration, ppbv	Recovery, %
10	100	a	11.2	11.4	102.0
10	100	b	11.3	10.8	95.9
10	100	c	11.2	8.9	79.2
10	100	d	11.2	10.8	96.9
10	100	e	11.2	10.0	89.4
10	100	average			92.7
10	100	std dev			8.8
10	1000	a	11.2	10.6	94.8
10	1000	b	11.3	10.8	96.0
10	1000	c	11.2	10.3	91.8
10	1000	d	11.2	11.1	99.4
10	1000	e	11.2	10.5	93.7
10	1000	average			95.1
10	1000	std dev			2.9
50	100	a	55.0	32.8	59.6
50	100	b	56.2	66.1	117.6
50	100	c	56.8	63.1	111.2
50	100	d	56.2	63.9	113.7
50	100	e	55.4	64.3	116.2
50	100	average			103.7
50	100	std dev			24.8

Table 4.6 summarizes the percentage recoveries measured for check standards containing H_2S, methyl mercaptan, and dimethyl disulfide at approximately the 50 ppbv level. Five canisters (a through e) containing the three compounds at the levels shown above were each analyzed in triplicate during this study. The average percentage recoveries for hydrogen sulfide, methyl mercaptan, and dimethyl disulfide were 108, 122, and 98%, respectively.

Table 4.6 Check Standard Results for Hydrogen Sulfide, Methyl Mercaptan, and Dimethyl Sulfide

Canister	Anal No.	Hydrogen Sulfide, ppbv			Methyl Mercaptan, ppbv			Dimethyl Sulfide, ppbv		
		Actual	Measured	% Rec	Actual	Measured	% Rec	Actual	Measured	% Rec
a	1		48.6			48.8			44.3	
	2		48.2			48.8			43.0	
	3		48.5			48.5			44.3	
	Ave.	45.2	48.4	107.2	40.5	48.7	120.2	44.0	43.9	99.7
b	1		52.6			53.0			44.5	
	2		51.5			53.0			42.2	
	3		51.9			52.9			37.2	
	Ave.	48.4	52.0	107.3	43.5	53.0	121.9	47.2	41.3	87.5
c	1		49.6			55.1			49.5	
	2		49.9			55.0			51.2	
	3		54.0			57.0			49.1	
	Ave.	49.2	51.2	104.0	44.2	55.7	126.2	48.0	49.9	104.0
d	1		54.9			54.9			47.7	
	2		54.7			54.6			45.6	
	3		57.4			55.7			44.5	
	Ave.	50.0	55.7	111.4	44.8	55.1	122.9	48.7	46.0	102.5
e	1		55.1			54.3			45.3	
	2		54.8			54.2			50.1	
	3		55.0			54.3			44.7	
	Ave.	49.9	55.0	110.3	44.7	54.3	121.3	48.6	46.7	96.1
Average % Rec.				108.0			122.5			98.0
Std. Dev				2.9			2.3			6.6
RSD				2.7			1.9			6.7

Table 4.7 summarizes the results of hydrogen sulfide matrix spikes for five samples collected at two kraft mill WWTPs. The canisters were analyzed to determine the native concentrations, and then they were first spiked to add approximately 10 ppbv to the native concentration and analyzed to determine spike recovery. Following the analyses to determine the recovery of the approximately 10 ppbv H_2S spikes, the canisters were spiked again to yield approximate final spike concentrations of 50 ppbv and analyzed again to determine the recovery of the 50 ppbv spikes. For the 10 ppbv spikes, the canisters were analyzed with concentration volumes of 100 mL and 1000 mL. For the 50 ppbv spikes, the canisters were only analyzed with a 100 mL concentration volume. For the 10 ppbv spike samples analyzed with a 100 mL concentration volume, the average recovery was 78.8% with a standard deviation of 13.7%. For the 10 ppbv spike samples analyzed with a 1000 mL concentration volume,

the average recovery was 79.7% with a standard deviation of 21.7%. For the 50 ppbv spike samples, the average recovery was 98.3% with a standard deviation of 10.3%.

Table 4.7 H_2S Matrix Spike Results for Evaluation of the Gas Analysis Method Using the PFPD

Approximate Spike Concentration, Ppbv	Analytical Volume, mL	Canister Sample	Actual Spike Concentration, ppbv	Measured Spike Concentration, ppbv	Recovery, %
10	100	101a	10.50	10.41	99.11
10	100	51b	11.34	8.68	76.57
10	100	52b	11.39	8.94	78.50
10	100	53b	11.28	6.82	60.48
10	100	6a	11.16	8.88	79.55
10	100	average			78.8
10	100	std dev			13.7
10	1000	101a	10.50	8.40	79.96
10	1000	51b	11.34	9.90	87.31
10	1000	52b	11.39	4.83	42.42
10	1000	53b	11.28	10.65	94.42
10	1000	6a	11.16	10.54	94.47
10	1000	average			79.7
10	1000	std dev			21.7
50	100	101a	55.72	50.40	90.45
50	100	51b	55.85	59.59	106.68
50	100	52b	59.29	64.08	108.07
50	100	53b	54.37	46.01	84.62
50	100	6a	56.11	57.16	101.88
50	100	average			98.3
50	100	std dev			10.3

5.0 EVALUATION OF THE OVERALL ACCURACY AND PRECISION OF THE EMISSIONS MEASUREMENT METHOD

In this necessarily complex method for measuring small emissions of extremely reactive compounds from large, aqueous, heterogeneous emissions sources with complex geometry and topography, there are many potential contributors to bias and variability. Relative to bias, there are two major questions that must be considered: 1) are the measured analyte concentrations representative of the actual ambient air concentrations at the time of sampling, and 2) does the spatial ambient air sampling and emissions calculation technique accurately calculate the total emissions flux from the source? To answer the first question, sampling system H_2S train spike and recovery tests were routinely performed, and the H_2S concentrations measured in canister-contained ambient air samples were compared to concentrations measured on site, at the time of sample collection with another measurement technique. The results of these tests are summarized in Section 5.1. Ideally, to answer the second question, a tracer gas would be used; however, for situations typically encountered at kraft mill WWTPs, it is very difficult to appropriately release a tracer gas over the surface area of the sources. Therefore, for this method an alternate technique was used for assessing the accuracy of the emissions flux determination. This technique was a quantitative measure of how well the vertical concentration profile calculation procedure fit the measured vertical concentration data. The results of this comparison are contained in Section 5.2.

The precision of the ambient air sampling and analysis method was assessed via the collection and analysis of duplicate ground-level canister samples for almost every sampling run conducted over the course of the study. The precision of the overall method, including sampling, analysis and the spatial ambient air sampling and calculation procedure, was evaluated by calculating the percent relative standard deviation for every situation in which three or more test runs were conducted on the same source during the same day. This approach gives a worst case analysis of overall method variability because it includes any variations in the source emissions that may have occurred during each single day test period, as well as the variability of the measurement method. The results relative to method precision are summarized in Section 5.3.

5.1 Evaluation of H_2S Concentration Measurement Accuracy

A Jerome® 631-X™ handheld, portable H_2S analyzer (Arizona Instrument LLC), as shown in Figure 5.1, was used to help assess various aspects of the overall method accuracy. Therefore, initially, the accuracy of the Jerome analyzer itself had to be assessed. The Jerome analyzer uses the resistance across a thin gold film sensor to measure the amount of hydrogen sulfide in a specific volume of air passed over the sensor. The electrical resistance across the sensor increases with exposure to H_2S. The instrument automatically re-zeros before each new sample is taken.

For evaluation of the Jerome H_2S analyzer, a system similar to the one shown in Figure 4.1. was used to generate dry and humidified test gas streams. This system was used to test the response of the instrument to various levels of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The results from these tests are summarized in Table 5.1. For H_2S, the test gas concentrations ranged from 11 ppbv to 6 ppmv, whereas for the organic reduced sulfur compounds, the test gas concentrations ranged from approximately 10 ppbv to 180 ppbv. For the relatively high concentrations of H_2S, the entire test gas stream was bubbled through an acidified impinger, rather than just bubbling the dilution air through a water-containing impinger as shown in Figure 4.1.

The results of the Jerome analyzer evaluation show that the instrument had overall good, linear response characteristics for H_2S in both dry and humidified air, with a response factor of approximately one; however, the instrument also responds to the organic reduced sulfur compounds to varying degrees. The response factors for the organic reduced sulfur compounds ranged from 0 to 0.73 depending on compound, concentration, and humidity Humidity had more effect on the response factors for the organic reduced sulfur compounds than for H_2S. Additionally, it was noticed in these tests that exposure of the instrument to DMDS can contaminate it such that intermittent, spurious and high-biased readings can occur during subsequent measurements. To clear the instrument, repeated sampling of clean air is required until it consistently reads zero.

Figure 5.1 Jerome® 631-X™ H_2S Analyzer

Table 5.1 Jerome Analyzer Response to Individual Reduced Sulfur Gases

Compound	Test Gas Conc., ppbv	Jerome Response to Dry Gas, ppbv	Jerome Response to Humidified Gas, ppbv	Response Factor for Dry Gas	Response Factor for Humidified Gas
H_2S	11	13	6	1.18	0.55
	48	50	43	1.04	0.90
	130	120	130	0.92	1.00
	187	200	200	1.07	1.07
	4103	4900	5000	1.19	1.22
	5951	6600	6900	1.11	1.16
MeSH	11	8	0	0.73	0.00
	55	30	22	0.55	0.40
	114	61	51	0.54	0.45
	165	89	83	0.54	0.50
DMS	11	7	0	0.64	0.00
	45	9	0	0.20	0.00
	117	16	7	0.14	0.06
	181	20	11	0.11	0.06
DMDS	14	9	0	0.64	0.00
	44	22	12	0.50	0.27
	119	45	71	0.38	0.60
	182	56	99	0.31	0.54

The Jerome H_2S analyzer was also used to assess the accuracy of the overall canister sampling and GC/PFPD analysis methods at four WWTP sources, which had significant H_2S emissions and essentially no organic reduced sulfur compound emissions. This was accomplished by making multiple, collocated, downwind ambient air measurements with the Jerome analyzer, while the canister samples were being collected, and comparing the average of the Jerome analyzer measurements to the analysis values obtained from the integrated canister samples. At each downwind sampling location, generally three Jerome analyzer readings were obtained concurrent with the canister sampling, which lasted from one to seven minutes at each sampling location, with a total sample collection time for each run of 45 minutes. The average Jerome reading at each sampling location was adjusted relative to the amount of canister sampling time at each location. Then, the sample time-adjusted readings for each location were summed to yield an approximately integrated concentration that could be compared to the average of the measured integrated canister H_2S concentration. The results of that comparison are summarized in Table 5.2. The canister method concentrations are actually the average from the duplicate ground-level canisters that are routinely collected for each test run. For the 11 test runs, the average canister method bias, as referenced to the pseudo-integrated Jerome readings, was +10 %. The standard deviation associated with that value was ±40 %. The variability associated with calculating approximately-integrated Jerome readings, as well as the variabilities associated with both of the methods, were likely all significant contributors to the standard deviation associated with calculating the average bias.

A test gas generation system similar to the one shown in Figure 4.1 was used periodically to perform H_2S train spike and blank tests on three ambient air sampling systems similar to the one shown in Figure 3.1. The Jerome H_2S analyzer was used to measure H_2S concentration at the flow controller outlet. The results of the train spike tests are shown in Table 5.3. For a total of 16 tests with H_2S concentrations ranging from 20 to 60 ppbv, the sampling system bias ranged from +2.8% to -9.8%, and averaged -2.7%. The train blank tests associated with the train spike tests yielded Jerome H_2S analyzer blank values of 0 to 1 ppbv.

Table 5.2 Comparison of On-Site Pseudo-Integrated Jerome Analyzer Measurements to Canister Method Results

Mill	Source	Run No.	Total No. of Jerome Meas.	H_2S Conc., ppbv		Bias (Jerome Relative to Canister), %
				Jerome	Canister	
EJ	SP1	1	26	113	182	-38
		2	26	92	125	-26
		3	24	128	167	-23
EJ	SP2	1	22	159	122	30
		2	36	92	72	28
		3	15	80	49	63
EJ	ASB	1	30	36	29	24
		2	30	21	19	11
		3	36	22	12	83
BH	EP	1	27	487	590	-17
		2	27	263	355	-26
					Average	10
					Std. Dev.	40

Table 5.3 Ambient Air Sampling System Bias Check for H_2S

	Upwind No. 1			Downwind			Upwind No. 2		
	H_2S Conc., ppbv			H_2S Conc., ppbv			H_2S Conc., ppbv		
Date	Measured	Expected	Bias, %	Measured	Expected	Bias, %	Measured	Expected	Bias, %
1/28/2005	37	41	-9.8						
2/8/2005				59	63	-6.3			
4/6/2005	56	59	-5.1						
4/27/2005	49	48	2.1	47	47	0.0			
7/20/2005	45	46	-2.2						
7/21/2005				45	45	0.0			
11/7/2005	34	34	0.0						
11/10/2005							37	36	2.8
11/29/2005							20	21	-4.8
11/30/2005	30	32	-6.3						
12/30/2005	51	55	-7.3	48	50	-4.0	51	50	2.0
3/24/2006				55	56	1.8	54	51	-5.9
Average			-4.1			-1.7			-1.5

5.2 Evaluation of the Vertical Concentration Profile Curve Fitting Procedure

As described in Section 2.4.1, the horizontally integrated concentration values obtained from four vertical elevations were used to calculate the horizontally integrated shape of the vertical concentration profile of the emission plume at the sample path. To do this, the concentration data were fit to the following equation.

$$C(z) = C_o\left(1 - \frac{Z}{Z_b}\right)^b$$

where:

$C(z)$ = concentration at elevation z, g/m^3
C_o = concentration at ground level (elevation 0) , g/m^3
Z_b = height of the emission plume at the sample path, m
b = vertical concentration profile exponent

In order to solve for b and C_o, the natural logarithm was taken of both sides of the equation to yield

$$\ln[C(z)] = \ln C_o + b\ln\left[1 - \frac{Z}{Z_b}\right]$$

Linear regression was then used to solve for b and C_o. The correlation coefficient (R squared) determined from this linear regression can be used to quantitatively determine how well the vertical concentration profile curve generated from this procedure fits the measured data. The DMDS data from run no. 20 on the No. 1 ASB at Mill A was used for the following example. Table 5.4 shows the sampling height and concentration data. Figure 5.2 shows the linear plot of the logarithmic relationship. Thus, the vertical concentration profile exponent (b) is equal to the slope, which is 5.332, and the natural logarithm of the ground level DMDS concentration is equal to the y-intercept, which is -7.572. Since these values are now known, the vertical concentration profile curve can be calculated as shown on Figure 5.3. Also shown on Figure 5.3 are the measured concentrations which track closely with the curve and show a very good fit between the shape of the vertical concentration profile curve and the measured concentrations. The correlation coefficient (0.983) calculated on Figure 5.2 is a quantitative measure of the curve fit.

In Tables 5.5 through 5.7, the correlation coefficients are summarized for primary clarifiers, aerated basins and un-aerated basins. Correlation coefficients were included from all of the test runs which had detectable concentrations measured at three or four levels, or which had detectable concentrations measured at two levels used in conjunction with one-half the non-detect concentration at the next highest level. For each source type, the correlation coefficients are averaged for each analyte. With the exception of DMDS and methane at the primary clarifiers, all of the average correlation coefficients were in the range of 0.8 to 1.0, which indicates an overall good fit of the measured concentration data with the vertical concentration profile curve fitting procedure.

Table 5.4 DMDS Concentration and Sampling Height Data for Run No. 20 on the No. 1 ASB at Mill A

Height (Z), m	ln[1-Z/Zb]	Conc. [C(z)], ppbv	Conc. [C(z)], g/m^3	ln[C(z)]
0.6	-0.011	149.4	5.68E-04	-7.472
8.5	-0.165	51.0	1.94E-04	-8.548
17.1	-0.364	15.8	5.99E-05	-9.722
25.6	-0.611	6.0	2.30E-05	-10.682

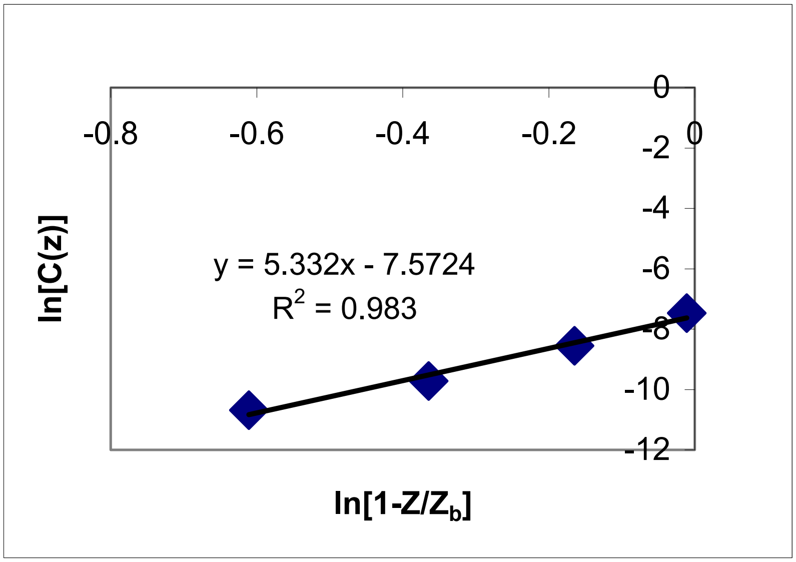


Figure 5.2 Logarithmic Plot of Vertical Concentration Data

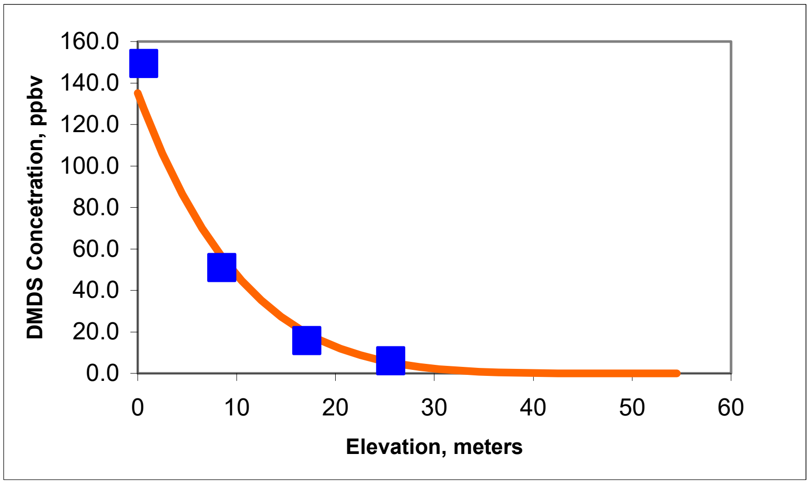


Figure 5.3 Calculated Vertical Concentration Profile and Measured Vertical Concentration Data

Table 5.5 Quality of the Vertical Concentration Profile Curve Fitting Procedure for Primary Clarifiers

Mill	Run No.	P-G Stab. Class	Zb Used for Calc., m	High Sample Line Height, % of Zb	RSQ*				
					H_2S	MM	DMS	DMDS	CH_4
A	1	C	16	91	0.97	--	--	--	--
B	1	C	14	53	0.94	---	---	---	--
B	2	C	16	48	0.98	---	---	---	--
B	3	C	12	61	0.94	---	---	---	--
B	4	C	13	60	---	---	---	---	0.98
B	6	C	14	73	0.96	--	---	---	--
B	7	C	11	89	0.83	--	---	---	--
D	1	C-D	14.4	68	0.89	0.84	---	---	0.23
D	2	C	12.6	78	--	---	---	0.68	0.77
D	3	C-D	12.2	80	0.61	1.00	---	0.96	--
D	4	D-E	12	82	0.87	---	---	0.69	--
D	5	D	12	82	0.77	---	---	0.90	--
F	1	C	13	54	0.84	0.99	0.84	0.64	0.95
F	2	C	11	63	0.73	0.68	0.78	0.74	--
F	3	C	14	51	0.90	0.90	0.80	0.91	--
Average				69	0.86	0.88	0.81	0.79	0.73

*square of the Pearson product moment correlation coefficient

Table 5.6 Quality of the Vertical Concentration Profile Curve Fitting Procedure for Aerated Basins

Mill	Run No.	P-G Stab. Class	Z_b Used for Calc., m	High Sample Line Height, % of Zb	RSQ*				
					H_2S	MM	DMS	DMDS	CH_4
A	2	D	33	62	--	--	1.00	0.98	--
A	4	C	55	62	--	--	--	0.98	--
A	6	A	125	13	--	--	0.99	0.97	--
A	7	A	557	3	--	--	0.97	0.96	--
A	8	A	320	16	--	--	0.79	0.76	--
A	9	A	408	13	--	--	0.93	0.98	--
A	10	A	366	14	--	--	0.90	0.95	--
A	11	A	249	21	--	--	0.98	1.00	--
A	12	A	366	14	--	--	0.90	0.96	--
A	13	A	124	13	--	--	0.96	1.00	--
A	14	A	173	11	--	--	0.96	0.91	--
A	15	B	79	23	--	--	0.98	0.96	--
A	16	C	70	26	--	--	0.88	0.97	--
A	17	A	227	5	--	--	1.00	0.98	--
A	18	A	264	7	--	--	0.94	1.00	--
A	19	B	75	24	--	--	0.95	0.98	--
A	20	C	56	46	--	--	0.98	0.98	--
A	21	C	55	38	--	--	0.97	0.93	--
A	22	D	32	66	--	--	0.95	0.91	--
B	1	D-E	32	57	0.88	1.00	1.00	1.00	--
B	2	D-E	31	58	0.92	1.00	1.00	0.98	--
B	3	C	68	27	0.96	0.99	1.00	0.98	--
D	1	A	363	11	0.12	0.91	0.87	0.74	--
D	2	A	160	9	---	1.00	---	---	--
D	3	A	175	9	0.76	0.97	---	0.97	--
D	4	A	181	8	0.93	0.98	1.00	0.96	--
D	5	A	120	12	---	---	---	1.00	--
D	6	A-B	103	14	0.77	0.99	---	0.64	--
D	7	B-C	129	26		---	---	0.98	--
D	9	A	124	27	0.98	---	---	--	--
D	10	A	140	24	0.94	--	--	--	--
D	11	B-C	113	30	0.98	--	--	--	--
E	1	E	30	64	--	--	--	--	0.99
E	2	D	41	47	--	--	--	--	0.92
E	3	A	512	6	--	--	--	--	0.99
E	4	D	31.3	44	0.96	--	--	--	1.00

(Continued on next page.)

Table 5.6 Continued

Mill	Run No.	P-G Stab. Class	Z_b Used for Calc., m	High Sample Line Height, % of Zb	RSQ* H_2S	MM	DMS	DMDS	CH_4
E	5	E	29.7	46	1.00	--	--	--	1.00
E	6	C	50.4	27	1.00	--	--	--	0.97
F	1	C	15	59	--	--	0.94	--	--
F	2	C	14	64	--	--	0.97	--	--
F	3	B-C	21	44	--	--	0.99	--	--
Average				29	0.86	0.98	0.95	0.94	0.98

*square of the Pearson product moment correlation coefficient

Table 5.7 Quality of the Vertical Concentration Profile Curve Fitting Procedure for Unaerated Basins

Mill	Source	Run No.	P-G Stab. Class	Z_b Used for Calc., m	High Sample Line Height, % of Zb	RSQ*				
						H_2S	MM	DMS	DMDS	CH_4
B	No. 1 Ret. Pond	2	A	288	8	---	---	---	---	0.94
B	No. 1 Ret. Pond	3	A-B	308	7	---	---	---	---	0.93
B	Spill Pond	1	B-C	71	32	0.94	---	---	---	
B	Spill Pond	2	B-C	65	35	0.99	---	---	---	0.95
B	Spill Pond	3	A	101	18	0.95	---	---	---	0.99
B	Spill Pond	4	A	106	17	0.94	---	---	---	0.99
B	Spill Pond	5	D	32	43	0.59	0.99	---	---	---
B	Spill Pond	6	D	34	40	0.45	--	---	---	---
B	Spill Pond	7	C - D	38	36	0.73	---	---	---	
E	No. 1 Settling Pond	1	B	88	38	0.86	--	--	--	0.86
E	No. 1 Settling Pond	2	A	210	16	0.86	--	--	--	0.55
E	No. 1 Settling Pond	3	D	36	32	0.78	--	--	--	0.79
E	No. 1 Settling Pond	4	C-D	46	25	-	--	--	--	0.56
E	No. 1 Settling Pond	5	D	42	28	0.90	--	--	--	NA
E	No. 1 Settling Pond	6	C-D	49	28	0.94	--	--	--	0.95
E	No. 1 Settling Pond	7	D	35.9	38	0.84	--	--	--	0.95
E	No. 1 Settling Pond	8	D	36.4	38	0.91	--	--	--	0.94
E	No. 2 Settling Pond	1	D	32	72	0.87	--	--	--	---
E	No. 2 Settling Pond	2	C-D	38	61	0.61	--	--	--	0.52
E	No. 2 Settling Pond	3	C-D	34	69	0.88	--		--	---
E	No. 2 Settling Pond	4	C-D	27	50	0.91	--	--	--	0.57
E	No. 2 Settling Pond	5	C-D	27	50	0.90	--	--	--	0.92
E	No. 2 Settling Pond	6	E	21.3	43	0.84	--	--	--	1.00
E	No. 2 Settling Pond	7	A	270	3	0.86	--	--	--	0.96
E	No. 2 Settling Pond	8	A	234	8	0.62	--	--	--	0.95
Average					33	0.83	0.99	---	---	0.85

*square of the Pearson product moment correlation coefficient

5.3 Overall Method Precision

The overall method precision was assessed in two ways. In Section 5.3.1 the precision of the ambient air sampling and analysis method was evaluated from the concentrations measured in duplicate canisters collected at the ground-level for most of the field test runs conducted in this study. In Section 5.3.2 the precision of the overall emissions measurement method was evaluated by comparing the results obtained from multiple test runs conducted on the same source on the same day.

5.3.1 *Precision of the Ambient Air Sampling and Analysis Method*

The precision of the ambient air sampling and analysis method was assessed by calculating the percent difference in measured concentrations between field ground-level duplicate samples collected throughout the study. The percent difference between duplicates is calculated by dividing the absolute value of the difference between the duplicate concentrations by the average of the two concentrations, and then multiplying the result by 100. The results of those calculations are summarized for the reduced sulfur compounds in Table 5.8. For all of the test runs, the overall percent difference between duplicates for H_2S, MM, DMS, and DMDS were 24%, 13%, 4,%, and 8%, respectively. For the reduced sulfur compounds, H_2S was followed by methyl mercaptan with the highest variabilities, which are believed to be due to their highly reactive nature.

For methane, the situation is different than for the reduced sulfur compounds. As shown in Table 5.9, there was always a high background ambient air concentration of methane, which was generally in the range of 2000 ppbv to 2500 ppbv. The average background concentration for all of the test runs was 2126 ppbv, whereas the average concentration downwind was 2795 ppbv. Therefore, to calculate the source emissions of methane, the background concentration was always subtracted from the concentration downwind of the emission source to arrive at the concentration value to use in the emission rate calculations. Thus, the source contribution to the downwind concentration was a relatively small difference between two large numbers. This calculation can introduce additional variability, beyond the analytical variability, into the background-corrected concentrations. Therefore, for the calculation of the percent difference between duplicate values in Table 5.9, the background-corrected downwind concentrations were used so that the variability due to subtracting the high background correction is included in the percent difference values. For all of the test runs, the overall percent difference between the background-corrected duplicates for methane was 27%.

5.3.2 *Precision of the Overall Emissions Measurement Method*

The overall precision of the emissions measurement method was assessed by calculating the percent relative standard deviation of the emission rates for each compound whenever there were three or more test runs conducted at the same source on the same day. Therefore, the percent relative standard deviation values include any variability in the source emissions, as well as all of the variability associated with the test method. Several factors that either were known, or had the potential, to affect the source emission rates of the reduced sulfur compounds during the test periods were variability in the source loading rate associated with the liquid input, variability in the inlet pH, and variations in horizontal wind velocity (especially for the large, quiescent basins). For example, the total sulfide input with the liquid influent to the primary clarifier at Mill F increased from 18 to 27 mg/L during the test period.

In Tables 5.10 through 5.12, the percent relative standard deviations are summarized for primary clarifiers, aerated basins and un-aerated basins, respectively. The percent relative standard deviations for H_2S emissions from un-aerated basins were calculated from the measured emission rates, and after they had been normalized to a horizontal wind velocity of ≤ 3.25 m/s. The normalization procedure is discussed in Technical Bulletin No 956 (NCASI 2008j).

The average percent relative standard deviations, of the combined spatial ambient air sampling technique, sample analyses and emissions calculation procedures, ranged from 14% for H_2S emissions from un-aerated basins to 63% for methane emissions from primary clarifiers. This difference is largely a result of relatively high ambient air H_2S concentrations downwind of the un-aerated basins, and relatively small differences between the upwind and downwind methane concentrations at the primary clarifiers. In general, relatively high emissions and ambient air concentrations corresponded to low relative standard deviations; conversely, relatively low emissions and ambient air concentrations corresponded to high relative standard deviations. Methane emissions were not expected to vary significantly within the single day test periods, or to have been significantly affected by horizontal wind velocity. The overall average percent relative standard deviations for methane were 63, 46, and 21% for primary clarifiers, aerated basins and un-aerated basins, respectively. When evaluating how these precision values for the overall method relate specifically to the spatial ambient air sampling technique and calculation procedures, it is important to take the analytical variability into consideration. The analytical precision, as represented by the average percent difference between duplicate downwind background-corrected methane concentration values, was 27%. Since the highest downwind concentrations are found at the ground-level, the average analytical precision would be even less at the higher sampling elevations. Therefore, when the analytical precision is taken into account, the results indicate remarkably precise results for the spatial ambient air sampling technique and calculation procedures used in the NCASI study.

Table 5.8 RSC Ground Level Field Duplicate Ambient Air Concentrations

			H_2S			MeSH			DMS			DMDS		
Mill	Source	Run No.	GN	GD	Diff.,* %	GN	GD	Diff.,* %	GN	GD	Diff.,* %	GN	GD	Diff.,* %
A	No. 1 ASB	6	7.71	6.27	20.6	99.3	91.1	8.6	109.34	101.87	7.1	79.65	78.21	1.8
		7	4.04	3.88	4	9.45	8.18	14.4	37.72	37.9	0.5	45.46	44.95	1.1
		8	3.58	3.63	1.4	ND[1.45]	4.98	NC	32.44	34.72	6.8	35.77	37.4	4.5
		9	3.51	3.66	4.2	ND[1.42]	4.37	NC	39.28	41.17	4.7	41.58	44.26	6.2
		10	3.63	--	NC	ND[1.43]	--	NC	38.51	--	NC	46.2	--	NC
		11	4.14	4.35	4.9	6.94	12.39	56.4	54.14	56.43	4.1	63.18	63.1	0.1
		12	3.56	3.79	6.3	ND[1.42]	ND[1.42]	NC	40.5	43.31	6.7	47.94	48.26	0.7
		13	ND[0.47]	--	NC	11.8	--	NC	25.61	--	NC	21.57	--	NC
		17	ND[0.47]	ND[0.47]	NC	11.08	11.81	6.4	26.65	26.82	0.6	27.2	27.12	0.3
		18	25.81	27.54	6.5	35.37	37.04	4.6	77.86	75.53	3	82.89	81.14	2.1
		19	20.33	22.28	9.2	33.18	35.36	6.4	105.49	110.3	4.5	98.63	99.77	1.1
		20	18.98	21.32	11.6	27.13	29.06	6.9	79.62	78.15	1.9	121.32	120	1.1
		21	18.78	16.19	14.8	25.9	24.45	5.8	51.94	45.68	12.8	93.5	93.26	0.3
		22	53.08	60.93	13.8	56.32	60.76	7.6	137.44	137.83	0.3	201.76	200.33	0.7
		23	16.77	--	--	33.86	--	NC	95.73	--	NC	149.39	--	NC
		24	18.13	19.5	7.3	27.3	27.9	2.2	84.71	92.95	9.3	147.78	139.95	5.4
		25	18.75	19.9	6	27.22	28.04	3	81.42	81.93	0.6	133.51	133.6	0.1
B	ASB	1	54.81	51.84	5.57	68.89	64.52	6.55	11.49	11.26	2.02	6.51	6.64	1.98
		2	16.76	17.04	1.66	49.54	50.95	2.81	10.65	10.74	0.84	50.67	49.52	2.3
		3	12.86	10.08	24.24	45.6	49.42	8.04	10.46	10.75	2.73	16.65	16.31	2.06
	No. 1 Ret. Pond	1	1.75	ND[0.97]	NC	ND[2.31]	ND[2.32]	NC	ND[1.72]	ND[1.72]	NC	ND[1.16]	ND[1.16]	NC
		2	ND[0.98]	1.54	NC	ND[2.33]	ND[2.39]	NC	ND[1.73]	ND[1.77]	NC	ND[1.16]	ND[1.19]	NC
		3	6.54	6.24	4.69	ND[2.32]	ND[2.34]	NC	ND[1.72]	ND[1.74]	NC	ND[1.16]	ND[1.17]	NC

(Continued on next page. See notes at end of table.)

Table 5.8 Continued

			H_2S			MeSH			DMS			DMDS		
Mill	Source	Run No.	GN	GD	Diff.,* %	GN	GD	Diff.,* %	GN	GD	Diff.,* %	GN	GD	Diff.,* %
B	Spill Pond	1	63.8	264.98	122.38	ND[2.31]	ND[2.35]	NC	ND[1.71]	ND[1.74]	NC	ND[1.16]	ND[1.17]	NC
		2	307.94	289.19	6.28	ND[2.34]	ND[2.34]	NC	ND[1.74]	ND[1.74]	NC	ND[1.17]	ND[1.17]	NC
		3	273.47	260.5	4.86	ND[2.33]	ND[2.33]	NC	ND[1.73]	ND[1.73]	NC	ND[1.16]	ND[1.17]	NC
		4	335.57	574.51	52.51	ND[2.32]	ND[2.34]	NC	ND[1.72]	ND[1.73]	NC	ND[1.16]	ND[1.17]	NC
		5	487.0	708.5	37.1	0.71	0.68	4.3	ND	ND	NC	ND	ND	NC
		6	843.6	430.5	64.9	0.58	ND	NC	ND	ND	NC	ND	ND	NC
		7	355.0	365.4	2.9	0.41	ND	NC	ND	ND	NC	ND	ND	NC
	Primary Clarifier	1	33.71	ND[0.98]	NC	ND[2.32]	ND[2.35]	NC	ND[1.72]	ND[1.74]	NC	ND[1.16]	ND[1.17]	NC
		2	35.12	31.4	11.18	ND[2.33]	ND[2.34]	NC	ND[1.73]	ND[1.74]	NC	ND[1.17]	ND[1.17]	NC
		3	ND[0.97]	50.73	NC	ND[2.32]	ND[2.33]	NC	1.87	2.1	11.59	ND[1.16]	ND[1.16]	NC
		4	56.78	54.51	4.08	ND[2.31]	ND[2.34]	NC	2.01	2	0.5	ND[1.15]	ND[1.17]	NC
		5	NA	59.5	NC	NA	ND	NC	NA	ND	NC	NA	0.22	NC
		6	78.9	73.6	6.9	ND	ND	NC	ND	ND	NC	ND	0.19	NC
		7	NA	88.3	NC	ND	ND	NC	ND	ND	ND	0.19	0.26	31.1
D	ASB	1	14.91	14.27	4.4	5.79	5.23	10.2	2.44	2.44	0	4.66	4.35	6.9
		2	31.71	48.52	41.9	10.07	12.62	22.5	4.28	4.78	11	5.08	4.48	12.6
		3	126.33	116.48	8.1	12.15	12.15	0	6.34	6.15	3	3.96	3.68	7.3
		4	34.8	8.81	119.2	11.32	3.56	104.3	6	5.65	6	4.2	6.21	38.6
		5	37.93	ND	---	10.06	ND	---	4.34	ND	---	1.7	ND	---
		6	45.52	48.04	5.4	11.15	11.18	0.3	4.37	4.43	1.4	2.45	2.29	6.8
		7	12.95	10.12	24.5	8.57	8.82	2.9	3.89	3.82	1.8	5.32	5.28	0.8
		8	58.46	38.98	40	12.76	10.15	22.8	4.57	4.68	2.4	5.09	6.63	26.3
		9	70	46.05	41.3	15.1	12.51	18.8	5.61	5.32	5.3	6.39	8.14	24.1
		10	27.03	22.19	19.7	11.28	10.1	11	4.13	4.22	2.2	4.96	5.27	6.1
		11	37.74	23.14	48	21.91	16.5	28.2	8.16	7.98	2.2	6.61	6.9	4.3

(Continued on next page. See notes at end of table.)

Table 5.8 Continued

			H_2S			MeSH			DMS			DMDS		
		Run			Diff.,*			Diff.,*			Diff.,*			Diff.,*
Mill	Source	No.	GN	GD	%	GN	GD	%	GN	GD	%	GN	GD	%
	Primary Clarifier	1	52.39	6.05	158.6	21.3	22.5	5.5	6.48	7.64	16.4	57.17	37.39	41.8
		2	35.26	72.4	69	15.72	14.84	5.8	4.46	4.27	4.4	52.89	53.02	0.2
		3	15.35	12	24.5	9.16	9.16	0	4.98	4.68	6.2	48.65	49.26	1.2
		4	39.8	---	---	10.97	---	---	5.92	---	---	52.47	---	---
		5	57.91	61.23	5.6	11.69	11.49	1.7	5	4.9	2	38.66	41.17	6.3
E	No. 1 Settling Pond	1	49.9	50.11	0.4	ND	ND	NC	ND	ND	NC	ND	ND	NC
		3	14.83	15	1.1	ND	ND	NC	ND	ND	NC	2.72	ND	NC
		6	208.0	156.7	28.2	ND	ND	NC	ND	ND	NC	ND	ND	NC
		7	155.6	95.2	48.2	ND	ND	NC	ND	ND	NC	ND	ND	NC
		8	184.1	150.6	20.0	ND	ND	NC	ND	ND	NC	ND	ND	NC
	No. 2 Settling Pond	2	41.69	101.61	83.6	ND	ND	NC	ND	ND	NC	ND	ND	NC
		4	57.66	62.94	8.8	ND	ND	NC	ND	ND	NC	ND	ND	NC
		6	118.2	126.7	7.0	ND	ND	NC	ND	ND	NC	ND	ND	NC
		7	75.1	69.2	8.2	ND	ND	NC	ND	ND	NC	ND	ND	NC
		8	45.7	51.4	11.7	ND	ND	NC	ND	ND	NC	ND	ND	NC
	ASB	1	7.24	6.51	10.6	ND	ND	NC	ND	ND	NC	ND	ND	NC
		2	4.73	5.15	8.5	ND	ND	NC	ND	ND	NC	ND	ND	NC
		3	8.76	11.01	22.8	ND	ND	NC	ND	ND	NC	ND	ND	NC
		4	31.9	26.2	19.4	ND	ND	NC	ND	ND	NC	ND	ND	NC
		5	20.0	17.8	11.7	ND	ND	NC	ND	ND	NC	ND	ND	NC
		6	11.8	12.5	5.9	ND	ND	NC	ND	ND	NC	ND	ND	NC
Average					24.0			13.0			4.4			7.7

GN = Ground Normal, GD = Ground Duplicate, NA = Not Available, NC = Not Calculable, ND[xxx] = Not Detected at a detection limit of xxx

*Diff. (Difference) is the absolute value of the difference between the two values divided by the average of the two values.

Table 5.9 Methane Overall Precision Data for Ground-Level Field Duplicates

Mill	Source	Run No.	Background CH$_4$ Conc., ppbv	Background-Corrected Downwind CH$_4$ Conc., ppbv		Difference,* %
				Normal	Duplicate	
A	No. 1 ASB	1	1845	791	NA	NA
		2	1888	716	NA	NA
		3	1846	368	NA	NA
		4	2477	NA	NA	NA
		5	1835	527	NA	NA
		6	2716	335	286	15.8
		7	2582	416	371	11.4
		8	2650	283	354	22.3
		9	2617	331	331	0.0
		10	2502	313	NA	NA
		11	2587	248	259	4.3
		12	2503	614	467	27.2
		13	1944	NA	NA	NA
		14	2113	307	178	53.2
		15	1930	376	258	37.2
		16	1893	393	297	27.8
		17	2059	231	97	81.7
		18	2058	101	NA	NA
		19	2081	184	NA	NA
		20	2009	271	NA	NA
		21	1905	292	NA	NA
		22	2133	NA	NA	NA
	Primary Clarifier	1	2175	NA	NA	NA
		2	2337	NA	NA	NA
B	No. 1 Ret. Pond	1	2123	161	114	34.5
		2	2026	217	251	14.2
		3	2097	567	417	30.4
	Spill Pond	1	2007	647	475	30.5
		2	2002	621	506	20.3
		3	2006	565	464	19.7
		4	1983	1076	948	12.6
		5	2045	NA	93	NA
		6	1993	118	134	12.6
		7	2032	116	30	118.7

(Continued on next page. See note at end of table.)

Table 5.9 Continued

Mill	Source	Run No.	Background CH$_4$ Conc., ppbv	Background-Corrected Downwind CH$_4$ Conc., ppbv Normal	Duplicate	Difference,* %
	Primary Clarifier	1	2198	107	4	185.6
		2	2174	209	40	135.9
		3	2174	137	122	11.7
		4	2105	213	149	35.2
		5	2104	NA	29	NA
		6	2028	177	134	27.8
		7	2087	142	167	16.1
D	No. 1 ASB	1	2150	42	26	48.6
		2	NA	NA	NA	NA
		3	2130	169	145	15.2
		4	2144	NA	259	NA
		5	2086	140	239	52.1
		6	2049	324	330	2.0
		7	2126	19	112	142.6
		8	1758	317	394	21.8
		9	1985	72	65	10.2
		10	2023	53	51	3.5
		11	2088	NA	17	NA
	Primary Clarifier	1	2204	431	438	1.6
		2	2037	443	501	12.2
		3	2124	371	NA	NA
		4	2127	322	NA	NA
		5	2086	443	511	14.2
E	No. 1 Settling Pond	1	2251	1210	998	19.2
		2	1956	1002	NA	NA
		3	2204	1064	1055	0.9
		4	2049	1256	NA	NA
		5	2724	NA	NA	NA
		6	2056	1666	1758	5.4
		7	2011	1435	1297	10.1
		8	2052	1362	1278	6.4

(Continued on next page. See note at end of table.)

Table 5.9 Continued

Mill	Source	Run No.	Background CH_4 Conc., ppbv	Background-Corrected Downwind CH_4 Conc., ppbv Normal	Duplicate	Difference,* %
	No. 2 Settling Pond	1	2263	1788	NA	NA
		2	2126	2168	2191	1.1
		3	2136	NA	NA	NA
		4	1945	1610	1424	12.2
		5	2127	1747	NA	NA
		6	1957	2392	2437	1.9
		7	2354	3820	4041	5.6
		8	2142	4663	4629	0.7
	ASB	1	2283	305	531	54.2
		2	2110	691	670	3.1
		3	2165	891	1218	31.0
		4	2349	858	758	12.4
		5	2204	856	886	3.5
		6	2186	840	NA	NA
F	Primary Clarifier	1	2089	564	533	5.8
		2	2187	452	437	3.3
		3	1577	880	992	11.9
	AST	1	2013	179	156	13.7
		2	2027	158	194	20.4
		3	2010	156	188	19.0
Average			2126			27.2

*Diff. (Difference) is the absolute value of the difference between the two values divided by the average of the two values.

Table 5.10 Overall Method Precision for Primary Clarifiers

Mill	Run No.	Date	Wind Direction, degrees	Wind Speed, m/s	P-G Stability Class	Emissions, g/s				
						H_2S	MeSH	DMS	DMDS	CH_4
B	1	8/21/2005	291	2.38	C	9.58E-03	[9.24E-04]	[8.84E-04]	[9.04E-04]	3.19E-03
	2	8/21/2005	286	2.41	C	9.23E-03	[8.09E-04]	[7.74E-04]	[7.91E-04]	9.25E-03
	3	8/21/2005	312	2.59	C	2.61E-02	[1.88E-03]	2.08E-03	[1.84E-03]	3.51E-02
	4	8/21/2005	310	2.38	C	1.21E-02	[7.13E-04]	7.94E-04	[6.98E-04]	2.14E-02
	RSD, %	-	-	-	-	56	NA	85	NA	82
	5	4/25/2006	245	4.15	C	1.04E-01	[2.42E-04]	[7.01E-04]	3.54E-04	1.03E-02
	6	4/25/2006	238	3.46	C	4.36E-02	[2.73E-04]	[8.36E-04]	3.35E-04	3.80E-02
	7	4/25/2006	212	3.18	C	3.20E-02	[2.84E-04]	[6.52E-04]	3.70E-04	2.36E-02
	RSD, %	-	-	-	-	65	NA	NA	5	58
D	1	5/12/2005	258	3.27	C-D	4.18E-02	2.70E-02	1.18E-02	1.25E-01	1.28E-01
	2	5/12/2005	286	3.59	C	6.57E-02	3.59E-02	1.33E-02	1.58E-01	3.18E-01
	3	5/12/2005	284	3.33	C-D	2.12E-02	1.13E-02	6.76E-03	1.09E-01	1.26E-01
	4	5/12/2005	293	3.63	D-E	7.13E-02	1.16E-02	8.06E-03	5.47E-02	1.13E-01
	5	5/12/2005	285	3.5	D-E	4.45E-02	1.36E-02	7.48E-03	8.88E-02	8.80E-02
	RSD, %	-	-	-	-	41	56	30	36	60
F	1	4/29/2006	119	3.80	C	1.47E-01	5.44E-02	8.40E-02	3.07E-03	8.67E-02
	2	4/29/2006	117	4.90	C	3.26E-01	3.70E-02	1.33E-01	5.18E-03	1.55E-01
	3	4/29/2006	112	4.98	C	4.81E-01	3.46E-02	9.48E-02	2.21E-03	2.65E-01
	RSD, %	-	-	-	-	53	26	25	44	53
	Average RSD, %	-	-	-	-	54	41	47	28	63

[xxx] = Not Detected at a Detection Limit of xxx; NA = Not Available

Table 5.11 RSC Overall Method Precision for Aerated Basins

Mill	Run No.	Date	Wind Direction, degrees	Wind Speed, m/s	P-G Stability Class	Emissions, g/s				
						H_2S	MeSH	DMS	DMDS	CH_4
A	3	6/23/2004	226	6.07	D	[7.51E-01]	[3.21E+00]	4.41E+00	9.05E+00	2.80E+00
	4	6/23/2004	224	5.95	C	3.41E+00	[7.52E+00]	9.55E+00	1.10E+01	NA
	5	6/23/2004	226	4.84	D	1.82E+00	[2.75E+00]	6.03E+00	7.09E+00	3.39E+00
	RSD, %	-	-	-	-	81	NA	40	22	NA
	8	7/29/2004	94	2.37	A	[3.59E-01]	[1.54E+00]	4.11E+00	7.17E+00	1.12E+01
	9	7/29/2004	99	2.33	A	[1.70E-01]	[7.26E-01]	2.39E+00	4.08E+00	5.54E+00
	10	7/29/2004	103	2.48	A	[2.28E-01]	[9.73E-01]	2.83E+00	5.48E+00	7.10E+00
	11	7/29/2004	107	2.89	A	[1.69E-01]	[7.19E-01]	3.34E+00	6.19E+00	4.18E+00
	12	7/29/2004	122	2.87	A	[2.21E-01]	[9.45E-01]	3.22E+00	5.86E+00	1.20E+01
	RSD, %	-	-	-	-	NA	NA	20	20	63
	14	10/12/2004	138	1.98	A	[2.75E-02]	[1.18E-00]	2.94E+00	4.47E+00	6.69E+00
	15	10/12/2004	202	4.05	B	3.37E-01	6.46E-01	1.74E+00	2.69E+00	1.88E+00
	16	10/12/2004	215	4.78	C	3.53E-01	8.01E-01	2.82E+00	4.29E+00	2.69E+00
	RSD, %	-	-	-	-	82	16	26	26	69
	17	10/13/2004	278	2.83	A	2.65E-01	5.21E-01	1.99E+00	4.67E+00	1.01E+00
	18	10/13/2004	281	2.69	A	2.84E-01	5.77E-01	1.43E+00	4.47E+00	7.68E-01
	19	10/13/2004	266	4.68	B	5.56E-01	8.06E-01	2.20E+00	5.39E+00	8.46E-01
	20	10/13/2004	255	5.84	C	3.14E-01	8.95E-01	2.71E+00	6.99E+00	2.39E+00

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Table 5.11 Continued

Mill	Run No.	Date	Wind Direction, degrees	Wind Speed, m/s	P-G Stability Class	Emissions, g/s				
						H_2S	MeSH	DMS	DMDS	CH_4
A	21	10/13/2004	247	5.73	C	2.66E-01	5.51E-01	2.07E+00	4.68E+00	1.94E+00
	22	10/13/2004	250	5.39	D	3.35E-01	6.75E-01	2.11E+00	5.14E+00	NA
	RSD, %	-	-	-	-	33	23	20	18	52
B	1	8/17/2005	29	5.22	D-E	5.20E-01	1.26E+00	2.74E-01	2.34E-01	NA
	2	8/17/2005	37	5.69	D-E	1.64E-01	7.81E-01	2.14E-01	1.43E+00	NA
	3	8/17/2005	35	3.23	C	1.31E-01	8.05E-01	2.24E-01	4.84E-01	NA
	RSD, %	-	-	-	-	79	28	14	88	NA
D	2	5/13/2005	29	3.85	A	8.49E-02	1.34E-01	6.90E-02	5.30E-02	NA
	3	5/13/2005	48	3.48	A	7.28E-01	3.19E-01	1.62E-01	2.33E-01	NA
	4	5/13/2005	50	3.37	A	1.05E+00	3.68E-01	1.96E-01	2.77E-01	NA
	5	5/13/2005	50	4.26	A	1.21E+00	7.47E-01	3.77E-01	6.28E-01	NA
	6	5/13/2005	57	4.41	A-B	5.84E-01	5.14E-01	2.43E-01	1.62E-01	NA
	RSD, %	-	-	-	-	60	55	54	80	NA
	7	5/14/2005	185	3.5	B-C	2.40E-01	5.97E-01	3.08E-01	5.21E-01	NA
	8	5/14/2005	204	3.87	A	6.40E-01	3.12E-01	2.49E-01	2.31E-01	1.62E+00
	9	5/14/2005	223	3.73	A	5.25E-01	2.58E-01	2.16E-01	2.80E-01	1.45E+00
	10	5/14/2005	217	3.56	A	6.24E-01	3.13E-01	1.92E-01	1.25E-01	2.85E+00
	11	5/14/2005	191	3.18	B-C	4.24E-01	2.46E-01	1.32E-01	1.10E-01	2.92E+00
	RSD, %	-	-	-	-	34	42	30	65	35

(Continued on next page.)

Table 5.11 Continued

Mill	Run No.	Date	Wind Direction, degrees	Wind Speed, m/s	P-G Stability Class	Emissions, g/s				
						H_2S	MeSH	DMS	DMDS	CH_4
E	1	4/18/2005	237	3.39	E	9.54E-02	[4.65E-02]	[4.46E-02]	[4.55E-02]	2.10E+00
	2	4/18/2005	225	2.74	D	6.13E-02	[7.65E-02]	[7.33E-02]	[7.49E-02]	9.08E+00
	3	4/18/2005	232	2.99	A	2.01E-01	[7.17E-02]	[6.86E-02]	[7.01E-02]	1.03E+01
	RSD, %	-	-	-	-	61	NA	NA	NA	62
	4	3/9/2006	213	4.79	D	5.01E-01	[1.19E-01]	[1.42E-01]	[6.75E-02]	5.71E+00
	5	3/9/2006	231	5.94	E	1.52E-01	[4.96E-02]	[5.90E-02]	[2.78E-02]	3.42E+00
	6	3/9/2006	219	6.34	C	1.60E-01	[8.68E-02]	[1.02E-01]	[4.76E-02]	4.31E+00
	RSD, %	-	-	-	-	74	NA	NA	NA	26
F	1		116	4.53	C	2.19E-02	4.81E-03	2.90E-01	3.73E-03	2.70E-01
	2		117	3.76	C	2.12E-02	3.96E-03	1.60E-01	3.96E-03	2.42E-01
	3		119	3.89	B-C	2.17E-02	3.63E-03	1.78E-01	3.80E-03	2.04E-01
	RSD, %	-	-	-	-	2	15	34	3	14
	Average RSD, %	-	-	-	-	53	30	28	43	46

[xxx] = Not Detected at a Detection Limit of xxx; NA = Not Available

Table 5.12 Overall Method Precision for Unaerated Basins

Mill	Source	Run No.	Date	Wind Direction, degrees	Wind Speed, m/s	P-G Stability Class	Emissions, g/s					
							H_2S	H_2S*	MeSH	DMS	DMDS	CH_4
B	Spill Pond	5	4/26/2006	38	6.09	D	6.74E+00	1.77E+00	1.58E-02	ND[2.01E-02]	ND[6.41E-03]	4.52E-01
		6	4/26/2006	25	5.14	D	7.46E+00	2.73E+00	1.16E-02	ND[1.87E-02]	ND[5.97E-03]	3.58E-01
		7	4/26/2006	54	3.9	C - D	3.52E+00	2.67E+00	1.07E-02	ND[1.59E-02]	ND[5.98E-03]	3.13E-01
		RSD, %	-	-	-	-	23	23	21	NA	NA	19
E	No. 1 Settling Pond	3	4/14/2005	31	5.57	D	3.40E-01	1.06E-01	[6.76E-02]	[6.47E-02]	1.50E-01	9.88E+00
		4	4/14/2005	39	5.64	C-D	6.92E-01	1.21E-01	[1.16E-01]	[1.11E-01]	[1.14E-01]	1.76E+01
		5	4/14/2005	48	6.74	D	5.70E-01	1.25E-01	[4.49E-02]	[4.30E-02]	[4.40E-02]	NA
		RSD, %	-	-	-	-	33	9	NA	NA	NA	NA
		6	3/9/2006	210	7.4	C-D	3.81E+00	7.17E-01	[1.62E-01]	[1.86E-01]	[8.21E-02]	1.65E+01
		7	3/9/2006	202	6.55	D	2.05E+00	4.72E-01	[1.40E-01]	[1.58E-01]	[6.89E-02]	1.11E+01
		8	3/9/2006	202	7.49	D	2.99E+00	5.52E-01	[1.55E-01]	[1.74E-01]	[7.38E-02]	1.16E+01
		RSD, %	-	-	-	-	30	22	NA	NA	NA	23
	No. 2 Settling Pond	1	4/14/2005	49	8.48	D	4.42E+00	4.05E-01	[2.26E-01]	[2.16E-01]	[2.21E-01]	4.77E+01
		2	4/14/2005	46	8.39	C-D	2.65E+00	4.01E-01	[1.85E-01]	[1.77E-01]	[1.81E-01]	3.80E+01
		3	4/14/2005	38	8.32	C-D	3.13E+00	3.77E-01	[1.52E-01]	2.66E-01	[1.48E-01]	NA
		RSD, %	-	-	-	-	27	4	NA	NA	NA	NA
		Avg. RSD, %	-	-	-	-	28	14	21	NA	NA	21

[xxx] = Not Detected at a Detection Limit of xxx; NA = Not Available

*Normalized to a horizontal wind velocity, at 10 meters elevation, of ≤ 3.25 m/s.

6.0 SUMMARY AND CONCLUSIONS

Spatial ambient air sampling, meteorological data collection and sample analysis methods were developed along with calculation procedures to quantify emissions of RSCs and methane from the various components of kraft mill WWTPs. These methods were used in an extensive study aimed at quantifying and understanding RSC and methane emissions from kraft mill WWTPs. The results of that study are published in NCASI Technical Bulletin No. 956 (NCASI 2008j).

The spatial ambient air sampling and calculation procedures were based on those used in a study of TRS emissions from three kraft mill WWTP basins in Canada (Esplin 1988, 1989). This technique used a helium-filled balloon tethered to mobile cart to hoist sampling lines to multiple elevations within the downwind dispersion plume. Ambient air samples were collected at multiple horizontal and vertical locations by moving the cart crosswind through the plume. The concentrations determined from the ambient air samples were used in conjunction with meteorological and geographical data to calculate the emission flux. Some modifications of Esplin's techniques were made in this study.

To measure RSC concentrations in ambient air downwind of kraft mill WWTP components, an analytical method had to be developed that would provide quantitation down to very low levels in the range of 1 to 2 ppbv. To meet the resource availability and logistical needs of this study, the ambient air samples had to be shipped off site for analysis, and be compatible with an automated analytical system. The method selected to meet the needs of this study involved ambient air sample collection in specially coated six-liter stainless steel canisters followed by connection of the canisters to a commercially available autosampler and cryogenic pre-concentration system. This system delivered concentrated ambient air samples to a gas chromatograph equipped with a pulsed-flame photometric detector. Extensive method development work was required to develop the techniques required for obtaining dependable analytical results from this system.

Method development, evaluation and performance data contained in this technical bulletin document the ability of the analytical method to produce reasonably accurate results for RSC concentrations in ambient air. Initial tests indicated that the Silonite^{TM} coated canisters sold by Entech Corp. had the best storage stability; however, even in these canisters the stability of the RSC compounds (especially H_2S) was still not adequate in unconditioned ambient air samples. To achieve adequate storage stability, the use of a permeation dryer to remove moisture before the sample entered the canister was coupled with post-sampling pressurization of the canister with nitrogen. Laboratory tests demonstrated quantitative passage of the analytes through the permeation dryer, and storage stability studies with field-collected samples indicated adequate storage stability up to 10 days. Regular sampling train spikes carried out throughout the course of the study indicated an overall average sampling train bias of -2% for H_2S. Multiple analyses and matrix spikes of field-collected samples indicated acceptable analytical precision and accuracy.

The overall analytical method precision for the kraft mill WWTP study was assessed via the analysis of field duplicates. For most of the test runs conducted in this study, ground-level field duplicates were collected and analyzed. For H_2S, MM, DMS, and DMDS, this yielded 57, 29, 33, and 32 sets of duplicate samples for which differences could be calculated, respectively. For these compounds, the average percent differences between duplicates were 24%, 13%, 4%, and 8%, respectively. For methane, the average percent different between the background-corrected duplicate ground-level samples was 27%.

The overall analytical method accuracy for the kraft mill WWTP study was assessed via comparison to another method at four sources which, of the reduced sulfur compounds, had essentially only H_2S emissions. The absence of the organic reduced sulfur compounds from these sources was confirmed via GC analysis of liquid and ambient air samples. The results from the canister cryogenic pre-concentration GC-PFPD method were compared to on-site measurements made with a Jerome® 631-X™ H_2S Analyzer. This was accomplished by making multiple, collocated, downwind ambient air measurements with the Jerome analyzer, while the canister samples were being collected, and comparing the average of the Jerome analyzer measurements to the analysis values obtained from the integrated canister samples. Comparison of the results from the two methods indicated that the results were similar, with the results from the canister method an average of 10% lower than those obtained from the Jerome® 631-X™ H_2S Analyzer.

Two approaches were used to calculate the overall performance of the emissions measurement method, which includes the spatial ambient air sampling technique and calculation procedures, as well as the ambient air sample analyses. Those two approaches were 1) an evaluation of method accuracy via determination of how well the vertical concentration profile curve fitting procedure fit the measured multi-level concentration data, and 2) an evaluation of the overall method precision for multiple test runs conducted on the same day. The NCASI WWTP emissions study produced a large body of data which could be used for these purposes. The fit of the vertical concentration profile concentration curve fitting procedure was evaluated for H_2S, MM, DMS, DMDS and methane. The fit quality was evaluated by calculating the correlation coefficient (RSQ) of the linear logarithmic plots of elevation versus concentration. The average correlation coefficients for the five compounds are summarized in Table 6.1 for three source categories: primary clarifiers, aerated basins and un-aerated basins. The overall method precision for the five compounds and three source categories, as evaluated from sets of multiple test runs conducted on the same day, are summarized in Table 6.2. In general, analytical variability at low concentrations was a major contributor to the overall method variability. elatively high ambient air concentrations corresponded to low overall method relative standard deviations; conversely, relatively low ambient air concentrations corresponded to high overall method relative standard deviations.

Table 6.1 Quality of the Vertical Concentration Profile Curve Fitting Procedure

Source Type	Average RSQ* Value				
	H_2S	MM	DMS	DMDS	CH_4
Primary Clarifiers	0.86	0.88	0.81	0.79	0.73
Aerated Basins	0.86	0.98	0.95	0.94	0.98
Un-Aerated Basins	0.83	0.99	NA	NA	0.85

*square of the Pearson product moment correlation coefficient

Table 6.2 Overall Emissions Measurement Method Precision

Source Type	Average Percent Relative Standard Deviation				
	H_2S	MM	DMS	DMDS	CH_4
Primary Clarifiers	54	41	47	28	63
Aerated Basins	53	30	28	43	46
Un-Aerated Basins	28	21	NA	NA	21
Un-Aerated Basins*	14	NA	NA	NA	NA

*Normalized to a horizontal wind velocity, at 10 meters elevation, of ≤ 3.25 m/s
NA = not applicable

7.0 REFERENCES

Bontempo, W. and Kao, S. 2002. Performance of aged versus new glass-lined canisters and tedlar bags in the analysis of reduced sulfur species. In *Proceedings of the Symposium on Air Quality Measurement Methods and Technology* - Session 12, Presentation No. 104 (November 13-15), San Francisco, CA. Pittsburgh, PA: Air & Waste Management Association.

Catalan, L.J.J. 2006. Optimization and calibration of a GC-PFPD-cryogenic trapping system for the analysis of volatile sulfur compounds at trace levels in gases. In *Proceedings of Symposium on Air Quality Measurement Methods and Technology.* (May 9-11), Durham, NC. Pittsburgh, PA: Air & Waste Management Association.

Cheskis, A., Atar, E., and Amirav, A. 1993. Pulsed-flame photometer: a novel gas chromatography detector. *Analytical Chemistry* 65:539-555

Devai, I. and DeLaune, R.D. 1994. Changes in reduced gaseous sulfur compounds collected in glass gas sampling bulbs. *Analytical Letters* 27(12):2403-2411.

Ehhalt, D.H. and Heidt, L.E. 1973. Vertical profiles of CH_4 in the troposphere and stratosphere. *Journal of Geophysical Research* 78(24):5265-5271.

Esplin, G.J. 1988. Boundary layer emission monitoring. *Journal of Air Pollution Control Association* 38:9.

———. 1989. Total reduced sulphur (TRS) emissions from effluent lagoons. *Pulp and Paper Canada* 90:10.

Gifford, F.A. 1976. Turbulent diffusion typing schemes. A review. *Nuclear Safety* 17(1):68-85.

Haberhauer-Troyer, C., Rosenberg, E., and Grasserbauer, M. 1999. Investigation of membrane dryers and evaluation of a new ozone scrubbing material for the sampling of organosulphur compounds in air. *Journal of Chromatography A* 852(2):589-595.

Helmig, D. 1997. Ozone removal techniques in the sampling of atmospheric volatile organic trace gases. *Atmospheric Environment* 31(21):3635-3651.

Hoffnagle, G.F., Smith, M.E., Crawford, T.V., and Lockhart, T.J. 1981. On-site meteorological instrumentation requirements to characterize diffusion from point sources – A workshop. January 15-17, 1980, Raleigh, NC. *Bulletin of the American Meteorological Society* 62:255-261.

Inomata, Y., Matsunaga, K., Murai, Y., Osada, K. and Iwasaka, Y. 1999. Simultaneous measurement of volatile sulfur compounds using ascorbic acid for oxidant removal and gas chromatography–flame photometric detection**.** *Journal of Chromatography A* 864:111-119.

Irwin, J.S. 1983. Estimating plume dispersion – A comparison of several sigma schemes. *Journal of Climate and Applied Meteorology* 22:92-114.

Ki-Hyun, K., Gyoo-Hoon, C., Ye-Jin, C., Hee-Nam, S., Yang, H.-S. and Oh, J.-M. 2006. The effects of sampling materials selection in the collection of reduced sulfur compounds in air. *Talanta***,** 68(5): 1713-1719.

Kunkel, B.A. 1985. *Development of an atmospheric diffusion model for toxic chemical releases*. NTIS: AD/A169-135. Air Force Geophysics Laboratory, Hanscom AFB.

Kuster, W. and Goldan, C., P.D. 1987. Quantitation of the losses of gaseous sulfur compounds to enclosure walls. *Environmental Science and Technology* 21:810-815.

Lau, Y.K. 1989. Measurement of sulphur gases in ambient air. *Environmental Monitoring and Assessment* 13:69-74.

MacTaggart, E.L., Farwell, S.O., Burdge, J.R., Cai, Z.-T., Haakenson, T.J., and Bamesberger, W.L. 1999. A continuous monitor-sulfur chemiluminescence detector (CM-SCD) system for the measurement of total gaseous sulfur species in air. *Atmospheric Environment* 33:625-632.

NCASI. 2005. *Methods Manual – Reduced sulfur compounds by direct injection GC/PFPD.* www.ncasi.org

———. 2008a. Emissions of Reduced Sulfur Compounds from the Mill A Wastewater Treatment Plant. Final Draft. www.ncasi.org.

———. 2008b. Emissions of Reduced Sulfur Compounds and Methane from the Mill B Wastewater Treatment Plant Phase I Testing. Final Draft. www.ncasi.org.

———. 2008c. Emissions of Reduced Sulfur Compounds and Methane from the Mill B Wastewater Treatment Plant Phase II Testing. Final Draft. www.ncasi.org.

———.2008d. Emissions of Reduced Sulfur Compounds and Methane from the Mill D Wastewater Treatment Plant. Final Draft. www.ncasi.org.

———. 2008e. Emissions of Reduced Sulfur Compounds and Methane from the Mill E Wastewater Treatment Plant Phase I Testing. Final Draft. www.ncasi.org.

———. 2008f. Emissions of Reduced Sulfur Compounds and Methane from the Mill E Wastewater Treatment Plant Phase II Testing. Final Draft. www.ncasi.org.

———. 2008g. Emissions of Reduced Sulfur Compounds from Wastewater Treatment Plant at Mill E: Phase III Testing. Final Draft. www.ncasi.org.

———. 2008h. Emissions of reduced sulfur compounds and methane from the mill F wastewater treatment plant. Final Draft. www.ncasi.org.

———. 2008i. Screening Study of Reduced Sulfur Compound Emissions from the Wastewater Treatment Plant at Mill T. Final Draft. www.ncasi.org.

NCASI. 2008j. *Emissions of reduced sulfur compounds and methane from kraft mill wastewater treatment plants*. Technical Bulletin No. 956. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Ochiai, N., Takino, M., Daishima, and Cardin, D.B. 2001. Analysis of volatile sulphur compounds in breath by gas chromatography–mass spectrometry using a three-stage cryogenic trapping preconcentration system. *Journal of Chromatography B*. 762(1):67-75.

Parmer, S. 1991. A study of "holding times" for H_2S, COS and CH_3SH samples (gas phase) in different containers. In *Proceedings of the 1991 U.S. EPA/A&WMA international symposium on the measurement of toxic and related air pollutants*, 544-551. Pittsburgh, PA: Air & Waste Management Association.

Quang, T. and Tang, Y.-Z. 1994. Stability of reduced sulphur compounds in whole air samplers. In *Proceedings of the 1994 U.S. EPA/A&WMA international symposium on the measurement of toxic and related air pollutants,* 1005-1010. Pittsburgh, PA: Air & Waste Management Association.

Rodrigues, B.A., Pitombo, L.R.M., Cardoso, A.A. 2000. Study on the use of oxidant scrubbers for elimination of interferences due to nitrogen dioxide in analysis of atmospheric dimethyl sulfide. *Journal of the Brazilian Chemical Society* 11(1):71-77.

Shelow, D. and Stidsen, G. 1998. Analysis of low-level 1 ppb to 20 ppb reactive sulfurs in air samples. Slide presentation, Pittsburgh Conference. www.restekcorp.com.

Sugawara, S., Nakazawa, T., Shirakawa, Y., Kawamura, K., Aoki, S., Machida, T., and Honda, H. 1997. Vertical profile of the carbon isotopic ratio of stratospheric methane over Japan. *Geophysical Research Letters* 24(23):2989-2992.

Sulyok, M., Haberhauer-Troyer, C., Rosenberg, E., Grasserbauer, M. 2001. Investigation of the storage stability of selected volatile sulfur compounds in different sampling containers. *Journal of Chromatography A* 917:367-374.

Sulyok, M., Haberhauer-Troyer, C., and Rosenberg, E. 2002. Observation of sorptive losses of volatile sulfur compounds during natural gas sampling. *Journal of Chromatography A* 946:301-305.

Talbert, B., Benesch, R., Haouchine, M., and Jacksier, T. 2004. A study of regulators for delivering gases containing low concentrations of hydrogen sulfide. *LC GC North America* 22:6.

Turner, D.B. 1994. *Workbook of atmospheric dispersion estimates: An introduction to dispersion modeling*. 2nd ed. Boca Raton, FL: CRC Press.

United States Environmental Protection Agency (USEPA). 1999. *Compendium of methods for the determination of toxic organic compounds in ambient air*. EPA-625/R-96-0106. Cincinnati, OH: United States Environmental Protection Agency.

———. 2000. *Meteorological monitoring guidance for regulatory modeling applications*. EPA-454/R-99-005. Research Triangle Park, NC: United States Environmental Protection Agency Office of Air Quality Planning and Standards.

Walter, B.P., Heimann, M., and Matthews, E. 2001. Modeling modern methane emissions from natural wetlands - 1. Model description and results. *Journal of Geophysical Research* 106(D24):34,189-34,206.

Wardencki, W. 1998. Problems with the determination of environmental sulfur compounds by gas chromatography. *Journal of Chromatography A* 793:1-19.

Winegar, E. D. 2002. An integrated analytical system for the low-level determination of hydrogen sulfide in the field. In *Proceedings of the symposium on air quality measurement methods and technology*. Session No. 12, Presentation No. 4 (November 13-15), San Francisco, CA. Pittsburgh, PA: Air & Waste Management Association.

APPENDIX A

EXAMPLE AIR EMISSION CALCULATION

Quantitation of reduced sulfur compound emissions from wastewater treatment plants is accomplished through the use of the spatial ambient air sampling technique described in Section 2.0. This appendix provides an example set of calculations to demonstrate how each equation is applied and how the spreadsheet tools are used. The example problem is illustrated in Figure A-1.

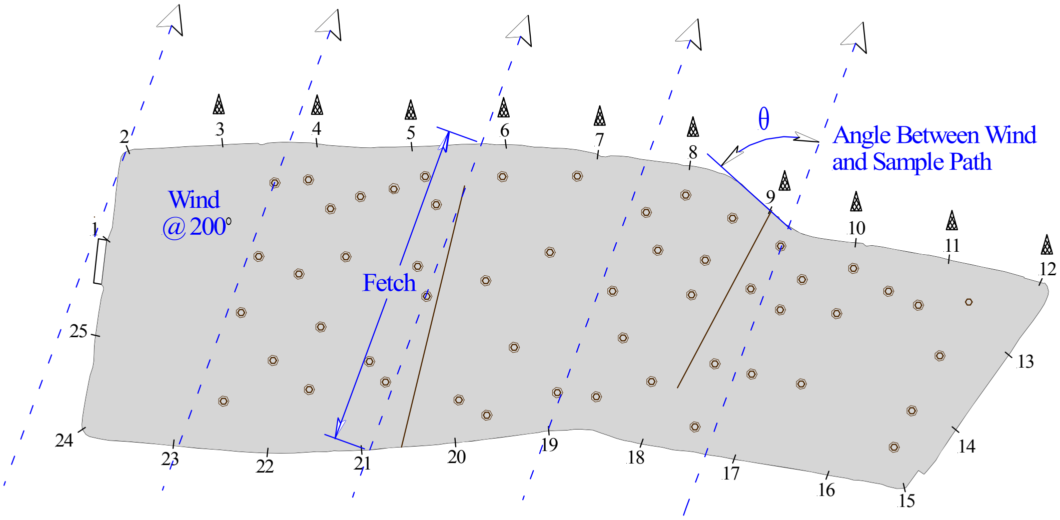

Figure A-1 Example Problem for Area Source Emission Quantitation Using the Spatial Ambient Air Sampling Technique

Input parameters are obtained from observations of wind speed, wind direction, and incoming solar radiation, which were used to estimate atmospheric stability class. This project utilized two sonic anemometers, one at 10 meter height and one at 2 meter height, along with an ambient temperature probe to generate site-specific meteorological data.

A.1 Calculation of Sampling Station Locations, Sample Line Heights, and Sampling Times

Basin Perimeter = 8325 ft (measured)

Distance Between Sampling Stations = 8325/25 = 333 ft

Date/ Time/ Latitude and Longitude = 3-9-06 / 8:10 DST / N35°52' W76°45'

Solar Altitude Angle = 8° *(from U.S. Naval Observatory Altitude and Azimuth Tables available online @: http://aa.usno.navy.mil/data/docs/AltAz.html)*

Average Wind Speed = 3.6 m/s
Azimuth = 200°

} Site-specific data collected from anemometer at 10-meter height

Average wind speed and azimuth are predicted for the test run set-up and sampling period (one to one and a half hours) based on the preceding 10 or more minutes.

P-G Stability Class = D *(from Turner's Key to Pasquill Stability Categories, Table 2.1.1.1)*

Fetch, x = 1150 ft = 0.35 km *(scaled from map)*

σ_z = 14.0 meters *(from Pasquill-Gifford curve, Table 2.1.1.2)*

$Z_b = 2.15\ \sigma_z =$ 30.1 meters = 99 ft

Sample line heights:
$0.15\ Z_b = 0.15\ (99) = 14.8$ ft
$0.30\ Z_b = 0.30\ (99) = 29.6$ ft
$0.45\ Z_b = 0.45\ (99) = 44.4$ ft

Round sample line heights up to multiples of 5:
low = 15 ft
mid = 30 ft
high = 45 ft

Sampling Station IDs for Sample Run with 200° wind: 3 through 12

Calculation of Sampling Times at Each Station:

> Angles between the wind direction and sample path at each sampling station are measured from a scale drawing of the source. See Figure A-1 for definition of the angle. Forty-five minutes of sample collection results in sample runs of approximately 60 minutes once time required to move between sample collection points is added. A calculation summary is provided in Table A-1.

Table A-1 Calculation of Sampling Times at Each Sampling Station

Azimuth	Station ID	Angle Between Wind and Sample Path θ deg.	sin θ	Sampling Time Each Station $\frac{\sin\theta}{\Sigma(\sin\theta)}$ x (total sampling time)
200°	3	68	0.927	(0.927/9.650) x (45) = 4 : 19 (min:sec)
	4	74	0.961	(0.961/9.650) x (45) = 4 : 29
	5	70	0.940	(0.940/9.650) x (45) = 4 : 23
	6	73	0.956	(0.956/9.650) x (45) = 4 : 28
	7	78	0.978	(0.978/9.650) x (45) = 4 : 34
	8	83	0.993	(0.993/9.650) x (45) = 4 : 38
	9	68	0.927	(0.927/9.650) x (45) = 4 : 19
	10	79	0.982	(0.982/9.650) x (45) = 4 : 35
	11	82	0.990	(0.990/9.650) x (45) = 4 : 37
	12	85	0.996	(0.996/9.650) x (45) = 4 : 39
		Σ (sin θ)	= 9.650	

A.2 Calculation of Vertical Dispersion, Path Width and Wind Profile Exponent

Dispersion parameters are calculated for the sample run based on actual meteorological conditions during the sample run. Summary data for the 10-meter and 2-meter anemometers are shown in Tables A.2.1 and A.2.2, respectively, for the example sample run. P-G stability class is first estimated from the standard deviation of the azimuth angle and standard deviation of the elevation angle during the test run (Gifford 1976; Kunkel 1985). The vertical dispersion coefficient, σ_Z, is then calculated from the standard deviation of the vertical component of the wind velocity using Irwin's model (Irwin 1983). The pollutant boundary layer height, Z_b, can then be determined. The wind profile exponent, p, is calculated using site-specific wind velocity data at 10 and 2 meters. In lieu of the site-specific data, the values given in Table 2.3.1 may be used.

Table A.2.1 Summary Data for the 10-meter Sonic Anemometer

		WIND SPEED						SPEED OF	SONIC
DATE	TIME	u (m/s)	V (m/s)	w (m/s)	2-D (m/s)	AZIMUTH (deg.)	ELEV. (deg.)	SOUND (m/s)	TEMP (°C)
Start	8:11								
Stop	9:09								
Avg		-2.57	-3.94	0.03	4.79	212.71	0.80	338.71	11.55
Std Dev		1.01	0.91	0.38	1.01	10.98	4.89	0.57	0.96
Min		-5.77	-6.74	-1.56	2.48	185.10	-14.40	337.62	9.70
Max		-0.28	-1.88	1.05	7.67	240.20	18.40	339.60	13.04
No. of data points		705							
		Avg. Wind 1st half of run			4.67	205.71	Avg. Azimuth 1st half of run		
		Avg. Wind 2nd half of run			4.91	219.73	Avg. Azimuth 2nd half of run		
	Difference between 1st half and 2nd half				5.16%	-14.02	degrees		

Table A.2.2 Summary Data for the 2-meter Sonic Anemometer with Ambient Temperature Probe

		WIND SPEED						SPEED OF	SONIC	AMBIENT
DATE	TIME	u (m/s)	V (m/s)	w (m/s)	2-D (m/s)	AZIMUTH (deg.)	ELEV. (deg.)	SOUND (m/s)	TEMP (°C)	TEMP (°F)
Start	8:11									
Stop	9:09									
Avg		-2.16	-2.64	-0.05	3.51	219.20	-0.53	338.30	10.86	52.57
Std Dev		0.81	0.79	0.23	0.81	13.06	4.07	0.59	0.99	1.84
Min		-5.15	-5.25	-0.86	1.44	185.00	-15.80	337.10	8.83	49.00
Max		-0.28	-0.62	0.79	6.16	251.20	16.80	339.42	12.75	55.20
No. of data points		705								
		Avg. Wind 1st half of run			3.51	212.65	Avg. Azimuth 1st half of run			
		Avg. Wind 2nd half of run			3.50	225.77	Avg. Azimuth 2nd half of run			
	Difference between 1st half and 2nd half				0.26%	-13.12	degrees			

(ι) Determination of P-G Stability Class Using σ_A

σ_A = standard deviation of 10-m azimuth angle = 10.98 *(from site-specific data, Table A.2.1)*

Run Time = 9:09 – 8:11 = 0:58

$(\sigma_A)_{60} = (\sigma_A)_t\ (60 / t)^{0.2} = (10.98)(60/58)^{0.2} = 11.05$

σ_E = standard deviation of 10-m elevation angle = 4.89 *(from site-specific data, Table A.2.1)*

P-G Stability Class = D neutral *(from Table 2.3.2)*

(ιι) Calculation of Vertical Dispersion Coefficient and Pollutant Boundary Layer Height

σ_W = standard deviation of 10-m vertical wind = 0.38 *(from site-specific data, Table A.2.1)*

U_{10} = 4.79 m/s *(from site-specific data, Table A.2.1)*

Fetch, x = 396 meters *(scaled from map using actual wind direction during sampling run)*

T = travel time = fetch / U_{10} = 396 / 4.79 = 82.67 seconds

$$f_Z(stable) = \frac{1}{1 + 0.9(T/50)^{0.5}} = \frac{1}{1 + 0.9(82.67/50)^{0.5}} = 0.464$$

$\sigma_Z = \sigma_W\, T\, f_z = (0.38)(82.67)(0.464) = 14.6$ meters

$Z_b = 2.15\ \sigma_Z = 2.15(14.6) = 31.3$ meters

(ιιι) Calculation of Sample Path Width

W = 1352 ft = 412 meters *(scaled from map as shown in Figure A-2)*

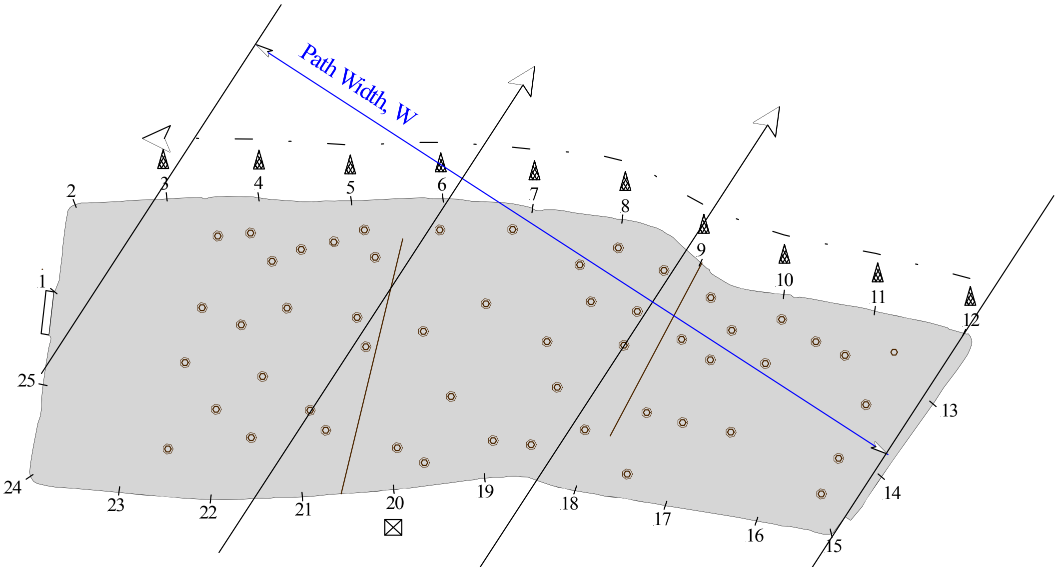

Figure A-2 Illustration of Path Width Defined By Wind Direction

(ιν) Calculation of Wind Profile Exponent

$$p = \frac{\ln(U_{10}) - \ln(U_2)}{\ln(10) - \ln(2)} = \frac{\ln(4.79) - \ln(3.51)}{1.6094} = 0.19$$

A.3 Calculation of Concentration Profile

The emission calculation workbook is used to calculate concentration profiles and emission rates once the canister samples have been analyzed and compound concentration data is available. An example of one worksheet is shown in Figure A-3. Items to be input are marked with boxes.

At the top of each worksheet, the following sample run data is input: Mill code, source, run number, date, start time, stop time, pollutant boundary layer height (Z_b), low- mid- and high- sample line heights, crosswind sample path width, wind profile exponent (p), 10-meter horizontal wind velocity (U_{10}), ambient temperature (°C), and atmospheric pressure (atm). In the mid-section of the worksheet, sample ID codes and post-run (initial) canister pressures and post-pressurization (final) canister pressures are input for each canister. The canister dilution factor is calculated as the ratio of final-to-initial pressures; e.g., for sample JAB1GD shown in Figure A-3, the dilution factor due to pressurizing the samples with nitrogen is 47.76 / 12.76 = 3.74.

The analysis concentration factor is calculated as the ratio of analysis volume-to-calibration curve volume. In the example shown in Figure A-3, the analytic concentrations input into the worksheet were previously corrected for analysis volume and hold time, so the analysis concentration factor is 1.

For each input analytic concentration,

$$\text{Ambient Conc. (ppbv)} = \text{Analytic Conc. (ppbv)} \times \text{Canister Dilution Factor} \;/\; \text{Analysis Concentration Factor}$$

If background corrections are applied,

$$\text{Background Corrected Ambient Concentration (ppbv)} = \text{Ambient Concentration (ppbv)} - \text{Background Concentration (ppbv)}$$

In the example shown in Figure A-3, background reduced sulfur compound concentrations were below the quantitation limit, and background corrections were not applied to reduced sulfur compound concentrations. Background correction was applied to methane concentrations.

Values shown in brackets in Figure A-3 are non-detect and represent the method quantitation limit (MQL) for each compound in the three ground-level canisters (background B, ground normal GN, and ground duplicate GD). Values shown in brackets for the upper-level canisters (low L, mid M, and high H) are non-detect and represent one-half MQL.

A6

Mill	Source	Run No.	Date	Start Time	Stop Time	Zb (m)	SAMPLING HEIGHT (m) L	M	H	Path Width (m)	p	U10 (m/s)	T (°C)	P (atm)
J	ASB	1	3/9/06	8:11	9:09	31.3	4.6	9.1	13.7	412	0.19	4.79	11.4	1.00

Canister	Compound	Initial Pres., (in Hg)	Final Pres., (in Hg)	Canister Dilution Factor	Cal. Curve Vol. (mL)	Analysis Vol. (mL)	Analysis Conc. Factor	Anal. Conc. (ppbv)	Ambient Conc. (ppbv)	Bkgrd Corrected Ambient Conc. (ppbv)	Avg. Bkgrd Corrected Ambient Conc. (ppbv)
JAB1BNB	H2S	13.94	52.22	3.75	1000	1000	1	[1.34]	~~[5.02]~~		
	MeSH	13.94	52.22	3.75	1000	1000	1	[1.29]	~~[4.79]~~		
	DMS	13.94	52.22	3.75	1000	1000	1	[1.19]	~~[4.42]~~		
	DMDS	13.94	52.22	3.75	1000	1000	1	[0.37]	~~[1.39]~~		
	CH4	13.94	52.22	3.75	1	1	1	627	2348.78		
JAB1GDDUP	H2S	12.76	47.76	3.74	1000	1000	1	7.01	26.24	26.24	
	MeSH	12.76	47.76	3.74	1000	1000	1	[1.28]	[4.79]	[4.79]	
	DMS	12.76	47.76	3.74	1000	1000	1	[1.18]	[4.42]	[4.42]	
	DMDS	12.76	47.76	3.74	1000	1000	1	[0.37]	[1.38]	[1.38]	
	CH4	12.76	47.76	3.74	1	1	1	830	3106.65	757.87	
JAB1GNG	H2S	17.21	64.55	3.75	1000	1000	1	8.50	31.88	31.88	29.06
	MeSH	17.21	64.55	3.75	1000	1000	1	[1.28]	[4.80]	[4.80]	[4.80]
	DMS	17.21	64.55	3.75	1000	1000	1	[1.18]	[4.43]	[4.43]	[4.42]
	DMDS	17.21	64.55	3.75	1000	1000	1	[0.37]	[1.39]	[1.39]	[1.39]
	CH4	17.21	64.55	3.75	1	1	1	855	3206.87	858.09	807.98
JAB1LNL	H2S	18.89	70.83	3.75	1000	1000	1	4.74	17.77	17.77	
	MeSH	18.89	70.83	3.75	1000	1000	1	[0.64]	[2.40]	~~[2.40]~~	
	DMS	18.89	70.83	3.75	1000	1000	1	[0.59]	[2.21]	~~[2.21]~~	
	DMDS	18.89	70.83	3.75	1000	1000	1	[0.19]	[0.71]	~~[0.71]~~	
	CH4	18.89	70.83	3.75	1	1	1	682	2557.23	208.45	
JAB1MNM	H2S	19.41	73.28	3.78	1000	1000	1	3.53	13.33	13.33	
	MeSH	19.41	73.28	3.78	1000	1000	1	[0.64]	[2.42]	~~[2.42]~~	
	DMS	19.41	73.28	3.78	1000	1000	1	[0.59]	[2.23]	~~[2.23]~~	
	DMDS	19.41	73.28	3.78	1000	1000	1	[0.19]	[0.72]	~~[0.72]~~	
	CH4	19.41	73.28	3.78	1	1	1	616	2325.63	~~-23.15~~	
JAB1HNH	H2S	21.21	79.58	3.75	1000	1000	1	2.30	8.63	8.63	
	MeSH	21.21	79.58	3.75	1000	1000	1	[0.64]	[2.40]	~~[2.40]~~	
	DMS	21.21	79.58	3.75	1000	1000	1	[0.59]	[2.21]	~~[2.21]~~	
	DMDS	21.21	79.58	3.75	1000	1000	1	[0.19]	[0.71]	~~[0.71]~~	
	CH4	21.21	79.58	3.75	1	1	1	616	2311.23	0.001	@ 0.95 Zb

Compound	Canister	C(z), g/m^3	ln[c(z)]	Z	Zb	ln[1-(z/Zb)]	b	Co, g/m^3	r^2
H2S	0.02 Zb	3.85E-05	-10.16586	0.5	31.3	-0.0161	2.142	4.2E-05	0.960

	b		Emissions, g/s
	2.142	H2S	7.26E-01

	0.02 Zb	4.67E-05	-9.97106	0.5	31.3	-0.0161		28.41	ppbv
	0.15 Zb	2.61E-05	-10.55539	4.6	31.3	-0.1579			
	0.29 Zb	1.95E-05	-10.84328	9.1	31.3	-0.3454			
	0.44 Zb	1.26E-05	-11.27787	13.7	31.3	-0.5764			
MeSH	0.02 Zb	[9.91E-06]	-[11.52177]	0.5	31.3	-0.0161		[8.6E-06]	
	0.02 Zb	[9.93E-06]	-[11.51969]	0.5	31.3	-0.0161		[4.18]	ppbv
	0.15 Zb	[4.96E-06]	-[12.21314]	4.6	31.3	-0.1579			
	0.29 Zb	[5.00E-06]	-[12.20629]	9.1	31.3	-0.3454			
	0.44 Zb	[4.97E-06]	-[12.21250]	13.7	31.3	-0.5764			
DMS	0.02 Zb	[1.18E-05]	-[11.34829]	0.5	31.3	-0.0161		[1.0E-05]	
	0.02 Zb	[1.18E-05]	-[11.34622]	0.5	31.3	-0.0161		[3.85]	ppbv
	0.15 Zb	[5.91E-06]	-[12.03967]	4.6	31.3	-0.1579			
	0.29 Zb	[5.95E-06]	-[12.03282]	9.1	31.3	-0.3454			
	0.44 Zb	[5.91E-06]	-[12.03903]	13.7	31.3	-0.5764			
DMDS	0.02 Zb	[5.61E-06]	-[12.09159]	0.5	31.3	-0.0161		[4.9E-06]	
	0.02 Zb	[5.62E-06]	-[12.08952]	0.5	31.3	-0.0161		[1.21]	ppbv
	0.15 Zb	[2.88E-06]	-[12.75629]	4.6	31.3	-0.1579			
	0.29 Zb	[2.90E-06]	-[12.74945]	9.1	31.3	-0.3454			
	0.44 Zb	[2.89E-06]	-[12.75565]	13.7	31.3	-0.5764			
CH4	0.02 Zb	5.23E-04	-7.55681	0.5	31.3	-0.0161	4.495	4.7E-04	0.997
	0.02 Zb	5.92E-04	-7.43261	0.5	31.3	-0.0161		688	ppbv
	0.15 Zb	1.44E-04	-8.84761	4.6	31.3	-0.1579			
	~~0.29 Zb~~	-1.60E-05		~~9.1~~	~~31.3~~	~~-0.3454~~			
	0.95 Zb	6.89E-10	-21.09508	29.7	31.3	-2.9957			

		MeSH	
		DMS	
		DMDS	
	4.495	CH4	4.30E+00
Combined emission profile exponent	3.236	H2S	5.01E-01
	3.236	MeSH	ND[1.04E-01]
	3.236	DMS	ND[1.24E-01]
	3.236	DMDS	ND[5.91E-02]
	3.236	CH4	5.71E+00

Figure A-3. Example Worksheet for Concentration Profile and Emission Rate Calculation

Concentrations by volume (ppbv) are converted to mass (g/m^3) in the lower left of the spreadsheet using the following equation:

$$C(z) = \begin{pmatrix} ambient \\ conc. \\ ppbv \end{pmatrix} / 10^6\, xMW \left[\frac{P_{atm}}{0.0821(T + 273)} \right]$$

Thus, for H_2S (MW = 34.08):

C(0.5) = (26.24 ppbv)/10^6 x (34.08) x (1.00)/((0.0821)(11.4 + 273)) = 3.85 x 10^{-5} g/m^3
C(0.5) = (31.88 ppbv)/10^6 x (34.08) x (1.00)/((0.0821)(11.4 + 273)) = 4.67 x 10^{-5} g/m^3
C(4.6) = (17.77 ppbv)/10^6 x (34.08) x (1.00)/((0.0821)(11.4 + 273)) = 2.61 x 10^{-5} g/m^3
C(9.1) = (13.33 ppbv)/10^6 x (34.08) x (1.00)/((0.0821)(11.4 + 273)) = 1.95 x 10^{-5} g/m^3
C(13.7) = (8.63 ppbv)/10^6 x (34.08) x (1.00)/((0.0821)(11.4 + 273)) = 1.26 x 10^{-5} g/m^3

for MeSH (MW = 48.1):

C(0.5) = ([4.79] ppbv)/10^6 x (48.1) x (1.00)/((0.0821)(11.4 + 273)) = [9.91 x 10^{-6}] g/m^3
C(0.5) = ([4.80] ppbv)/10^6 x (48.1) x (1.00)/((0.0821)(11.4 + 273)) = [9.93 x 10^{-6}] g/m^3
C(4.6) = ([2.40] ppbv)/10^6 x (48.1) x (1.00)/((0.0821)(11.4 + 273)) = [4.96 x 10^{-6}] g/m^3
C(9.1) = ([2.42] ppbv)/10^6 x (48.1) x (1.00)/((0.0821)(11.4 + 273)) = [5.00 x 10^{-6}] g/m^3
C(13.7) = ([2.40] ppbv)/10^6 x (48.1) x (1.00)/((0.0821)(11.4 + 273)) = [4.97 x 10^{-6}] g/m^3

for DMS (MW = 62.06):

C(0.5) = ([4.42] ppbv)/10^6 x (62.06) x (1.00)/((0.0821)(11.4 + 273)) = [1.18 x 10^{-5}] g/m^3
C(0.5) = ([4.43] ppbv)/10^6 x (62.06) x (1.00)/((0.0821)(11.4 + 273)) = [1.18 x 10^{-5}] g/m^3
C(4.6) = ([2.21] ppbv)/10^6 x (62.06) x (1.00)/((0.0821)(11.4 + 273)) = [5.91 x 10^{-6}] g/m^3
C(9.1) = ([2.23] ppbv)/10^6 x (62.06) x (1.00)/((0.0821)(11.4 + 273)) = [5.95 x 10^{-6}] g/m^3
C(13.7) = ([2.21] ppbv)/10^6 x (62.06) x (1.00)/((0.0821)(11.4 + 273)) = [5.91 x 10^{-6}] g/m^3

for DMDS (MW = 94.12):

C(0.5) = ([1.38] ppbv)/10^6 x (94.12) x (1.00)/((0.0821)(11.4 + 273)) = [5.61 x 10^{-6}] g/m^3
C(0.5) = ([1.39] ppbv)/10^6 x (94.12) x (1.00)/((0.0821)(11.4 + 273)) = [5.62 x 10^{-6}] g/m^3
C(4.6) = ([0.71] ppbv)/10^6 x (94.12) x (1.00)/((0.0821)(11.4 + 273)) = [2.88 x 10^{-6}] g/m^3
C(9.1) = ([0.72] ppbv)/10^6 x (94.12) x (1.00)/((0.0821)(11.4 + 273)) = [2.90 x 10^{-6}] g/m^3
C(13.7) = ([0.71] ppbv)/10^6 x (94.12) x (1.00)/((0.0821)(11.4 + 273)) = [2.89 x 10^{-6}] g/m^3

for CH_4 (MW = 16.03):

C(0.5) = (757.87 ppbv)/10^6 x (16.03) x (1.00)/((0.0821)(11.4 + 273)) = 5.23 x 10^{-4} g/m^3
C(0.5) = (858.09 ppbv)/10^6 x (16.03) x (1.00)/((0.0821)(11.4 + 273)) = 5.92 x 10^{-4} g/m^3
C(4.6) = (208.45 ppbv)/10^6 x (16.03) x (1.00)/((0.0821)(11.4 + 273)) = 1.44 x 10^{-4} g/m^3
C(9.1) = (-23.15 ppbv)/10^6 x (16.03) x (1.00)/((0.0821)(11.4 + 273)) = -1.60 x 10^{-5} g/m^3
C(13.7) = (-37.55 ppbv)/10^6 x (16.03) x (1.00)/((0.0821)(11.4 + 273)) = -2.59 x 10^{-5} g/m^3
C(0.95Z_b) = (0.001 ppbv)/10^6 x (16.03) x (1.00)/((0.0821)(11.4 + 273)) = 6.89 x 10^{-10} g/m^3

The concentration data at four elevations is then fit to the equation $c(z) = c_o\left(1 - \frac{z}{Z_b}\right)^b$.

Since this equation is non-linear, it is transformed by taking the natural logarithm of each side, yielding the following equation:

$$\ln c(z) = \ln c_o + b \ln\left(1 - \frac{Z}{Z_b}\right)$$

which is of the form y = A + Bx. Linear regression is used to solve for b and c_o.

A calculation summary is provided in Table A-3. The r^2 values are also given to indicate the degree of correlation between the measured data set and the linearized curve. It can be seen that, for the data sets where compound concentrations are equal to MQL at ground-level and ½ MQL at higher elevations, there is poor correlation. Thus, in this example, emission rates for these compounds (MeSH, DMS, and DMDS) were not calculated using the individual concentration profile exponents shown in Table A-3, but rather, a combined emission profile exponent that is the average of the emission profile exponents for H_2S and CH_4 was used.

Table A-3. Calculation of Concentration Profile Exponent, b

Compound	C(z), g/m^3	ln[c(z)]	ln[1 – z /Z$_b$]	b	Intercept	c$_o$, g/m^3	r^2
H2S	c(0.5) = 3.85 x 10^{-5}	-10.16586	-0.0161	2.142	-10.086	4.2E-05	0.960
	c(0.5) = 4.67 x 10^{-5}	-9.97106	-0.0161				
	c(4.6) = 2.61 x 10^{-5}	-10.55539	-0.1579				
	c(9.1) = 1.95 x 10^{-5}	-10.84328	-0.3454				
	c(13.7) = 1.26 x 10^{-5}	-11.27787	-0.5764				
MeSH	c(0.5) = [9.91 x 10^{-6}]	-[11.52177]	-0.0161	1.239	-11.659	[8.6E-06]	0.617
	c(0.5) = [9.93 x 10^{-6}]	-[11.51969]	-0.0161				
	c(4.6) = [4.96 x 10^{-6}]	-[12.21314]	-0.1579				
	c(9.1) = [5.00 x 10^{-6}]	-[12.20629]	-0.3454				
	c(13.7) = [4.97 x 10^{-6}]	-[12.21250]	-0.5764				
DMS	c(0.5) = [1.18 x 10^{-5}]	-[11.34829]	-0.0161	1.239	-11.486	[1.0E-05]	0.617
	c(0.5) = [1.18 x 10^{-5}]	-[11.34622]	-0.0161				
	c(4.6) = [5.91 x 10^{-6}]	-[12.03967]	-0.1579				
	c(9.1) = [5.95 x 10^{-6}]	-[12.03282]	-0.3454				
	c(13.7) = [5.91 x 10^{-6}]	-[12.03903]	-0.5764				
DMDS	c(0.5) = [5.61 x 10^{-6}]	-[12.09159]	-0.0161	1.191	-12.224	[4.9E-06]	0.617
	c(0.5) = [5.62 x 10^{-6}]	-[12.08952]	-0.0161				
	c(4.6) = [2.88 x 10^{-6}]	-[12.75629]	-0.1579				
	c(9.1) = [2.90 x 10^{-6}]	-[12.74945]	-0.3454				
	c(13.7) = [2.89 x 10^{-6}]	-[12.75565]	-0.5764				
CH_4	c(0.5) = 5.23 x 10^{-4}	-7.55681	-0.0161	4.495	-7.653	4.7E-04	0.997
	c(0.5) = 5.92 x 10^{-4}	-7.43261	-0.0161				
	c(4.6) = 1.44 x 10^{-4}	-8.84761	-0.1579				
	c(9.1) = -1.60 x 10^{-5}	–	-0.3454				
	c(13.7) = -2.59 x 10^{-5}	–	-0.5764				
	c(29.7) = 6.89 x 10^{-10}	-13.6023	-2.9957				

Correcting for background concentrations of methane resulted in negative concentrations at the mid and high levels. In order to have a minimum of three data points for regression, a value of 0.001 ppbv was input at 0.95 Z$_b$.

A.4 Calculation of Emission Rates

Emission rates are calculated using the following equation:

$$E = C_o W U_{10} \int_0^{Z_b} \left(\frac{Z}{10}\right)^p \left(1 - \frac{Z}{Z_b}\right)^b dz$$

where:

E = emission rate, g/s
C_o = ground level pollutant concentration, g/m^3
W = crosswind length of the sample path, m
U_{10} = average wind velocity at 10 meters, m/s
Z_b = pollutant boundary layer height, m
p = wind profile exponent
b = emission profile exponent

The integral is calculated numerically using 0.1 meter increments for Z. In the emission calculation workbook, the numeric integration is done using a Visual Basic for Applications macro. Input data required for calculation is read from specific cells on the active worksheet. The result of the calculation, along with key input data used in the calculation, is output to the worksheet. An example of the code used for calculation and summation of the integral is shown below.

```
For J = 1 To nElem
    rscH2SArr(z) = ((z / 10) ^ p) * ((1 - (z / Zb)) ^ b5) * dz
    SumIntegralrscH2S = SumIntegralrscH2S + rscH2SArr(z)
    z = z + dz
Next
```

The array, in this example “rscH2SArr(z)”, is a dynamic array whose dimensions (number of elements) are dependent on the height Z_b. The number of elements in the array is given by the following equation:

```
nElem = Fix(Zb) * 10 + 1
```

Coded calculation loops, such as the one above for hydrogen sulfide with a combined emission profile exponent, are created for each compound. Values of p, Z_b, and b are read into the macro from the cells on the worksheet. All other variables and counters in the calculation loop are initially set to zero before calculation begins. The increment for numeric integration, dz, equals 0.1. The loop will be executed ‘nElem’ times. An abbreviated sample of code loop execution is shown below for this one case. Content of the “rscH2SArr(z)” array is plotted in Figure A-4.

nElem = Fix(31.31) * 10 + 1 = 31 x 10 + 1 = 311

J = 1, z = 0 rscH2SArr(z) = ((0 / 10) ^ 0.19) * ((1 - (0 / 31.31)) ^ 3.236) * 0.1 = 0
SumIntegralrscH2S = 0 + 0 = 0
z = 0 + 0.1 = 0.1

J = 2, z = 0.1 rscH2SArr(z) = ((0.1 / 10) ^ 0.19) * ((1 - (0.1 / 31.31)) ^ 3.236) * 0.1 = 0.040504612
SumIntegralrscH2S = 0 + 0.040504612 = 0.040504612
z = 0.1 + 0.1 = 0.2

J = 3, z = 0.2 rscH2SArr(z) = ((0.2 / 10) ^ 0.19) * ((1 - (0.2 / 31.31)) ^ 3.236) * 0.1 = 0.045855809
SumIntegralrscH2S = 0.040504612 + 0.045855809 = 0.086360421
z = 0.2 + 0.1 = 0.3

J = 4, z = 0.3 rscH2SArr(z) = ((0.3 / 10) ^ 0.19) * ((1 - (0.3 / 31.31)) ^ 3.236) * 0.1 = 0.04909436
SumIntegralrscH2S = 0.086360421 + 0.04909436 = 0.135454781
z = 0.2 + 0.1 = 0.3

J = 5, z = 0.4 rscH2SArr(z) = ((0.4 / 10) ^ 0.19) * ((1 - (0.4 / 31.31)) ^ 3.236) * 0.1 = 0.051372495
SumIntegralrscH2S = 0.135454781 + 0.051372495 = 0.186827276
z = 0.3 + 0.1 = 0.4

.

.

.

.

J = 311, z = 31.0 rscH2SArr(z) = ((31.0 / 10) ^ 0.19) * ((1 - (31.0 / 31.31)) ^ 3.236) * 0.1 = 4.07 x 10^{-8}
SumIntegralrscH2S = 6.233202258 + 4.07 x 10^{-8} = 6.233202299
z = 31 + 0.1 = 31.1

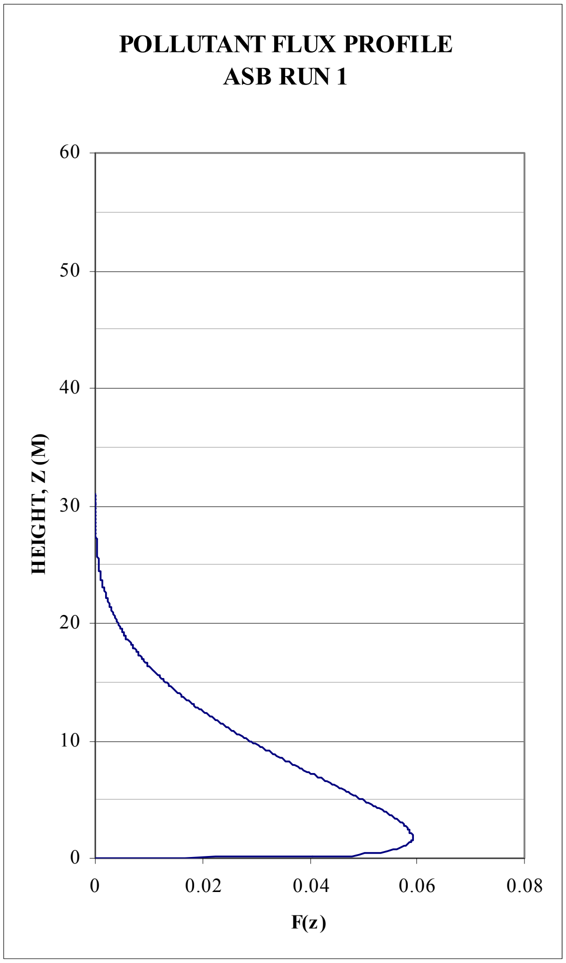

Figure A-4 Pollutant Flux Profile Plot for the Example Problem

Once numeric integration is complete, the emission rate is calculated by multiplying the result by the ground-level concentration (c_o), the crosswind path width (W), and the 10-m horizontal velocity (U_{10}).

rscH2Semission = C0H2S * W * U10 * SumIntegralrscH2S
rscH2Semission = $(4.26 \times 10^{-5}) \times (412) \times (4.79) \times (6.233202299) = 0.524$ g/s

REFERENCES

Gifford, F.A. 1976. Turbulent diffusion typing schemes. A review. *Nuclear Safety* 17(1):68-85.

Kunkel, B.A. 1985. *Development of an atmospheric diffusion model for toxic chemical releases*. NTIS: AD/A169-135. Air Force Geophysics Laboratory, Hanscom AFB.

APPENDIX H – NCASI TB NO. 1000, MECHANISTIC APPROACH FOR ESTIMATING HYDROGEN SULFIDE EMISSIONS FROM WASTEWATER TREATMENT PLANTS

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NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

MECHANISTIC APPROACH FOR ESTIMATING HYDROGEN SULFIDE EMISSIONS FROM WASTEWATER TREATMENT PLANTS

TECHNICAL BULLETIN NO. 1000
DECEMBER 2012

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Acknowledgments

This bulletin was prepared by James Palumbo, Senior Research Engineer at the NCASI Northern Regional Center and Zach Emerson, Senior Research Engineer at the NCASI Southern Regional Center. Rob Crawford, Ann Crapo, Ed Hopwood, Bill Rice, Derek Sain, and Jim Stainfield of the NCASI Southern Regional Center collected the emissions data for model testing. Brad Upton and Diana Cook of the NCASI West Coast Regional Center supervised the laboratory experiments which characterized sulfide generation and oxidation processes in pulp and paper wastewaters. Van Maltby and Laurel Eppstein of the NCASI Northern Regional Center collected the data characterizing the gas emissions from accumulated sludge in wastewater treatment basins.

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Cite this report as:

National Council for Air and Stream Improvement, Inc. (NCASI). 2012. *Mechanistic approach for estimating hydrogen sulfide emissions from wastewater treatment plants*. Technical Bulletin No. 1000. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.

PRESIDENT'S NOTE

NCASI has maintained a long-standing research focus on the origin and ultimate fate of reduced sulfur compounds in forest product industry wastewaters. This research has included the development of aqueous measurement methods, odor investigation procedures, and large-scale emissions studies. An extension to this work is the development of a model to estimate hydrogen sulfide emissions from wastewater treatment basins. This Technical Bulletin describes such a model composed of various observed relationships developed by NCASI staff and selected from the published literature describing the fate, transport, and atmospheric emissions of hydrogen sulfide at wastewater treatment basins. This bulletin serves primarily as a user manual, providing step-by-step instruction for the first-time user. However, it also includes substantive documentation regarding model algorithms, experience with model performance, sensitivity of model predictions to input variables, and use of the model for making predictions of sulfide emission rate changes that may occur due to alterations in wastewater composition or wastewater treatment plant configuration.

The model presented is intended for use as a method for estimating the emission rate of hydrogen sulfide from wastewater treatment basins and has been designed and tested on aerated stabilization basins and primary settling basins. Six processes are included in the model: wastewater transport, sulfide dissociation, generation, oxidation, volatilization, and benthic gas release. The hydrogen sulfide emissions rate is estimated based upon various basin chemical and physical properties such as pH, dissolved oxygen concentration, and aerator configuration. A field testing program indicated that the model can make reasonable predictions of the average daily hydrogen sulfide emission rate at industry aerated stabilization basins and non-aerated primary settling basins.

The model has been developed to run on computers with Microsoft Excel and is available to members on NCASI's website. This software is designed for use by industry personnel familiar with wastewater treatment processes but not necessarily with computer modeling or hydrogen sulfide chemistry. This model may be useful to those wishing to make estimates of hydrogen sulfide emissions from wastewater treatment basins for various regulatory purposes, such as the Toxics Release Inventory (TRI) Program or the National Pollutant Release Inventory (NPRI) reporting, or as part of an odor management study.

Technical Bulletin No. 1000. As NCASI approaches its 70th anniversary (in 2013), the publication of Technical Bulletin No. 1000 represents a significant milestone in the organization's history. This report serves as a bookend with NCASI's first Technical Bulletin, titled *Sampling and Analysis of Air-Borne Gaseous Effluents Resulting from Sulfate Pulping,* prepared under the direction of Dr. E. R. Hendrickson and released in 1957, which consisted of a review of the literature on the analysis of gaseous sulfur compounds. The publication of NCASI Technical Bulletin No. 1 led to subsequent development of field sampling methods and field testing at a kraft mill in the southern U.S.

During the half-century between these two reports, the industry has achieved a dramatic reduction of its environmental footprint, and NCASI has played a key role in providing support to its member companies along the way. Originally conceived as an organization focused exclusively on pulp mill effluents, the National Council has since expanded its technical capabilities to provide expertise in issues associated with other media, together with capabilities in wood products issues, matters related to product stewardship, and environmental aspects related to forest management. Publishing 1000 comprehensive reports is a significant milestone for any organization, but NCASI's accomplishment is even more significant, given the important role that these publications have played in reshaping the environmental practices of an entire industry over a period of nearly seven decades. The long list of NCASI Technical Bulletins reflects the growth of societal expectations in regard to environmental and sustainability issues, as well as the extraordinary progress that the forest products industry has made in responding to those expectations.

Ron Yeske

Ronald A. Yeske

December 2012

NOTE DU PRÉSIDENT

Depuis plusieurs années, NCASI a placé une priorité importante sur les travaux de recherches liés à la compréhension de l'origine et du devenir ultime des composés de soufre réduit dans les effluents de l'industrie des produits forestiers. Ces recherches comprenaient entre autre le développement de méthodes de mesure en milieux aqueux, de procédures d'investigation des odeurs ainsi que d'études à grande échelle des émissions à l'atmosphère. Par extension, ce travail a ainsi mené au développement d'un modèle permettant d'estimer les émissions de sulfure d'hydrogène des bassins de traitement des effluents. Ce bulletin technique décrit ce modèle qui comprend diverses corrélations observées et développées par le personnel de NCASI ainsi que d'autres corrélations tirées de littérature pertinente et décrivant les émissions de sulfure d'hydrogène des bassins de traitement des effluents ainsi que leur devenir dans l'environnement. Ce bulletin est en fait un manuel d'utilisation du modèle, offrant des instructions étape-par-étape pour les utilisateurs débutants. Par ailleurs, ce bulletin inclut aussi des informations détaillées à propos des algorithmes utilisés dans le modèle, des essais réalisés pour évaluer la performance du modèle, la sensibilité des prédictions du modèle en fonction des variables de modélisation et finalement, la possibilité d'utiliser le modèle pour prédire la variation probable des taux d'émissions de sulfure d'hydrogène due à des changements de composition de l'effluent ou à des modifications de configuration du système de traitement des effluents.

Ce modèle constitue un outil d'estimation des taux d'émission de sulfure d'hydrogène provenant de bassins de traitement des effluents; il a été conçu et testé pour des bassins de stabilisation aérés et des bassins de décantation primaire. Six procédés sont compris dans le modèle: mouvements des effluents, dissociation du sulfure, génération, oxydation, volatilisation et libération de gaz benthique. Le taux d'émission du sulfure d'hydrogène est estimé à partir de diverses propriétés chimiques et physiques des bassins telles que : pH, concentration d'oxygène dissout et configuration des aérateurs. Un programme de mesures sur le terrain a permis de confirmer que le modèle procurait des estimations réalistes des taux d'émissions journaliers moyens de sulfure d'hydrogène provenant des bassins aérés de stabilisation et de bassins non-aérés de décantation primaire présents dans l'industrie.

Le modèle a été conçu de façon à être utilisé sur des ordinateurs équipés de Microsoft Excel et est disponible aux membres sur le site web de NCASI. Ce logiciel est conçu pour le personnel de l'industrie ayant une connaissance des procédés de traitement des effluents sans pour autant être familier avec les algorithmes de modélisation logicielle, ni avec la chimie du sulfure d'hydrogène. Ce modèle sera utile aux personnes désirant effectuer une estimation des émissions de sulfure d'hydrogène des bassins de traitement des effluents à des fins de déclarations réglementaires des rejets de polluants tel que le Toxics Release Inventory (TRI) des États-Unis ou l'Inventaire national des rejets de polluants (INRP) du Canada ou encore pour des études de gestion des odeurs.

Bulletin technique n^{o} 1000. À l'approche du soixante-dixième anniversaire de fondation du NCASI (en 2013), la publication du bulletin technique n^{o} 1000 représente un jalon important dans l'histoire de l'organisation. Ce rapport peut être vu comme une progression dans une longue lignée de documents produits par NCASI et débutant par le tout premier bulletin technique intitulé *Échantillonnage et analyse des effluents atmosphériques gazeux générés par le procédé de pâte kraft,* préparé sous la direction du Dr. E. R. Hendrickson et publié en 1957. Ce premier bulletin technique présentait une revue de littérature sur l'analyse des composés de soufre à l'état gazeux. La publication du bulletin technique n^{o} 1 de NCASI a mené au développement ultérieur de méthodes d'échantillonnage et ensuite suivi de programmes d'échantillonnage dans des fabriques de pâtes kraft du sud-est des États-Unis.

Durant les cinq décennies qui séparent ces deux rapports, l'industrie a réalisé une réduction dramatique de son empreinte environnementale et NCASI a joué un rôle clé dans le soutien à ses entreprises membres en cours de route. Conçue à l'origine comme une organisation focalisée exclusivement sur les effluents des fabriques de pâtes et papiers, NCASI a depuis élargi ses capacités techniques afin d'apporter une expertise pour les questions liées à d'autres médias environnementaux, ainsi que des capacités pour soutenir l'industrie des produits du bois, aux questions liées à la gestion des produits et aux aspects environnementaux de la gestion des forêts. La publication de 1000 rapports exhaustifs est une étape importante pour toute organisation, mais l'accomplissement de NCASI est encore plus significatif, compte tenu du rôle important que ces publications ont joué dans la refonte des pratiques environnementales d'une industrie tout entière sur une période de près de sept décennies. La longue liste de bulletins techniques de NCASI reflète la croissance des attentes de la société en ce qui concerne les questions environnementales et le développement durable, ainsi que les progrès extraordinaires que l'industrie des produits forestiers a fait pour répondre à ces attentes.

Ronald A. Yeske

Décembre 2012

MECHANISTIC APPROACH FOR ESTIMATING HYDROGEN SULFIDE EMISSIONS FROM WASTEWATER TREATMENT PLANTS

TECHNICAL BULLETIN NO. 1000
DECEMBER 2012

ABSTRACT

The National Council for Air and Stream Improvement (NCASI) has developed a model (H2SSIM) of sulfide fate and transport in wastewater treatment basins. H2SSIM provides hydrogen sulfide emissions estimates from wastewater treatment basins used by the forest products industry. This bulletin serves as the user manual and documentation for H2SSIM and provides step-by-step instructions for the user interested in estimating H_2S emissions from an industry wastewater treatment basin. The documentation section describes the underlying model equations, parameters, and inputs. Included in the documentation section are the results of a model testing program comparing H_2S emissions estimates from H2SSIM to those measured in the field at several industry wastewater treatment basins. The testing indicates that H2SSIM estimated the daily average H_2S emission rate at four industry ASBs with an estimated average relative error of +/- 27%. Limited testing at two primary settling basins and one primary clarifier indicated a similar error range at these basins. A sensitivity analysis performed on the model inputs indicated that wastewater pH and oxidation reduction potential are critical to model performance and thus should be characterized as accurately as possible. Information describing the sulfide load, dissolved oxygen concentration, temperature, geometry, and aeration characteristics of the basin is also necessary to run the model.

KEYWORDS

emissions, hydrogen sulfide, model, wastewater, wastewater treatment basins

RELATED NCASI PUBLICATIONS

Technical Bulletin No. 956 (September 2008). *Emissions of Reduced Sulfur Compounds and Methane from Kraft Mill Wastewater Treatment Plants.*

Technical Bulletin No. 949 (May 2008). *Summary of Industry Experience with Odor Measurements at Wastewater Treatment Plants.*

Technical Bulletin No. 933 (June 2007). *Development and Application of a Method for Measuring Reduced Sulfur Compounds in Pulp and Paper Wastewaters.*

Technical Bulletin No. 849 (August 2002). *Compilation of Speciated Reduced Sulfur Compounds and Total Reduced Sulfur Emission Data for Kraft Mill Sources.*

Technical Bulletin No. 511 (January 1986). *Simulation of Organic Compound Removal in Biological Wastewater Treatment Processes.*

Technical Bulletin No. 458 (January 1985). *User Manual for NCASI Aerated Stabilization Basin Model and Guidance for its Use.*

APPROCHE MÉCANISTE POUR ESTIMER LES MISSIONS DE SULFURE D’HYDROGÈNE DE SYSTÈMES DE TRAITEMENT DES EFFLUENTS

BULLETIN TECHNIQUE N^{O} 1000
DÉCEMBRE 2012

RÉSUMÉ

Le Conseil national pour l’amélioration de l’air et des cours d’eau (NCASI) a développé un modèle (H2SSIM) permettant d’estimer le devenir dans l'environnement du sulfure émis des bassins de traitement des effluents. H2SSIM fournit des estimations des émissions de sulfure d’hydrogène provenant des bassins de traitement des effluents utilisés dans l’industrie des produits forestiers. Ce bulletin sert de manuel d’utilisation et de document de référence pour le modèle H2SSIM et offre des instructions étape-par-étape pour les utilisateurs désirant estimer les émissions de H_2S de bassins de traitement des effluents dans l’industrie des pâtes et papiers. La section de la documentation décrit les équations sous-jacentes du modèle et les paramètres et données à entrer dans celui-ci. Les résultats d'un programme d'essais comparant les émissions de H_2S estimées par le modèle H2SSIM à celles mesurées sur le terrain à plusieurs bassins de traitement des effluents sont inclus dans la section documentation. Les tests ont démontré que le modèle H2SSIM estimait des taux quotidiens moyens d'émission de H_2S de quatre BSA avec une erreur relative moyenne de + / - 27%. Des tests limités réalisés à deux bassins de décantation primaires et à un clarificateur primaire indiquaient une erreur relative semblable pour ces bassins. Une analyse de sensibilité effectuée sur les données d'entrée du modèle a indiqué que le pH des effluents et le potentiel d'oxydoréduction sont des paramètres critiques à la performance adéquate du modèle et devraient donc être caractérisées aussi précisément que possible. Des données décrivant la charge de sulfure, la concentration en oxygène dissous, la température, la géométrie et les caractéristiques du bassin sont également nécessaires pour faire fonctionner le modèle.

MOTS-CLÉS

émissions, sulfure d’hydrogène, modèle, effluents, bassins de traitement des effluents

AUTRES PUBLICATIONS DE NCASI

Bulletin technique n^{o} 956 (septembre 2008). *Emissions of Reduced Sulfur Compounds and Methane from Kraft Mill Wastewater Treatment Plants*.

Bulletin technique n^{o} 949 (mai 2008). *Summary of Industry Experience with Odor Measurements at Wastewater Treatment Plants.*

Bulletin technique n^{o} 933 (juin 2007). *Development and Application of a Method for Measuring Reduced Sulfur Compounds in Pulp and Paper Wastewaters.*

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Bulletin technique n^{o} 511 (janvier 1986). *Simulation of Organic Compound Removal in Biological Wastewater Treatment Processes*.

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MECHANISTIC APPROACH FOR ESTIMATING HYDROGEN SULFIDE EMISSIONS FROM WASTEWATER TREATMENT PLANTS

1.0 INTRODUCTION

The National Council for Air and Stream Improvement (NCASI) has developed a model of sulfide (H_2S, HS^-, S^{2-}) fate and transport in wastewater treatment basins used by the pulp and paper industry. The primary objective for this model is to provide the industry a tool which allows for the accurate estimation of hydrogen sulfide emissions to the atmosphere from wastewater treatment basins. The model is also designed for predicting future hydrogen sulfide emissions under modified wastewater basin operating conditions. Operating in this predictive mode, the model provides the user the ability to study the effect of alternative strategies for managing hydrogen sulfide emissions from wastewater treatment systems.

The sulfide model discussed in this bulletin is a computer program designed to solve differential equations describing the sulfide fate and transport processes in wastewater treatment basins at a steady state condition. The model equations represent a synthesis of the research conducted by NCASI and others as reported in the scientific literature. The model structure is based upon NCASI's BOD and TSS removal model, SASBV4 (NCASI 1985a), which has been thoroughly documented and tested. The sulfide model simulates sulfide loading and transport in a manner similar to the way SASBV4 simulates BOD loading and transport while incorporating the fate processes that are specific to sulfide. These processes include sulfide generation, dissociation, oxidation, volatilization, and benthic gas release.

This bulletin serves two primary purposes. The first is as a user manual providing an overview and guidance for users interested in setting up and running the model for a specific wastewater basin. The second purpose is to document the model as well as describe its testing at several pulp and paper wastewater treatment basins where measured hydrogen sulfide emission rates are available.

2.0 MODEL APPLICABILITY

2.1 Applicable Wastewater Treatment Basins

The model is applicable to most flow-through wastewater treatment basins and has been designed to offer flexibility towards the adaptation of the model to the wide range of design and operational configurations of wastewater treatment basins encountered in the pulp and paper industry. However, most development work and testing to this point has focused on aerated stabilization basins (ASBs). These ASBs have the following characteristics.

- The hydraulic residence time ranges from 2.4 to 9.6 days.
- They contain mechanical surface aeration equipment.
- The total sulfide concentration of the inlet ranges from 0.5 to 41 mg/L.
- Wastewater temperatures range from 20.5 to 43°C.
- Wastewater pH ranges from 6.4 to 8.8.
- Front zone wastewater dissolved oxygen concentration ranges from 0.1 to 0.5 mg/L.

Emission predictions are likely most reliable for ASBs with conditions similar to those observed at the ASBs which were used to test the model. Additional caution should be used when applying the model to ASBs which exhibit conditions outside the above ranges.

H2SSIM has undergone limited testing at industry primary settling basins but not at primary clarifiers. While the model is designed to simulate emissions from these basin types, the user is advised to apply appropriate caution with the results until the model can be more thoroughly evaluated. H2SSIM has not been tested for activated sludge basins. However, emissions measurements by NCASI (2008b) have indicated that these basins emit relatively small amounts of H_2S. Additional information regarding model testing is contained in Section 7 of this bulletin.

2.2 Applicable Types of Model Analyses

There are two general types of analyses applicable with H2SSIM. The first is the estimation of H_2S emissions at current operating conditions. In this type of analysis, the user enters information into the model that reflects the current state of the basin and the model provides an estimate of hydrogen sulfide emissions at these conditions. Possible applications under this type of analysis include

- screening of several basins to identify primary sources of hydrogen sulfide emissions;
- documentation of hydrogen sulfide emissions; and
- understanding the root causes of hydrogen sulfide emissions in a basin.

The second type of analysis is the prediction of hydrogen sulfide emissions under a change to the existing system. Examples of system changes that could be evaluated by the model include

- pretreatment of influent to reduce the sulfide load;
- addition of aeration equipment; and
- adjustment of basin pH or temperature.

This type of analysis offers the model user a means of evaluating the effectiveness of various hydrogen sulfide control options prior to the expenditure of capital or operating resources.

3.0 MODEL OVERVIEW

H2SSIM is a computer program which numerically solves differential equations describing sulfide and sulfate transport through a pulp and paper wastewater treatment basin at steady state conditions. The state variables modeled are flow, sulfide, and sulfate. Sulfide in this context is defined as total sulfide (NCASI 2007); however, the dissociated forms of sulfide (H_2S, HS^-, S^{2-}) are considered in the model processes. The model approximates non-ideal flow patterns by utilizing a segmented framework (i.e., continuously stirred tank reactors in series) with advective flow and mixing between segments. In addition to liquid transport, the model considers external sulfide loads, liquid to air mass transfer, and chemical and biochemical reactions that generate and remove sulfide. A generalized model control volume depicted on a sulfide mass balance basis is shown in Figure 3.1.

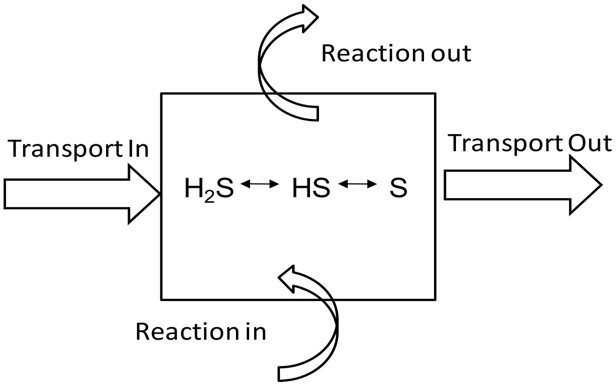

Figure 3.1 Generalized Sulfide Mass Balance around a Control Volume

The model estimates hydrogen sulfide emission rates by utilizing a mass balance approach to solve for the liquid total sulfide and sulfate concentrations. The model inputs which describe the mass transfer reaction rates are imported by the user to reflect site-specific conditions. The equations are then solved numerically for the steady state condition providing estimates of water column sulfide concentrations and transport and reaction rates. The general mass balance equation for a single model volume is shown in Equation 3.1.

$$V\frac{dc}{dt} = W + (Q_{i-1} + E_{i-1})c_{n-1} - (Q_i + E_i + E_{i-1})c_n + E_i c_{n+1} \pm R_{1,2,3} \qquad \text{Equation 3.1}$$

Where: V = Volume (L^3)
c = Concentration (M/L^3)
t = Time (T)
W = Load (M/T)
Q = Advective Flow (L^3/T)
E = Flow due to mixing (L^3/T)
$R_{1,2,3}$ = Reactions (generation, oxidation, stripping) (M/T)
n = Model segment number
i = Flow number

And: L = length
M = mass
T = time

Equation 3.1 states that the control volume mass rate of change is equal to the sum of several individual rates that add or remove mass from the volume. These rates include influent loading, advective transport, and mixing from adjacent model segments and reactions. At steady state, the control volume's mass rate of change is equal to zero and the steady state liquid concentration is computed. Using the computed sulfide concentration and other site-specific information, the H_2S emission rate from volatilization is calculated. The emissions contribution from benthic gas bubbles is calculated separately from Equation 3.1 and summed with the emission rate from volatilization to produce the total basin emission estimate.

Sulfate is included as a state variable in the model because the sulfide generation rate can be limited by very low sulfate concentrations. The model describes sulfate as being transformed to sulfide through the generation reaction and sulfide being transformed to sulfate by oxidation. This interaction between state variables is simulated by the coupled nature of the differential equations describing the sulfide and sulfate accumulation rate.

The mathematical forms of the sulfide and sulfate equations excluding the transport and temperature correction terms and assuming aerobic conditions are presented in Equations 3.2 and 3.3.

$$\frac{dS(-II)}{dt} = k_{Gen}\left(\frac{SO_4}{SO_4+K_{SO_4}}\right)\left(\frac{K_{DO}}{DO+K_{DO}}\right) - k_{ox}S(-II)^m DO^n - K_L A\left(S(-II)F_{H2S}\right) \quad \text{Equation 3.2}$$

$$\frac{dSO_4}{dt} = -k_{Gen}\left(\frac{SO_4}{SO_4+K_{SO_4}}\right)\left(\frac{K_{DO}}{DO+K_{DO}}\right) + k_{ox}S(-II)^m DO^n \quad \text{Equation 3.3}$$

Where: S(-II) = Total sulfide (M/L^3)
SO_4 = Sulfate (M/L^3)
DO = Dissolved oxygen (M/L^3)
k_{gen} = Sulfide generation rate (M/L^3T)
K_{SO4} = Sulfate half saturation coefficient (M/L^3)
K_{DO} = Dissolved oxygen half saturation coefficient (M/L^3)
k_{ox} = Aerobic sulfide oxidation rate (T^{-1})
m = Order of reaction with respect to total sulfide (-)
n = Order of reaction with respect to dissolved oxygen (-)
K_L = Liquid-air mass transfer coefficient (L/T)
A = Surface area (L^2)
F_{H2S} = Fraction of total sulfide as H_2S (-)

The individual terms in Equations 3.2 and 3.3, along with the benthic gas generation rate, are further described in the following section.

3.1 Sulfide Transport within the Wastewater Treatment Basin

Wastewater treatment basin hydraulics differ greatly across the pulp and paper industry. A basin rarely exhibits ideal plug flow or a completely mixed hydraulic regime. In addition, many treatment systems have additional complexities such flow baffles, multiple influent points to a single basin, parallel basins or basins in series, and quiescent zones. Model hydraulics must be flexible enough to accommodate the variety of basins encountered in the industry.

An approach to model hydraulics that has been found useful for simulating wastewater basins is the tanks in series approach. The tanks in series approach models the system as a number of completely stirred tank reactors (CSTRs) arranged in series where the sum of volumes from the CSTRs is equal to the volume of the wastewater treatment basin of interest. The SASBV model for ASBs (NCASI 1985a) is a tank in series model which also includes the ability to simulate mixing (i.e., backmixing). The tank in series with backmix approach was selected as the hydraulic basis for the H2SSIM because it has proven to be flexible and effective in simulating industry wastewater treatment basin hydraulics. A single tank model will provide completely mixed hydraulics, while increasing the number of tanks allows to user to simulate incompletely mixed to approximate plug type regimes.

Additional capabilities were added for H2SSIM because the SASBV hydraulics proved limiting for certain industry basins. These cases often involved multiple influent loads such as condensate hard piping. To provide the user with tools to address this complexity, H2SSIM includes the capability to simulate multiple influent loads to a single wastewater basin.

3.2 Sulfide Dissociation

Inorganic, free sulfide can exist in three forms, the concentrations of which depend upon the wastewater pH. H2SSIM calculates the effect of pH on the predominant sulfide form present in the wastewater. This calculation is significant because only H_2S is a volatile form of sulfide.

At the near neutral pH conditions encountered in most wastewaters undergoing biological treatment, hydrogen sulfide dissociates to yield a hydrogen ion and hydrogen sulfide ion (Equation 3.4).

$$H_2S \leftrightarrow H^+ + HS^- \qquad \text{Equation 3.4}$$

At very high pH levels, the hydrogen sulfide ion can dissociate again to a hydrogen ion and sulfur ion (Equation 3.5).

$$HS^- \leftrightarrow H^+ + S^{2-} \qquad \text{Equation 3.5}$$

When the reaction is considered to be at equilibrium, the reaction and concentration products can be defined by Equations 3.6 and 3.7.

$$K_1 = \frac{[H^+][HS^-]}{H_2S} \qquad \text{Equation 3.6}$$

$$K_2 = \frac{[H^+][S^{2-}]}{HS^-} \qquad \text{Equation 3.7}$$

If the reactions represented in Equations 3.4 and 3.5 are considered to occur much faster than the other processes in the overall mass balance equation, a local equilibrium holds (Chapra 1997) and the sulfide dissociation reaction can be solved outside of the sulfide mass balance equation.

If a local equilibrium exists for sulfide dissociation, the fraction of total sulfide that exists as each species at the specified pH can be calculated (Equations 3.8 through 3.10).

$$F_{HS} = \frac{K_1[H^+]}{1+K_1[H^+]+K_1K_2[H^+]^2} \qquad \text{Equation 3.8}$$

$$F_{H_2S} = \frac{K_1K_2[H^+]^2}{1+K_1[H^+]+K_1K_2[H^+]^2} \qquad \text{Equation 3.9}$$

$$F_S = \frac{1}{1+K_1[H^+]+K_1K_2[H^+]^2} \qquad \text{Equation 3.10}$$

Where: F_{HS} = Fraction of total sulfide as HS^-

F_{H2S} = Fraction of total sulfide as H_2S

F_S = Fraction of total sulfide as S^{2-}

The fraction of each sulfide species calculated by these equations with pKa1 = 7.04 and pKa = 11.96 is shown in Figure 3.2.

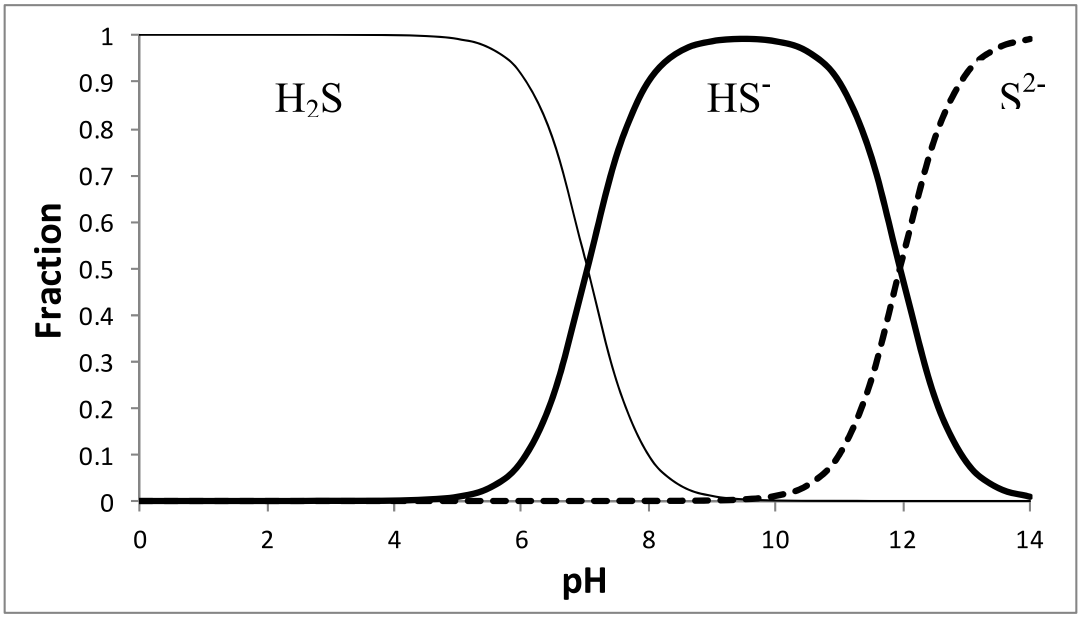

Figure 3.2 Fraction of Sulfide Species as a Function of Wastewater pH

The fractions of each sulfide species are calculated internally by H2SSIM and used to define the concentration of each dissociated form as a function of pH and total sulfide concentration. A critical use of these fractions is calculating the amount of sulfide available to volatilize to the atmosphere as H_2S (i.e., the volatilization term in Equation 3.2).

3.3 Generation of Sulfide in Wastewater

Sulfide can be generated in wastewater when conditions are favorable. These conditions include sufficient concentration of the reactants and an anoxic (i.e., dissolved oxygen is near zero) environment. A quantitative expression relating the sulfide generation rate to temperature, sulfate concentration, and oxygen concentration in pulp and paper wastewaters has been developed based on laboratory batch reactor experiments. The technical details of that study and subsequent equation development are reported in Appendix A.

The expression for sulfide generation in pulp and paper wastewaters is presented in Equation 3.11.

$$R_1 = k_{gen}\left(\frac{SO_4}{K_{SO_4} + SO_4}\right)\left(\frac{K_{DO}}{K_{DO} + DO}\right) \qquad \text{Equation 3.11}$$

Where: R_1 = Sulfide generation rate (M/L^3T)
SO_4 = Sulfate concentration (M/L^3)
DO = Dissolved oxygen concentration (M/L^3)
k_{gen} = Generation rate coefficient at 20 °C (M/L^3T)
K_{SO4} = Sulfate half saturation coefficient (M/L^3)
K_{DO} = Oxygen half saturation coefficient (M/L^3)

Equation 3.11 states that the rate of sulfide generation is proportional to an empirical rate coefficient and may be limited by low sulfate concentrations or the presence of oxygen.

The rate of sulfide generation is also affected by temperature. The optimal temperature for sulfate reducing bacteria has been reported as 25 to 35°C. The temperature correction should account for bacterial inhibition at temperatures greater than 35°C as in Equations 3.12 and 3.13.

When the wastewater temperature is 35°C or less, the model uses

$$\mathrm{k_{Temp}} = k_{20}\theta^{Temp-20} \qquad \text{Equation 3.12}$$

Where θ = Temperature coefficient
k_{Temp} = Rate coefficient at actual temperature
k_{20} = rate coefficient at 20°
Temp = Temperature °C

When the wastewater temperature is greater than 35°C, the model uses

$$k_{Temp} = k_{20}\theta^{15} * \theta_2^{Temp-35} \qquad \text{Equation 3.13}$$

Where: θ_2 = Second temperature coefficient

The overall effect of Equations 3.12 and 3.13 is an increasing rate coefficient up to 35 °C. As temperatures increase further, the rate coefficient decreases. Details concerning Equation 3.13 can be found in NCASI (1985b).

3.4 Sulfide Oxidation

Sulfide is oxidized rapidly to sulfate and several intermediate sulfur species when exposed to aerobic conditions. A commonly used sulfide oxidation rate equation was found to adequately describe sulfide oxidation data from pulp and paper mill wastewaters (Palumbo, Brown, and Stratton 2010). This equation is presented here as Equation 3.14.

$$R_2 = k_{ox} S_{-II}{}^{m} (DO)^{n} \qquad \text{Equation 3.14}$$

Where: R_2 = Rate of sulfide oxidation (M/L^3T)
k_{ox} = Aerobic sulfide oxidation coefficient (T^{-1})
S_{-II} = Sulfide concentration (M/L)
DO = Dissolved oxygen concentration (M/L)
m = order of reaction with respect to sulfide (-)
n = order of reaction with respect to oxygen (-)

The sulfide oxidation rate changes as a function of pH. This change is represented in the model through a varying oxidation rate coefficient. The relationship between the rate coefficient and pH is shown in Equation 3.15. The derivation of Equation 3.15 is described in Appendix B.

$$k_{ox} = 7.16 * (1 - \exp(-0.84 * (pH - 6.15)) \qquad \text{Equation 3.15}$$

In Equation 3.15, it is assumed that the oxidation rate coefficient is zero below a pH value of 6.15.

When oxygen is absent, sulfide is more slowly oxidized in wastewaters. The rate of sulfide oxidation under anoxic conditions can be modeled using a modification of Equation 3.14. The development of this equation is presented in Appendix B.

$$R_2 = k_{anox} S_{-II}^{m} \qquad \text{Equation 3.16}$$

Where k_{anox} = Anoxic sulfide oxidation rate coefficient (T^{-1})

H2SSIM selects which oxidation equation to use based upon the redox condition ("aerobic" or "anoxic") input by the user. In most basins that contain aeration equipment, the redox condition is aerobic and Equation 3.15 is used to specify the oxidation rate. In many primary settling ponds and primary clarifiers which are not aerated, the redox condition is anoxic. In these basins, Equation 3.16 is used to specify the oxidation rate.

Aerobic and anoxic oxidation rates are affected by temperature. Equation 3.12 is used to adjust both the anoxic and aerobic rate coefficients to account for temperature effects.

3.5 Sulfide Volatilization

H_2S is volatile in aqueous systems and can be emitted from the surface of wastewater treatment basins. The rate of sulfide (as H_2S) volatilization is mathematically represented by Equation 3.17. In Equation 3.17, F_{H2S} modifies the total sulfide concentration (S_{-II}) so that only sulfide which exists as H_2S is volatilized.

$$R_3 = K_L A * (S_{-II} F_{H2S}) \qquad \text{Equation 3.17}$$

Where: R_3 = Rate of sulfide volatilization (M/L^3T)
S_{-II} = Total sulfide concentration (M/L^3)
F_{H2S} = Fraction of total sulfide that is H_2S (-)
K_L = Overall mass-transfer coefficient (L/T)
A = Surface area (L^2)

The mass transfer coefficient is estimated using semi-empirical methods developed by Thibodeaux 1996, Thibodeaux and Parker 1974, and Thibodeaux, Parker, and Heck 1982. In an industrial wastewater treatment basin, the mass-transfer coefficient is dependent upon basin dimensions, aeration characteristics, meteorological conditions and the physical and chemical characteristics of the air/water/sulfide system. A summary of the mass-transfer estimation methods is presented in Appendix C.

3.6 H_2S Release from Accumulated Sludge

The sludge which often accumulates at the bottom of wastewater treatment units such as ASBs and primary settling basins is devoid of oxygen. Because an abundance of sulfate and organic matter is typically available in pulp and paper wastewaters, the accumulated sludge possesses conditions suitable for sulfide generation in the porewater. A significant transport pathway from the sludge porewater to the atmosphere is via gas bubbles which escape the sludge bed and rise to the surface of the water column. These gas bubbles are composed primarily of methane, carbon dioxide, and nitrogen; however, in many cases they also contain a small percentage of hydrogen sulfide. An NCASI study (Owens 2005) determined an average benthic gas H_2S flux rate as 0.0145 gm m^{-2} day^{-1} at 20°C in an ASB. In a primary settling basin study a benthic gas H_2S flux rate was estimated at 0.130 gm m^{-2} day^{-1} at 20°C. These flux rates are incorporated into the H2SSIM model.

H2SSIM estimates the benthic gas H_2S emission rate by the estimated flux rate as a function of basin area (Equation 3.18).

$$E_B = \Phi A \qquad \text{Equation 3.18}$$

Where: E_B = Benthic H_2S Emissions (gm/s)

Φ = Benthic H_2S Flux Rate (gms/m^2 s)

A = Area (m^2)

The flux rate is adjusted for temperature using Equation 3.12 and a temperature correction coefficient of 1.06. This coefficient is comparable to those used for temperature correction of other benthic processes (Chapra 1997).

3.7 Numerical Integration

After the variables in Equations 3.2 and 3.3 are defined by the user, the program solves these equations for the steady state condition in each zone. These differential equations can be generally described by Equation 3.19.

$$\frac{dc}{dt} = \frac{Q}{V}(c_{in} - c) - R \qquad \text{Equation 3.19}$$

Where: $\frac{Q}{V}(c_{in} - c)$ = Net flux of c into segment (M/T)

R = Reaction occurring in segment (M/T)

In general, R is a function of c as well as the other model constituents. At steady state $\frac{dc}{dt}$ is zero and the computer program finds a value of c at which the change rate of c due to the reaction term is equal to the net influx of c due to the transport in and out of the segment.

If the loadings were time variable, the value of $\frac{dc}{dt}$ would not be zero and the value of c would be of interest at all times. In this case c can be calculated as a function of time by integration as in Equation 3.20.

$$c_{t+1} = c_t + \int_i^{i+1} \frac{dc}{dt} dt \qquad \text{Equation 3.20}$$

In H2SSIM, Equation 3.20 is used to find a steady state solution to the differential equations. At constant loads and appropriate values of total simulation time and calculation step (*dt*), c_{t+1} will eventually equal c_t for all segments, resulting in a steady state solution. The discrete form of Equation 3.20 is shown in Equation 3.21.

$$c_{t+1} = c_0 + \sum_{i=1}^{n} \left(\frac{dc}{dt}\right)_i dt \qquad \text{Equation 3.21}$$

Where: n = number of integration steps

The model uses a numerical integration procedure based on Euler's Method (Chapra 1997) to solve Equation 3.21. The order of the solution is from the upstream segment to the downstream segment. Because the derivative of a segment constituent is a function of the upstream segment concentration, the concentrations calculated at time *t* are saved in a temporary array until all the segment concentrations have been calculated for that time step, after which time the segment concentrations are updated to the temporary array values. This is done to ensure mass balances on the model constituents.

4.0 MODEL INPUT AND OUTPUT DESCRIPTIONS

There are multiple user inputs to the model which are used to describe the wastewater treatment basin's site-specific characteristics. In H2SSIM, these inputs can be divided into three general categories:

- *Basin characterization inputs* are developed by the user and describe the physical and chemical state of the basin.

- *Parameters* describe the processes occurring in the basin and may vary depending upon the nature (i.e., municipal vs. industrial) of the system. However, H2SSIM has been developed and tested for the pulp and paper industry and it is believed that the parameters do not need to be adjusted from their default values when applied to those systems.
- *Constants* are values which also describe the modeled system but are considered to be universal.

4.1 Basin Characterization Inputs

Basin characterization inputs are developed by the user from site-specific information. They are entered into H2SSIM via the H2SSIM tab. The basin characterization inputs are distributed over five numbered “Data Types” which contain related information.

4.1.1 *Data Type 1 - Site Identification Inputs*

Company Name, Facility Name, Basin Name - These inputs identify the specific wastewater treatment basin which is being modeled. These inputs are used for identification purposes and are not required to run the model.

4.1.2 *Data Type 2 - Model Zone Information*

Number of Zones- This input defines the number of model zones (1-4) that are used to characterize the basin. Guidance for setting the number of modeled zones is provided in Section 5 of this bulletin. The number of zones defaults to one if the user selects PC (primary clarifier) in the type of basin query.

Zone Location of Hardpipe- This input locates the position of a hard piped condensate stream. If no hardpipe exists the user should select “none.”

Type of Basin - This input queries the user regarding the type of system to be modeled. If the system is a primary clarifier, the model defaults to a single zone and requires the user to enter a weir height.

4.1.3 *Data Type 3 - Load Characteristics*

Flow, Sulfide, Sulfate - The load characteristic inputs set the steady state flow rate as well as the sulfide and sulfate influent concentrations for the main influent and any condensate stream. If no hardpipe condensate input stream exists (i.e., “none” is selected for the zone location of hardpipe), the hardpipe load information is not read by the model. Flow can be entered in units of MGD, MLD, cfs, or cms. Sulfide and sulfate concentrations can be entered in units of mg/L or ppb. A discussion regarding development of load characteristics and the simulation period of interest is presented in Section 5 of this bulletin.

4.1.4 *Data Type 4 - Atmospheric Conditions*

Wind speed, Ambient Temperature - The atmospheric conditions used by the model are wind speed and ambient air temperature. These values are required and should represent an average of the time period which is being simulated. Wind speed can be entered as mph or m/s. Temperature can be entered as degrees Fahrenheit or Celsius.

4.1.5 *Data Type 5 – Zone Physical and Water Column Chemical Conditions*

Dissolved Oxygen, Temperature, pH - Water column conditions characterizing dissolved oxygen concentration, temperature, and pH must be entered for each zone. These values are required and should represent an average of the time period which is being simulated (A discussion regarding development of water chemistry conditions and the simulation period of interest is presented in

Section 5 of this bulletin). Dissolved oxygen is entered as mg/L and pH is entered as standard pH units. Temperature may be entered as degrees Fahrenheit or Celsius.

Redox Status – The water column redox status of each zone is specified by the user as "aerobic" or "anoxic." Typically, mechanically aerated wastewaters such as ASBs are considered aerobic and non-aerated basins such as primary clarifiers and settling basins are considered anoxic. Additional guidance regarding the assignment of redox status to zones is presented in Section 5 of this bulletin.

Length, Width, Depth – The user must specify the physical dimensions of the zone in units of meters, feet, or yards. These dimensions characterize the volume of the basin taken up by wastewater and do not include any accumulated sludge in the basin.

Mixing – The user characterizes the mixing between zones by specifying either "none," "low," "moderate," or "high" mixing. Guidance on the selection of a mixing value is provided in Section 5.3.5.

Number of Aerators, Total Horsepower, Impellor Size, Impellor RPM, Diffused Air Flow- If the aeration equipment is surface mechanical, then the number of aerators, total horsepower, impellor size, and impellor RPMs must be specified. If the aeration equipment is diffused air only, total horsepower and diffused air flow is needed. If both types of aeration equipment are present, all entries must be used. Information regarding aerator impellor design is likely available from the manufacturer.

Weir Height – If the model is simulating emissions from a primary clarifier, the user must supply the height of the weir in meters, yards or feet. This length is the measurement of the water freefall from the top of the weir to the water surface.

4.2 Model Parameters

Model parameters can be viewed and adjusted by clicking the View Parameters button on the H2SSIM tab. The recommended default parameters have been developed and tested by NCASI through various research programs; thus, under most circumstances, changes to these values are not advised.

4.2.1 *Sulfide Generation Parameters*

k_{gen} – Sulfide Generation Rate Coefficient at 20 °C; (units = mg/L hr^{-1}) - This input parameter characterizes the maximum generation rate of sulfide in the water column. NCASI studies described in Appendix A have estimated the value of this parameter as 0.25 mg/L hr^{-1}.

KSO4 – Sulfate Half Saturation Coefficient; (units = mg/L) - This parameter identifies the concentration of sulfate at which the sulfide generation rate is halved due to limited quantities of sulfate. The value for this parameter is estimated as 10 mg/L SO_4. The basis for this value is presented in Appendix A.

KDO – Oxygen Half Saturation Coefficient; (units = mg/L) – The suggested value for this parameter is 0.05 mg/L O_2. The basis for this value is presented in Appendix A.

ThetaGen1 – Sulfide Generation Temperature Correction Factor; (units = unitless) - This correction factor is used to scale the sulfide generation rate coefficient to the water temperature of the wastewater basin. The value of this parameter has been reported at 1.06 as noted in Appendix A.

ThetaGen2 – Second Sulfide Generation Temperature Correction Factor; (units = unitless) - The correction factor is used to scale the sulfide generation rate coefficient when water temperatures are greater than 35°C. The value of this parameter has been reported at 0.965 as noted in NCASI (1985a).

4.2.2 *Sulfide Oxidation Parameters*

k_{ox} – Aerobic Sulfide Oxidation Rate Coefficient; (units = min^{-1}) – This parameter characterizes the rate of sulfide oxidation at 20°C in aerobic wastewater. The average value of the aerobic sulfide oxidation rate coefficient at neutral pH as estimated in pulp and paper wastewaters is 0.047 (Palumbo, Brown, and Stratton 2010). Because H2SSIM internally calculates the parameter as a function of pH, it is not available for adjustment by the user.

k_{anox} –Anoxic Sulfide Oxidation Rate Coefficient; (units = min^{-1}) – This parameter characterizes the rate of sulfide oxidation at 20°C in anoxic wastewater. The estimated value of the anoxic sulfide oxidation rate coefficient is 0.006 as described in Appendix B.

m – Reaction order of HS^- and H_2S with respect to sulfide; (units = unitless) - The reaction order with respect to sulfide has been estimated as 1.0 for previous sulfide oxidation research. Studies of pulp and paper wastewater oxidation (Palumbo, Brown, and Stratton 2010; Appendix B) found that a value of 1.0 for this parameter was satisfactory for these wastewaters.

n - Reaction order of HS^- and H_2S with respect to oxygen; (units = unitless) – Previous studies have reported a range of 0.1 – 0.2 (Wilmot et al. 1988; Nielsen, Vollertsen, and Hvitved-Jacobsen 2003, 2006) for this parameter. Studies focusing on pulp and paper wastewaters (Palumbo, Brown, and Stratton 2010) did not estimate this parameter with statistical significance but did indicate that the value of this parameter was likely in the range indicated by the above noted literature. The suggested value of this parameter is 0.20.

ThetaOx - Oxidation Temperature Correction Factor; (units = unitless) - The correction factor is used to scale the sulfide oxidation rate coefficients to the water temperature of the wastewater basin. The value of this parameter has been reported at 1.05 as noted in Appendix B.

4.2.3 *Aeration Parameters*

Oxygen Transfer Coefficient – Standard Oxygen Transfer Rate; (units = lbs O_2/HP/hour) - This is the clean water oxygen transfer rate of the aeration equipment tested at standard conditions. The typical value for surface aerators is 2.0.

Alpha1 – Wastewater Oxygen Transfer Ratio; (units = none) - This is the relative rate of oxygen transfer of wastewater compared to clean water. The default value for this parameter is 0.83.

Alpha 2 - Wastewater Sulfide Transfer Ratio (units = none) - This is the relative rate of hydrogen sulfide transfer of wastewater compared to clean water. The suggested value for this parameter is 0.60.

4.3 Model Constants

Model constants are defined internally and are not adjustable by the user.

pKa1 – Dissociation Constant for HS^- and H_2S; (units = unitless) – The dissociation constant for HS^- and H_2S at 25 °C is 7.04 (Ebbing 1996).

pKa2 – Dissociation Constant for HS^- and S^2; (units = unitless) – The dissociation constant for HS^- and S^{2-} at 25 °C is 11.96 (Ebbing 1996).

H_{CP} - Henry's Law Constant for H_2S in Water; (units = L atm/mol) – This constant represents the volatility of H_2S in water in a dilute system. The Henry's law constant for H_2S in water is 0.009861 L atm/mol at 30 °C (Staudinger and Roberts 1996).

$D_{H2S,Water}$ – Diffusivity of H_2S in Water; (units = cm^2/s) – The liquid-phase diffusivity of H_2S in water at 20 °C is 1.61 E-5 cm^2/s (USEPA 1994).

$D_{O2,Water}$ – Diffusivity of Oxygen in Water; (units = cm^2/s) – The liquid-phase diffusivity of oxygen in water at 20 °C is 2.40 E-5 cm^2/s (Reid and Sherwood 1958).

$D_{H2S,Air}$ – Diffusivity of H_2S in Air; (units = cm^2/s) – The gas-phase diffusivity of H2S in air at 20 °C is 0.176 cm^2/s (USEPA 1994).

$D_{Ether,Water}$ – Diffusivity of Ether in Water; (units = cm^2/s) – The liquid-phase diffusivity of ether in water at 20 °C is 8.50 E-6 cm^2/s (USEPA 1994).

ρ_{Water} – Density of Water; (units = g/mL) – The density of water is 0.9928 g/mL at 20 °C (Geankoplis 1993).

ρ_{Air} – Density of Air; (units = g/m^3) – The density of air is 1.204 g/m^3 at 20 °C (Geankoplis 1993).

ν_{Water} – Viscosity of Water; (units = kg m/s) – The viscosity of water is 1.01 E-3 kg m/s at 20 °C (Geankoplis 1993).

ν_{Air} – Viscosity of Air; (units = kg m/s) – The viscosity of air is 1.81 E-5 kg m/s at 20 °C (Geankoplis 1993).

4.4 Model Output

Model output is displayed on the Output tab. Estimates of H_2S emissions are presented in several different formats in two tables. The Basin Emissions table displays the emission estimates from the entire wastewater treatment basin (i.e., the sum of all zones). The emissions rate is presented in units of gm/s, lbs/yr, US tons/yr, metric tonnes/yr, and gm/m^2 -yr, which is the emissions rate normalized to the total basin area. The Zone Emissions table presents emissions for each individual zone in units of gm/s, lbs/yr, and gm/m^2 yr. This table also includes liquid total sulfide concentration estimates for each zone. The model parameters that were used to generate the output in the results tables are presented in the table to the right of the emissions output.

5.0 PREPARATION AND EXECUTION OF H2SSIM

This section provides instruction for users who wish to set up and properly execute H2SSIM to estimate hydrogen sulfide emissions for wastewater treatment basins. Various example scenarios are provided to help users adapt specific scenarios to the model.

There are eight general steps from the initiation of a sulfide emissions estimation project to obtaining final results.

1. Opening and initializing software
2. Selection of the desired simulation period
3. Data collection and data set assembly
4. Model zone specification
5. Input influent loads and atmospheric conditions
6. Input basin physical and chemical information
7. Model execution
8. Review output

To assist with input development, it is suggested that the user create a sketch in plan view at an approximate scale and locate physical features (such as influent and effluent locations, aerator positions, flow diversion curtains) and wastewater sample locations and results. Such a sketch can be useful when setting model zone locations and characteristics as described later.

5.1 Opening and Initializing Software

H2SSIM is contained in the Microsoft Excel spreadsheet environment and the user must have a valid copy of this program installed on their computer in order to run H2SSIM. The H2SSIM file can be downloaded into a Windows file folder from the NCASI website (www.ncasi.org). The user may create a distinct H2SSIM folder in which multiple model runs and supporting data are contained. Once H2SSIM is downloaded, it is advisable to copy and rename files (e.g., H2SSIM_Basin1) that have been modified by the user to allow for easy identification.

To open the model, double click the H2SSIM icon in the previously created folder. When the file is opened in Excel, it will be scanned for viruses and the model code will be recognized as a supplementary macro. If the system's security level is set to high, the H2SSIM code will be disabled. For the model to run, the macro security level should be set to allow macros. Depending upon the user's version of Excel, the security level can be changed via different menu options and the user is advised to consult the Help section provided in their version of Excel.

All other spreadsheet functions including saving are performed as with a typical Excel spreadsheet. The user has the option to modify the H2SSIM spreadsheet to save multiple model runs or the field data used to develop model inputs. However, certain cells which contain important information for the user are write-protected and cannot be modified. The H2SSIM source code can be viewed by pressing ALT-F11 while in the Excel environment.

5.2 Selection of a Simulation Period

The selection of the simulation period is important because the period of interest defines the scope of the data collection and the applicability of the results. Some examples of simulation periods that may be of interest to a user are

- annual average hydrogen sulfide emissions;
- emissions during low basin dissolved oxygen concentrations occurring during the summer; and
- emissions during peak BOD loading periods.

In each of the above cases, the model inputs must reflect the simulation period of interest. For example, the annual average conditions should be calculated from data collected at a frequency so that the data set truly represents an annual average and is not biased by a majority of data points collected during a brief timeframe. Another example of matching the simulation period of interest to appropriate model inputs is when estimating H_2S emissions during peak BOD loading conditions. During peak BOD loads, it is likely that not only will BOD loads increase but wastewater oxygen concentrations will decrease. It is also possible that wastewater pH and influent sulfide loads may change relative to average conditions. Thus, annual average pH and sulfide loading values would not be appropriate inputs for the peak BOD loading scenario. It is important that a user identify their simulation period of interest and define inputs that are specific for that period.

5.3 Data Collection and Database Assembly

Table 5.1 lists the site-specific data needs for the successful estimation of hydrogen sulfide emissions from a wastewater treatment basin. As discussed above these data should be collected to accurately reflect the simulation period of interest.

Table 5.1 Site-Specific Data Requirements for Sulfide Fate Model

Category	Specific Measurement
Physical Characteristics	Length, width, average depth, hydraulic tracer study[a]
Chemical Characteristics	Basin longitudinal profiles of temperature, pH, ORP, and dissolved oxygen.
Aeration Characteristics	Number of active aerators, nameplate horsepower, impellor size, impellor RPMs, diffused air flow
Meteorological Conditions	Wind speed, ambient air temperature
Loading Conditions	Influent flow rate, sulfide and sulfate concentrations

[a] Hydraulic tracer studies are not necessary if other reliable estimates of basin volume are available.

5.4 Defining Model Zones

H2SSIM partitions heterogeneous wastewater treatment basins into a series of three dimensional zones which have homogenous characteristics. Defining the number, size, and mixing characteristics of these zones is critical for properly simulating H_2S emissions. There are three main steps when setting up model zones for H2SSIM:

- selecting the number of zones;
- specifying the physical dimensions of model segments; and
- setting hydraulic mixing parameters between segments.

A guidance document published by EPA provides additional information regarding basin mixing zones for the reader interested in a thorough discussion of this topic (USEPA 1999).

5.4.1 *Selecting the Proper Number of Zones*

In cases where the user is not simulating a primary clarifier, the number of zones must be selected in Data Type 2 on the Inputs tab. When deciding upon the appropriate number of model zones, the user must balance multiple factors. In general, the user should seek the minimum number of zones that accounts for physical characteristics and chemical gradients while maintaining an accurate hydraulic regime. The following list, in order of priority, identifies the factors that the user should consider when setting model zones.

- Physical boundaries
- Dissolved oxygen and pH gradients
- Mechanical aeration density
- Temperature gradients
- Hydraulic regime considerations

Physical boundaries are man-made impediments to water transport. Examples include weirs and pipes between basins and also in-basin curtains. The presence of a physical boundary is in most cases an appropriate location for the end of a model zone because the effect of the physical boundary is to create two distinct volumes. Figures 5.1 and 5.2 illustrate the proper placement of model zones with the presence of a pipe and curtain, respectively.

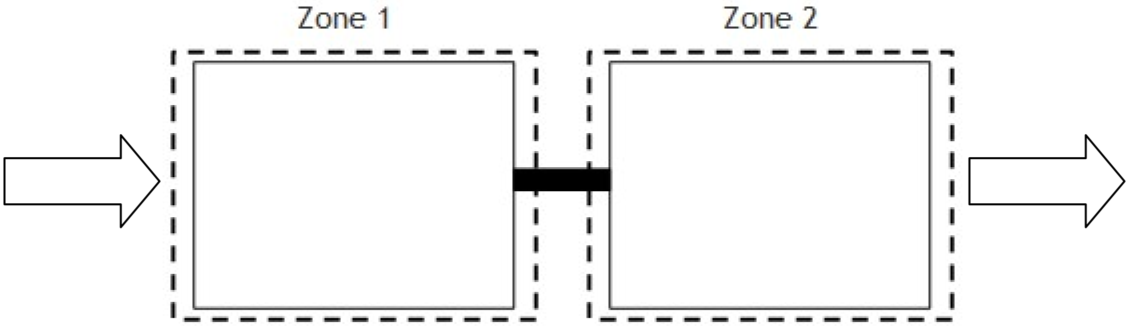

Figure 5.1 Suggested Model Zone Placement with Pipe/Weir Present
[The arrows depict the flow direction.]

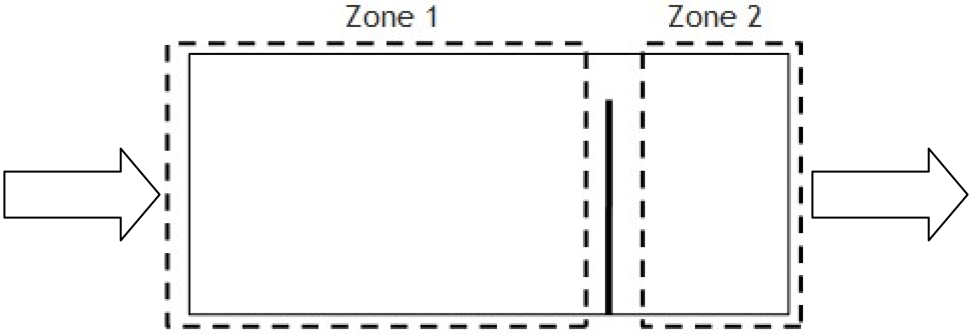

Figure 5.2 Suggested Model Zone Placement with Flow Curtain Present

In both of the above examples, model zones are placed so that a physical boundary in the basin is properly represented and two separate and distinct zones are simulated.

After physical boundaries are accounted for, the basin can be further zoned based on chemical gradients and mechanical aeration density. Dissolved oxygen and pH gradients should be accounted for first, followed by aeration density. Figure 5.3 continues the example in Figure 5.2 by placing model zones around measured pH gradients.

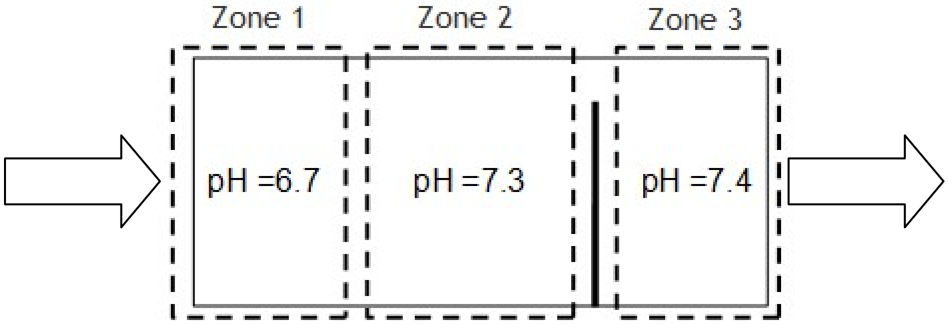

Figure 5.3 Suggested Model Zone Placement When Flow Curtain and pH Gradients Are Present

Mechanical aeration density should be accounted for if there is a large quiescent area (i.e., lack of mechanical turbulence) in an aerated basin. Continuing the example from Figure 5.3, the quiescent area can be simulated by splitting Zone 3 into two zones based upon aerator density as shown in Figure 5.4. In this figure, surface aerators are represented by a star.

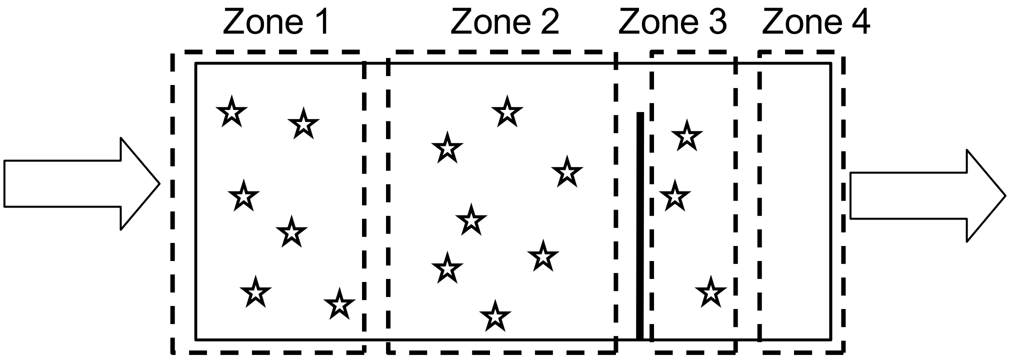

Figure 5.4 Suggested Model Zone Placement When Flow Curtain, pH Gradients, and Aeration Density Gradients Are Present

Deciding upon the number and location of zones is an exercise in professional judgment informed by the available data. It is in making these types of decisions that a sketch of the basin with sample locations, values, and aerator locations can be useful.

5.4.2 *Effect of Model Segmentation on Simulated Hydraulics*

The number of model segments selected will affect the type of flow that the model simulates. For a detailed discussion of modeling basin hydraulics, see NCASI Technical Bulletin 458 (NCASI 1985a). In general, the modeled hydraulic regime moves from a complete mix to plug flow as more segments are added to the model, as shown in Figure 5.5. This figure shows tracer curves generated under identical load and basin conditions for three different zone arrangements.

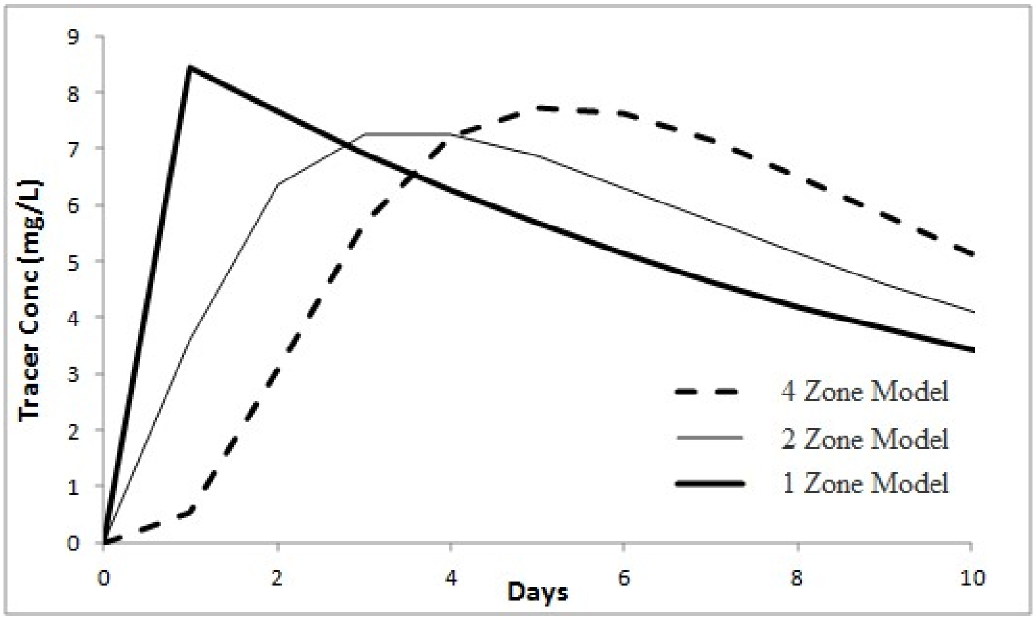

Figure 5.5 Example of Residence Time Curves for Various Numbers of Model Zones

As seen in Figure 5.5, the number of zones in the model can have some effect upon the concentration and timing of load at the effluent location. In practice, it should be the goal of the user to achieve a reasonable characterization of the basin's hydraulics. As discussed in Section 5.4.1, the user should set the number of model segments based first on any physical boundaries, then on chemical and aeration considerations.

5.4.3 *Specification of Model Segment Dimensions*

Once the user has determined the number of zones to be used, those zones must be appropriately sized. Zone dimensions (length, width, and depth) are critical in defining both the residence time of the system and the area of the air/water interface. Zone dimensions are input by the user in Data Type 5 of the Inputs tab.

To define the length and width, the user may consult a scale drawing of the system. The geometry of the model segment is rectangular by default, so for systems that are trapezoidal or circular, an approximation must be made. An average water column depth (excluding any accumulated sludge) must also be entered for each segment. As depths across basins often vary, it is suggested that the number and location of the model segments are considered so that each segment is representative of an average water depth.

5.4.4 S*election of Mixing*

Mixing ("high," "moderate," "low," "none") must be specified between each adjacent model zone in Data Type 5. Mixing is internally set to "none" for boundaries with the influent and effluent; thus, the mixing for Zone 1 characterizes the interface between Zones 1 and 2 and the mixing for Zone 2 characterizes the interface between Zones 2 and 3. This pattern repeats until the final zone, which interfaces with the effluent and therefore is internally set to "none."

A conservative tracer study can assist the user in specifying the amount of mixing. If a tracer study is not available, the physical characteristics of the boundary between the model segments can be used as a general guide. This guidance is summarized in Table 5.2.

Table 5.2 Suggested Mixing Settings Based upon Zone Interface Conditions

Conditions at Interface Between Zones	Suggested Mixing Setting
Physical separation of adjacent basins such as by weir, pipe, or curtain.	None
Moderate separation of adjacent basins or adjacent basins are quiescent.	Low
Adjacent basins are not physically separated; basins are lightly to moderately agitated (< 30 HP/MG).[a]	Moderate
Adjacent basins are not separated; basins are moderately to heavily agitated (> 30 HP/MG).	High

[a] Based upon NCASI experience using conventional wastewater treatment models.

5.5 Inputting Influent Loads and Atmospheric Conditions

The flow of wastewater into the basin and the concentration of sulfide and sulfate in the wastewater are specified in Data Type 3 on the H2SSIM tab. The values entered in this section should be characteristic of the wastewater just prior to entering Zone 1.

As noted earlier, the flows and concentrations entered should be representative of the simulation period of interest. For determining the sulfide concentration during that period, multiple samples should be taken to account for variability. Several methods for quantifying total sulfide are available including those which may be performed on site (NCASI 2005, 2006). A highly accurate estimate of the sulfate concentration is not necessary if it is believed that the concentration is above 100 mg/L.

Atmospheric conditions are entered in Data Type 4. These conditions should represent average wind speed and temperature from the simulation time period of interest. The data for the atmospheric conditions can be acquired from a local meteorological station and do not need to be recorded on site in most cases.

5.5.1 *Defining the Location of a Condensate Hardpipe Influent*

The location of a condensate hardpipe is specified in Data Type 3. If a hardpipe is present, it can be located in any of the model zones. The decision as to where the hardpipe is located can be assisted by superimposing the approximate hardpipe location on the basin sketch with the model zones overlaid. In cases where the hardpipe enters near the boundary between two zones, it may be more accurate to place the hardpipe in the downstream zone, as that is where the hardpipe will likely have the largest impact.

5.6 Inputting Basin Physical and Chemical Information

The physical and chemical conditions of the wastewater basin are input in Data Type 5. These values are entered by zone. The model will only read the values in the number of zones specified in Data Type 2 (i.e., if three zones are specified, the model will disregard any input under Zone 4).

5.7 Running the Model and Reviewing Output

After all model inputs have been entered, the user may run the model by clicking the Run icon located in the model controls section. The user may then review the output on the Output tab. Unusual output values such as negative or very high emission rates can usually be traced to errors made in the input section. The user should always double check both the value and units of all entered inputs and verify that the correct model parameters were used prior to accepting the results of the simulation.

6.0 PREDICTING FUTURE EMISSIONS USING H2SSIM

This section is intended to provide the user with examples of predicting future H_2S emissions as a function of a planned change to the treatment basin or its operation. Examples of possible changes to the treatment system include pretreatment of influent sulfide loads, changes to existing aeration, and adjustment of basin pH.

The first step to preparing the model to predict future emissions is to go through the process of setting the model up for existing conditions as described in Section 5 in this bulletin. This run of the model is referred to as the base case model. Once the base case model is deemed to be satisfactorily estimating existing emissions, model inputs can be systematically changed in order to simulate the effect of anticipated modifications to the treatment system. The rest of this section describes how model inputs can be changed to simulate some common treatment system changes.

6.1 Simulation of Influent Sulfide Load Pretreatment

In many wastewater treatment basins, the primary source of sulfide to an aerated basin is anoxic upstream processes such as primary clarifiers and settling ponds. A mill may consider pretreatment through the addition of some oxidizing agent (e.g., peroxide, oxygen) to the anaerobic waste stream. The NCASI sulfide model does not estimate the effect of pretreatment to these waste streams, but if the effect is known or generally known, the sulfide model can estimate the reduction in H_2S emissions that would be realized by pretreatment.

The user can simulate pretreatment in the model by reducing the concentration of sulfide in Data Type 3. Because in many cases the exact effect of pretreatment on influent sulfide concentration may not be known, a range of removals may be input to the sulfide model to reflect this uncertainty. Table 6.1 presents the results of several model runs made at varying influent sulfide concentrations which reflect a range of pretreatment effectiveness.

Table 6.1 Example Model Results over a Range of Pretreatment Efficiencies

Percentage of Existing Sulfide Load Removed by Pretreatment	Predicted ASB Emissions (gms/s)
0%	2.15
25%	1.71
50%	1.26
75%	0.83
100%	0.39

The results of the modeling yield several useful pieces of information. Estimated emission rates as a result of pretreatment can be used to determine if pretreatment is a feasible option for attaining a particular target emission rate. For example if it is known that pretreatment will reduce the influent sulfide load by as much as 50% and that the target emission rate is 1.0 gms/sec, it can be assumed that pretreatment alone will not attain target emission rates. Another useful piece of information is the estimate of emissions at 100% sulfide removal by pretreatment. This result indicates that while the major source of emitted sulfide is the influent load, some sulfide is likely being formed in the ASB itself and this portion of sulfide is responsible for the emissions when influent sulfide loads are eliminated.

An important aspect of performing predictive modeling is understanding the effect of treatment basin changes and reflecting those changes in the model inputs. For example, in the pretreatment scenario described above, it would be prudent to determine if the pretreatment process would significantly change any other basin characteristics, such as basin pH or dissolved oxygen. If such changes are deemed likely, proper adjustments to these additional model inputs would need to be made.

6.2 Simulation of pH Adjustment

Low basin pH values can lead to higher emissions of H_2S. This occurs primarily because H_2S predominates at lower pH values (see Figure 3.2) and is more volatile than HS^-. While pH control in large treatment basins is challenging, it can be an effective means of reducing H_2S emissions. To simulate pH adjustment, the user would change the existing zone pH values (Data Type 5) to the values which are anticipated after the relevant modifications are made.

6.3 Simulation of Additional Aeration

Treatment basins with low oxygen concentrations typically have higher sulfide concentrations. This occurs because reducing environments can exist when oxygen levels are low and these environments are conducive to sulfide generation and can slow sulfide oxidation. One operational strategy to increase the dissolved oxygen in a basin is to install additional aeration equipment. In this case, H2SSIM can be used to estimate H_2S emissions as a function of the basin's anticipated dissolved oxygen concentration.

In order to simulate a scenario of additional aeration, the user would go to Data Type 5 and modify three inputs for each model segment that was impacted: the number of aerators, horsepower, and dissolved oxygen. It should be noted that the sulfide model does not predict dissolved oxygen concentrations as a function of additional aeration. The user must estimate resulting dissolved oxygen either through oxygen transfer calculations or the use of a wastewater treatment model such as SASBV4 (NCASI 1985a).

7.0 MODEL PERFORMANCE TESTING AND SENSITIVITY ANALYSIS

The ability of a model to predict an accurate response is directly related to the ability of the model algorithm to accurately describe the mechanisms affecting the form and fate of the modeled parameter. The model algorithm can be tested indirectly by applying the model to multiple systems where the response of interest has been measured. If the model successfully predicts the measured response, it is said to be "confirmed" for the range of system inputs used in testing. While this testing does not positively determine that the model algorithm is correct, it does provide increased confidence in its reliability. In Sections 7.1 and 7.2, H2SSIM emissions predictions for four different ASBs and three primary wastewater treatment units are compared to measured[1] H_2S emission rates. The results of these comparisons help to inform the user regarding the amount of error expected when using H2SSIM.

Model accuracy is also related to input data quality. While it is always desirable to collect the best data possible, time and resources can often limit data collection activities. Sensitivity analysis is a useful means of identifying the inputs that can most significantly impact model accuracy. Available time and resources can then be optimized by targeting the data collection towards the most sensitive inputs. A sensitivity analysis of H2SSIM's user inputs is presented in Section 7.3

7.1 Performance Testing: Aerated Stabilization Basins

H2SSIM testing for ASBs is presented in two phases. The first summarizes comparisons of H_2S model predictions to emission rates measured by NCASI during a 2005–2006 wastewater emissions survey (NCASI 2008a, 2008b). During this survey, H_2S emissions were measured several times per day for one to two days. Wastewater conditions (i.e., pH, temperature, DO) were measured at a single time to characterize average conditions. The second phase of measurements focused on a single ASB with two to three emission measurements per day over three days. During this phase, an attempt was made to record multiple wastewater conditions and make emission measurements at similar points in time.

Over both phases of testing, seven comparisons of the measured daily average H_2S emissions rate to the H2SSIM estimate can be made at four different ASB systems. For each comparison, model inputs were developed to characterize the sulfide loading rate, basin physical dimensions, aeration, and chemical conditions for the surveyed ASB based on information collected at the nearest point in time to the H_2S emissions measurement. Model parameters were held constant to the values recommended in Section 4. Table 7.1 summarizes the measured emission rates and model predictions for both phases of the testing.

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[1] Throughout this document the term "measured" is used to describe the field derived H_2S emission rates. NCASI (2008a, 2008b) discusses the development and implementation of the field method.

Table 7.1 Summary of NCASI H_2S Emissions Measurements and Model Estimates at ASBs

Mill ID	Model Testing Phase	Daily Average Measured H_2S Emissions Rate (g/s)	Standard Deviation of Measured Emissions Rate (g/s)	Number of Emission Measurements	Model Predicted Daily Average Emissions Rate (g/s)	Percent Model Error from Average
Mill E 2005	1	0.12	0.07	3	0.15[a]	21%
Mill E 2006	1	0.27	0.20	3	0.15[a]	-84%
Mill B	1	0.27	0.22	3	0.24[a]	-13%
Mill D	1	0.60	0.32	11	0.68[a]	12%
Mill H Day 1	2	0.47	0.06	3	0.40[b]	-16%
Mill H Day 2	2	0.58	0.20	3	0.62[b]	6%
Mill H Day 3	2	0.22	0.09	2	0.34[b]	35%

[a] This estimated emission rate is based upon a single characterization of ASB conditions.

[b] This estimated emission rate is the average of multiple model estimates based upon multiple characterizations of ASB conditions.

The comparison between modeled and measured emission rates is presented for Phase I testing in Figure 7.1 and for Phase II testing in Figure 7.2. In these figures, the measured average daily emission rate and standard deviation is depicted by a point and error bars respectively. Model estimates are represented by points. Multiple points appear in Figure 7.2 because in Phase II, ASB condition data were collected several times per day and these points represent the model predictions based on that data.

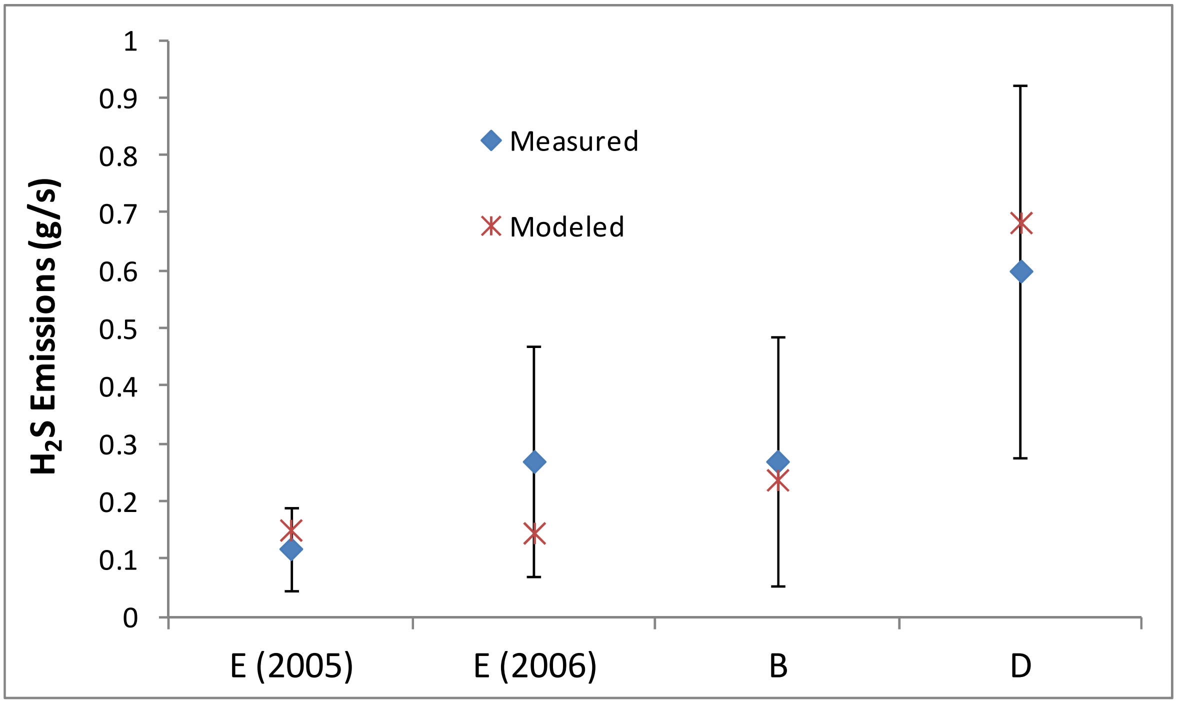


Figure 7.1 Measured H_2S Emission Rates Compared to Model Predicted Rates for Phase I Model Testing at ASBs
[Error bars depict the standard deviation from the mean of the emissions measurements.]

Figure 7.1 indicates that the model is able to estimate the magnitude of the measured average daily emission rates to within one standard deviation of the measured rate. Based upon visual inspection, the model does not appear to systematically under- or over-predict the average emission rates. The estimated relative model error as a percentage of the average measured daily emission rate ranges from -84 to 21%.

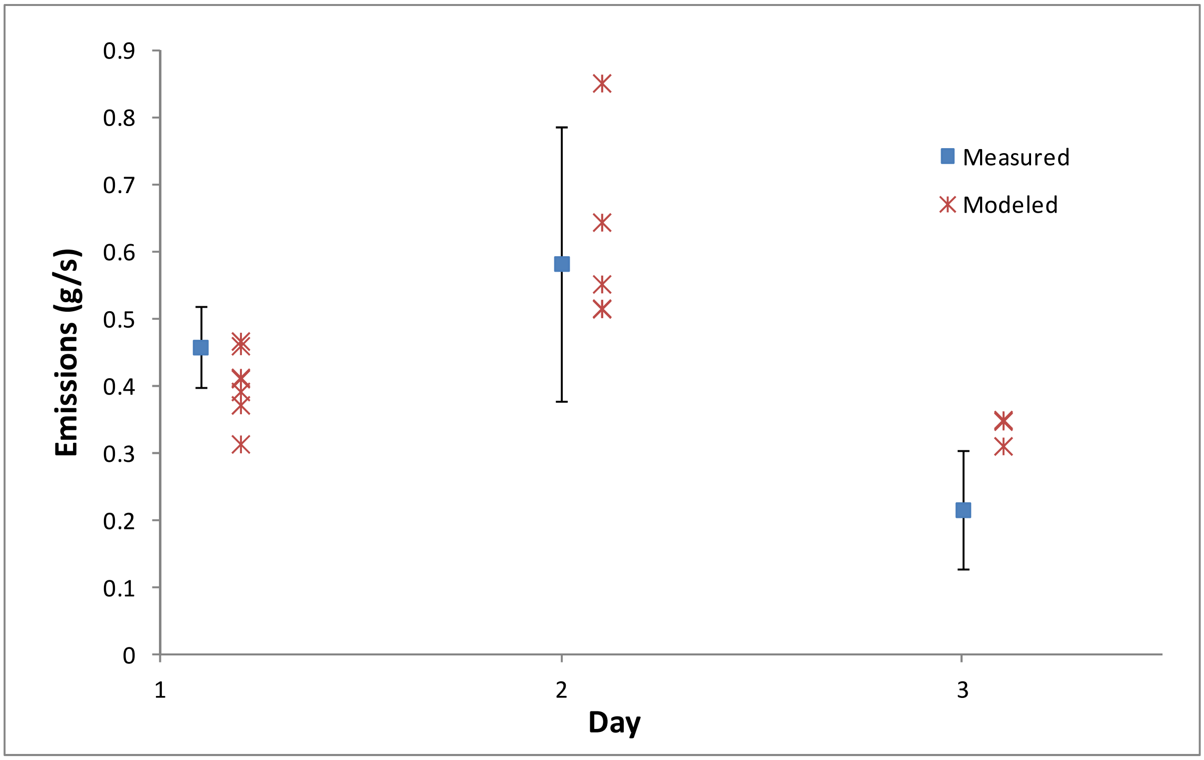


Figure 7.2 Measured H_2S Emission Rates Compared to Model Predicted Rates for Phase II Model Testing at ASBs [Error bars depict the standard deviation from the mean of the emissions measurements. (Modeled and measured points are slightly offset for visualization purposes).]

Figure 7.2 shows that the model is able to simulate the general magnitude of the emissions measurements. It also appears that the day-to-day trend of the measurements is captured by the model. The estimated relative model error as a percentage of the average measured daily emission rate ranges from -16 to 35%.

7.2 Performance Testing: Primary Settling Basins

The model was tested on two primary settling basins using data collected from pulp and paper industry wastewater treatment plants (NCASI 2008a). These types of basins are modeled in much the same way as ASBs. However a key difference is the redox condition of the wastewater. Because primary wastewater has a high organic content and the basins typically contain no aeration equipment, these wastewaters are most likely anoxic. To account for slower oxidation under anoxic conditions, the model uses a different oxidation rate equation for anoxic wastewaters. To account for the more favorable sulfide generation conditions, the oxygen concentration is assumed to be zero, causing the sulfide generation rate to approach its maximum.

Table 7.2 Summary of NCASI H_2S Emissions Measurements and Model Estimates at Primary Settling Basins

Mill ID	Daily Average Measured H_2S Emissions Rate (g/s)	Standard Deviation of Measured Emissions Rate (g/s)	Number of Measurements	Model Predicted Daily Average Emissions Rate (g/s)	Percent Model Error from Average
Mill E Pond 1	1.01	0.71	5	1.03	2%
Mill E Pond 2	1.40	0.30	2	1.94	28%

The results of the model testing on the primary treatment units are shown in Figure 7.3.

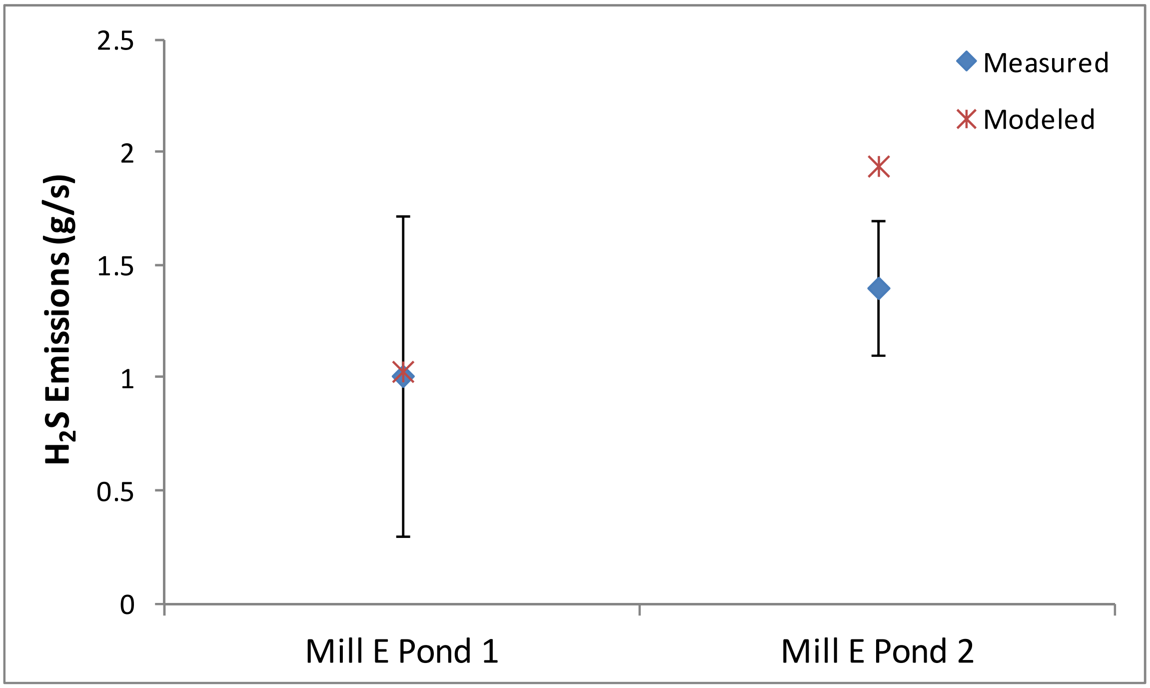


Figure 7.3 Measured H_2S Emission Rates Compared to Model Predicted Rates for Primary Settling Basin Model Testing [Error bars depict the standard deviation from the mean of the emissions measurements.]

Figure 7.3 indicates that the modeled rate is higher than the standard deviation of the measured daily emission rate for Pond 2. During the emissions rate sample event (NCASI 2008a), this pond was partially covered with floating fiber which formed a mat. This mat may have impeded volatilization of H_2S and caused the model to over-predict emissions.

7.3 Performance Testing: Sensitivity Analysis

Sensitivity analysis can be used to identify model inputs which have the greatest effect on model output. A more detailed description of how sensitivity analysis is performed is available in NCASI (2002). In general, a base case is developed which characterizes the original state of the model. To assess the sensitivity of an input, that input is adjusted by a certain percentage. The output of the model using the adjusted input is then compared relative to the output of the base case model. Inputs which significantly change the model output are considered to be sensitive and worthy of increased attention.

A sensitivity analysis of the H2SSIM basin characterization inputs was performed using a data set from the Phase II testing. The results are presented in Table 7.3. It is important to note that input parameter sensitivities may change relative to the value of other inputs and also to its own value. While the sensitivities presented in Table 7.3 are likely representative of most input data sets, it is advised that users perform sensitivity analyses using their own unique input data sets to best identify the most sensitive inputs.

Table 7.3 Sensitivity Analysis of H2SSIM Basin Characterization Inputs

Model Input Name	Model Input Base Case Value	Percent Change in Emissions from 25% Decrease in Input Value	Percent Change in Emissions from 25% Increase in Input Value
Flow (MGD)	45	0.2%	-0.2%
Sulfide Load (lbs/day)	612	-9.8%	12.3%
Sulfate Concentration (mg/L)	438	-0.2%	0.2%
Windspeed (mph)	1.25	0.0%	0.0%
Ambient Temperature (C°)	23.8	0.2%	-0.2%
Dissolved Oxygen in Zone 1, Zone 2, Zone 3 (mg/L)	0.48, 0.37, 0.4	12.5%	-10.2%
Temperature (C°)	43.5, 40.4, 38	9.8%	-10.7%
pH[a]	6.5, 7, 7.1	272.7%	-44.1%
Redox Condition[b]	Aerobic	2177.3%	N/A
Length (m)	108, 252, 360	6.6%	-3.9%
Width (m)	160, 160, 160	6.6%	-3.9%
Depth (m)	3.5, 3.5, 3.5	10.5%	-8.6%
Mixing[c]	High, None, Low	0.2%	0.0%
Number of Aerators	8, 12, 16	2.3%	-2.0%
Total Horsepower	600, 900, 1200	-17.0%	21.3%
Impellor Size (m)	0.6, 0.6, 0.6	1.0%	-1.0%
Impellor RPMs	1200,1200,1200	0.6%	-0.4%
Benthic Flux Rate (gm/m^2 s)	0.0145	-2.5%	3.1%

[a] The basin pH was changed by +/- 5% in order to keep the values within a typical wastewater range.

[2] The redox condition used for the base case is “aerobic” across the basin. The condition used for the 25% decrease is “anoxic” across the basin.

[c] The mixing condition used for the 25% decrease is “none” across the basin. The condition used for the 25% increase is “high” across the basin.

The results of the input sensitivity analysis indicate that the most important inputs to the sulfide emissions model are zone pH and redox condition. Based on their observed sensitivities, it is critical that these inputs are measured accurately and are representative of the conditions in the basin.

Inlet sulfide load, basin dissolved oxygen concentration, temperature, basin geometry, and aeration are moderately sensitive inputs indicating that resources would be well spent collecting data to accurately characterize these inputs. Sulfate concentration, wind speed, ambient temperature, mixing, impellor size, and RPMs are not sensitive inputs. As such, it is likely that in most cases, these inputs can be developed using indirect sources of information (literature values, local meteorological stations, professional judgment).

REFERENCES

Chapra, S.C. 1997. *Surface water quality modeling*. New York: McGraw-Hill.

Ebbing, D.D. 1996. *General chemistry*. 5th ed. Boston: Houghton Mifflin Company.

Geankoplis, C.J. 1993. *Transport processes and unit operations*. Englewood Cliffs, NJ: PTR Prentice Hall.

National Council [of the Paper Industry] for Air and Stream Improvement, Inc. (NCASI). 1985a. *User manual for NCASI aerated stabilization basin model and guidance for its use.* Technical Bulletin No. 0458. New York: National Council of the Paper Industry for Air and Stream Improvement, Inc.

———. 1985b. *Modification of the NCASI ASB treatment plant model for simulating conditions when basin temperatures exceed 35°F.* Technical Bulletin No. 0477. New York: National Council of the Paper Industry for Air and Stream Improvement, Inc.

———. 2002. *Sensitivity analysis for water quality model development and application*. Technical Bulletin No. 0854. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

———. 2005. *Evaluation of sulfide ion detector tubes for determining sulfide concentrations in pulp and paper mill wastewaters*. Special Report No. 05-01. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

———. 2006. *An evaluation of a colorimetric method for the determination of total sulfide in pulp and paper mill wastewaters.* Special Report No. 06-02. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

———. 2007. *Development and application of a method for measuring reduced sulfur compounds in pulp and paper mill wastewaters*. Technical Bulletin No. 0933. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

———. 2008a. *Emissions of reduced sulfur compounds and methane from kraft mill wastewater treatment plants*. Technical Bulletin No. 956. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.

———. 2008b. *Spatial ambient air sampling and analysis methods for quantifying reduced sulfur compound and methane emissions from kraft mill wastewater treatment plants*. Technical Bulletin No. 0957. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Nielsen, A.H., Vollertsen, J., Hvitved-Jacobsen, T. 2003. Determination of kinetics and stoichiometry of chemical sulfide oxidation in wastewater of sewer networks. *Environmental Science and Technology* 37: 3853-3858. http://dx.doi.org/10.1021/es034035l

———. 2006. Kinetics and stoichiometry of aerobic sulfide oxidation in wastewater from sewers—Effects of pH and temperature. *Water Environment Research* 78:275-283. http://dx.doi.org/10.2175/106143005X94367

Owens, M. 2005. *A Study of gas emissions and porewater from a pulp mill waste treatment system.* Prepared for NCASI by Chesapeake Biogeochemical Associates.

Palumbo, J.E., Brown, L.C., and Stratton, S.C. 2010. Modeling the oxidation of sulfide in pulp and paper wastewaters. *Journal of Environmental Engineering* 136: 1171-1179. http://dx.doi.org/10.1061/(ASCE)EE.1943-7870.0000248

Reid, R.C. and Sherwood, T.K.. 1958. *Properties of gases and liquids*. New York: McGraw-Hill Book Company, Inc.

Staudinger, J. and Roberts, P.V. 1996. A critical review of Henry's law constants for environmental applications. *Critical Reviews in Environmental Science and Technology* 26: 205-297. http://dx.doi.org/10.1080/10643389609388492

Thibodeaux, L.J. 1996. *Environmental chemodynamics: Movement of chemicals in air, water, and soil.* 2nd ed. New York: Wiley Interscience.

Thibodeaux, L.J. and Parker, D.G. 1974. Desorption limits of selected industrial gases and liquids from aerated basins. Paper 30d, presented at 76th AIChE National Meeting, Tulsa, OK.

Thibodeaux, L.J., Parker, D.G., and Heck, H.H. 1982. *Measurement of volatile chemical emissions from wastewater basins*. EPA-600/2-82-095. Cincinnati, OH: United States Environmental Protection Agency, Industrial Environmental Research Laboratory.

United States Environmental Protection Agency (USEPA). 1994. *Air emissions models for waste and wastewater.* EPA-453/R-94-080A. Research Triangle Park, NC: United States Environmental Protection Agency, Office of Air Quality Planning and Standards.

———. 1999. *Technical support document for the evaluation of aerobic biological treatment units with multiple mixing zones*. www.epa.gov/ttn/atw/pulp/mulmix5.pdf

Wilmot, P.D, Cadlee, K., Katinic, J.J., and Kavanagh, B.V. (1988) Kinetics of sulfide oxidation by dissolved oxygen. *Journal of the Water Pollution Control Federation* 60: 1264-1270.

APPENDIX A

DEVELOPMENT OF THE SULFIDE GENERATION RATE EQUATION

NCASI has undertaken research to understand sulfide generation in pulp and paper mill wastewaters. The emphasis of this research is on developing a quantitative expression to predict the rate of sulfide generation in wastewater treatment basins. To assist in this development, an experimental program was initiated. The focus of this program was documenting sulfide generation in bench-scale reactors held at anoxic conditions over a period of 10 – 18 days. The specific research objectives are as follows:

- Observe and document the generation of sulfide in pulp and paper wastewaters under anoxic conditions.
- Based on observations of sulfide generation, identify applicable generation rate equation forms for use in wastewater treatment basins.
- Propose an equation for estimating the sulfide generation rate.
- Estimate rate equation parameters from batch reactor data.

Literature Review

Sulfide can be produced by several reactions; however, the most significant in nature is dissimilatory sulfate reduction. This reaction occurs only under anoxic conditions indicated by the lack of oxygen. In this biologically mediated reaction, sulfate reducing bacteria (SRB) transfer electrons from an electron donor to an electron acceptor, generating energy for metabolism along with the reduced sulfide. SRB can use both organic and inorganic compounds as an electron donor. If hydrogen is the electron donor, carbon monoxide or carbon dioxide is used as a carbon source. The most common organic electron donors are simple fermentation products such as alcohols and short-chain volatile fatty acids, but SRB have been observed to utilize a wide variety of organic substrates for sulfate reduction (Hansen 1988). Nitrogen and trace metals are also needed for SRB metabolism (Postgate 1984). Some investigations have noted a strong relationship between fermentative bacteria and SRB in activated sludge (Ingvorsen and Nielsen 2003). It is likely that fermentative bacteria provide simple substrates to SRB in these systems by breaking down the more complex organic molecules. Sulfate is the typical compound used as an electron acceptor during the reduction, but some SRB can also utilize sulfite, thiosulfate, and elemental sulfur (Colleran, Finnegan, and Lens 1995). In general, SRB have been observed to function well between 25 and 35°C. Sulfate reduction has been observed in wetland soils across a wide range of pH values (Feng and Hsieh 1998).

In the typical reaction, sulfate is reduced to sulfide through the transfer of electrons. The following reaction equation demonstrates sulfate reduction with acetate as the electron donor.

$$CH_3COO^- + SO_4^- \Leftrightarrow HS^- + 2HCO_3^- \qquad \text{Equation A1}$$

A common modeling approach for biologically mediated reactions is the use of Monod kinetics. In this approach, the growth rate of biomass is considered to be at a maximum when all reactants are in excess above a certain saturated concentration. Biomass growth increasingly slows as concentrations decrease below this saturation value. The half saturation constant is the concentration of a particular reactant at which the reaction is slowed by 50% of its maximum rate. This type of model adapted to SRBs including terms for the electron acceptor and donor is presented in Equation A2.

$$\frac{dX}{dt} = \mu_{\max} X \left(\frac{S}{S + K_S} \right) \left(\frac{SO_4}{SO_4 + K_{SO_4}} \right) \qquad \text{Equation A2}$$

Where: μ_{max} = Maximum specific growth rate ($time^{-1}$)
X = SRB biomass (mg/L)
S = Substrate concentration (mg/L)
K_S = Substrate half saturation constant (mg/L)
SO_4 = Sulfate concentration (mg/L)
K_{SO4} = Sulfate half saturation constant (mg/L)
t = time

Equation A2 implies that the growth rate of SRB biomass (and by inference, the sulfide generation rate) is a function of substrate and sulfate below certain “saturation” concentrations. Boon (1995) has reported a range in the scientific literature for the sulfate half saturation constant as between 0.27 and 4.6 mg S/L. A few sources of kinetic information on freshwater sulfate reducers are available for substrate limitation. In one, Oude Elferink et al. (1998) reported a half saturation value for acetate degrading SRB in bioreactors of 35.4 mg/L. Visser (1995) determined a half saturation value of 18 mg/L for mixed culture system fed with acetate. Moosa, Nemati, and Harrison (2002) reported that the substrate half saturation value for a continuous reactor fed with acetate varied linearly with initial sulfate concentration. They estimated a half saturation value of 27 mg/L at an initial sulfate concentration of 1000 mg/L. This value rose to 125 mg/L at an initial sulfate concentration of 10,000 mg/L. Using the data from Moosa et al. and assuming the relationship holds at lower sulfate concentrations, a half saturation value can be extrapolated to typical kraft pulp and paper mill wastewater sulfate concentrations. Using a typical initial sulfate concentration for this study of 450 mg/L, a substrate half saturation value of 6.8 mg/L is calculated with this relationship.

Some investigators have modified the approach of Equation A2 and included a threshold concentration for the reactants. Instead of a slowing decline in rate as reactant concentrations decrease, this approach assumes that the rate slows with decreasing concentration but at some time, reaches a substrate or sulfate concentration where the reaction ceases completely. This concentration is referred to the threshold concentration and is shown in Equation A3.

$$\frac{dX}{dt} = \mu_{\max} X \left(\frac{S - S_t}{(S - S_t) + K_S} \right) \left(\frac{SO_4 - SO_{4t}}{(SO_4 - SO_{4t}) + K_{SO_4}} \right) \qquad \text{Equation A3}$$

Where: S_t = Substrate threshold concentration (M/L^3)
SO_{4t} = Sulfate threshold concentration (M/L^3)

Investigations by Oude Elferink et al. (1998) suggest that the acetate threshold value for two types of SRB is less than 0.89 mg/L. Ingvorsen, Zehnder, and Jorgensen (1984) reported data that suggested a threshold value for sulfate as less than 4 mg/L. It is speculated that these low half saturation and threshold values for acetate and sulfate allow SRB to out-compete methane producing bacteria in most environments.

The above kinetic expressions are applicable to environments that are entirely anoxic. Working with sewer waters that may alternate between aerobic and anaerobic conditions, Yongsiri et al. (2003) included an inverse Monod kinetics saturation term in their model to adjust for the potential presence of oxygen. The value of the inverse Monod term for oxygen is at a maximum when oxygen concentration is zero, is half of its value at an oxygen concentration equal to the half saturation coefficient, and approaches zero as oxygen concentration increases beyond the half saturation coefficient. Yongsiri et al. (2003) suggest a dissolved oxygen half saturation coefficient of 0.05 mg/L. The behavior of the inverse Monod term for oxygen is depicted in Figure A1 with the suggested half saturation coefficient value.

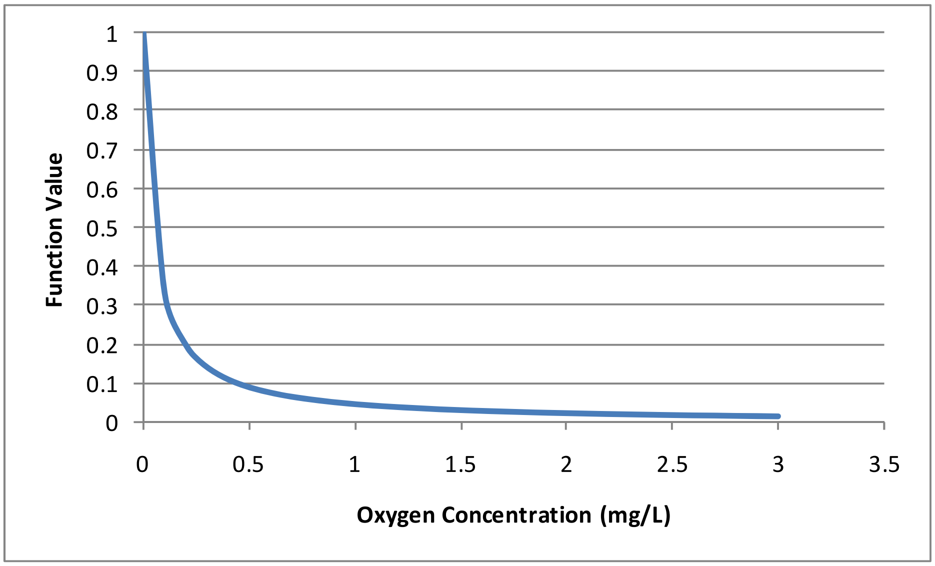


Figure A1 Value of Inverse Monod Function for Dissolved Oxygen Concentration

When the inverse Monod term is added to an equation simulating sulfate reduction, it has the effect of allowing unlimited SRB growth (assuming no other limiting factors) when zero oxygen is present. As the oxygen concentration increases, the amount of sulfate reduction is limited until it approaches zero. Equation A4 presents Equation A2 with the inverse Monod oxygen term added.

$$\frac{dX}{dt} = \mu_{\max} X \left(\frac{S}{S + K_S} \right) \left(\frac{SO_4}{SO_4 + K_{SO_4}} \right) \left(\frac{K_{DO}}{K_{DO} + DO} \right) \qquad \text{Equation A4}$$

Where: O_2 = Oxygen concentration (M/L^3)
K_{SO4} = Oxygen half saturation coefficient (M/L^3)

The key information from the sulfide generation literature review is as follows:

- Sulfide is predominately formed by sulfate reducing bacteria (SRB) in anoxic environments.
- SRB can use various sulfur compounds as electron acceptors and large variety of compounds as electron donors.
- The reported value of the sulfate half saturation coefficient varies between 0.27 and 4.6 mgS/L.
- The reported value of the substrate half saturation coefficient varies between 6.8 and 35 mg/L for acetate under various experimental conditions.
- SRB growth in environments that may alternate between aerobic and anaerobic has been modeled in sewers using an inverse Monod kinetic function.
- SRB function optimally at temperatures between 25 and 35 °C and a wide range of pH values.

Lab Procedures

Experiments to characterize sulfide generation in pulp and paper wastewaters from three mills were conducted at the NCASI West Coast Regional Center laboratory. The specific lab procedures are included at the end of this report. In general, the experiments were conducted by filling a 20 L reactor with wastewater obtained from the front end of an aerated stabilization basin treating pulp and paper mill effluent. The reactors were kept anoxic and held at a constant temperature of about 35 °C. The reactors were sampled over a period of several weeks for sulfide, sulfate, and various other potential substrates (i.e., BOD_5, MeOH). A probe in the reactor measured dissolved oxygen, ORP, and pH.

Experimental Results and Generation Model Development

Plotted results of measured sulfide and sulfate are shown in Figures A2 through A5. These plots illustrate the general trends between sulfate and sulfide under anoxic conditions.

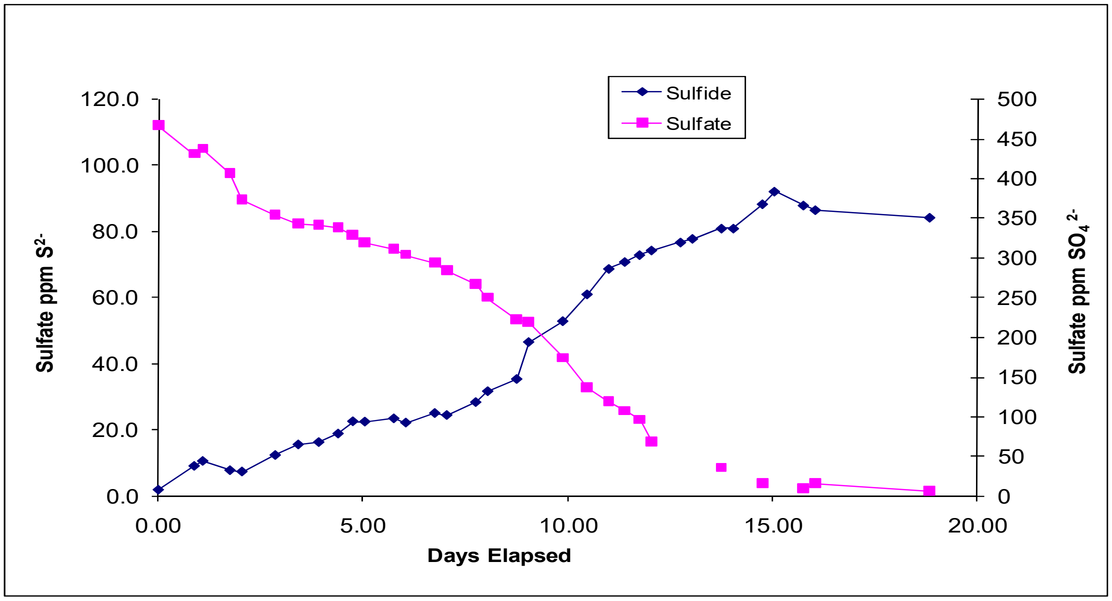


Figure A2 Mill A: Sulfide and Sulfate Concentrations (mg/L)

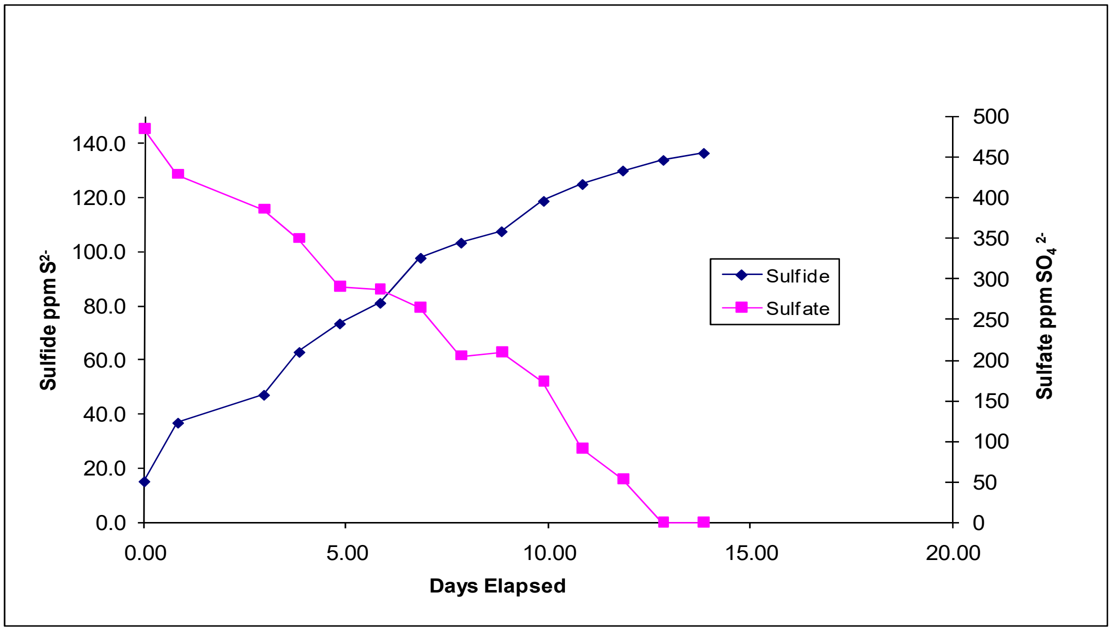


Figure A3 Mill B: Sulfide and Sulfate Concentrations (mg/L)

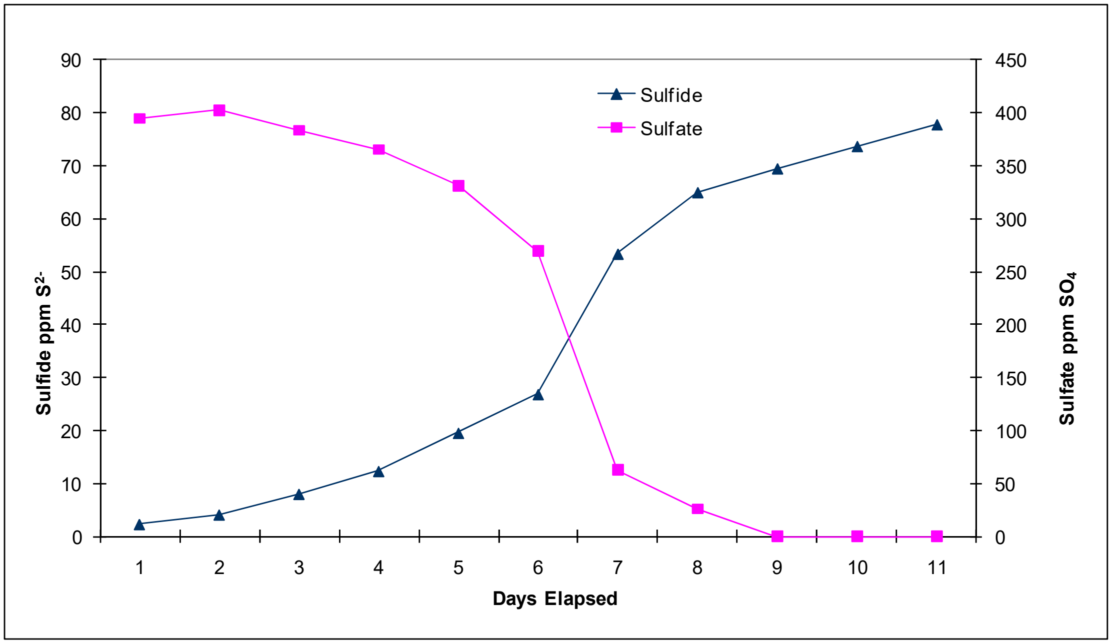


Figure A4 Mill C Reactor 1: Sulfide and Sulfate Concentrations (mg/L)

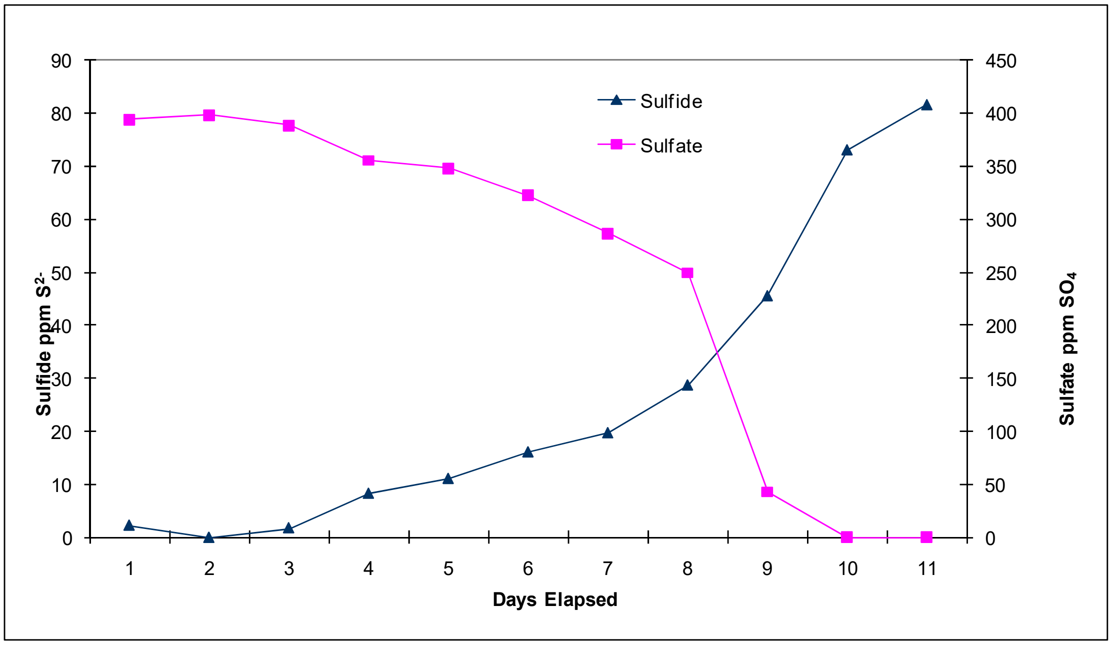


Figure A5 Mill C Reactor 2: Sulfide and Sulfate Concentrations (mg/L)

The figures show that the sulfide generation rate is not consistently linear. In three of the four reactors, a noticeable increase in reaction rate is observed as the reaction proceeds. This rate reaches a maximum and then slows again. This is especially noticeable in Figures A4 and A5. This "S" shape to the sulfide time series is characteristic of microbiological processes where the initial slow rate or lag is caused by biomass acclimation. Other possible reasons for the lag are the presence of more favorable electron acceptors such as nitrate or a specific compound which needs to be formed by fermentative reactions prior to the SRB becoming fully active. After the lag phase, the reaction proceeds at its maximum rate and then slows as some reagent becomes scarce and limits the reaction. If the theory associated with Equation A2 is correct, this observation would suggest that over a long-term anoxic incubation, sulfate may be depleted more quickly than substrate. To confirm this possibility, substrate concentrations must also be monitored. The next section discusses measurement of various substrates in the reactors.

Observations on Substrate Limitation

Experiments were conducted to determine the likelihood of substrate limiting SRB activity in pulp and paper wastewaters. A sulfide reactor was sampled for several measures of substrate including BOD_5, methanol, ethanol, and volatile fatty acids (acetic, propionic, butyric, valeric, isobutyric, and isovaleric). The results for these reactors are shown in Figures A6 to A8.

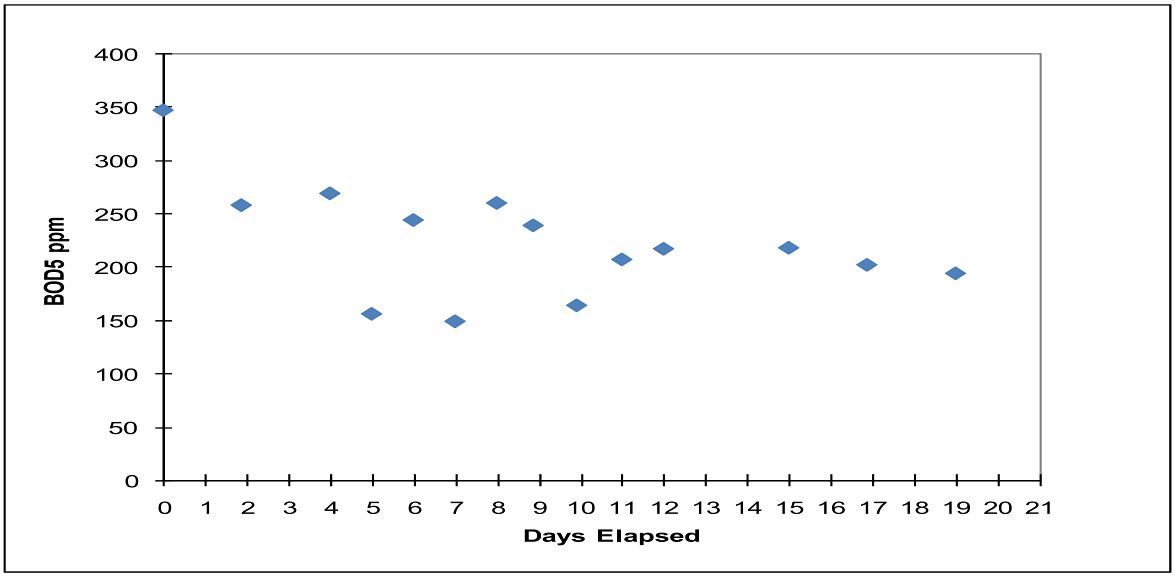


Figure A6 Observed BOD_5 Concentrations from Anoxic Batch Reactor

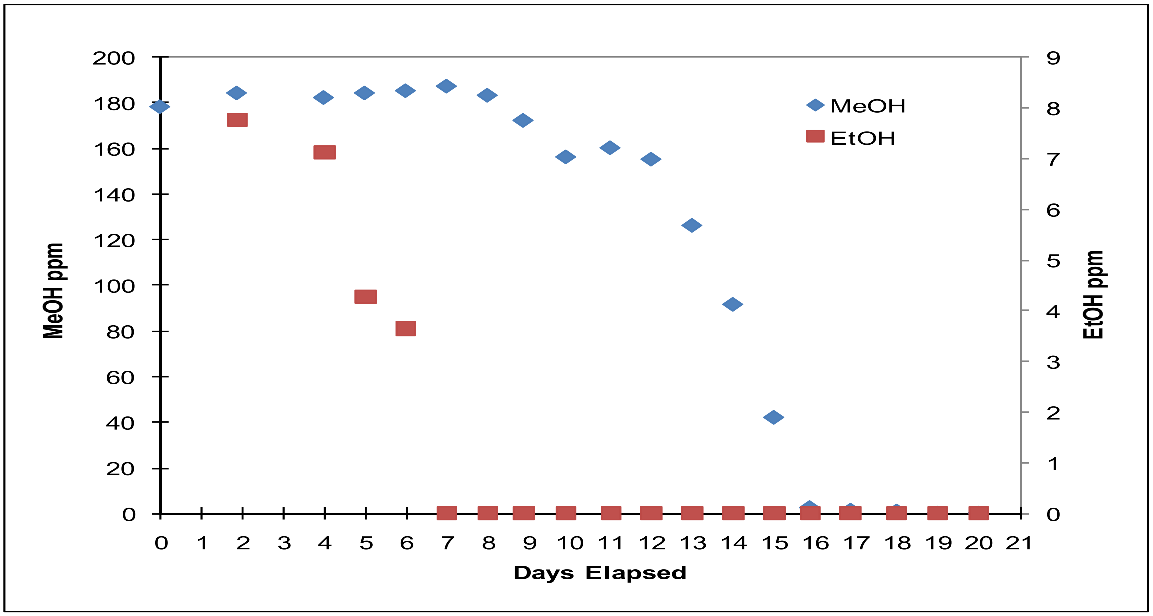


Figure A7 Observed Methanol and Ethanol Concentrations from Anoxic Batch Reactor

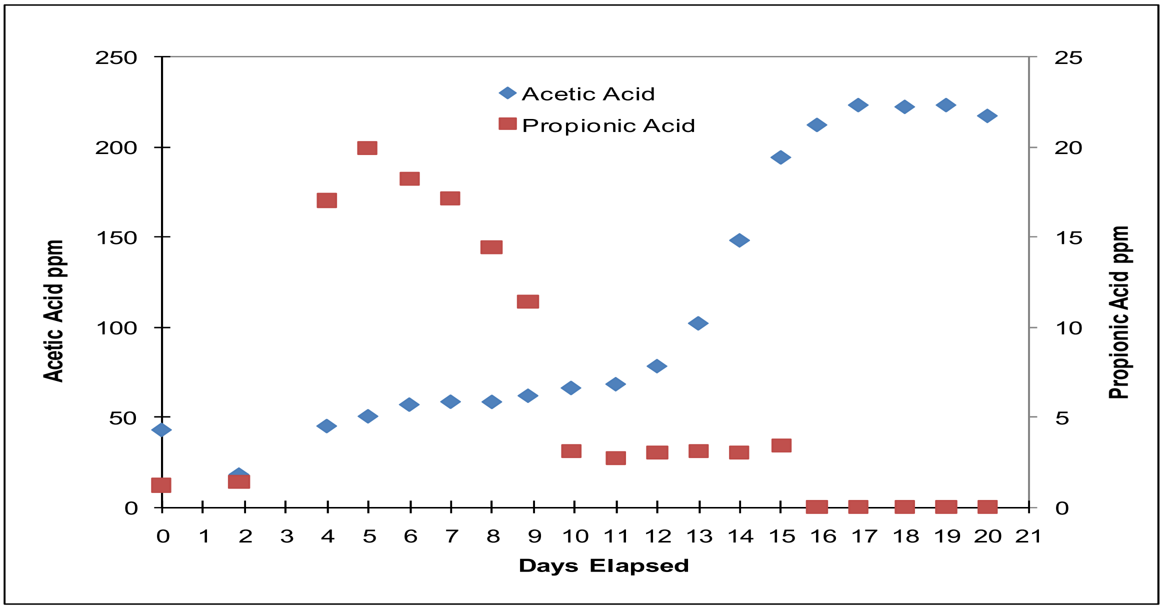


Figure A8 Observed Acetic and Propionic Acid Concentrations from Anoxic Batch Reactor

Figure A6 shows BOD_5 concentration over the course of the experiment. These data indicate that BOD_5 decreased slowly over the course of the experiment and reached a concentration of about 200 mg/L at the conclusion. It does not appear likely that BOD_5 ever reached a concentration in this experiment that could be considered to limit sulfide generation considering the published half saturation coefficients for acetate which are less than 40 mg/L. Similar observations are apparent for methanol, ethanol, and the VFAs. Considering the wide variety of substrates that SRBs are reported to consume and the high concentration of organic materials in untreated wastewater, it is unlikely that substrate will limit sulfide generation in most circumstances. It is more likely that sulfate will be completely consumed prior to depletion of substrate.

These observations about substrate in the reactors suggest that it may not be necessary to include substrate limitation as part of a sulfide generation rate equation. This is likely true for sections of a wastewater treatment basin that receive untreated or lightly treated wastewater such as settling ponds and the front ends of ASBs. However, these experiments do not address conditions likely to occur at the back end of aerobic treatment basins, namely, adequate sulfate concentrations and low substrate concentrations due to rapid aerobic treatment. This scenario, combined with the anaerobic conditions necessary for SRB activity, is not likely to occur in treatment ponds to any great extent, but at this point in time, there is little understanding as to sulfide generation under these conditions.

Model Development

A theoretical kinetic model for sulfate reduction can be developed based on general principles of bacterial growth and sulfate reduction. The rate of sulfide production is related to the rate of sulfate reduction.

$$\frac{dS^{2-}}{dt} = \frac{dSO_4}{dt} * Y_{S^{2-}/SO_4} \qquad \text{Equation A5}$$

Where: S^{2-} = Sulfide (mg/L)
SO_4 = Sulfate (mg/L)
$Y_{S^{-2}/SO4}$ = Unit of sulfide produced per unit of sulfate reduced.

The rate of sulfate reduction is related to the rate of biomass formation.

$$\frac{dSO_4}{dt} = \frac{dX}{dt} * \frac{1}{Y_{X/SO4}} \qquad \text{Equation A6}$$

Where: X = SRB Biomass (mg/L)
$Y_{X/SO4}$ = Unit of biomass produced per unit of sulfate reduced

The rate of biomass formation can be expressed by

$$\frac{dX}{dt} = (\mu - k_d) * X \qquad \text{Equation A7}$$

Where: μ = Specific growth rate (time^{-1})
k_d = decay rate coefficient (time^{-1})

The specific growth rate can be estimated by

$$\mu = \mu_{\max} \frac{S}{K_S + S} * \frac{SO_4}{K_{SO4} + SO_4} \qquad \text{Equation A8}$$

Where: $\mu_{\max}$ = maximum specific growth rate (time^{-1})
K_S = Substrate half saturation constant (mg/L)
K_{SO4} = Sulfate half saturation constant (mg/L)

The above equations can be interpreted as follows: Biomass (as SRB) grows at a maximum rate when substrate and sulfate are in excess. Sulfate is removed and sulfide is produced proportionally to the growth of the biomass. Biomass growth slows as either sulfate or substrate becomes limiting. Sulfate reduction and sulfide generation rates are reduced in proportion to this slowed growth.

The type of model described above is typically applied to laboratory results, where conditions are controlled. The substrate is often only a single substrate such as acetate, and the biomass may be cultured to result in a single species. As such, many of the parameters that are estimated are only applicable to a specific set of conditions that may be different from those in an actual treatment basin where SRB cultures and available substrates are mixed.

The complexities associated with a complete model of sulfide generation may be avoided by making assumptions about the uniformity of the conditions in pulp and paper wastewater treatment basins. These assumptions (listed below), if valid, would allow the model to be simplified to a useful predictor of sulfide generation in basins.

- The ratio of sulfide produced to sulfate removed is constant and at its theoretical value of 1 mol of sulfide produced per 1 mol of sulfate reduced.
- The effect of biomass concentration on sulfide generation rate is constant and therefore implicitly incorporated into the rate coefficient.
- Substrate is not limiting sulfide generation.

If these assumptions hold, Equations A5 to A8 simplify to the expression in Equation A9.

$$\frac{dS^{2-}}{dt} = k\left(\frac{SO_4}{K_{SO_4} + SO_4}\right) \qquad \text{Equation A9}$$

Where k = Zero order rate coefficient (mg S/L time)

To account for the effect of varying oxygen concentrations, the inverse Monod oxygen term can be added to develop the final model.

$$\frac{dS^{2-}}{dt} = k\left(\frac{SO_4}{K_{SO_4} + SO_4}\right)\left(\frac{K_{DO}}{K_{DO} + DO}\right) \qquad \text{Equation A10}$$

Estimation of Sulfide Generation Rate Coefficient

If the above assumptions are valid, sulfate is in excess and oxygen concentration is zero, a kinetic rate equation emerges in which the conditions are such that the rate of reaction is independent of the concentration of reactants. Because it is expected that Equation A10 will be applied mostly under conditions of low oxygen and high sulfate concentrations, the most important parameter to estimate is the rate coefficient *k.*

In the reactor experiments, the timeframe of interest is after the lag period and before sulfate limitation (i.e., the middle leg of the "S"). This timeframe corresponds to the maximum observed sulfide generation rate. Because the lag period is not expected in wastewater treatment systems and Equation A10 accounts for sulfate limitation, the generation rate during this timeframe is a good estimate of *k.*

To precisely determine *k* in the reactor experiments, a segmented regression procedure was applied to the reactor sulfide data. This procedure estimates three discrete rates and two breakpoints in the data that separate the three rates. The initial rate is assumed to be the acclimation or lag phase. The middle rate between the breakpoints is the maximum rate (*k*), and the final rate is assumed to be sulfate limitation. The purpose of the procedure is to systematically identify the part of the sulfide generation curve that represents the maximum generation rate. The procedure was carried using the non-linear regression capabilities of the R software (R Development Core Team 2011). Results of the regression are presented in Table A1. The results of the procedure are presented graphically in Figures A9 through A12.

Table A1 Results of Segmented Regression of Sulfide Generation Reactors
(95% confidence interval in parentheses)

Mill	Lag Rate (mg/L day)	Breakpoint 1 (Days)	Max Rate[d] (mg/L day)	Breakpoint 2 (Days)	Limit Rate[d] (mg/L day)
A	4.0[a] *(3.6,4.3)*	8.0 *(7.3,8.7)*	11.3 *(9.6,13.1)*	11.0 *(10.5, 11.5)*	1.5 *(0.2,3.0)*
B	NA[b]	8.9 *(7.0,10.7)*	11.3 *(10.7,12)*	NA[b]	4.5 *(1.0,7.9)*
C	0.52[c] *(0.47,0.57)*	6.9 *(6.7,7.1)*	26.5 *(23.2,29.8)*	8.3 *(8.1,8.5)*	4.3 *(3.2,5.3)*
C – Replicate	0.31[c] *(0.25,0.37)*	8.9 *(8.5,9.3)*	22.1 *(18.5,25.7)*	NA[e]	NA[e]

[a] The lag rate for these data was fitted with a linear model of the form $y = k*t$.

[b] A significant fit was not found for a three-segment model; thus, a two-segment model was applied and no lag phase was determined.

[c] The lag rate for these data was fitted with a polynomial model of the form $y = k*t^2$.

[d] The maximum rate and limit rate were fitted with a linear model of the form $y = k*t$.

[e] A significant fit was not found for a three-segment model; thus, a two-segment model was applied and no limit phase was determined.

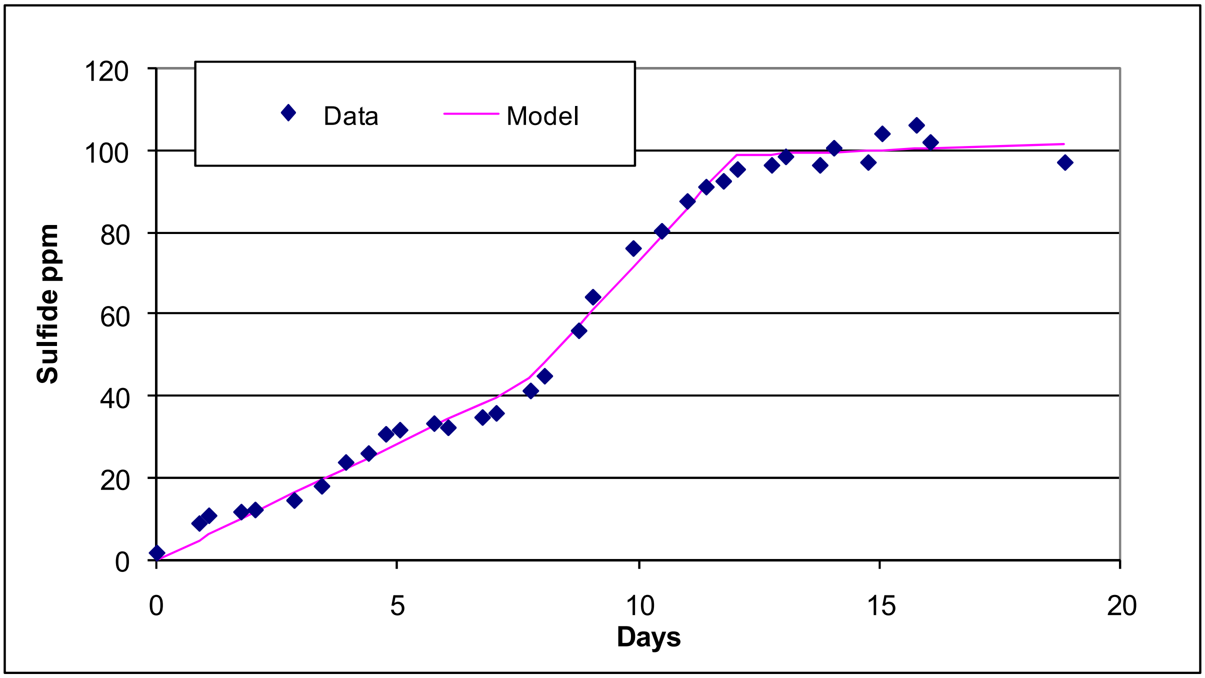


Figure A9 Fit of Segmented Model to Mill A Data

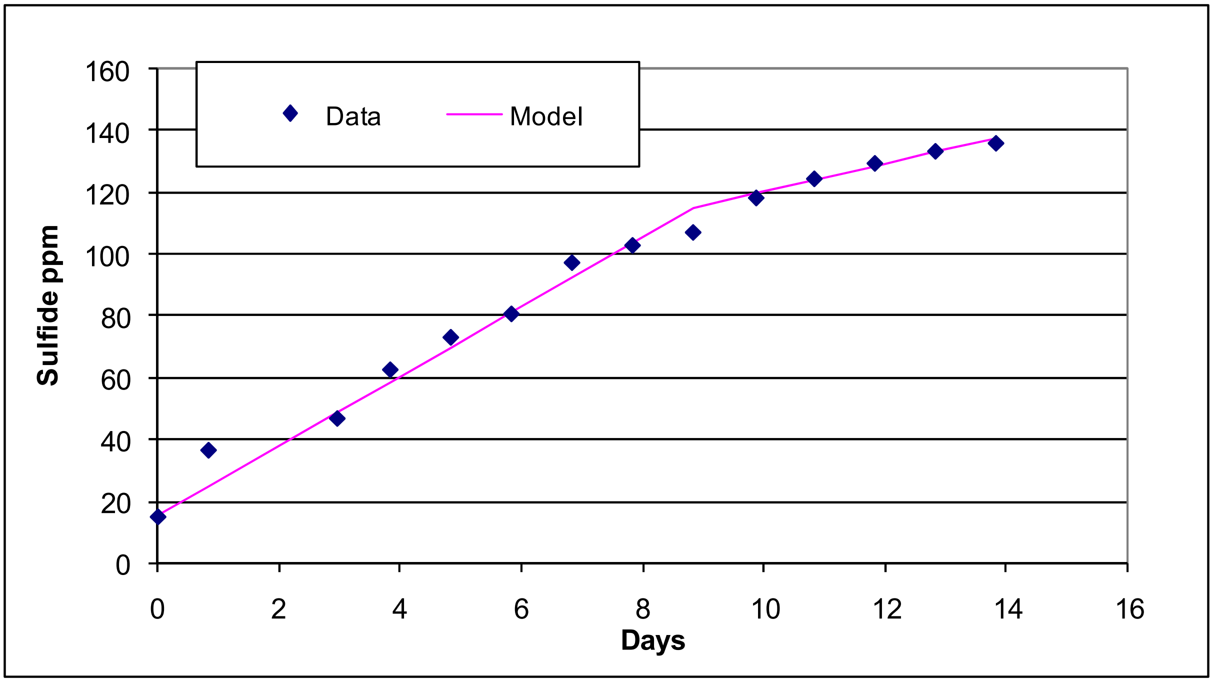


Figure A10 Fit of Segmented Model to Mill A Data

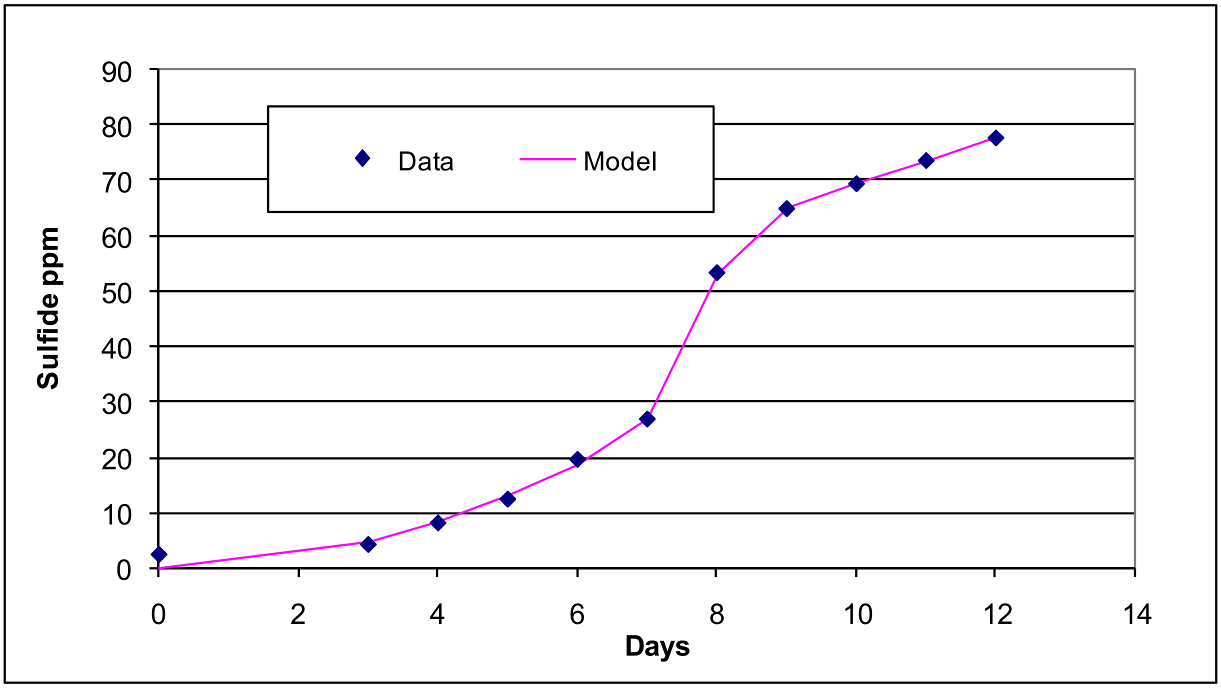


Figure A11 Fit of Segmented Model to Mill C Data

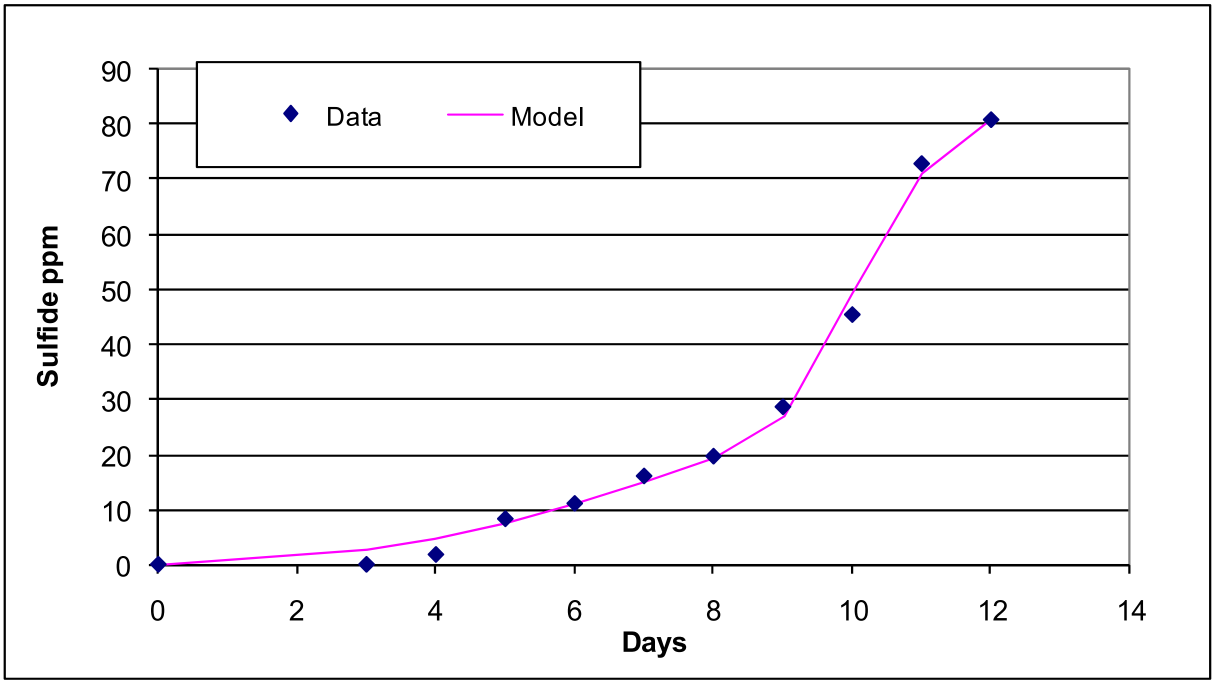


Figure A12 Fit of Segmented Model to Mill C Replicate Data

The results presented in Table A1 indicate that the rate of sulfide generation under optimal conditions varied between 11.3 and 26.5 mg/L day. This result suggests some variability in maximum sulfide generation rates that may be due to some unknown effect that promotes sulfide generation in Mill C or acts as an inhibitor in Mills A and B.

Effect of Temperature

The effect of temperature on biochemical reactions is often modeled using the Arrhenius equation.

$$k_T = k_{20} * \theta^{T-20} \qquad \text{Equation A11}$$

Where θ = Temperature coefficient
k_T = Rate coefficient at actual temperature
k_{20} = rate coefficient at 20 °

The experiments described here did not investigate the value of the temperature coefficient, but temperature effects were observed qualitatively in reactors run at different temperatures. Moosa, Nemati, and Harrison (2005) reported on the effect of temperature between 20 and 35 °C on sulfate reduction in continuous reactors fed with acetate. From this work, a temperature correction coefficient of 1.06 can be estimated. Using Equation A11 with a temperature coefficient of 1.06 and substituting the average measured generation rate from the experiments, an average sulfide generation rate for the three mill wastewaters of 0.25 hr^{-1} can be calculated for 20°C.

Summary

The results of the lab work to characterize sulfide generation are as follows:

- Sulfide generation was likely limited by sulfate after 7 to 11 days of incubation under anoxic conditions. Measurement of available substrates indicates that likely substrates (BOD_5, VFAs) remained at significant concentrations after sulfate had been depleted.

- The above observation suggests that under the vast majority of conditions encountered in pulp and paper wastewaters, it is unlikely that substrate would limit sulfide generation.
- A model was developed that relates the sulfide generation rate to a maximum generation rate, sulfate concentration, oxygen concentration, and temperature.
- Results from batch reactor experiments were used to estimate the value of the maximum generation rate coefficient for three mills as between 11.3 and 26.5 mg/L day^{-1}. Using the average of the three mills and a temperature coefficient of 1.06, an average generation coefficient of 0.25 mg/L hr^{-1} can be calculated for 20°C.
- Based upon a literature review, a reasonable estimate of the sulfate half saturation coefficient is 10 mg/L.

REFERENCES FOR APPENDIX A

Boon, A.G. 1995. Septicity in sewers: Causes, consequences and containment. *Water Science and Technology* 31:237-253. http://dx.doi.org/10.1016/0273-1223(95)00341-J

Colleran, E., Finnegan, S., and Lens, P. 1995. Anaerobic treatment of sulphate-containing waste streams. *Antonie van Leeuwenhoek* 67: 29-46. http://dx.doi.org/10.1007/BF00872194

Feng, J. and Hsieh, Y.P. 1998. Sulfate reduction in freshwater wetland soils and the effects of sulfate and substrate loading. *Journal of Environmental Quality* 27:968:972.

Hansen, T.A. 1988. Physiology of sulphate-reducing bacteria. *Microbiological Sciences* 5(3):81-84.

Ingvorsen, K. and Nielsen, M.Y. 2003. Kinetics of bacterial sulfate reduction in an activated sludge plant. *FEMS Microbiology Ecology* 46:129-137. http://dx.doi.org/10.1016/S0168-6496(03)00209-5

Ingvorsen, K., Zehnder, A.J.B., and Jorgensen, B.B. 1984. Kinetics of sulfate and acetate uptake by Desulfobacter postgatei. *Applied and Environmental Microbiology* 47: 403-408.

Moosa, S., Nemati, M., and Harrison, S.T.L. 2002. A kinetic study on anaerobic reduction of sulphate, Part I: Effect of sulphate concentration. *Chemical Engineering Science* 57:2773:2780.

———. 2005. A kinetic study on anaerobic reduction of sulphate, Part II: Incorporation of Temperature Effects in the Kinetic Model. *Chemical Engineering Science* 60:3517:3524.

Oude Elferink, S.J.W.H., Luppens, S.B.I., Marcelis, C.L.M., and Stams, A.J.M. 1998. Kinetics of acetate oxidation by two sulfate reducers isolated from anaerobic granular sludge. *Applied and Environmental Microbiology* 64:2301-2303.

Postgate, J.R. 1984. *The sulfate-reducing bacteria*. 2nd ed. London: Cambridge University Press.

R Development Core Team 2011. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0. http://www.R-project.org/

Visser, A. 1995. The anaerobic treatment of sulfate containing wastewater. PhD diss. Wageningen Agricultural University.

Yongsiri, C., Hvitved-Jacobsen, T., Vollertsen, J., and Tanaka, N. 2003. Introducing the emission process of hydrogen sulfide to a sewer process model (WATS). *Water Science and Technology* 47(4):85-92

APPENDIX B

DEVELOPMENT OF THE SULFIDE OXIDATION RATE EQUATIONS

Experiments designed to determine an appropriate rate equation and parameters for sulfide oxidation in aerobic pulp and paper mills were performed at the NCASI West Coast Center Laboratory. The methods and results of these experiments are reported in Palumbo, Brown, and Stratton (2010). The experiments determined that a commonly used rate equation for sulfide oxidation was applicable to pulp and paper wastewaters. This rate expression is presented in Equation B1.

$$\frac{dS}{dt} = k_{ox}S^m O^n \qquad \text{Equation B1}$$

Where: S = Total sulfide (mg/L)
O = Oxygen concentration (mg/L)
k_{ox} = Rate coefficient
m = Order of reaction with respect to total sulfide
n = Order of reaction with respect to oxygen

Parameters for the rate expression were estimated based on the results of the lab experiments. These parameters are presented in Table B1.

Table B1 Summary of Estimated Sulfide Oxidation Rate Parameters (Palumbo, Brown, and Stratton 2010)

Study Site	k_{ox} (min^{-1} @20°C)	m[a]	n[b]
Mill A	0.058	1	0
Mill B	0.039	1	0
Mill C	0.045	1	0

[a] The order of the reaction with respect to sulfide was assumed to be 1 for this study based on the findings in the reported literature.

[b] The order of the reaction with respect to oxygen could not be estimated with statistical confidence in these experiments. The value is likely less than 0.2, which is consistent with previous reports.

Effect of Temperature

Various studies in wastewaters (Wilmot et al. 1988; Nielsen, Vollertsen, and Hvitved-Jacobsen 2006) have found that the effect of temperature on the sulfide oxidation rate can be described by Equation B2.

$$k = k_{20} * \theta^{T-20} \qquad \text{Equation B2}$$

Where: k_{20} = oxidation rate coefficient at 20°C (hr^{-1}).
θ = Temperature coefficient
T = Temperature (°C)

The temperature coefficient has been reported as 1.04 (Wilmot et al. 1988) and 1.06 (Nielsen, Vollertsen, and Hvitved-Jacobsen 2006) in wastewaters. A value of 1.05 is selected for the NCASI model based on an average of these two reports.

Effect of pH

The oxidation of sulfide occurs more rapidly at higher pH vales. This is likely due to the relative ease with which HS is oxidized compared to H_2S. Several additional reactor experiments were performed to estimate the effect of pH changes on the oxidation rate in pulp and paper wastewater. Similar to literature reports, these experiments found that sulfide oxidation occurred much more rapidly at high pH values. These observed values (hr^{-1} @ 20°C) are plotted against pH in Figure B1.

Based on the shape of the data, an exponential model was chosen to estimate the oxidation rate coefficient as a function of a pH range. The exponential model was fitted to the reactor data to estimate parameter values. This fitted model is shown in Figure B1 as "predicted."

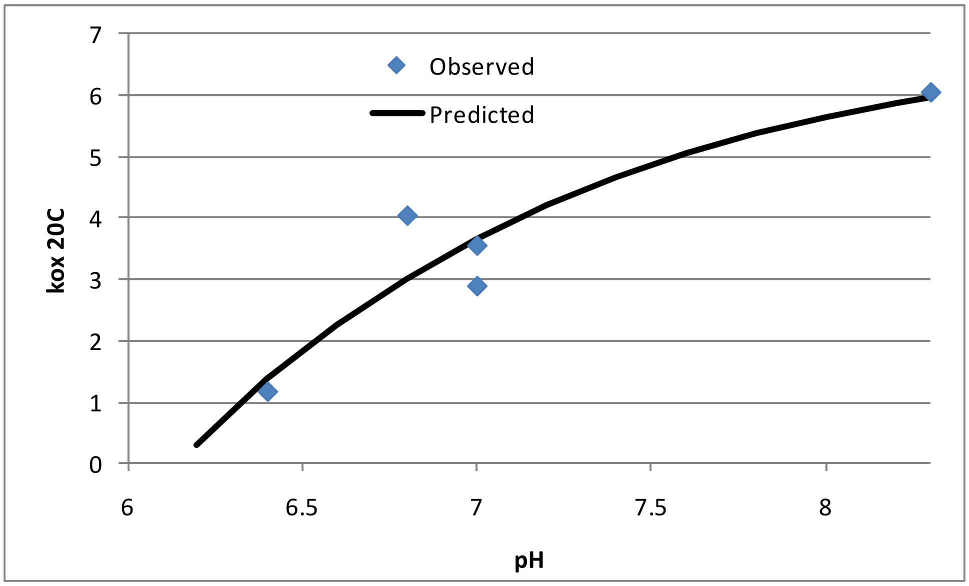


Figure B1 Sulfide Rate Coefficient in Sulfide Model as a Function of pH (T=20°C)

The exponential model has the general form of Equation B3.

$$k_{ox} = \gamma_1(1 - \exp(\gamma_2(pH - \gamma_3)) \qquad \text{Equation B3}$$

The values of the parameters fitted to the observed data are $y_1 = 7.16$, $y_2 = -0.84$, and $y_3 = 6.15$. In the sulfide emissions model, Equation B3 defaults to zero at pH values less than 6.15.

Oxidation Rate under Anoxic Conditions

In laboratory experiments performed in a similar manner to those reported in Palumbo, Brown, and Stratton (2010), sulfide has been shown to oxidize more slowly under anoxic conditions. The rate of sulfide oxidation under anoxic conditions can be modeled using a modification of Equation B1.

$$\frac{dS}{dt} = k_{anox}S^m \qquad \text{Equation B4}$$

This equation can be fit to sulfide depletion data under anoxic conditions to estimate the coefficients. This fit of Equation B4 to data is shown in Figure B2.

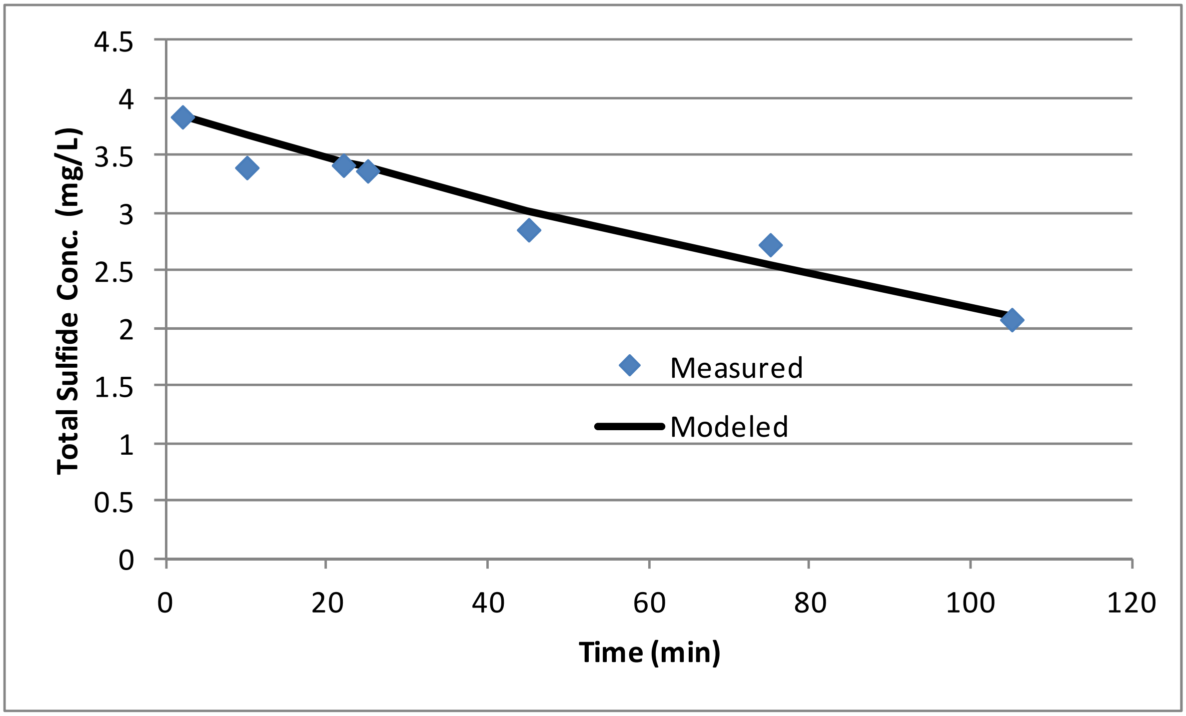


Figure B2 Equation B4 Fit to Sulfide Depletion Data Collected Under Anoxic Wastewater Conditions (pH = 6.9, Temperature = 20 °C)

The resulting coefficients are $k_{anox} = 0.006\ \text{min}^{-1}$ and $m = 1$. Additional experiments are planned to confirm the results of this experiment and also characterize the anoxic rate coefficient at various pH values.

REFERENCES FOR APPENDIX B

Nielsen, A.H., Vollertsen, J., and Hvitved-Jacobsen, T. 2006. Kinetics and stoichiometry of aerobic sulfide oxidation in wastewater from sewers—Effects of pH and temperature. *Water Environment Research* 78:275-283. http://dx.doi.org/10.2175/106143005X94367

Palumbo, J.E., Brown, L.C., and Stratton, S.C. 2010. Modeling the oxidation of sulfide in pulp and paper wastewaters. *Journal of Environmental Engineering* 136: 1171-1179. http://dx.doi.org/10.1061/(ASCE)EE.1943-7870.0000248

Wilmot, P.D, Cadlee, K., Katinic, J.J., and Kavanagh, B.V. (1988) Kinetics of sulfide oxidation by dissolved oxygen. *Journal of the Water Pollution Control Federation* 60: 1264-1270.

APPENDIX C

DEVELOPMENT OF THE SULFIDE STRIPPING RATE EQUATION

Modeling of Sulfide Stripping

The mass transfer of sulfide from a treatment basin is modeled by using procedures similar to those outlined in EPA's background document *Air Emissions Models for Waste and Wastewater* (USEPA1994). The estimation methods described in this document form the backbone of the mass transfer components of EPA's Water9 software and 40 CFR Appendix C to Part 63 calculation procedures. Mass transfer modeling of these systems follows a semi-empirical approach based upon the two resistance model of multiphase interfacial transport. This section will outline the calculation procedures performed by the sulfide model software to estimate mass-transfer coefficients for the system.

The Two-Resistance Model

The two-resistance model has been recognized as the most appropriate method to represent and quantify the volatilization of organic components from water bodies to the atmosphere (Whitman 1923; Treybal 1980). This model is also the basis for the aerated system model used in EPA WATER9 and Appendix C emissions estimation procedures outlined in Part 63. Using this model, environmental volatilization can be represented as a sequence of the following two processes (Liss and Slater 1974; Geankoplis 1993; Thibodeaux 1996).

- Transfer of the compound from the liquid phase to the interface separating the liquid from air
- Transfer of the compound from the interface to the air

In this system, the concentration in the air phase can be assumed to be zero due to constant surface renewal, so there is no mass transfer barrier due to a concentration gradient. The removal rate can be therefore be expressed in terms of an overall mass transfer coefficient.

$$\boldsymbol{E = K_L A \cdot C_{H2S,L}} \qquad \text{Equation C1}$$

where,

E = Emission rate from the area of interest (g/s)
K_L = Overall mass transfer coefficient (m/s)
A = Area associated with mass transfer (m^2)
$C_{H2S,\,L}$ = Concentration of sulfide in the liquid phase, (g/m^3)

The overall mass transfer coefficient is further expressed as the sum of the individual mass transfer coefficients in the liquid and gas phases.

$$\frac{1}{\boldsymbol{K_L}} = \frac{1}{\boldsymbol{k_l}} + \frac{1}{\boldsymbol{K_{eq} k_g}} \qquad \text{Equation C2}$$

where,

k_l = Liquid phase mass transfer coefficient (m/s)
k_g = Gas phase mass transfer coefficient (m/s)
K_{eq} = Partition Coefficient, expressed as $K_{eq} = H_{CP}/RT$

H_{CP} = Henry's law constant (represents the vapor-liquid equilibrium of sulfide in the dilute concentration range, in atm-m^3/mol)
R = Universal gas constant (atm-m^3/mol K)
T = Temperature (K)

This expression represents the two resistances to mass transfer, i.e., the liquid phase resistance ($1/k_l$) and the gas phase resistance (RT/Hk_g). The sum of the two individual resistances gives the overall resistance to mass transfer ($1/K_L$). The individual mass transfer coefficients k_l and k_g are estimated using empirical correlations that relate these parameters to system conditions and fluid/organic compound properties. Knowing the Henry's law constant H, the overall mass transfer coefficient and the resulting mass transfer rate can be calculated.

Volatilization from Aerated Stabilization Basins (ASBs)

Aerated stabilization basins (ASBs) are used in the pulp and paper industry to biologically treat the organic compounds in process effluents. Mechanical surface aerators are commonly used to improve the oxygen transfer into the ASB, thereby enhancing the biological treatment in the system and reducing the organic compound concentrations in treated effluents.

The two-resistance model described above can be used to represent the mass transfer occurring from the surface of aerated treatment systems. In the case of aerated systems, mass transfer occurs through two parallel mechanisms: desorption from "forced convection" (turbulent region) and desorption from "natural convection" (non-turbulent region). The zones of forced convection and natural convection in these aerated systems, as defined during this study, are reproduced in Figure C1 (Thibodeaux 1996). The turbulent area is defined as the impingement area of the aerator spray.

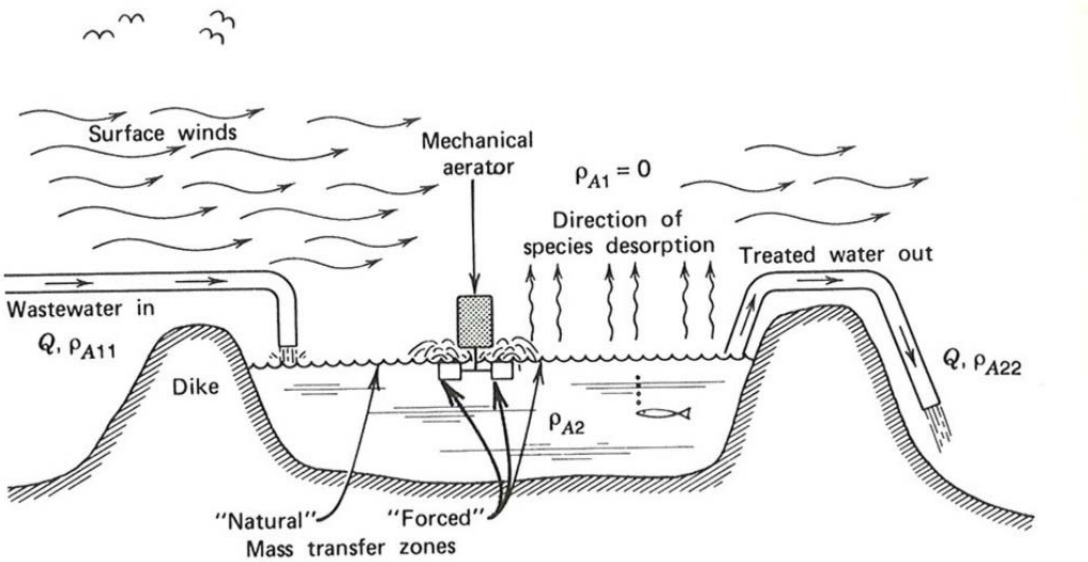


Figure C1 Forced Convection and Natural Convection Zones as Illustrated by Thibodeaux [Figure reproduced from Thibodeaux 1996, p. 174]

The overall mass transfer coefficient K_L for the two regions can be expressed as a function of the individual liquid and gas phase mass transfer coefficients.

Forced convection (turbulent region)

$$\frac{1}{K_{L,Turb}} = \frac{1}{k_{l,Turb}} + \frac{1}{K_{eq} k_{g,Turb}} \qquad \text{Equation C3}$$

Natural convection (defined as the quiescent region in USEPA 1994 and Appendix C to Part 63)

$$\frac{1}{K_{L,Quiescent}} = \frac{1}{k_{l,Quiescent}} + \frac{1}{K_{eq} k_{g,Quiescent}} \qquad \text{Equation C4}$$

The overall mass transfer coefficient ($K_{L,Overall}$) for the entire zone is subsequently calculated as a weighted average of the individual mass transfer coefficients for the forced convection and natural convection zones. This quantity is corrected for an effluent system by multiplying by α, the sulfide mass transfer correction factor. For hydrogen sulfide, experimental studies in sewage transport systems and municipal wastewater treatment indicate this value is approximately 0.6 (Yongsiri, Vollertson, and Hvitved-Jacobsen 2005). NCASI experiments verify this result for kraft mill effluents.

$$K_{L,Overall} = \frac{K_{L,Turb} A_{Turb} + K_{L,Quiescent} A_{Quiescent}}{A_{Turb} + A_{Quiescent}} \cdot \alpha \qquad \text{Equation C5}$$

where,

A_{Turb} = Turbulent area
$A_{Quiescent}$ = Quiescent area

Several previous studies have attempted to correlate these individual mass-transfer coefficients to system properties, aeration conditions, and organic compound properties. Calculations deriving from these studies are summarized in the 1994 EPA background document. The equations developed during these studies are used in the WATER9 model and also in the Appendix C Forms, to estimate the individual mass transfer coefficients.

The important mass transfer mechanisms differ for the turbulent and the quiescent regions. Mass transport in the turbulent region is driven by constant regeneration of the sulfide at the liquid surface (through surface renewal); transfer in these regions is thus proportional to the diffusivity of sulfide raised to the one-half power (Hsieh, Ro, and Stenstrom 1993; White 1991; Thibodeaux 1996). Transfer in quiescent regions is driven by diffusion through the boundary layer at the air-water interface and is proportional to the sulfide diffusivity raised to the two thirds power (Treybal 1980; White 1991; Geankoplis 1993).

Mass Transfer in the Turbulent Region

Mass transfer in the turbulent region is driven by a complex combination of the spraying action of the aerators, mechanically generated waves, and surface renewal of the air water interface. While the turbulent area can make up less than 1% of the surface area of a typical ASB, the mass transfer in the turbulent region often represents the vast majority of volatilization of a compound in the basin.

Liquid Phase Mass Transfer Coefficient for the Turbulent Region ($k_{l,\ turb}$)

Both EPA WATER9 and Appendix C Forms utilize a semi-empirical relationship, developed by Thibodeaux et al., to estimate the liquid phase mass transfer coefficient for the turbulent region ($k_{l,\ Turb}$) (Thibodeaux and Parker 1974; Thibodeaux et al. 1982). The turbulent liquid phase mass transfer coefficient is the most highly system-specific of the four relevant coefficients. The coefficient is expressed as

$$\boldsymbol{k}_{\boldsymbol{L,Turb}} = 8.22 \cdot 10^{-9} \cdot \boldsymbol{J} \cdot \boldsymbol{P} \cdot \ (1.024^{\boldsymbol{T}-20}) \cdot \boldsymbol{O}_{\boldsymbol{T}} \cdot \frac{18 \cdot 10^{6}}{\boldsymbol{A}_{\boldsymbol{S,Turb}} \cdot \rho_{\boldsymbol{Water}}} \cdot \left(\frac{\boldsymbol{D}_{\boldsymbol{H2S,Water}}}{\boldsymbol{D}_{\boldsymbol{Oxygen,Water}}} \right)^{1/2} \qquad \text{Equation C6}$$

where,

J = Oxygen transfer rating of the aerators (lb O_2 / HP hour)
P = Total power to the aerators in the zone (HP)
T = Liquid phase temperature (°C)
O_T = Oxygen transfer correction factor
$A_{S,Turb}$ = Surface area of the turbulent region (in ft^2)
ρ_{Water} = Density of water (g/cm^3)
$D_{H2S,\ Water}$ = Diffusivity of H2S in water (m^2/s)
$D_{Oxygen,Water}$ = Diffusivity of oxygen in water (m^2/s)

The estimated mass transfer in the turbulent area is thus very sensitive to the amount of applied horsepower in the basin.

Gas Phase Mass Transfer Coefficient for the Turbulent Region

The gas phase mass transfer coefficient for the turbulent region is calculated based upon the work of Reinhardt (1977). An empirical relationship for the coefficient was developed from lab studies of ammonia absorption into acidified water agitated by a surface impeller. The gas phase mass transfer coefficient for the turbulent region is a function of several dimensionless groups.

$$\boldsymbol{k}_{\boldsymbol{g,Turb}} = 3.9 \cdot 10^{-4} \cdot \frac{\boldsymbol{D}_{\boldsymbol{H2S,Air}}}{\boldsymbol{d}_{\mathrm{Im}\boldsymbol{peller}}} \mathrm{Re}^{1.42} \cdot \boldsymbol{Sc}^{0.5} \cdot \boldsymbol{Po}^{0.4} \cdot \boldsymbol{Fr}^{-0.21} \qquad \text{Equation C7}$$

$D_{H2S,\ Air}$ is the gas phase diffusivity of hydrogen sulfide (in m^2/s) and $d_{Impeller}$ is the size of the agitator (in m). The dimensionless quantities *Re*, Sc_{Gas}, *Po*, and *Fr* are the Reynolds, Schmidt, Power, and Froude numbers of the gas phase turbulent system, respectively, and are defined as the following.

$$\mathrm{Re} = \frac{\left(\boldsymbol{d}_{\mathrm{Im}\boldsymbol{peller}}\right)^{2} \cdot \omega}{\nu_{\boldsymbol{Air}}} \qquad \text{Equation C8}$$

$$\boldsymbol{Sc}_{\boldsymbol{Gas}} = \frac{\nu_{\boldsymbol{Air}}}{\boldsymbol{D}_{\boldsymbol{H2S,Air}}} \qquad \text{Equation C9}$$

$$\boldsymbol{Po} = \frac{\boldsymbol{HP} \cdot \varepsilon}{\boldsymbol{d}_{\mathrm{Im}\boldsymbol{peller}}^{5} \cdot \rho_{\boldsymbol{Air}} \cdot \omega} \qquad \text{Equation C10}$$

$$\boldsymbol{Fr} = \frac{\left(\boldsymbol{d}_{\mathrm{Im}\,\boldsymbol{peller}}\right) \cdot \omega^2}{\boldsymbol{g}} \qquad \text{Equation C11}$$

In these expressions, ω is the rotational speed (in radians/s), ν_{Air} is the kinematic viscosity of air, ρ_{Air} is the air density, *HP* is the nameplate horsepower of the aerator, ε is the mechanical efficiency of the aerator, and g is the gravitational acceleration (9.8 m/s^2).

Mass Transfer in the Quiescent Region

Volatilization of a compound from the quiescent region of an ASB is primarily driven by transport through the boundary layer at the surface of the air liquid interface. The primary mechanism is thought to be natural convection at the liquid surface generated by air flow.

Liquid Phase Mass Transfer Coefficient for the Quiescent Region

The fetch-to-depth (*F/D*) ratio plays an important role in the liquid side of mass transfer in the quiescent region. The *F/D* value is a measure of the length of the basin in the windward direction divided by the depth of the basin. This value indicates the degree to which wind-generated micro- and macro-sized waves will migrate across the basin, increasing mass transfer. For all of the cases of interest, the liquid phase mass transfer coefficient of sulfide in the quiescent region is driven by boundary layer phenomena (White 1991). The resistance to mass transfer on the liquid side is the ability of sulfide to reach the surface of the liquid-air interface through the boundary layer, not the ability of sulfide to leave the surface.

At low wind speeds (< 3.25 m/s), the liquid phase mass transfer coefficient is independent of wind speed and *F/D*. The coefficient is correlated by application of the liquid phase diffusivity of sulfide, $D_{H2S,\ Water}$ (in m^2/s) to experimental results for ether volatilization by using the following relationship.

$$\boldsymbol{k}_{\boldsymbol{l,Quiescent}} = 2.78 \cdot 10^{-6} \left(\frac{\boldsymbol{D}_{\boldsymbol{H}2\boldsymbol{S,Water}}}{\boldsymbol{D}_{\boldsymbol{Ether,Water}}}\right)^{2/3} \qquad \text{for } v_{wind} < 3.25 \text{ m/s, All } F/D \qquad \text{Equation C12}$$

For wind speeds over 3.25 m/s and intermediate *F/D* values ranging from 14 to 51.2, the following expression is used to estimate the coefficient.

$$\boldsymbol{k}_{\boldsymbol{l,Quiescent}} = \left[2.78 \cdot 10^{-9} \cdot \boldsymbol{F}/\boldsymbol{D} + 1.277 \cdot 10^{-7}\right] \cdot \boldsymbol{v}_{\boldsymbol{wind}}{}^{2} \cdot \left(\frac{\boldsymbol{D}_{\boldsymbol{H}2\boldsymbol{S,Water}}}{\boldsymbol{D}_{\boldsymbol{Ether,Water}}}\right)^{2/3} \qquad \text{Equation C13}$$

for $v_{wind} > 3.25$ m/s, $14 < F/D < 51.2$

For all other applicable conditions, the liquid phase mass-transfer coefficient is estimated from

$$\boldsymbol{k}_{\boldsymbol{l,Quiescent}} = \left[2.611 \cdot 10^{-7}\right] \cdot \boldsymbol{v}_{\boldsymbol{wind}}{}^{2} \cdot \left(\frac{\boldsymbol{D}_{\boldsymbol{H}2\boldsymbol{S,Water}}}{\boldsymbol{D}_{\boldsymbol{Ether,Water}}}\right)^{2/3} \qquad \text{Equation C14}$$

for $v_{wind} > 3.25$ m/s, $F/D > 51.2$

Gas Phase Mass Transfer Coefficient for the Quiescent Region

Estimates of the gas phase mass transfer coefficient in the quiescent region are based upon the work of MacKay and Matsugu (1973). These authors developed an empirical relationship for the coefficient by studying the evaporation of benzene, gasoline, and water from still pools into air.

$$\boldsymbol{k}_{g,\boldsymbol{Quiescent}} = 4.82 \cdot 10^{-3} \cdot \boldsymbol{v}_{\boldsymbol{Wind}}{}^{0.78} \cdot \boldsymbol{Sc}_{\boldsymbol{Gas}}{}^{-\frac{2}{3}} \cdot \boldsymbol{d}_{\boldsymbol{Effective}}{}^{-0.11}$$ Equation C15

In this expression, the mass transfer coefficient is estimated from the wind speed (in m/s), the effective diameter of the basin ($d_{efective}$, in m), and the Schmidt number of the gas phase.

Temperature Correction of Physical Parameters

Each of the correlations is based upon physical parameters of one or more compounds. In order to make the model more site-specific and condition-specific, these physical quantities are corrected to simulate their dependence upon temperature. While the individual impact of the temperature dependence upon a parameter may be low, the combined impact can be large.

The temperature correction of the density of air (in g/m^3) is linearly dependent upon the ambient air temperature (in °C) and is derived from the ideal gas law.

$$\rho_{Air} = 1.204 \cdot \frac{293.15\,\boldsymbol{K}}{\boldsymbol{T}_{\boldsymbol{Ambient}} + 273.15}$$ Equation C.16

Water density (in kg/m^3) is found from the basin temperature (in °C) from the following.

$$\rho_{Water} = \left[\, 0.998203 - 0.000257 \cdot (\boldsymbol{T}_{\boldsymbol{ASB}} - 20)\right] \cdot 1000$$ Equation C17

The viscosity of air is calculated empirically from tabulated data (Geankoplis 1993, p. 855).

$$\mu_{Air} = 0.1 \cdot (0.0000004568 \cdot \boldsymbol{T}_{\boldsymbol{ASB}} + 0.00017209)$$ Equation C18

The temperature dependence of water viscosity is simulated by the following empirical relationship.

$$\mu_{Water} = 0.00174 - 0.0000452 \cdot \boldsymbol{T}_{\boldsymbol{ASB}} + 0.00000044 \cdot \boldsymbol{T}_{\boldsymbol{ASB}}{}^{2}$$ Equation C19

The liquid phase diffusivities of ether, oxygen, and sulfide are calculated from literature values at a set temperature (in this case 20°C) using the semi-empirical procedures outlined in Bird, Stewart, and Lightfoot (1960, p. 515). This relation is applicable for diffusion of a very dilute species in a liquid and is a function of the liquid viscosity at the appropriate temperature.

$$\boldsymbol{D}_{\boldsymbol{Ether,Water}} = 8.5 \cdot 10^{-10} \cdot \frac{\boldsymbol{T}_{\boldsymbol{ASB}} + 273.15}{293.15} \cdot \frac{0.000972}{\mu_{Water}} \ (\mathrm{m^2/s})$$ Equation C20

$$\boldsymbol{D}_{\boldsymbol{Oxygen,Water}} = 2.4 \cdot 10^{-9} \cdot \frac{\boldsymbol{T}_{\boldsymbol{ASB}} + 273.15}{293.15} \cdot \frac{0.000972}{\mu_{Water}} \ (\mathrm{m^2/s})$$ Equation C21

$$\boldsymbol{D}_{H2S,Water} = 1.61 \cdot 10^{-9} \cdot \frac{\boldsymbol{T}_{ASB} + 273.15}{293.15} \cdot \frac{0.000972}{\mu_{Water}} \ (\mathrm{m^2/s}) \qquad \text{Equation C22}$$

The temperature dependence of the gas phase diffusivity of sulfide is derived from molecular theory and varies with temperature raised to the 1.5 power. This relationship is only applicable at low concentrations (Bird, Stewart, and Lightfoot 1960, p. 511).

$$\boldsymbol{D}_{H2S,Air} = 1.76 \cdot 10^{-5} \cdot \left(\frac{\boldsymbol{T}_{ASB} + 273.15}{293.15}\right)^{1.5} \ (\mathrm{m^2/s}) \qquad \text{Equation C23}$$

The Henry's law constant of sulfide in an air/water system is calculated from the value at 30°C and is derived from thermodynamic modeling.

$$\ln \frac{\boldsymbol{H}_{CP}}{(\boldsymbol{H}_{CP})_{30}} = 2.3 \cdot 767.3886 \cdot \left(\frac{1}{30 + 249.09} - \frac{1}{\boldsymbol{T}_{ASB} + 249.09}\right) \cdot \ln 2.7182 \qquad \text{Equation C24}$$

Agitated Area Due to Surface Aeration

Thibodeaux et al. (1982) examined the transfer rates of volatile organics in wastewater treatment basins. The objective of this work was to determine the flux rate of organic compounds emitted into the air from wastewater treatment plants in the pulp and paper industry. The concentration profile (CP) technique was used to measure the organic compound concentrations in the boundary layer. Mass transfer models based on the two-resistance theory were used to generate predicted methanol emission rates. This study was also used to determine the appropriate turbulent areas for use with the two-zone approach outlined above.

The liquid phase mass transfer coefficient for the turbulent region ($k_{l,\ turb}$) was estimated using an expression similar to Equation C6. The results of a more elaborate study on the interfacial surface area (a_v) generated by high speed (1200 rpm) aerators had been published in literature (Freeman 1979).The interfacial areas generated due to surface aeration were found to be dependent on the aerator horsepower. According to this study, a 50-HP high speed aerator with a 60 cm impellor would generate 135 m^2 of agitated area. These data were considered appropriate for the high speed aerators typically used in wastewater treatment systems in the pulp and paper industry. These data have been used in the USEPA background document on air emission models to calculate "turbulent areas" for sample ASBs (USEPA 1994, pp. 5-40) and also provided in the Appendix C Forms, as a means to calculate the turbulent area applicable to the turbulent liquid phase mass transfer coefficient. Selected turbulent areas are presented in Table C1.

Table C1 Turbulent Areas for Various Aerator Horsepowers

Aerator Horsepower (HP)	**Turbulent Area (per Aerator)**
50	135 m^2
75	229 m^2
100	348 m^2
125	492 m^2

Volatilization from Primary Clarifiers

Sulfide is volatilized from the surface of industrial clarifiers along two pathways: from the surface of the clarifier and from trickling water at the weir. The overall mass transfer coefficient from a primary clarifier is expressed as the sum of the transfer along these two pathways.

$$(K_L A)_{Overall} = \left(K_{L,Surface} A_{Surface} + K_{L,Weir} A_{Weir}\right) \cdot \alpha \qquad \text{Equation C25}$$

In this expression, $K_{L,Surface}$ and $A_{Surface}$ are the mass transfer coefficient and interfacial area of the liquid-air interface for the surface of the clarifier. $K_{L,Weir}$ and A_{Weir} represent the mass transfer coefficient at the weir and the surface area of the weir waterfall.

The mass transfer from the surface liquid of the clarifier is driven by air flow. The mass transfer coefficient is calculated in the same manner as for aerated basins, described above.

Like the pond coefficients, the mass transfer coefficient at the weir is estimated using two-film theory as described in Equation C26.

$$\frac{1}{\boldsymbol{K}_{L,Weir}} = \frac{1}{\boldsymbol{k}_{l,Weir}} + \frac{1}{\boldsymbol{K}_{eq}\boldsymbol{k}_{g,Weir}} \qquad \text{Equation C26}$$

where $k_{l,Weir}$ and $k_{g,Weir}$ are the liquid side and gas side mass transfer coefficients and K_{eq} is the dimensionless Henry's constant. In this software tool, the transfer coefficients for a weir are calculated in the manner described by Pincince (1991). The liquid side transfer is calculated from the following empirical expressions.

$$\boldsymbol{R} = \exp\left(0.042 \cdot \boldsymbol{h}_{Weir}^{\;0.0872} \cdot \left(\frac{\dot{\boldsymbol{V}}}{\boldsymbol{C}_{Weir}}\right)^{0.509}\right) \qquad \text{Equation C27}$$

$$\boldsymbol{k}_{l,Weir} = \left(1 - \frac{1}{\boldsymbol{R}}\right) \cdot \frac{\dot{\boldsymbol{V}}}{3600 \cdot \boldsymbol{h}_{Weir}} \quad \left(\boldsymbol{m}^2/\boldsymbol{s}\right) \qquad \text{Equation C28}$$

In these expressions, h_{Weir} and C_{Weir} are the height and circumference of the clarifier weir in meters; $\dot{V}$ is the flow rate over the weir in m^3 per hour.

The gas side mass transfer coefficient is correlated from experimental results for benzene stripping using the diffusivity of sulfide in air, as shown in Equation C29.

$$k_{g,Weir} = 0.05 \cdot \left(\frac{D_{H2S,Air}}{D_{Benzene,Air}} \right)^{2/3} \quad \left(m^2 / s \right) \qquad \text{Equation C29}$$

Volatilization Due to Diffused Aeration

Sulfide can also be volatilized due to transfer from the liquid phase to bubbles that derive from the operation of subsurface aeration equipment. Generally, the depth at which these bubbles are created is much greater than their size; the bubble/liquid system can therefore be assumed to be at equilibrium with respect to dissolved H_2S. For dilute systems, the stripping rate due to bubble action is then related to the liquid concentration and gas flow rate through the system, as shown in Equation C30 (similar procedures are described in Geankoplis 1993).

$$\dot{m}_{H_2S} = \dot{V}_{Gas} \cdot K_{Eq} \cdot C_{H_2S} \qquad \text{Equation C30}$$

In this expression, the emission rate of sulfide (in g/s) is a function of the volume rate of gas through the system, V_{Gas} (in m^3/s), the dimensionless Henry's constant and the concentration of free sulfide (in g/m^3) in the liquid phase.

When estimating the volatilization rate due to subsurface aeration, a conservative assumption is to use the volume of injected air for V_{Gas} (i.e., assume no injected volume loss due to oxygen take-up or overwater pressure).

Mass Transfer Calculation Procedure

The model software calculates an overall mass transfer coefficient (K_LA) for each modeled zone. This parameter is then applied to the mass balance differential equations, and a sulfide emission rate is estimated from each zone. The calculation procedure for the mass-transfer mechanism is as follows:

1) Read zone-specific temperature, dimensions, number, and power of aerators.
2) Calculate temperature-dependent densities, viscosities, diffusivities, and Henry's Constant.
3) Calculate dimensionless quantities (Reynolds numbers, Schmidt Numbers, etc.).
4) Calculate the turbulent area from aeration information, allocate turbulent and quiescent area.
5) Calculate quiescent and turbulent liquid and gas phase mass-transfer coefficients.
6) Calculate and output overall mass-transfer coefficient for the zone.

REFERENCES FOR APPENDIX C

Bird, R.B., Stewart, W.E., and Lightfoot, E.N. 1960. *Transport phenomena*. New York: John Wiley and Sons.

Freeman, R.A. 1979. Stripping of hazardous chemicals from surface aerated waste treatment basins. Air Pollution Control Association – Water Pollution Control Federation Specific (Toxic) Pollutants Conference. February 13-16. Gainesville, FL.

Geankoplis, C.J. 1993. *Transport processes and unit operations*. Englewood Cliffs, NJ: PTR Prentice Hall.

Hsieh, C., Ro, K.S., and Stenstrom, M.K. 1993. Estimating emissions of 20 VOCs–Part I: Surface aeration. *Journal of Environmental Engineering* 119(6): 1077-1098. http://dx.doi.org/10.1061/(ASCE)0733-9372(1993)119:6(1077)

Liss, P.S. and Slater, P.G. 1974. Flux of gases across the air-sea interface. *Nature* 247: 181-184. http://dx.doi.org/10.1038/247181a0

MacKay, D. and Matsugu, R.S. 1973. Evaporation rates of liquid hydrocarbon spills on land and water. *Canadian Journal of Chemical Engineering* 51: 434-439. http://dx.doi.org/10.1002/cjce.5450510407

Pincince, A. 1991. Transfer of oxygen and emissions of volatile organic compounds at clarifier weirs. *Research Journal of the Water Pollution Control Federation* 63(2): 114-119.

Reinhardt, J.R. 1997. Gas-side mass-transfer coefficient and interfacial phenomena of flat-bladed surface agitators. Ph.D. Dissertation, University of Arkansas, Fayetteville.

Thibodeaux, L.J. 1996. *Environmental chemodynamics: Movement of chemicals in air, water, and soil.* 2nd ed. New York: Wiley Interscience.

Thibodeaux, L.J. and Parker, D.G. 1974. Desorption limits of selected industrial gases and liquids from aerated basins. Paper 30d, presented at 76th AIChE National Meeting, Tulsa, OK.

Thibodeaux, L.J., Parker, D.G., and Heck, H.H. 1982. *Measurement of volatile chemical emissions from wastewater basins*. EPA-600/2-82-095. Cincinnati, OH: United States Environmental Protection Agency, Industrial Environmental Research Laboratory.

Treybal, R. E. 1980. *Mass transfer operations*. 3rd ed. New York: McGraw Hill.

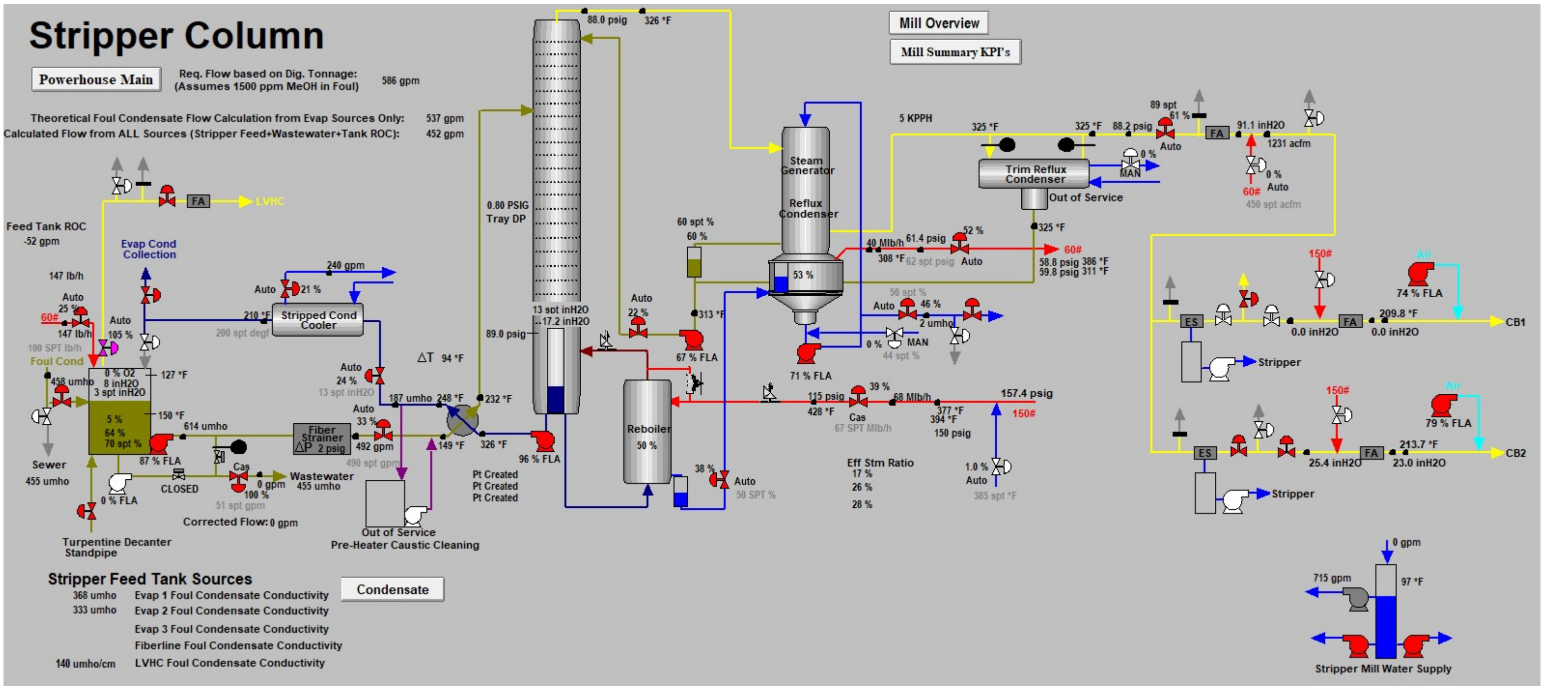
United States Environmental Protection Agency (USEPA). 1994. *Air emissions models for waste and wastewater.* EPA-453/R-94-080A. Research Triangle Park, NC: United States Environmental Protection Agency, Office of Air Quality Planning and Standards.

White, F. 1991. *Viscous fluid flow*. Boston: McGraw-Hill.

Whitman, W.G. 1923. Preliminary experimental confirmation of the two-film theory of gas absorption. *Chemical and Metallurgical Engineering* 29: 146-150.

Yongsiri, C., Vollertson, J., and Hvitved-Jacobsen, T. 2005. Influence of wastewater constituents on hydrogen sulfide emission in sewer networks. *Journal of Environmental Engineering* 131:1676-1683. http://dx.doi.org/10.1061/(ASCE)0733-9372(2005)131:12(1676)

ATTACHMENT B – STEAM STRIPPER FLOW DIAGRAM



Stripper Column

Powerhouse Main

Req. Flow based on Dig. Tonnage:
(Assumes 1500 ppm MeOH in Foul) 586 gpm

Theoretical Foul Condensate Flow Calculation from Evap Sources Only: 537 gpm
Calculated Flow from ALL Sources (Stripper Feed+Wastewater+Tank ROC): 452 gpm

Feed Tank ROC -52 gpm

Corrected Flow: 0 gpm

Stripper Feed Tank Sources

368 umho	Evap 1 Foul Condensate Conductivity
333 umho	Evap 2 Foul Condensate Conductivity
	Evap 3 Foul Condensate Conductivity
	Fiberline Foul Condensate Conductivity
140 umho/cm	LVHC Foul Condensate Conductivity