NEW INDY
CONTAINERBOARD

January 11, 2022

John Glass
Bureau of Air Quality- Modeling Section Manager
South Carolina Department of
Health and Environmental Control
2600 Bull Street
Columbia, South Carolina 29201

Re: Response to DHEC comments on New-Indy Catawba, LLC's Corrective Action Plan Air Dispersion Modeling Analysis

Dear John:

New-Indy Catawba LLC (New-Indy Catawba) submits this information in response to questions and comments by the South Carolina Department of Health and Environmental Control (DHEC) received via electronic mail on December 21, 2021. The DHEC questions pertain to the air dispersion modeling submittals from New-Indy Catawba to DHEC on August 30, 2021 and October 27, 2021. The DHEC questions and New-Indy Catawba responses are discussed below.

DHEC Comment 1: *December 2, 2021 responses, Item 6 - The individual H2SSIM runs in the August 2021 modeling analysis used temperatures of 135.8 F, 133.4 F, 130.6 F, for an average of 133.27 F. Where did this data come from if it is not source specific data? The average value of these temperatures is different than the "average" used in the October 2021 H2SSIM run of 111.9 F. Please explain. In the IPT results, 111.9 F is shown as the inlet to the ASB. Is it appropriate to use this temperature at the Clarifier? Does the stream temperature drop as it flows from the Clarifier to the ASB? Is using 111.9 F more conservative, i.e., results in higher emissions from the Primary Clarifier? Please explain in regard to the Closed Trench No. 1, Splitter and Open Sump No. 4, and Ditch O as well.*

New-Indy Catawba Response 1: The individual H2SSIM runs in the August 2021 modeling analysis utilized an overly conservative assumption of site-specific foul condensate temperatures in the primary clarifier model runs. The temperature was updated to a more accurate assumption of ASB inlet temperatures in the submittal of the Response to Comments: Condensate Collection and Treatment System: HAP, Methanol, and TRS Performance Test-Conducted June 23 – July 11, 2021 dated October 5, 2021 (provided as Attachment A). The temperatures utilized in the October 5 response were the following: 110.6°F (July 9, 2021), 112.8°F (July 10, 2021), and 112.3°F (July 11, 2021) which matches the calculated average of 111.9°F.

No site-specific temperature data exists for the Primary Clarifier, Closed Trench No. 1, Splitter and Open Sump No. 4, and Ditch 0. The closest directly-measured temperature source is the ASB inlet, and it was regarded as the best engineering estimate of the Primary Clarifier Temperature in the October 5 response. Stream temperature has the potential to drop between the Primary Clarifier and the ASB inlet; however, the drop is expected to be insignificant based on the ambient daytime temperature during the sampling period (the average high temperature during the sampling period was 90°F.). National Council for Air and Stream Improvement (NCASI) Technical Bulletin No. 1000 states that as temperature increases above 35°C (95°F) for anoxic environments (*i.e.*, dissolved oxygen near 0 mg/L), hydrogen sulfide generation decreases (provided as Attachment B, page 7). Therefore, 111.9°F is considered a more conservative temperature than 133.27°F for estimating air emissions of hydrogen sulfide in anoxic environments such as the units between the Primary Clarifier and the ASB.

DHEC Comment 2: *December 2, 2021 responses, Item 8 - The response indicates that the pH of 8.943333 was used as a surrogate in the H2SSIM model until specific source data was available. The individual H2SSIM runs in the August report seemed to use source specific data. See table below:*

	August 2021 report				October 2021 report	
	Run 1	Run 2	Run 3	Avg	Avg	Used in Water 9
pH	9.01	9.1	9.04	9.05	8.9433333	9.08

Where did the data in the August report come from and why was it used in the model runs for the August report? The 8.9433 pH was not used until the October 2021 report, which is from the inlet to the ASB. What is the correct source specific data that should be used in the H2SSIM and Water9 runs for the Primary Clarifier?

For informational purposes, here is a comparison of the three individual runs and the average from the August 2021 report to the average run in the October 2021 report (see table below). The average flow drops by about 2.5 MGD between the August 2021 and October 2021 reports. Why are the total sulfide values so different between the August and October reports? It was assumed that the information in the three runs from August were averaged and used as input to the October report. If the averages of the runs in the August report were not used as the inputs for the October report, please explain where the information came from that was used in the October report for the Primary Clarifier and reason for the differences in many of the parameters between the two reports?

Clarifier, H2SSIM model inputs						
	August 2021 report				October 2021 report	
Page=>	A-244	A-246	A-248		A-60	A-56
	Run 1	Run 2	Run 3	Avg	Avg	Used in Water9
Flow, MGD	24.06	23.98	23.14	23.73	21.35	--
Total Sulfide, mg/L	114.2	96.9	46.9	86	0.0200371	--
Sulfate, mg/L	390	390	390	390	390	--
Temperature , F	135.8	133.4	130.6	133.27	111.9	111.9
pH	9.01	9.1	9.04	9.05	8.9433333	9.08
Clarifier, length, ft	275	275	275	275	243.7	--
width, ft	275	275	275	275	243.7	--
depth, ft	5.41	5.41	5.41	5.41	5.41	--
Emissions, lbs/yr	167.6	123.3	72.3	121.07	15.2	--
Emissions flux, gms/m2-yr	10.8	8	4.7	7.83	1.3	--
Liquid Conc. (total sulfide), mg/L	5.076	4.61	2.47	4.05	0.452	--
Liquid Sulfide Load (lb/yr)	58,634.3	53,070.2	27,436.2	46,380.23	4,637.2	--

New-Indy Catawba Response 2: The August 2021 H2SSIM modeling analysis utilized daily average site-specific foul condensate pH data (average pH of 9.05) for the Primary Clarifier. The most representative source specific pH data for the Primary Clarifier is 9.08, which is based on the average readings of the Primary Clarifier pH PI tag from July 9-11,2021, as stated in New-Indy Catawba Response 8 in the December 2, 2021 Response to DHEC (provided as Attachment C).

The length and width of the Primary Clarifier was re-calculated in the October 2021 report as equivalent rectangular lengths and widths based on the Primary Clarifier's circular surface area to refine further the H2SSIM model inputs. The average flow was revised in the October 2021 report to reduce the full inlet raw water flow by 10% to account for evaporation, consistent with the Fbio calculations for 40 CFR Part 63, Subpart S. The total sulfide concentration for the October 2021 report was back-calculated using WATER9 (*i.e.*, the inlet total sulfide concentration to the Primary Clarifier was determined using an iterative approach utilizing the WATER9 program that resulted in the measured sulfide concentration at the ASB inlet).

These differences in the Primary Clarifier dimensions, flow rate, and total sulfide concentrations were documented in New-Indy Catawba Response 36 in the Response to DHEC comments dated October 5, 2021 and New-Indy Catawba Response 6 in the Response to DHEC comments dated December 2, 2021.

DHEC Comment 3: *December 2, 2021 responses, Item 12 -Table A-7 of the October 2021 modeling report indicates dates by each sampling run performed at the Post-Aeration Basin. The dates areRun 1 (7-15-21), Run 2 (7-21-21), Run 3 (7-28-21). These dates do not correspond to any testing dates or results in the Initial Performance Test (IPT). These results do not appear tomatch any of th[ose] in the IPT results. The response indicates results from measurements using the Scentroid portable monitor were not part of the IPT performed July 7-11, 2021. These measurements were not observed by DHEC personnel and this method was not the required method in the EPA's 114 letter, nor the method approved for use in the test reports. The results appear to indicate the Scentroid monitor results, which are air emissions, were used as inputs to the water models. Is this correct and, if so, please explainhow this is appropriate, what water model input(s) this air emissions data was used for, and how this air emissions data was converted to provide the input(s) used in the models. Also, please provide a detailed description of the sampling methodology used for the Scentroid measurements as well as information on the accuracy of the Scentroid data generated.*

New-Indy Catawba Response 3:

New-Indy Catawba installed a cover and carbon filtration system on the Post-Aeration Basin to capture and reduce potential H_2S/TRS emissions on June 9, 2021, prior to the IPT. EPA approved the temporary removal of the cover during the IPT to conduct the liquid sampling of the Post-Aeration Basin to determine the fraction biodegraded (Fbio) and fraction volatilized (Fair) for H_2S/TRS. The Post-Aeration Basin air emissions (Fair) in the IPT Report were calculated based on the liquid sampling conducted July 9-11, 2021 during the IPT as required by the EPA. The Post-Aeration Basin Fair values reported in the IPT Report do not account for the cover and carbon filtration system, as sampling for those emissions is not a requirement for 40 CFR Part 63, Subpart S. In its June 30, 2021 Section 114 Request, EPA required only liquid sampling of the Post-Aeration Basin; air emission testing of the Post-Aeration Basin was not required. Neither DHEC nor EPA specified a method for the measurement of air emissions from the Post-Aeration Basin.

New-Indy Catawba conducts periodic sampling of the outlet of the carbon filtration system using the Scentroid portable monitor to determine the need for replacement of the carbon filter.[1] To estimate the air emissions from the Post-Aeration Basin most accurately, New-Indy Catawba

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[1] The Consent Decree between EPA and New-Indy Catawba requires weekly monitoring of emissions from the Post-Aeration Tank (referred to herein as "Post-Aeration Basin") using the Scentroid TR8+ Pollutracker monitor. This is further support that the Scentroid monitor is the best available method for measuring air emissions from this source.

utilized three Scentroid portable monitor measurements collected following the IPT on July 15, 2021, July 21, 2021, and July 28, 2021, as reflected in Table A-7 of the October 2021 modeling report. The average of those three measurements was used to estimate the H_2S emissions from the Post-Aeration Basin for purposes of the air dispersion modelling. The Scentroid portable monitor results for H_2S were input to the air dispersion model, representing the H_2S emissions from the Post-Aeration Basin with the cover and carbon filtration system operating. In its June 30, 2021 Section 114 Request, EPA required Method RSK-175 to measure TRS compounds. Method RSK-175 is a wastewater analysis method, and is therefore not applicable to air measurements.

The Scentroid H_2S monitoring results were not used as inputs to the WATER9 emissions model. The WATER9 emissions model estimates for the remaining TRS compounds (dimethyl disulfide, dimethyl sulfide, and methyl mercaptan) are based on the Post-Aeration Basin liquid sampling conducted during the IPT, as described in Table A-39 (page A-175) of the October 2021 Modeling Report. The modeled TRS air emissions are based on the Scentroid H_2S measurement inputs combined with the WATER9 emissions model estimates for the remaining TRS compounds.

The Scentroid Operations and Maintenance Manual is provided as Attachment D. Appendix A, Row 13 of the Operations and Maintenance Manual states the lowest detection threshold for H_2S is 7 ppb, with a resolution of 1 ppb. The H_2S concentrations measured during July ranged from 38 to 68 ppb.

DHEC Comment 4: *Tables A-8 and A-9, Footnotes 2 and 3 of the October 2021 modeling report indicate the input data to the Water9 and H2SSIM models for Ditch O + Splitter Box and the Primary Clarifier came from the Subpart S Initial Performance Test (IPT) done July 9-11, 2021. These sources were not part of the IPT. From where did the input data to these models come? Was data from other sources in the IPT used instead? If so, please provide a detailed explanation, to include why this was done, why the substituted data is representative of these sources, what exact values were used and where, what conversions were done on the IPT results to make it useable for other sources and in the models? In particular, the concentrations presented in Table A-40, indicated as inputs to the Water9 model, could not be matched to concentrations from the IPT.*

New-Indy Catawba Response 4: The input data with explanation for data substitutions and assumptions for the WATER9 and H2SSIM model runs for Ditch 0 + Splitter Box and the Primary Clarifier were included beginning on page A-55 in the Corrective Action Plan Air Dispersion Modeling Analysis submitted October 2021 (provided in Attachment E).

In response to WATER9 model inputs listed in Table A-40, TRS compounds were not directly sampled from the Primary Clarifier, Ditch #0, and Splitter Box. The closest directly-measured parameters are at the ASB inlet, which were regarded as the best engineering estimates for locations from the Primary Clarifier to the ASB inlet unless otherwise noted in the tables in Attachment E. As stated in New-Indy Catawba Response 6 in the December 2 Response to DHEC, "The total sulfide concentration was back-calculated using the WATER9 (*i.e.*, the inlet total sulfide concentrations to each individual source was determined using an iterative approach utilizing the WATER9 program that resulted in the measured sulfide concentration at the ASB inlet)." The measured sulfide concentrations at the ASB inlet from July 9-11, 2021 were 25.4 ppb, 12.5 ppb, and 14.0 ppb, respectively. These measured concentrations were provided in Table 3-1 of Attachment IPT11 to New-Indy Catawba's October 5, 2021 Response to DHEC Questions and Comments to Test Reports.

Please feel free to contact me if you have any additional questions.

Sincerely,

Daniel J. Mallett
Environmental Manager

Enclosures

ATTACHMENT A
OCTOBER 5, 2021 RESPONSE TO COMMENTS: CONDENSATE COLLECTION AND TREATMENT SYSTEM: HAP, METHANOL, AND TRS PERFORMANCE TEST-CONDUCTED JUNE 23 – JULY 11, 2021

No. 3 Paper Machine Dryer Vents, Pulp Dryer, No. 2 and No. 3 Smelt Dissolving Tanks, and No. 1 and No. 2 Combination Boilers: TRS and SO_2 Testing- Conducted June 21- 27, 2021

1. *Please include in the report summaries of the H_2S emissions from the testing conducted on each source.*

   Response 1: The report has been updated to include summaries of the hydrogen sulfide (H_2S) emissions from the testing conducted from each source. The updated report is provided in Attachment ST1.

2. *Were any blank samples run to determine/verify the MDLs? If so, please provide.*

   Response 2: No.

3. *The MDL must be used in all calculations when the analysis of the sample is below the detection limit.*

   Response 3: The report will be revised to reflect the requested use of the minimum detectable level (MDL) following receipt of DHEC and EPA's final comments on the report. However, we believe these revisions are contrary to established EPA policy regarding appropriate treatment of samples below the detection limit. The EPA policy regarding handling of samples below the detection limit is provided in Attachment ST3.

4. *Provide a discussion as to why the SO_2 emissions were higher in Combination Boiler No. 1 when combusting NCGs only and no SOGs as compared to when both types were combusted together.*

   Response 4: The SO_2 emissions expressed in pounds per hour (lb/hr) were higher when combusting NCGs only (436.0 lb/hr) compared to when both types of gases (NCGs + SOGs) were combusted together (360.9 lb/hr) in Combination Boiler No. 1. The pulp production during the NCGs only test was 76.0 oven dried tons pulp per hour (ODTP/hr) compared to 55.9 ODTP/hr during the NCGs + SOGs test. At the higher pulp production the mass emissions rate is higher. When the SO_2 emissions are normalized to pulp production during the test, the NCGs + SOGs produced more SO_2 per ton of pulp (6.46 lb SO2/ODTP) compared to the NCGs only test (5.74 lb SO2/ODTP). This emissions data is available on page 664 of the Weston stack test report.

5. *Table 2-15 provided a summary of results for Paper Machine No. 3 whitewater sampling. The average H_2S concentration on 6/24/2021 was 184,285 micrograms per liter (ug/l), on 6/25/2021 was 154,444 ug/l, and on 6/26/2021 was 57,333 ug/1. Provide a detailed discussion as to why the concentration decreased. The discussion should include information as to any mill operational changes or Paper Machine No. 3 changes during the time the samples were taken.*

   Response 5: There were no operational changes to Paper Machine No. 3 during the time the whitewater samples were taken. Regarding other areas of the process and potential impact: The pulp mill was continuing to operate in the initial commencement phase during June when the testing was required to be conducted to comply with DHEC's Order to Correct Undesirable Level of Air Contaminants (Order). The pulp mill equipment suppliers were continuing to adjust pulp mill operations to complete checkout of the process equipment during June. These adjustments included addressing pulp washing effectiveness, which depends on the pulp mill equipment and the quality of the shower water. Some of the organic and sulfur compounds that are generated in the digester remain with the pulp after washing, and these organic and sulfur compounds are carried over to the paper machine. This would include organics and sulfur compounds remaining in the stripped condensates that are recycled to the washers. There is inherent variability in the range of concentration of organics and sulfur compounds and the distribution of the four TRS compounds (H_2S, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide). See also response to Question No.

7.

6. *Table 2-15 provided a summary of results for the paper machine #3 whitewater sampling. The sampling data for methyl mercaptan seems to show an increase in concentration on 6/26/2021. Provide a detailed discussion as to why the concentration increased. The discussion should include information as to any mill operational changes or paper machine #3 changes during the time the samples were taken.*

   Response 6: There were no operational changes to Paper Machine No. 3 during the time the whitewater samples were taken. The variation in methyl mercaptan concentration can be attributed to the pulp washing efficiency. See also responses to Question Nos. 5 and 7.

7. *Table 2-15 provided a summary of results for the paper machine #3 whitewater sampling, and table 2-17 provided a summary of results for the steam stripper inlet foul condensate sampling. Provide a detailed discussion as to why the H_2S concentration was higher in the paper machine #3 whitewater than the steam stripper inlet foul condensate.*

   Response 7: New-Indy Catawba, LLC (New-Indy Catawba) has verified with the lab (ALS Simi Valley, CA) that reported H_2S liquid concentration results for the No. 3 Paper Machine whitewater samples are accurate. However, these results are believed not to be representative of normal operations for the following reasons:

   - The foul condensate samples contain concentrated amounts of organics and sulfur compounds by design. It is not reasonable that the reported H_2S liquid concentration results for the No. 3 Paper Machine whitewater samples would be higher than the H_2S liquid concentration results for foul condensate samples, which were 120,000-190,000 ug/L.
   - The high H_2S liquid concentration results in the No. 3 Paper Machine whitewater samples are not consistent with the low air emissions measured at the No. 3 Paper Machine Vents (sum of all stacks from the No. 3 Paper Machine is approximately 1.0 lbs/hr total TRS). Furthermore, the measured TRS air emissions at the Pulp Dryer are low, approximately 0.2 lbs/hr, as are the Pulp Dryer whitewater concentrations, 5-10 µg/L H_2S. This also corroborates the expectation that the higher H_2S liquid concentrations reported for the No. 3 Paper Machine whitewater are not representative.

8. *The test report does not appear to provide any information about the sulfur recovery system for the NCGs and SOGs streams prior to being combusted in combination boiler #1 or combination boiler #2. Provide a discussion as to how the sulfur recovery system works, of how the system was operated during the test, and provide a block diagram of the sulfur recovery system.*

   Response 8: The NCG collection system has an NCG scrubber to recover sulfur from the low volume high concentration (LVHC) gases. The high volume low concentration (HVLC) gases and SOGs do not use a sulfur recovery system. The LVHC NCG scrubber uses 20% caustic to capture the sulfur from the collected gases and return the captured sulfur to the pulping process. Pages 664 and 666 of the Weston stack test report document that the NCG scrubbing liquid flow during each test run was maintained at 40 gallons per minute and the NCG scrubbing liquid pH was maintained at 10.9 during each test run. A block flow diagram of the NCG LVHC sulfur recovery system is included in Attachment ST8.

Condensate Collection and Treatment System: HAP, Methanol, and TRS Performance Test-Conducted June 23 - July 11, 2021

1. *The calibrations, recoveries, and other QA/QC information from the NCASI 94.03 and 99.01 lab reports are missing.*

   Response 1: Revised lab reports with NCASI 94.03 and 99.01 calibrations, recoveries, MDLs, and other QA/QC information results are included in this response in Attachment IPT1.

2. *The MLVSS lab report is missing.*

   Response 2: Lab reports are included in this response in Attachment IPT2.

3. *For the RSK-175 TRS analysis, the chain of custody and dimethyl disulfide calibrations are missing.*

   Response 3: The Chain of Custody has been included in this response in Attachment IPT3. Dimethyl disulfide calibrations were not provided by the laboratory. According to the laboratory, there is not a separate calibration for dimethyl disulfide. The response factor for this compound is set as two times the response factor for dimethyl sulfide. A separate calibration is not needed for dimethyl disulfide as the response factor can be estimated accurately.

4. *Please provide the following data on a 1-hour average for each collection and treatment sampling day.*
   a. *Steam stripper inlet foul condensate feed flow rate*
   b. *Steam stripper steam flow rate*
   c. *Foul condensate to steam stripper feed temperature*
   d. *Stripped condensate temperature*
   e. *Stripped condensate flow*

   Responses 4a-e: The 1-hour average data for the steam stripper parameters requested for the period of July 9-11, 2021 are provided in Attachment IPT4.

5. *Please provide the following data on a 24-hour average for each collection and treatment sampling day.*
   a. *ASB wastewater inlet flow (there is a table stating this parameter, but it matches with the total foul condensate flow only).*
   b. *ASB outlet flow rate.*
   c. *Number of aerators operating per zone.*
   d. *Post-Aeration tank flow*

   Responses 5a and b: The 24-hour average data for the ASB parameters requested in Questions 5a and 5b for the period of July 9-11, 2021 are provided in Attachment IPT5.

   Response 5c: During the IPT sampling period of July 9-11, 2021, there were the following 75 hp surface aerators running in Zones 1-3 of the aerated stabilization basin (ASB) during the day (7 am – 5:30 pm)/night (5:30 pm – 7 am):

   Zone 1: 12/19 (average = 16)
   Zone 2: 15/15
   Zone 3: 6/6
   Total: 33/40 (average = 37)

   Note: Certain surface aerators were turned off during the day for safety reasons to allow for ongoing surface solids removal in Zone 1 but were restarted at the end of each day and operated through the night. Figure 2-2 in Attachment IPT14 provides the location and operation status for the aerators during the IPT.

Responses 5d: 24-hour average data for the period July 9-11, 2021 for the Post-Aeration Tank flow requested in Question 5d is provided in Attachment IPT5.

6. *Please provide the following instantaneous data from each sampling day.*
   - a. *Post-Aeration tank number of aerators operating.*
   - b. *Post-Aeration tank total aerator hp-hrs*.

Response 6a: No instantaneous data is available for the IPT sampling period of July 9-11, 2021; however, run status is tracked visually by the operator in the 24-hour manned control room. Per the operator, during this period three aerators were operated continuously in the Post-Aeration Tank: one 75 hp surface aerator and two submerged aspirating aerator/mixers (one at 75-hp and one at 84 hp).

Response 6b: No instantaneous data is available for the IPT sampling period of July 9-11, 2021. However, the total each day was 5,616 hp-hrs (75 hp * 2 * 24 hrs/day + 84 hp * 24 hrs/day). See also response to Question 6a.

7. *What are the units for Dissolved Oxygen and Temperature on the sample property sheets? Pages 890- 896 in part 2 of the electronic report.*

Response 7: Dissolved Oxygen is in units of mg/L. Temperature is in units of degrees Fahrenheit.

8. *What does data in red mean on the sample property sheets? Pages 893-894 in part 2 of the electronic report.*

Response 8: This was internal formatting that did not get removed before submittal.

9. *When was the most recent depth survey of the ASB completed?*

Response 9: A complete bathymetric survey of the ASB was last completed in September 2015. In early December 2019, a bathymetric survey of the ASB was attempted using an unmanned drone boat equipped with a sonar echosounder, but the drone boat was only able to access and survey a small portion of the basin.

10. *Please revise the NCASI 94.03 and 99.01 data to reflect the MDL requirements from 63.457(j)(4)(i) & (ii).*

Response 10: 40 CFR §63.457(j)(4) applies to mass flow rate, mass per megagram of ODTP, or the mass percent reduction compliance determinations under 40 CFR §63.446. Compliance calculation methodologies for pulping condensates collection and treatment are summarized in section 2.3 of the IPT report submitted to DHEC on August 28, 2021. Hazardous air pollutant (HAP) concentrations are measured as methanol per 40 CFR §63.457(f)(2) for the purposes of compliance with the requirements for pulping condensates collection and treatment in the steam stripper in 40 CFR §63.446. All foul and stripped condensate methanol liquid concentration sampling results utilized in the mass flow rates (and mass per pounds ODTP) for compliance with the methanol collected and the percent removal calculations for the steam stripper system were above the MDL. For calculation of lb/ODTP removal in the hard pipe and ASB, calculations for the fraction biodegraded (Fbio) are based on methanol liquid concentrations; however, an “r” factor is applied that considers the ratio of the sum of acetaldehyde, methyl ethyl ketone (MEK), and propionaldehyde mass to the ratio of methanol mass in the foul condensate stream. There were several foul condensate samples that were less than the detection limit for MEK and propionaldehyde. However, the rule does not dictate that the compounds that meet the requirements 40 CFR §63.457(j)(4) be omitted from the calculations.

Rather the rule indicates that they are not required to be included in the calculations. New-Indy Catawba may choose to revise this approach for future performance tests.

11. *For the individual TRS compounds, the MDL must be used in all calculations when the analysis of the sample is below the detection limit.*

    Response 11: DHEC has requested that all results that were reported below the MDL be reported at the MDL (See stack testing question 3). To avoid underreporting the liquid concentration results, New-Indy Catawba has revised all liquid concentration results that were reported below the detection limit, which is also referred to as the "method reporting limit" (MRL), to be equal to the MRL rather than at the MDL.[1] All individual TRS calculations have been revised to reflect the use of the MRL for the liquid concentration sampling results that were reported below the detection limit. The revised results and supporting tables and documentation are provided in Attachment IPT11.

12. *For the various test methods, how were the MDLs established?*

    Response 12: The MDLs were established as follows for the various liquid concentration test methods performed and utilized to calculate the IPT results (responses provided directly by the laboratories):

    - Speciated TRS compounds via RSK-175 Method (ASTM D-5504) per Atmospheric Analysis and Consulting, Inc (AAC): MDLs are determined for the ASTM D-5504 method, which was used for the analysis of all RSK-175 samples. There are no separate MDLs for RSK-175. MDLs are determined by injecting a very low concentration of standard at an experimentally determined level multiple times over several days. The level that gives an estimated average value of 70%-130% the true value has its standard deviation multiplied by the Student's t-value to determine the MDL. See Attachment IPT12 for the results of the 2021 MDL study for ASTM D-5504.
    - Methanol via NCASI MeOH-94.03 Method and HAPs via NCASI HAPS-99.01 Method per ALS Laboratory in Kelso, WA: ALS utilizes a lab wide procedure for establishing new MDLs whereby they analyze 7 spiked samples at approximately 0.5 to 1 times the limit of quantification (LOQ), and 7 method blank samples. The statistical calculations and evaluations for the spiked and method blank samples establish the MDL. Existing MDLs are evaluated annually based on the collected Method blank data and quarterly MDL verification results. See Attachment IPT12 for the results of the for the most recent MDL study for the NCASI MeOH-94.03 and NCASI HAPS-99.01 Methods.

13. *In Table 2-10, the ASB inlet liquid flow rate does not match what is reported in Table G-4. Please explain.*

    Response 13: The ASB inlet liquid flow (gpm) in Table 2-10 has been updated to represent the total ASB inlet flow, which is the ASB inlet flow (gpm) plus the foul condensate flow (gpm) (See Attachment IPT13). The Foul Condensate Flow to the ASB (MGD) in Table G-4 includes foul condensates entering the ASB through the hardpipe, and these values are accurate.

14. *Please revise the ASB zone 1 sample locations to indicate the alternate location used on 7/10 and 7/11. Please provide the flight map for the drone as requested on-site.*

    Response 14: A revised Figure 2-1 has been provided in Attachment IPT14 showing the alternate

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[1] A Method Reporting Limit (MRL) is the limit of detection for a specific target analyte for a specific sample after any adjustments have been made (*e.g.*, for dilutions or percent moisture), whereas the Method Detection Limit (MDL) is lower than the MRL (often much lower) and is a statistical calculation.

sampling locations for Zone 1 of the ASB on July 10 and 11. The revised figure also incorporates the aerial photo taken by the drone just prior to the IPT that is representative of the surface areas for Zones 1-3. Figure 2-2 shows the location and operation status of the aerators in operation during the IPT (see also response to Questions 5c and 16). Figure 2-3 includes the flight map for the drone.

15. *Was hydrogen peroxide added to the ASB during the condensate collection and treatment test?*

    Response 15: No hydrogen peroxide was added to the streams entering the ASB nor was there any hydrogen peroxide added at any location in the ASB during the IPT for the condensate treatment period of July 9-11, 2021. Hydrogen peroxide was added near the outlet of the No. 1 Holding Pond during the IPT period of June 23 – July 11.

16. *During the site visit on 7/10, the Mill stated that the actual number of aerators operating was 29 during the daytime and 37 at night. For each day of testing, how many aerators were operating during the day vs. night?*

    Response 16: There were a total of 33 aerators operating during the daytime (7 am – 5:30 pm) and a total of 40 aerators operating at night (5:30 pm – 7 am) in the ASB. Attachment IPT14 provides Figure 2-2 showing the location of the aerators in Zones 1-3, with designation of which were running during the day versus the night. Note that there were three additional aerators operating in Zone 1 that were not included because they were not providing aerated treatment during the IPT. See also response to Question 5c.

17. *Was the density of any of the liquid condensate streams ever measured to confirm the density of 8.34lb/gal?*

    Response 17: No. The liquid streams sampled as part of this testing effort (*i.e.*, foul and stripped condensate, wastewater, and whitewater) are greater than 99.99 percent water, so using the density of water is reasonable

18. *For the RSK-175 report:*
    a. *In Table I-1, why were samples above the calibration curve not included in the duplicate averages?*
    b. *In Table I-1, please elaborate on the samples that were over diluted and did not meet the minimum peak requirements.*
    c. *Why were the RSK-175 TRS samples blank corrected?*
    d. *Why does the lab report not have sample times for samples dates 7-10 and 7-11?*
    e. *Where is the discussion of the sample preparation and analysis? Was the EPA's 114 requirement for acid preservation completed?*

    Responses 18a and b: Attachment IPT18 provides additional information from ACC regarding the calibration curves and an addendum to the original reports with a narrative that provides an explanation that addresses samples that were over diluted and did not meet the minimum peak requirements. The results that were shaded in grey in Table I-1 were not in included in the reported liquid concentration averages based on this additional information.

    Response 18c: Per information provided by AAC, all RSK-175 samples are blank corrected as a part of the routine procedure to correct for potential contamination from glassware, water, and sample injection setup. This procedure functions similarly to a system blank for other methods. The RSK-175 method is provided in Attachment IPT18.

    Response 18d: The lack of sample times for the samples from 7-10 and 7-11 are a reporting oversight from the lab; however, AAC verified that each set of samples was identified and analyzed based on its sample date and time. In addition, AAC provided a sample matrix map that includes the AAC ID and Date/Time of the sample in the Addendum to the original reports included in Attachment IPT18.

Responses 18e: Per information provided by AAC, the RSK-175 procedure was utilized for preparation of the liquid sample, with the exception that the lab acidified the samples to a pH of 5 prior to purging the sample. The purged sample was analyzed per method ASTM D-5504-20, which is modified for sulfur compounds (i.e., Gas Chromatography (GC) with Sulfur Chemiluminescence Detection (SCD) for sulfur compounds by Method ASTM D-5504-20 versus GC followed by a Flame Ionization Detector (FID) for compounds covered by the RSK-175 Method. The RSK-175 and ASTM D-5504-20 methods are provided in Attachment IPT18.

19. *For the Tracer Study report:*
    - a. *Is there a laboratory report for the Li analysis performed for the tracer study?*
    - b. *Please provide the daily flow rates for the ASB Inlet, ASB outlet, and Hardpipe from during the tracer study. This would apply for 6/8/2021 to 6/22/2021.*
    - c. *Are compounds that would interfere with the Li tracer study analysis present in the ASB?*
    - d. *How was it determined that 84% of the Li was recovered during the tracer study?*
    - e. *How was the calculated retention time determined?*
    - f. *What is "short-circuiting" in the context of the curtains that were once installed to direct flow in the ASB?*
    - g. *Please provide additional information regarding the selection of 3 zones for the ASB.*
    - h. *Why is the volume used for tracer study calculations from a depth survey performed in 2015?*

Response 19a: The Pace Analytical laboratory reports are included as Attachment IPT19a(1) and IPT19a(2).

Response 19b: There is no flow meter on the total raw wastewater flow into the primary clarifier or ASB. The ASB inlet flow was estimated based on the raw river water withdrawal flow with an evaporation factor applied for water losses during the production process. The hardpipe foul condensate flow is measured directly. The outlet flow is the sum of the ASB inlet flow and the hardpipe foul condensate flow. A table summarizing these flows is included in this response as Attachment IPT19b.

Response 19c: Lithium was selected as a tracer because it is less likely to have interference issues in pulp and paper wastewater as compared to other tracers, such as rhodamine dye. The laboratory reports for lithium samples during the pilot study are attached. The reports contain quality control information.

Response 19d: The lithium recovery was calculated according to NCASI Technical Bulletin 408. The mass balance for lithium recovery is based on integrating the area under the tracer curve and adding this amount to the residual mass of lithium in the mixing vessel at the end of the sampling period. During the tracer study, 141.65 lbs of lithium were added and 118.93 lbs of lithium were recovered. This represents an 84% recovery. To simplify, the percent lithium recovered is the cumulative pounds of lithium recovered divided by the pounds of lithium added, where the cumulative pounds of lithium is calculated by the sum of the Delta t (hrs) x adjusted Li concentration x flow x 8.34 for the duration of the sampling period. It is recommended to sample for a period of time equal to two Theoretical Retention Times (TRT) which is the estimated volume in millions of gallons divided by the average flow in millions of gallons per day, to improve the recovery of the tracer material; however, for this particular study, samples were collected for three times the TRT.

Response 19e: The retention time was also calculated according to NCASI Technical Bulletin 408. The mean Hydraulic Retention Time (HRT) is estimated by calculating the center of gravity of the tracer concentrations versus time of discharge under the curve (Figure 6 in the Tracer Study Report) for the particular mixing vessel during the sampling period. A mathematical calculation is then used to determine the retention time in days based off the Delta t, adjusted Li concentration, and the sampling time in days. The resulting data is then cumulated to provide the Mean Retention Time.

Response 19f: "Short-circuiting" is a condition that can occur in a basin when wastewater takes a more direct route from the basin inlet to the basin outlet resulting in a lower working residence time than may be calculated by dividing the basin volume by the wastewater flow rate. The use of flow curtains in a wastewater basin can direct flow through the basin to reduce short-circuiting.

Response 19g: The selection of the three zones in the ASB is not related to the tracer study but is supported by the results of the tracer study. The ASB was assumed to have three working zones based on data from the 2015 bathymetric survey that showed the settled solids formed three distinct depressions or zones of water. The number and density of aerators in these areas also supported the use of these three zones.

Response 19h: The volume estimated based on the bathymetric survey in 2015 was provided to EBS for the tracer study, but this value did not affect the tracer study results. It was used to calculate the theoretical hydraulic residence time, which is volume divided by flow. The 2015 volume estimate was used because it was the last complete survey available to estimate the basin's working volume. Dredging is currently being performed in the ASB, and a follow-up bathymetric survey is scheduled for late November or early December 2021.

20. *Why was the production on 7/5/2021 not representative of typical Mill operations?*

Response 20: The 7/5/2021 production was not representative of typical Mill operations because of an unanticipated pulp mill outage.

21. *Condensate report page 1-1, states that a hard pipe was installed to send the condensate from the condensate tank to the ASB. Provide the depth of the ASB when it was originally put into operation, the current depth of the ASB, and the depth of the liquid. Also provide the depth that the hard pipe for the foul condensate is discharged below the liquid surface.*

Response 21: While there are no known as-built or record drawings after construction, the construction drawing from 1967 indicates the average uniform basin depth was approximately 20 feet deep from the top of water surface to the bottom of the basin. The foul condensates hard pipe was installed out into the basin, and the discharge outlet is located eight feet below the water surface.

22. *Condensate report page 1-1, states that the mill will treat the condensate with a combined system of steam stripping and the ASB. Provide the regulatory citation in MACT subpart S that applies to using two control devises as a treatment option.*

Response 22: New-Indy Catawba is complying with 40 CFR 63 Subpart S in accordance with the treatment process approved by DHEC on May 3, 2021. That approval letter is attached as Attachment IPT22.

23. *Condensate report page 1-7, states that the continuous digester was modified. Provide a description of the modifications that were made. Also provide a list of federal regulations that apply to the digester.*

Response 23: The continuous digester was modified to support producing unbleached pulp at a kappa of 90 or higher. The modifications to the continuous digester included modifying or replacing the screens, heat exchangers, and pumps to accommodate the higher kappa pulp. Construction Permit 2440-0005-DF specifies the continuous digester (equipment ID 5210) is subject to 40 CFR

Part 60, Subpart BBa and 40 CFR Part 63, Subpart S.

24. *Condensate report page 1-7, states that the #1 evaporator train was modified. Provide a description of the modifications that were made. Also provide a list of federal regulations that apply to the #1 evaporator train.*

    Response 24: The piping of the No. 1 evaporator train (multi-effect evaporator set with concentrator) was reconfigured to operate as a five-effect system to increase the evaporation rate. The modifications included replacing some vapor duct work, new pumps and flash tank, and modifying the piping and controls. Construction Permit 2440-0005-DF specifies the No. 1 evaporator set (equipment ID 2400) is subject to 40 CFR Part 60, Subpart BBa and 40 CFR Part 63, Subpart S.

25. *Condensate report page 1-8 states that the turpentine underflow started to be collected on 7/19/2021. Provide a discussion of where the underflow was piped prior to 7/19/2021, and provide a discussion of why the mill began to collect the underflow after 7/19/2021.*

    Response 25: The turpentine decanter underflow was originally collected and piped to the stripper feed tank. This piping was abandoned after the change to a continuous digester demonstrated there was no longer sufficient decanter underflow being generated to produce a saleable turpentine byproduct. The condensates collected from the LVHC system and sent to the stripper feed tank have been found to contain turpentine, which can contribute to fouling the condensate steam stripper. Therefore, New-Indy Catawba plans to hardpipe the LVHC system condensates to the turpentine decanter, allowing the entrained turpentine to separate and the decanter underflow containing the foul condensates will return to the stripper feed tank. The decanter underflow piping was restored to service on 7/19/21 in anticipation of this change to reduce fouling of the condensate steam stripper.

26. *Page 2-6 states that curtains were installed in the ASB to direct flow in the ASB, and that sludge deposition has impacted the flow and not directing flow as originally designed. Provide the date the curtains were installed, a map of the location of the curtains and a discussion of the original design flow ofthe ASB. Provide a discussion as to how the sludge deposition has impacted the flow in the ASB, and provide a discussion of the corrective actions taken by the company to return the ASB flow back to the original design.*

    Response 26: It is believed that the curtains were installed in 2000 after approval from DHEC. A map showing their approximate location of installation of the curtains and intended flow pattern is provided as Attachment IPT26a. Curtains were not part of the original design or operation of the basin and were installed approximately 30 years after the ASB was placed into operation. While the engineering report submitted to DHEC in the late 1990's requesting a construction permit to install the curtains contains the specifics, the layout of the curtains indicates that the purpose was likely to direct flow into a serpentine pattern to take greater advantage of the basin's volume than the original design provided. A map showing the current flow through the ASB is attached as Attachment IPT26b. The Mill is currently dredging the ASB to return the flow to the original design.

27. *Page 2-8 states that the solids accumulation limits the amount of flow to some areas of the ASB. Provide a discussion of the corrective actions taken by the company to address this issue.*

    Response 27: The Mill has hired several contractors to remove floating and settled solids. Currently, two dredges are in operation, and the Mill continues to excavate accumulated solids using shore-based excavators (rim-cutting).

28. *Page 2-8 states that the mill could not exactly follow the guidance in the technical document to subdivide the ASB. Provide a detailed explanation as to why the mill could not follow the technical document. Also, provide a discussion and justification as to why the mill decided to divide the ASB into three zones.*

Response 28: New-Indy Catawba provided the basis for the determination that the ASB is non-thoroughly mixed and the justification for the selected three zones for the determination of Fbio utilizing Procedure 5 of 40 CFR 63 Appendix C in section 2.1.3 of the IPT report. New-Indy Catawba selected the three ASB zones based on historical information (including the 2015 bathymetric survey that showed the settled solids formed three distinct depressions or zones of water and ASB performance - see response to Question 19.g), and the July tracer study (the 5-hour and 24-hour tracer study profiles in conjunction with the most recent aerial imagery of the ASB). The 1999 technical guidance document presents several alternative approaches for evaluating the performance of a biological treatment process that is not considered to be "thoroughly mixed," with each procedure considered to provide an equally acceptable assessment. The ultimate goal is to select the zones based on uniform characteristics, such as organic compound concentrations, dissolved oxygen concentrations, and biomass concentrations. The 1999 technical document states that (1) it is not possible to use some of the procedures because of site specific conditions; (2) the procedures have been designed to allow, to the extent reasonable, the use of existing information and to minimize the amount of new information that is required to evaluate the mixing characteristics of the system; and (3) it is recommended that, cases where insufficient information is available to successfully define zones, the facility consider gathering additional information. As noted in emails with DHEC on July 2, 2021, and in the IPT report, the Mill initially planned to gather additional data to support the three zones selected by sampling from the center and outlet of each zone during the IPT (*i.e*., methanol liquid concentration, dissolved oxygen, pH, BOD). However, to accommodate the required three sampling events per day, only the center of each zone was sampled. The zones and all original and alternate sampling locations are shown in the revised Figure 2-1 provided in Attachment IPT14. New-Indy Catawba will gather additional data to support the three zones as part of the IPT scheduled for October 26-28, 2021, where sampling will be completed at locations at the inlet, center, and outlet of each zone.

29. *Page 2-13 and page 3-2 discuss the effective steam to feed ratio for the foul condensate steam stripper, and that the correlation would be used to monitor compliance with MACT Subpart S. Provide a discussion as to why the company wants to monitor this parameter, and provide the citation in MACT subpart S that requires this parameter.*

Response 29: In late April 2021, New-Indy Catawba received notification from DHEC requiring restart of the steam stripper system. As approved by DHEC, New-Indy Catawba restarted the steam stripper system on May 3, 2021, with operation consistent with the historic condensate feed rate (400-480 gpm) and effective steam to feed ratio (ESFR) (16-18 lbs steam per gallon of condensate feed) operating ranges existing prior to the conversion to unbleached paper products. The DHEC approval letter is attached as Attachment IPT22. Permit Condition No. E.5 of the current Title V Operating Permit (TVOP) No. TV-2440-0005 (issued May 7, 2019) requires that the facility monitor ESFR and demonstrate compliance with the daily HAP removed when operating the steam stripper utilizing the "daily ESFR applied to the effective steam efficiency curve established or reestablished using characterization studies and performance testing conducted in accordance with §63.453(n)." Therefore, New-Indy Catawba plans to re-establish the effective steam efficiency curve consistent with Permit Condition E.5 and 40 CFR §63.453(n). Pursuant to 40 CFR §63.453(m), DHEC approved the ESFR as an alternative operating parameter to measuring the steam stripper operating parameters required under 40 CFR §63.453(g)(1-3).

30. *Page 3-3, table 3-1, indicates that the foul condensate average H_2S concentration on 7/9/2021 was about 2.5 times higher than the average H_2S concentration on 7/11/2021. Provide a discussion as why there is a large variation in the concentrations.*

Response 30: There is inherent variability in the range of liquid concentration of organics and sulfur compounds in the foul condensate stream, including hydrogen sulfide. Accordingly, we believe that the issues regarding the over-dilution of samples played a role in the elevated liquid concentrations on July 9th. See response to Question 18.

31. *Pages 3-7 and 3-8 indicate that low oxygen levels and the sludge deposition in zone 1 of the ASB the model predicted H2S generation from anaerobic digestion. Provide a discussion of the corrective actions the company is taking to resolve low oxygen levels and sludge deposition in the ASB.*

Response 31: With the surface solids removed, the Mill has since returned all 52 aerators to operation. In addition, the Mill currently is conducting a pilot studying to improve dissolved oxygen by adding hydrogen peroxide and oxygen to the ASB inlet and hydrogen peroxide to the ASB directly. The Mill has hired several contractors to remove floating and settled solids. Currently, two dredges are in operation and the Mill continues to excavate accumulated solids using shore-based excavators (rim-cutting).

32. *Section 3.4 states in several locations that the results for the model were unexpected, and the summary of results in Table 3-3 appear to be inconsistent and unrepeatable. Provide a detailed explanation as to why the results were unexpected, and provide a detailed explanation to what the company expected the results to be. Also provide a discussion of the actions the company has taken to correct these issues, and timeline for the corrective measures to be completed.*

Response 32: In Question No. 1 of the June 2, 2021 Information Request issued by EPA pursuant to Section 114(a)(1) of the Clean Air Act (CAA) (U.S. EPA Information Request), EPA directed New-Indy Catawba to update the IPT Plan to: (1) take samples and analyze for hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide; and (2) utilize 40 CFR Part 63 Appendix C Procedure 5 to calculate the Fbio for hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. New-Indy Catawba's response submitted on June 15, 2021, recommended the use of the Hydrogen Sulfide Emissions Simulator, or "H2SSIM" model, developed by the NCASI for estimating hydrogen sulfide emissions and fraction hydrogen sulfide destroyed, rather than the Appendix C calculations. The H2SSIM model was utilized for calculating the hydrogen sulfide emissions and the fraction removed in the ASB, and these results were reasonable and expected because the H2SSIM Model is calibrated to measured data in the field. Regarding the remaining TRS compounds, New-Indy Catawba provided the following response to address use of Appendix C calculations:

> Similar to hydrogen sulfide, the situation is also more complicated for methyl mercaptan and dimethyl disulfide, as methyl mercaptan is easily oxidized to dimethyl disulfide. Liquid material balance data in conjunction with emissions data from the field study results published in NCASI Technical Bulletin No. 956 indicate that a significant fraction of the methyl mercaptan entering the ASB with the influent is oxidized to dimethyl disulfide. Therefore, methyl mercaptan and dimethyl disulfide results from the Appendix C calculations will be adjusted based on the field study results published in NCASI Technical Bulletin No. 956. Calculating Fbio for any individual TRS compound may be difficult or impossible in the event of non-detect results from the liquid sampling.

Air emissions (E), in grams per second (g/s), are calculated as follows for the ASB/ASB zones in the Appendix C/Form XIII worksheet and the EPA WATER9 emissions model:

E (g/s) = CL * KL * A

Where:
CL (mg/l) = Liquid concentration of the compound in the effluent of each ASB/ASB zone
KL (m/s) = Overall mass transfer coefficient of each ASB/ASB zone; and
A (m^2) = Liquid Surface Area of the ASB/ASB zone

The Appendix C/Form XIII calculation workbook and EPA's WATER9 model utilize the same emission model equations and site-specific data to calculate KL and A; however, the Appendix C, Form XIII worksheet utilizes the measured liquid concentration in the respective zones for CL, while the WATER9 model calculates CL from site-specific data and defaults provided in WATER9 for the maximum biorate, limiting first-order biorate constant, and the biomass concentration.

The Appendix C/Form XIII worksheet calculated air emissions for methyl mercaptan, dimethyl sulfide, and dimethyl disulfide are greater than the inlet loading to the ASB; therefore, the calculated fraction emitted to the air (Fair) is greater than 1.0, and thus, the calculated Fbio is a negative value. This was an unexpected outcome as the fraction emitted to the air should be less than 1.0, and the Fbio should be a value between zero and 1.0. The same air emissions results cannot be repeated utilizing the WATER9 model with the same zone data inputs and using the flow-weighted inlet concentration into the ASB for each compound (*i.e.*, calculated liquid concentration in the inlet to the ASB from the measured ASB inlet flow and liquid concentrations and the measured foul condensate flow and liquid concentrations). The WATER9 model calculates an outlet concentration for each zone based on the emission model equations instead of using the measured liquid concentrations in each zone.

New-Indy Catawba has performed revised calculations for E, Fair, and Fbio for methyl mercaptan, dimethyl sulfide, and dimethyl disulfide utilizing the WATER9 model with the same zone data inputs and flow-weighted inlet concentrations into the ASB. As the Zone 1 liquid concentration results for methyl mercaptan were in some cases higher in Zone 1 than the inlet concentration and results for dimethyl disulfide were lower in some cases in Zone 1 than the inlet concentration, we have not adjusted the WATER 9 output results for methyl mercaptan and dimethyl disulfide to incorporate the field study results published in NCASI Technical Bulletin No. 956. However, New-Indy Catawba may choose to revise this approach for future performance tests. All individual TRS calculations have been revised to reflect the use of the WATER9 emission model. The revised results and supporting tables and documentation are provided in Attachment IPT11.

33. *Appendix B, tracer study report table 1, indicates that the calculated retention time in the ASB was 3.7 days, and that the theoretical retention time was 4.7 days. Provide an explanation as to why there is a difference in retention time.*

    Response 33: The volume estimated based on the bathymetric survey in 2015 was provided to EBS for the tracer study, but this value did not affect the tracer study results. It was used to calculate the theoretical hydraulic residence time, which is volume divided by flow. The 2015 volume estimate was used to estimate the theoretical residence time in the tracer study report because it was the most recent survey available for estimating the basin's working volume. Dredging currently is being performed in the ASB, and a follow-up bathymetric survey is scheduled for late November or early December 2021. The calculated retention time is a statistical evaluation of the tracer curve.

34. *Appendix B, tracer study report page 2, indicates that the peak lithium concentration was detected in 1.3 days. Provide an explanation as the meaning and significance of the peak lithium concentration being detected more than 2 days prior to the calculated retention time of 3.7 days.*

    Response 34: At the time of peak concentration detection, the ASB still contained a significant amount of the lithium that was originally introduced, as shown in Appendix B of the tracer study report figure 6. The difference between peak concentration detection and the calculated retention time represents the additional time it took for lithium to reach the ASB effluent.

35. *Appendix F, Page F-2, Appendix C, Fbio, indicates the average depth of zone 1, 2 and 3 are 4.5 feet, 3.2 feet and 3 feet, respectively. Provide the depth of the zones when the ASB first began operation.*

Response 35: While there are no known as-built or record drawings after construction, the construction drawing from 1967 indicates the average uniform basin depth was approximately 20 feet deep from the top of the water surface to the bottom of the basin.

36. *Appendix F, Page F-4 indicates that the average residence times is 2.39 days (and appendix J indicates 2.15 days). Provide a discussion as to why the residence time is less than the calculated retention time of 3.7 days, and provide a discussion of the actions the company will take to increase the residence time.*

    Response 36: The retention times in Appendix F and J are calculated by the Appendix C/Form XIII spreadsheets. These retention times are based on the flow and calculated volume of the ASB during the IPT testing, using the free surface area and depth of each zone in the ASB. The calculated retention time of 3.7 days from the June 2021 tracer study is based on the time it took for lithium to reach the ASB effluent. Please note that New-Indy Catawba continues to dredge the ASB to increase the residence time. In addition, the individual TRS calculations have been revised to reflect the full inlet raw water flow adjusted for 10% evaporation rate, consistent with the Fbio calculations for Subpart S and the approved IPT Plan. The revised calculations and supporting tables and documentation are provided in Attachment IPT11.

37. *Appendix G, table G-2, provides condensate steam stripper information. Provide a discussion as to why the stripped condensate methanol concentration was not included for 6/26/2021 through 7/8/2021.*

    Response 37: Stripped condensate liquid concentration samples for methanol were not taken during the period from June 26 through July 8, 2021 because compliance testing was not performed for pulping condensates treatment during that period.

38. *Appendix I, table 1-1, provides a comparison of the original and duplicate data for hydrogen sulfide, dimethyl disulfide, dimethyl sulfide and methyl mercaptan. The data shows large variation between the original sample results and the duplicate sample results. Provide a discussion as the why there was a large variation in the results.*

    Response 38: Attachment IPT18 provides additional information from AAC regarding the calibration curves and an addendum to the original reports with a narrative that provides an explanation that addresses samples that were overdiluted and did not meet the minimum peak requirements. The results shaded in grey in Table I-1 were not in included in the reported liquid concentration averages based on this additional information. See also response to Questions 18a and b.

ATTACHMENT B
NCASI TECHNICAL BULLETIN 1000

ncasi

NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

MECHANISTIC APPROACH FOR ESTIMATING HYDROGEN SULFIDE EMISSIONS FROM WASTEWATER TREATMENT PLANTS

TECHNICAL BULLETIN NO. 1000
DECEMBER 2012

by
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serving the environmental research needs of the forest products industry since 1943

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.

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° 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.

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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.

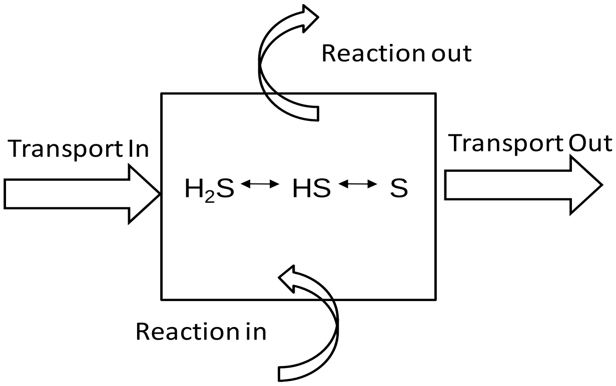

Figure 3.1 Generalized Sulfide Mass Balance around a Control Volume

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.

$$\frac{dS(-II)}{dt} = k_{Gen}\left(\frac{SO_4}{SO_4+K_{SO_4}}\right)\left(\frac{K_{DO}}{DO+K_{DO}}\right) - k_{ox}S(-II)^m DO^n - K_L A(S(-II)F_{H2S}) \quad \text{Equation 3.2}$$

$$\frac{dSO_4}{dt} = -k_{Gen}\left(\frac{SO_4}{SO_4+K_{SO_4}}\right)\left(\frac{K_{DO}}{DO+K_{DO}}\right) + k_{ox}S(-II)^m DO^n \quad \text{Equation 3.3}$$

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.

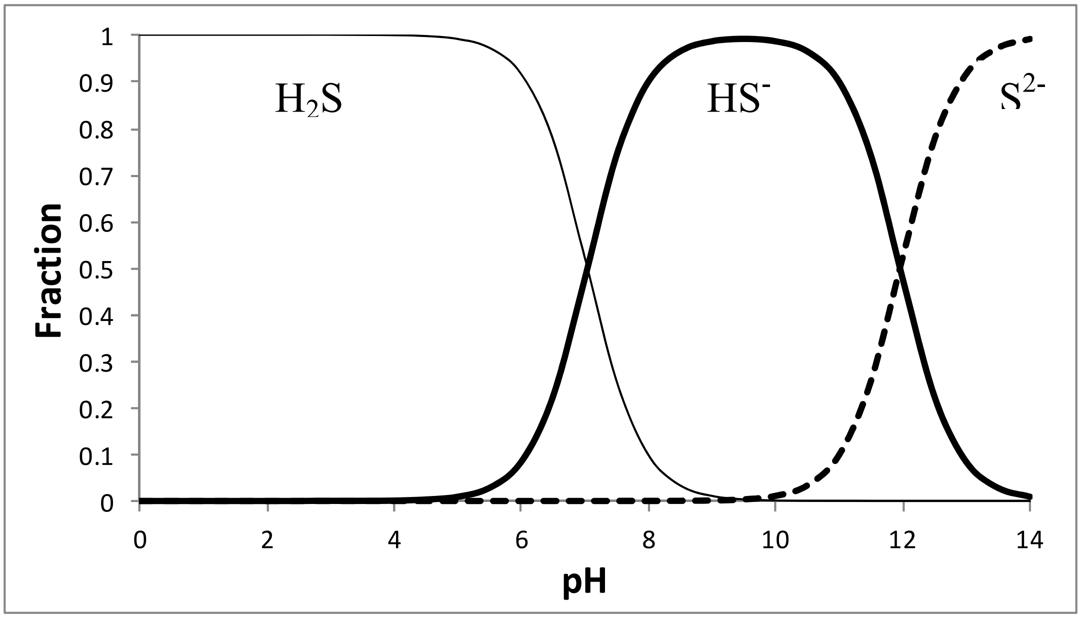

Figure 3.2 Fraction of Sulfide Species as a Function of Wastewater pH

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

$$\mathrm{k}_{\mathrm{Temp}} = k_{20}\theta^{Temp-20} \qquad \text{Equation 3.12}$$

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.

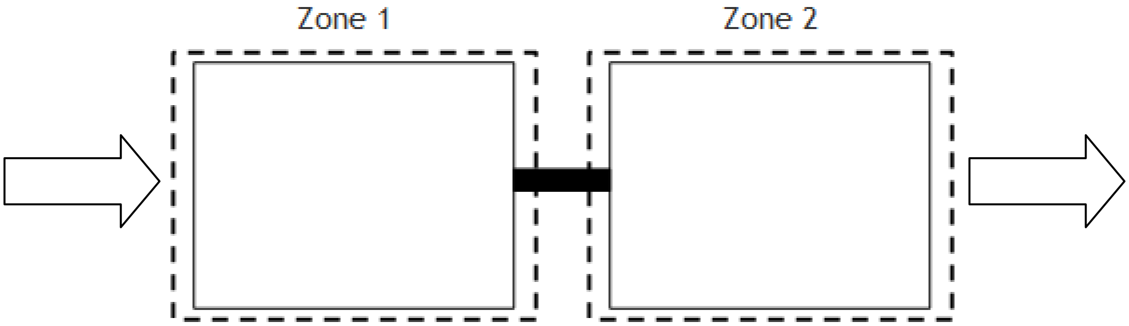

Figure 5.1 Suggested Model Zone Placement with Pipe/Weir Present [The arrows depict the flow direction.]

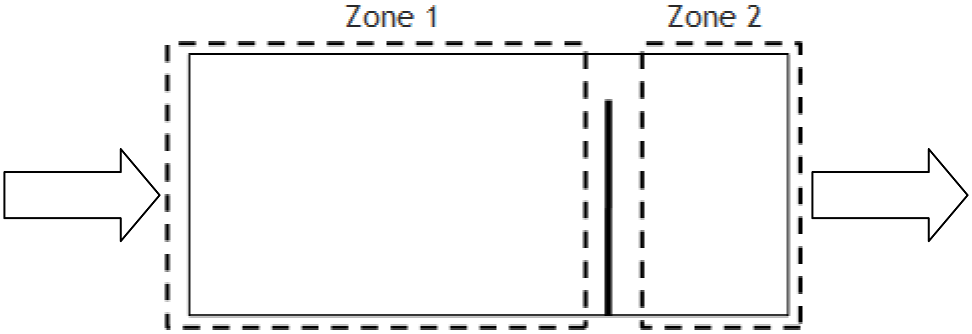

Figure 5.2 Suggested Model Zone Placement with Flow Curtain Present

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.

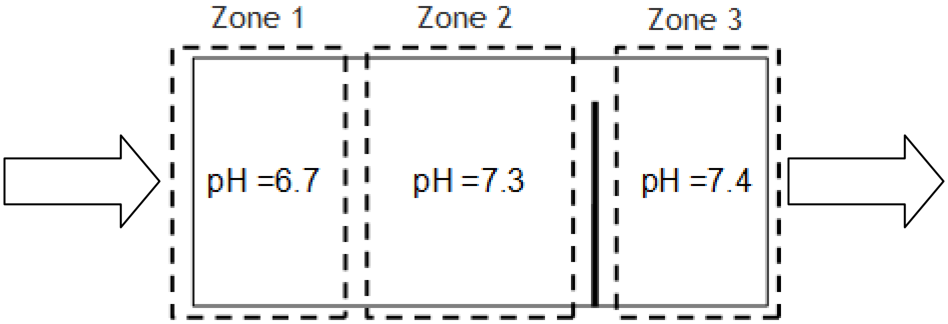

Figure 5.3 Suggested Model Zone Placement When Flow Curtain and pH Gradients Are Present

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.

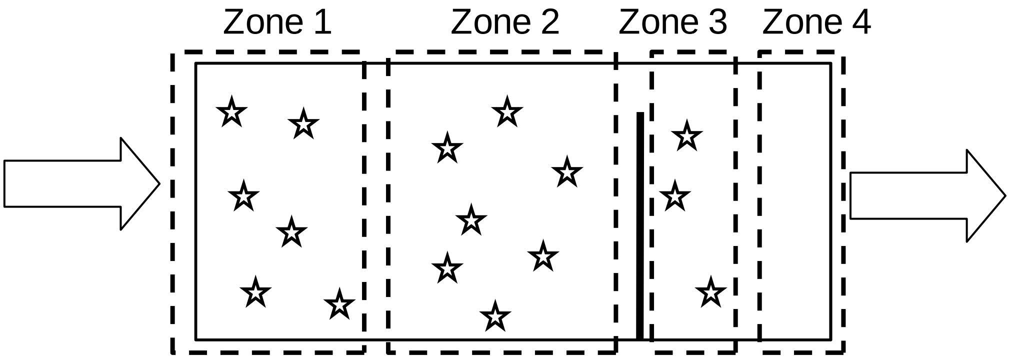

Figure 5.4 Suggested Model Zone Placement When Flow Curtain, pH Gradients, and Aeration Density Gradients Are Present

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.

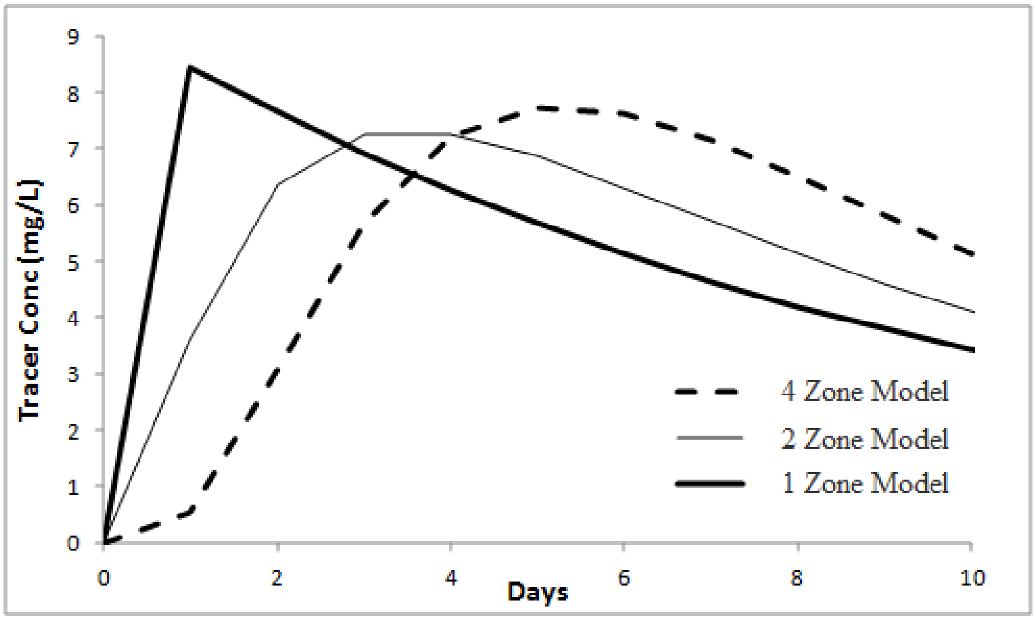

Figure 5.5 Example of Residence Time Curves for Various Numbers of Model Zones

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.

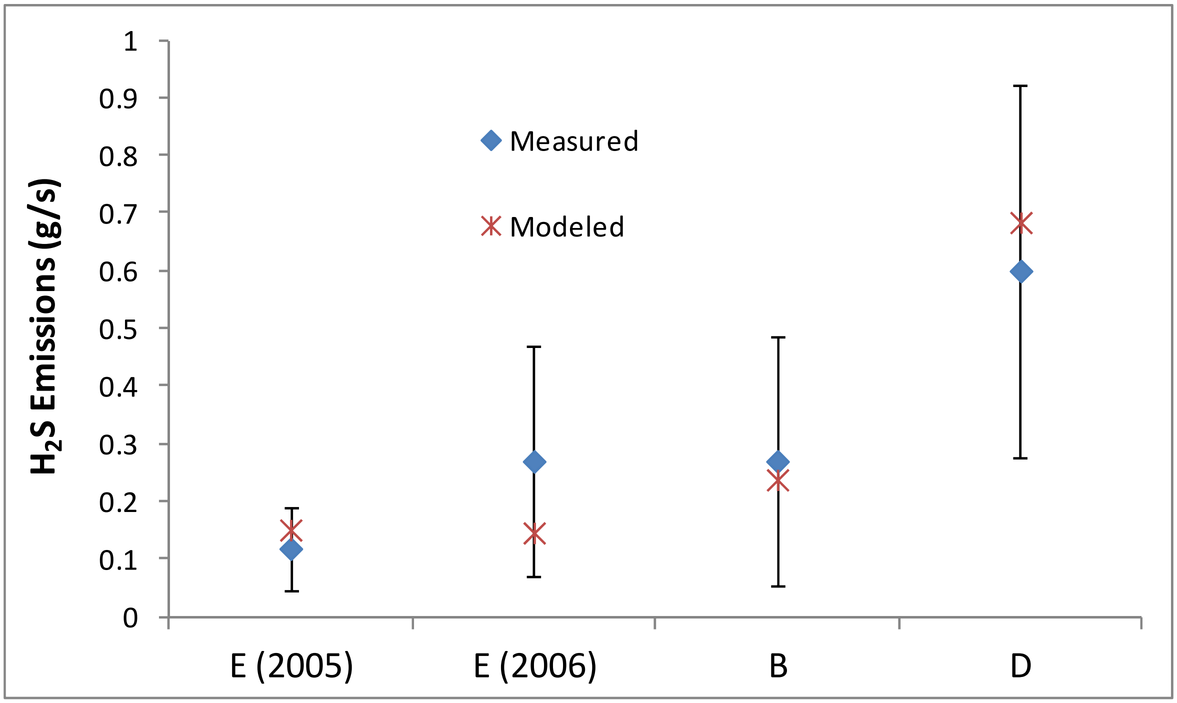

Figure 7.1 Measured H_2S Emission Rates Compared to Model Predicted Rates for Phase I Model Testing at ASBs
[Error bars depict the standard deviation from the mean of the emissions measurements.]

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%.

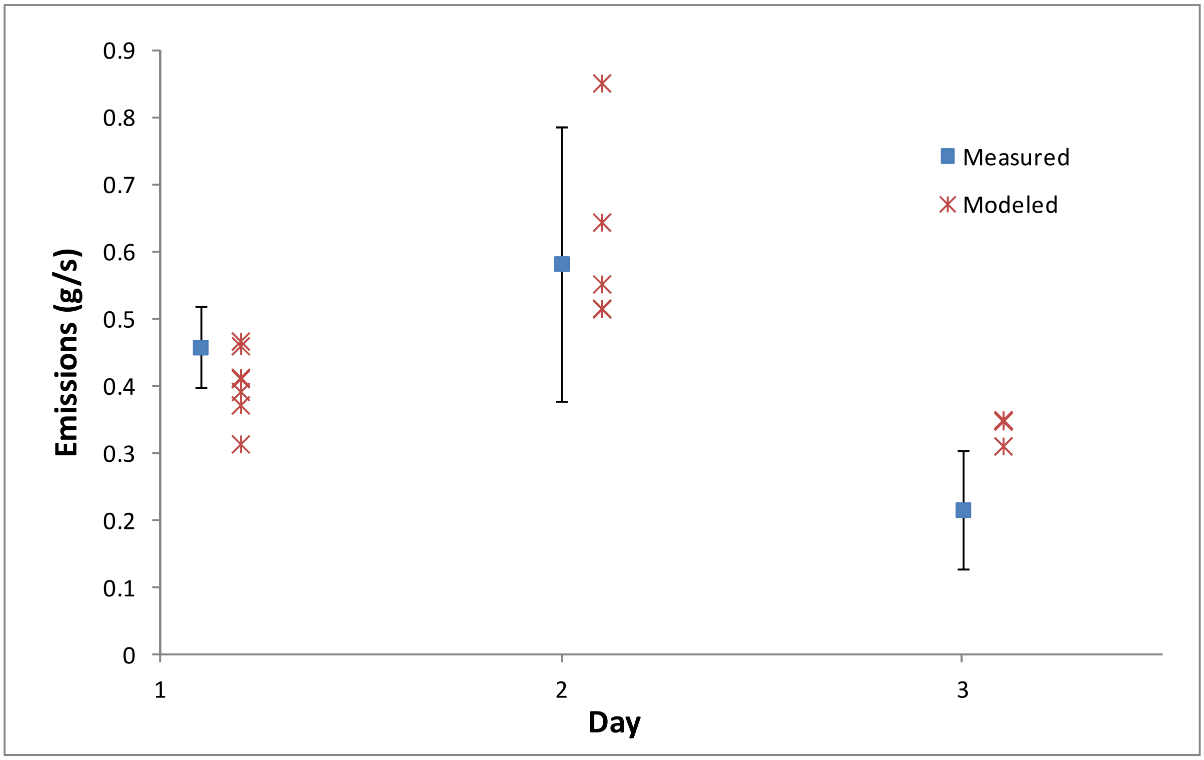

Figure 7.2 Measured H_2S Emission Rates Compared to Model Predicted Rates for Phase II Model Testing at ASBs [Error bars depict the standard deviation from the mean of the emissions measurements. (Modeled and measured points are slightly offset for visualization purposes).]

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.

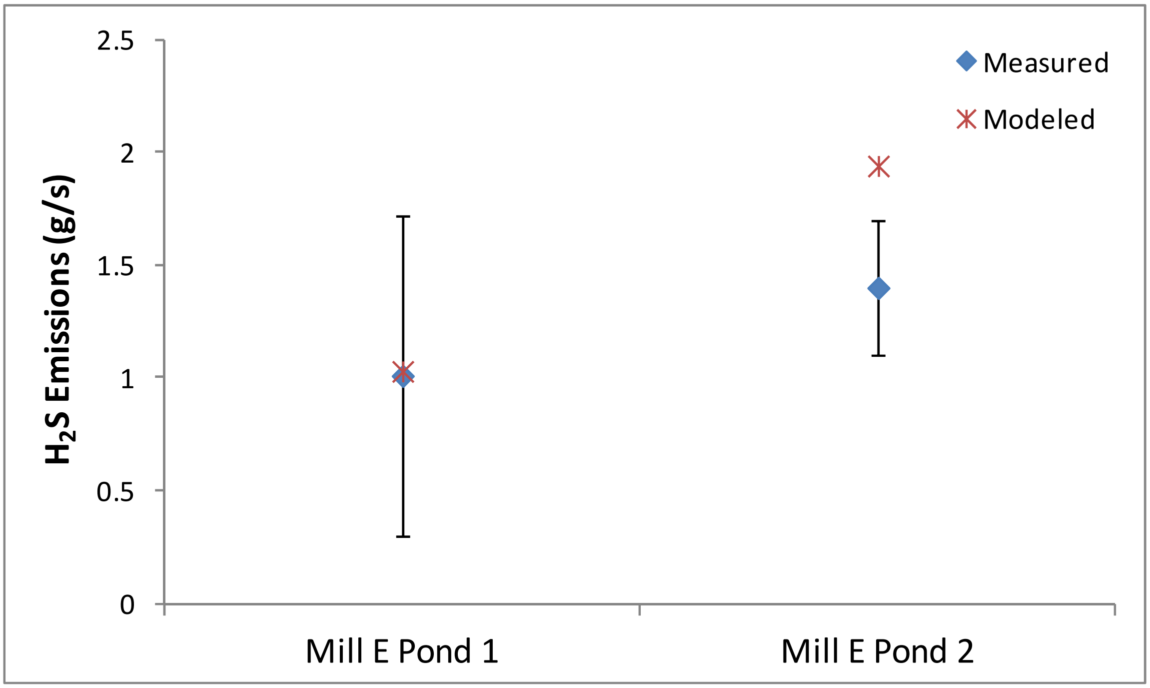

Figure 7.3 Measured H_2S Emission Rates Compared to Model Predicted Rates for Primary Settling Basin Model Testing [Error bars depict the standard deviation from the mean of the emissions measurements.]

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).

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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.

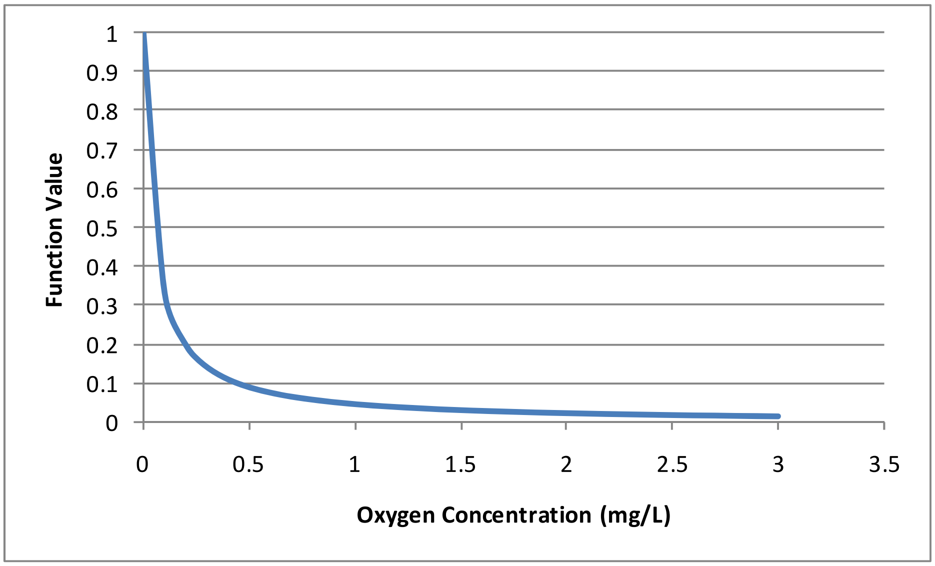

Figure A1 Value of Inverse Monod Function for Dissolved Oxygen Concentration

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.

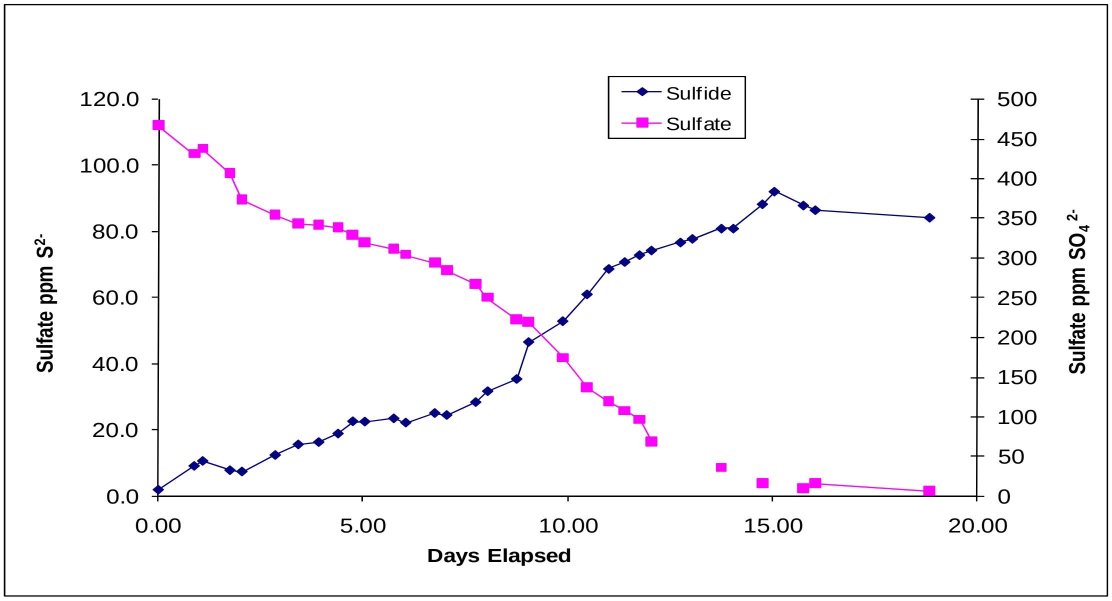

Figure A2 Mill A: Sulfide and Sulfate Concentrations (mg/L)

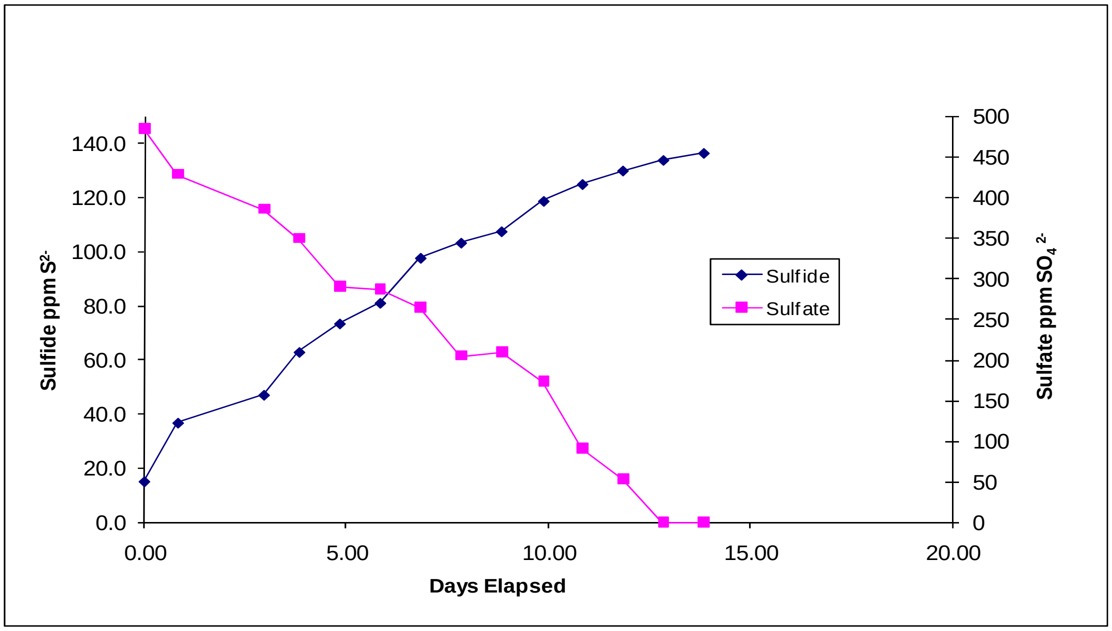

Figure A3 Mill B: Sulfide and Sulfate Concentrations (mg/L)

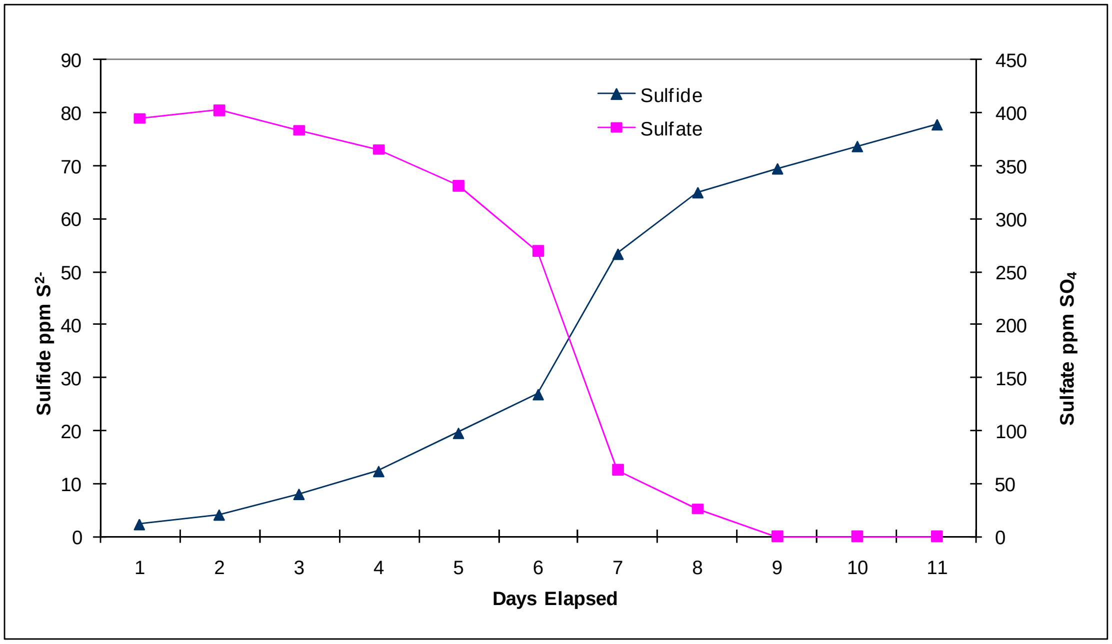

Figure A4 Mill C Reactor 1: Sulfide and Sulfate Concentrations (mg/L)

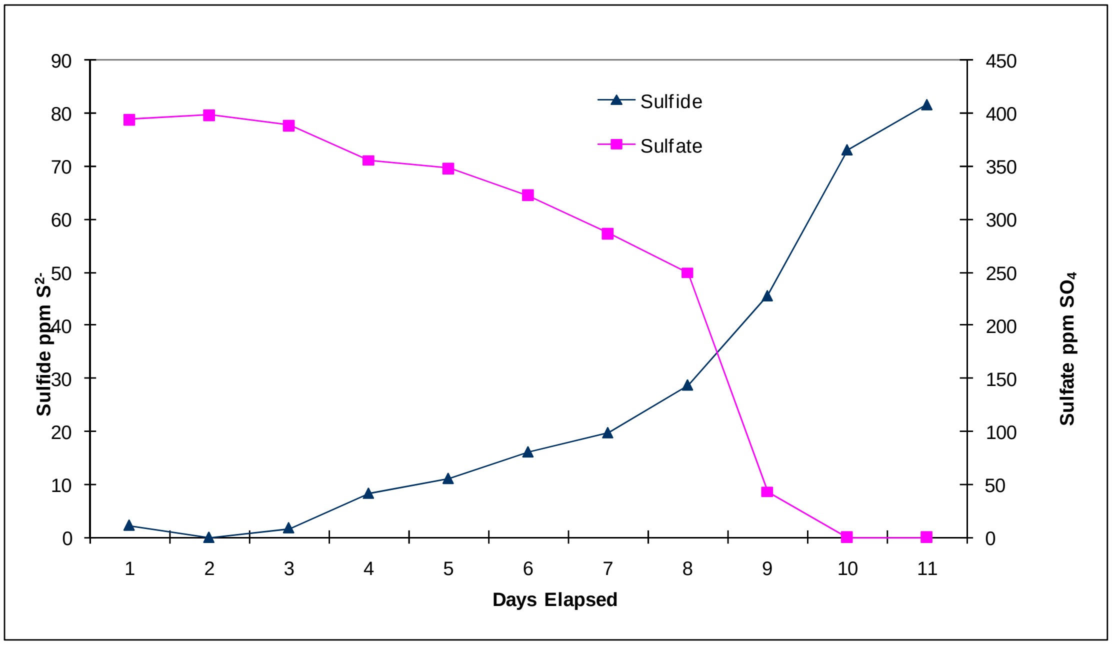

Figure A5 Mill C Reactor 2: Sulfide and Sulfate Concentrations (mg/L)

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.

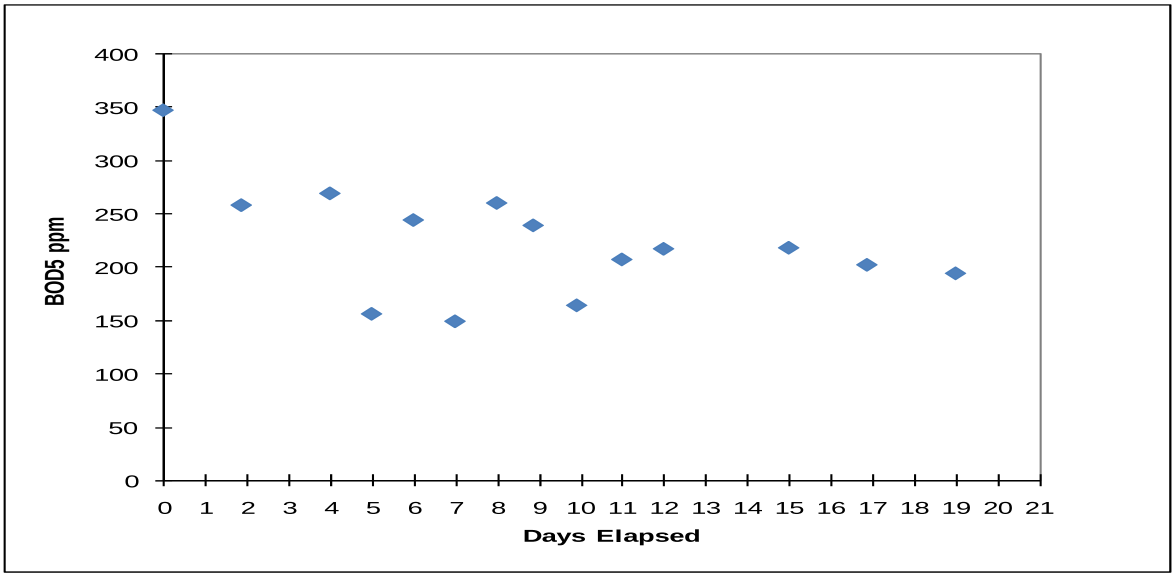

Figure A6 Observed BOD$_5$ Concentrations from Anoxic Batch Reactor

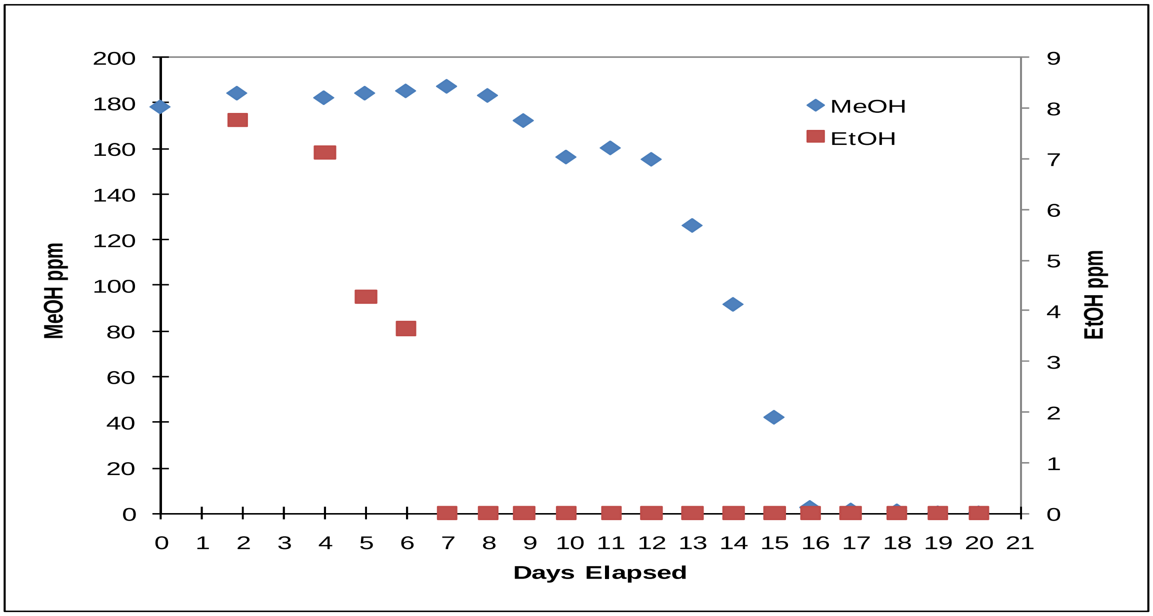

Figure A7 Observed Methanol and Ethanol Concentrations from Anoxic Batch Reactor

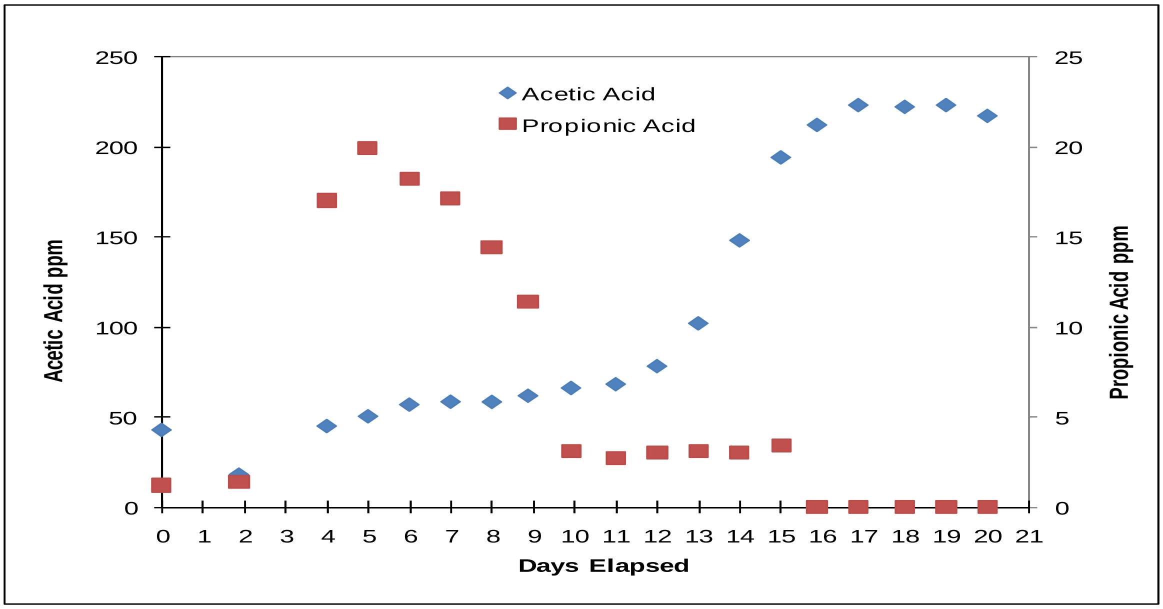

Figure A8 Observed Acetic and Propionic Acid Concentrations from Anoxic Batch Reactor

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: μ_{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.

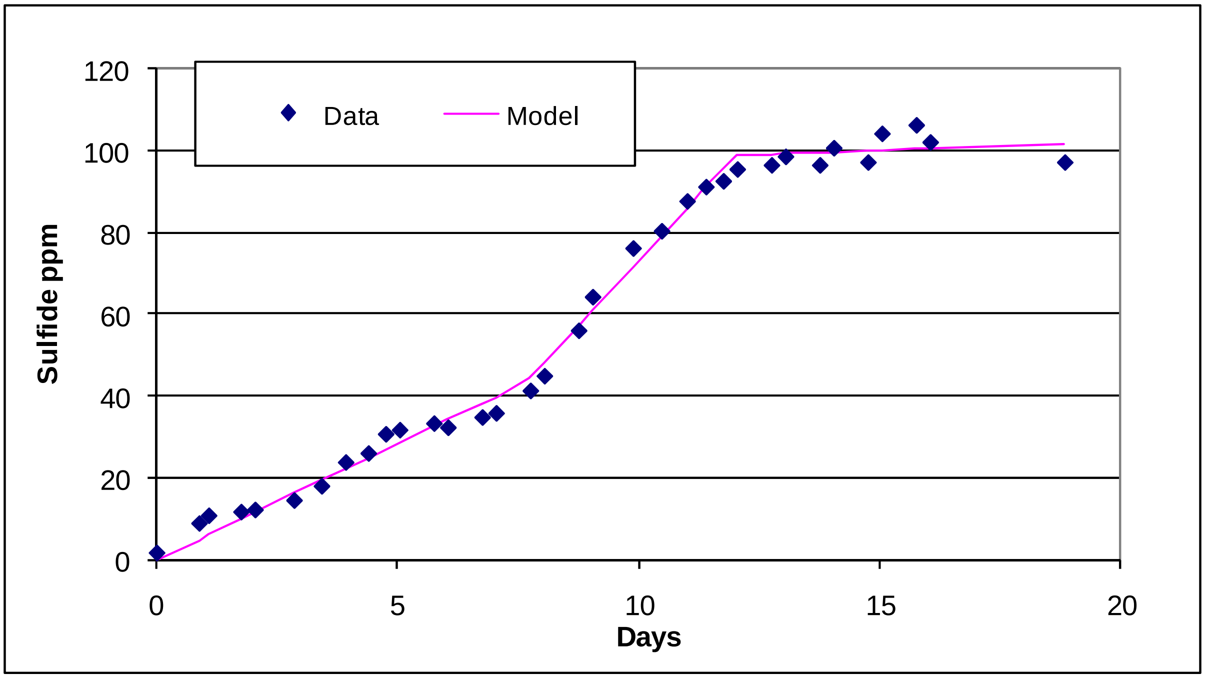

Figure A9 Fit of Segmented Model to Mill A Data

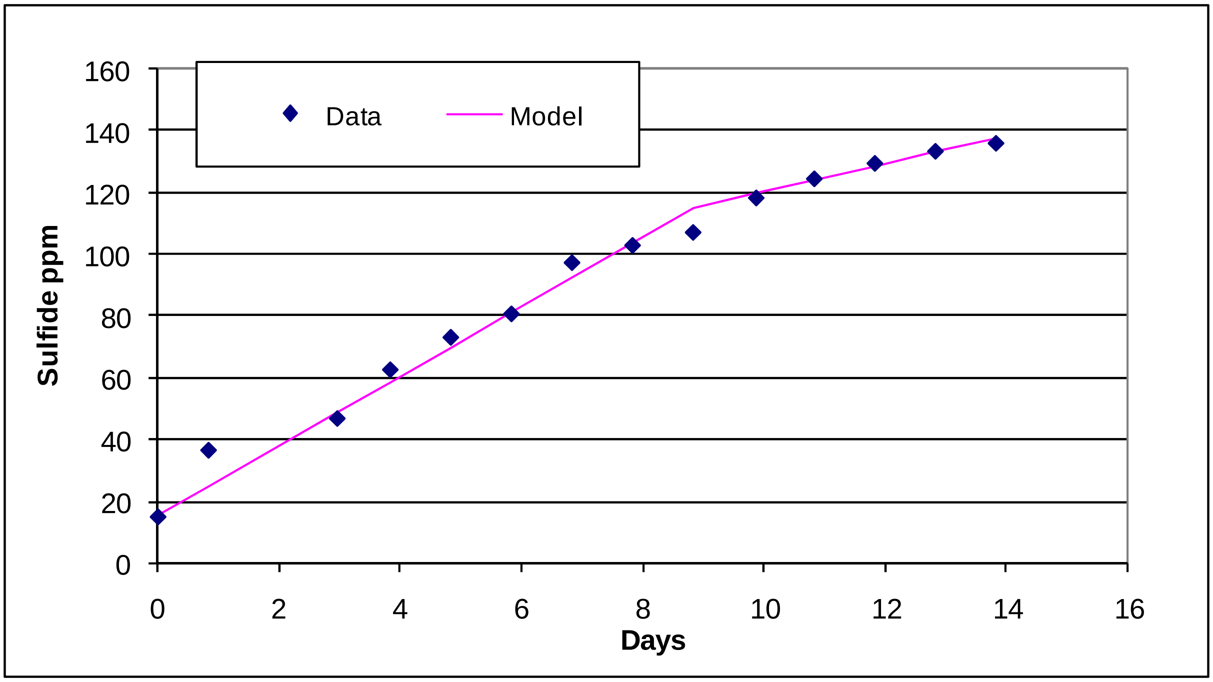

Figure A10 Fit of Segmented Model to Mill A Data

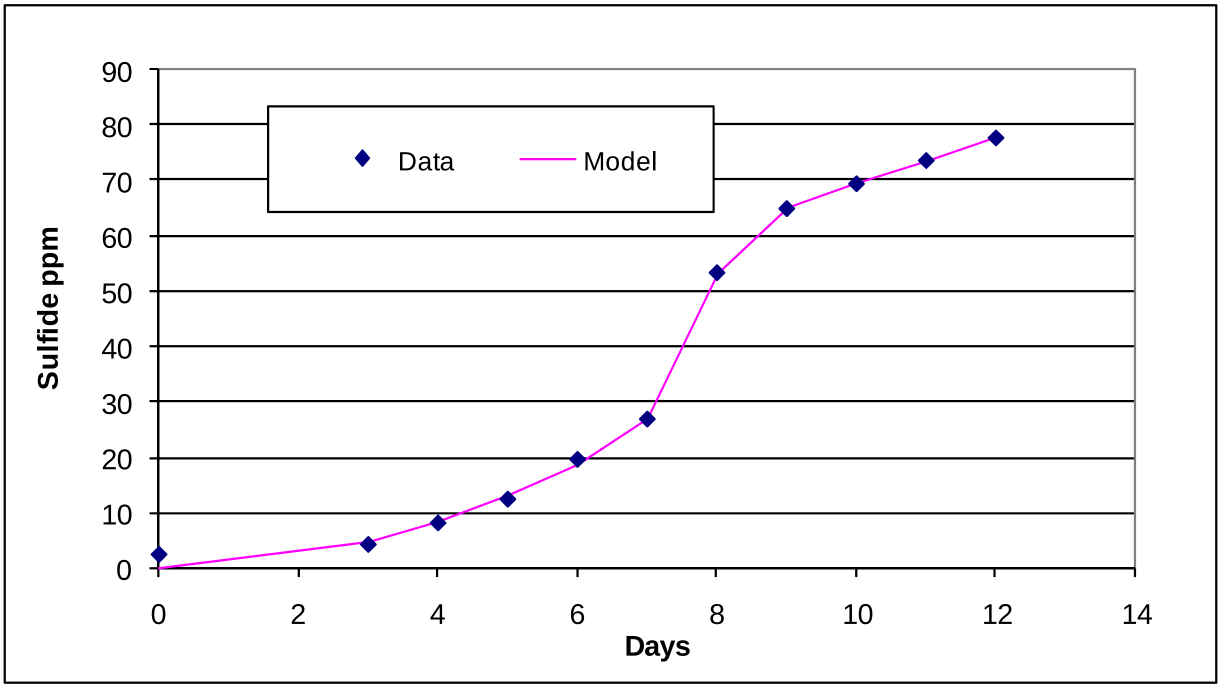

Figure A11 Fit of Segmented Model to Mill C Data

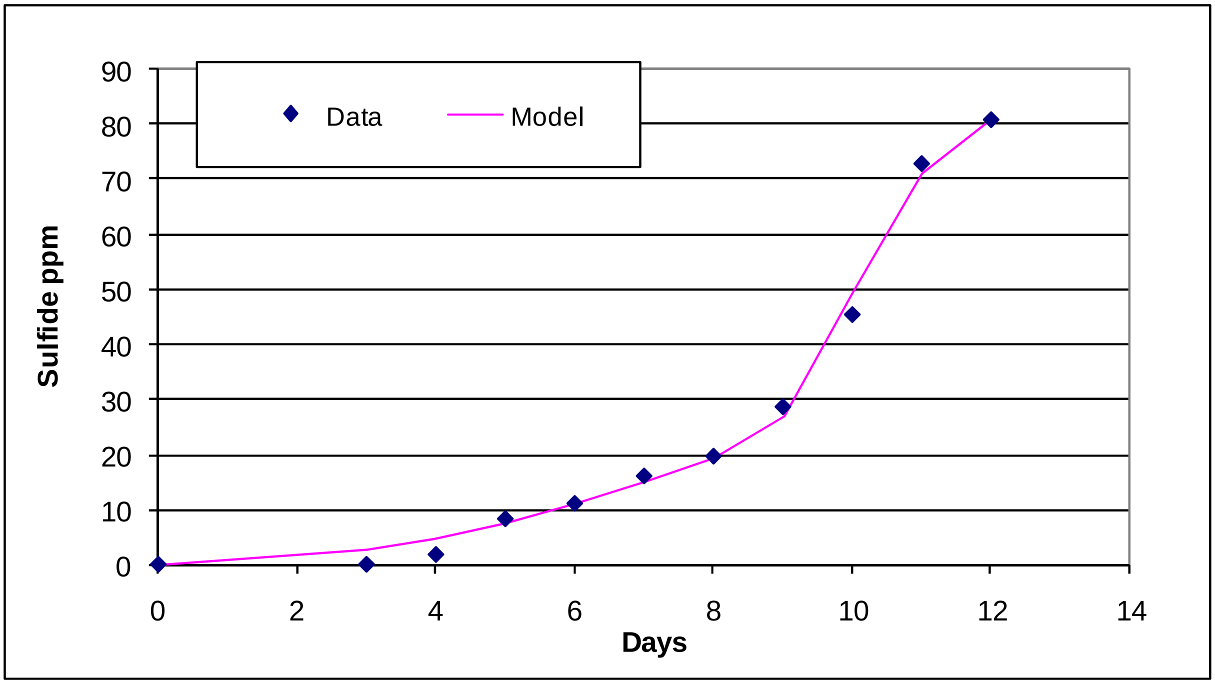

Figure A12 Fit of Segmented Model to Mill C Replicate Data

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.

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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."

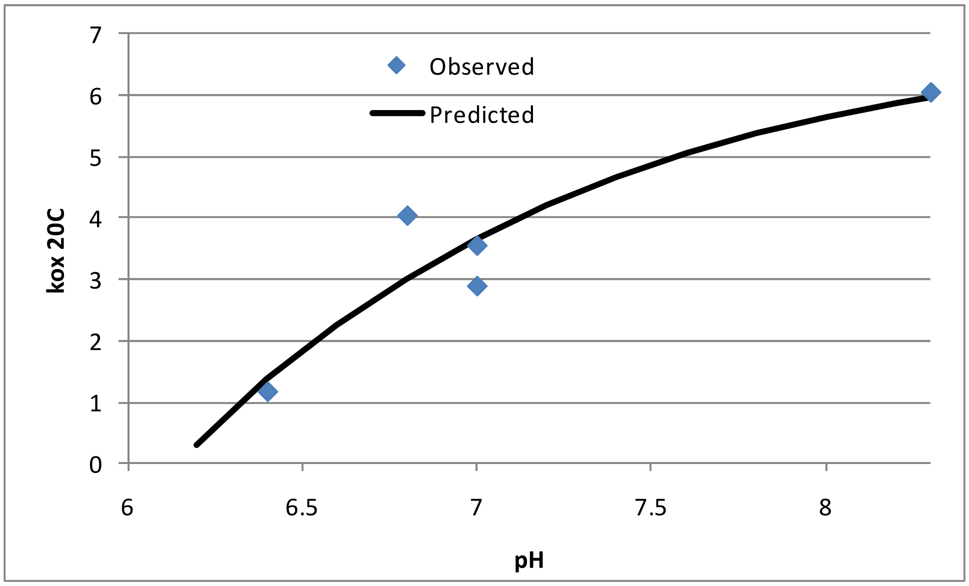

Figure B1 Sulfide Rate Coefficient in Sulfide Model as a Function of pH (T=20°C)

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.

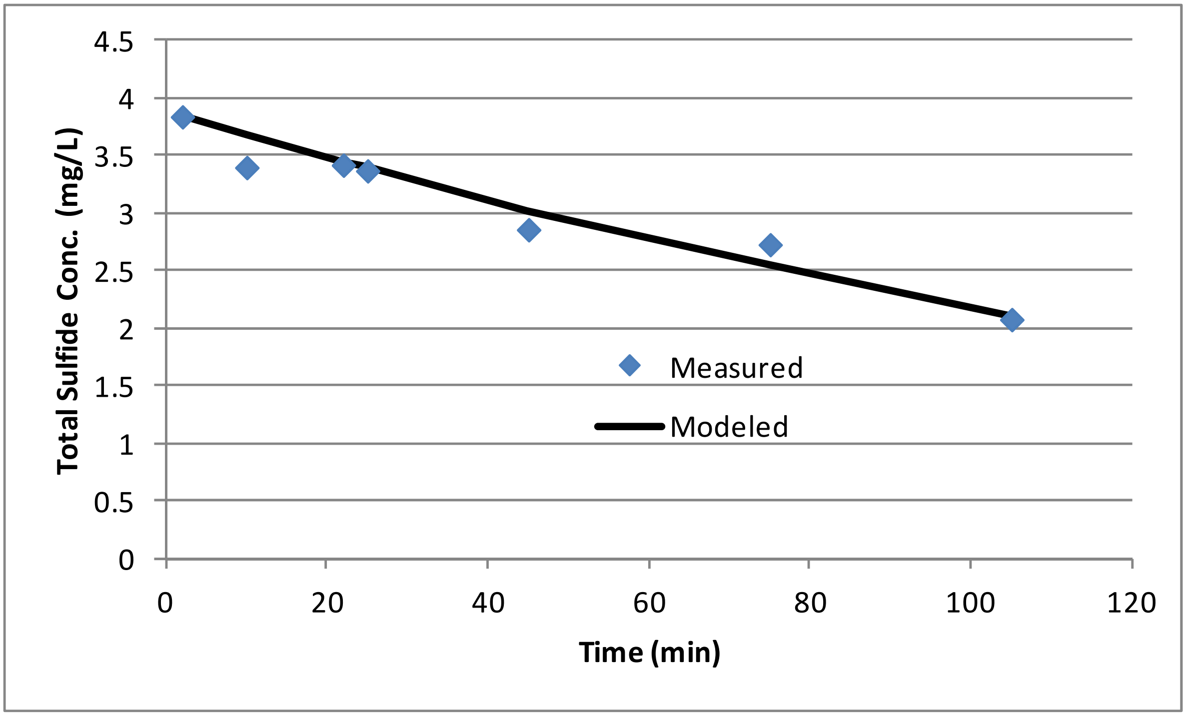

Figure B2 Equation B4 Fit to Sulfide Depletion Data Collected Under Anoxic Wastewater Conditions (pH = 6.9, Temperature = 20 °C)

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

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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.

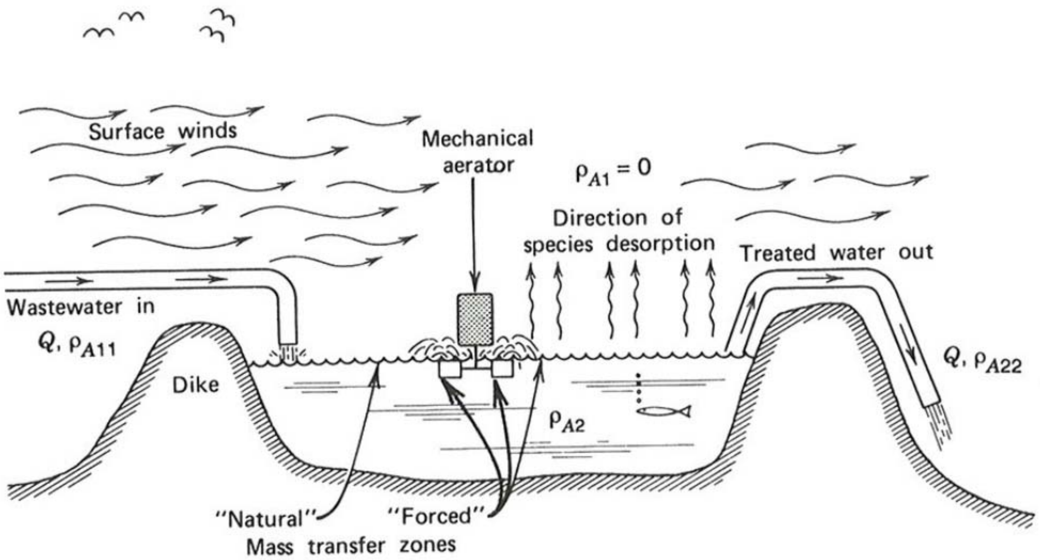

Figure C1 Forced Convection and Natural Convection Zones as Illustrated by Thibodeaux [Figure reproduced from Thibodeaux 1996, p. 174]

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.

$$\boldsymbol{k}_{\boldsymbol{l},\boldsymbol{Quiescent}} = 2.78 \cdot 10^{-6} \left(\frac{\boldsymbol{D}_{\boldsymbol{H}2\boldsymbol{S},\boldsymbol{Water}}}{\boldsymbol{D}_{\boldsymbol{Ether},\boldsymbol{Water}}} \right)^{2/3} \qquad \text{for } v_{wind} < 3.25 \text{ m/s, All } F/D \qquad \text{Equation C12}$$

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.

$$\boldsymbol{k}_{\boldsymbol{l},\boldsymbol{Quiescent}} = \left[2.78 \cdot 10^{-9} \cdot \boldsymbol{F} / \boldsymbol{D} + 1.277 \cdot 10^{-7}\right] \cdot \boldsymbol{v}_{\boldsymbol{wind}}{}^2 \cdot \left(\frac{\boldsymbol{D}_{\boldsymbol{H}2\boldsymbol{S},\boldsymbol{Water}}}{\boldsymbol{D}_{\boldsymbol{Ether},\boldsymbol{Water}}} \right)^{2/3} \qquad \text{Equation C13}$$

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

$$\boldsymbol{k}_{\boldsymbol{l},\boldsymbol{Quiescent}} = \left[2.611 \cdot 10^{-7}\right] \cdot \boldsymbol{v}_{\boldsymbol{wind}}{}^2 \cdot \left(\frac{\boldsymbol{D}_{\boldsymbol{H}2\boldsymbol{S},\boldsymbol{Water}}}{\boldsymbol{D}_{\boldsymbol{Ether},\boldsymbol{Water}}} \right)^{2/3} \qquad \text{Equation C14}$$

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.

$$\boldsymbol{k}_{g,Quiescent} = 4.82 \cdot 10^{-3} \cdot \boldsymbol{v}_{Wind}{}^{0.78} \cdot \boldsymbol{Sc}_{Gas}{}^{-\frac{2}{3}} \cdot \boldsymbol{d}_{Effective}{}^{-0.11} \qquad \text{Equation C15}$$

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.

$$\rho_{Air} = 1.204 \cdot \frac{293.15\,\boldsymbol{K}}{\boldsymbol{T}_{Ambient} + 273.15} \qquad \text{Equation C.16}$$

Water density (in kg/m^3) is found from the basin temperature (in °C) from the following.

$$\rho_{Water} = \left[\, 0.998203 - 0.000257 \cdot (\boldsymbol{T}_{ASB} - 20) \right] \cdot 1000 \qquad \text{Equation C17}$$

The viscosity of air is calculated empirically from tabulated data (Geankoplis 1993, p. 855).

$$\mu_{Air} = 0.1 \cdot (0.0000004568 \cdot \boldsymbol{T}_{ASB} + 0.00017209) \qquad \text{Equation C18}$$

The temperature dependence of water viscosity is simulated by the following empirical relationship.

$$\mu_{Water} = 0.00174 - 0.0000452 \cdot \boldsymbol{T}_{ASB} + 0.00000044 \cdot \boldsymbol{T}_{ASB}{}^{2} \qquad \text{Equation C19}$$

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.

$$\boldsymbol{D}_{Ether,Water} = 8.5 \cdot 10^{-10} \cdot \frac{\boldsymbol{T}_{ASB} + 273.15}{293.15} \cdot \frac{0.000972}{\mu_{Water}} \ (\text{m}^2/\text{s}) \qquad \text{Equation C20}$$

$$\boldsymbol{D}_{Oxygen,Water} = 2.4 \cdot 10^{-9} \cdot \frac{\boldsymbol{T}_{ASB} + 273.15}{293.15} \cdot \frac{0.000972}{\mu_{Water}} \ (\text{m}^2/\text{s}) \qquad \text{Equation C21}$$

$$\boldsymbol{D}_{\boldsymbol{H2S},\boldsymbol{Water}} = 1.61 \cdot 10^{-9} \cdot \frac{\boldsymbol{T}_{\boldsymbol{ASB}} + 273.15}{293.15} \cdot \frac{0.000972}{\mu_{\boldsymbol{Water}}} \ (\mathrm{m^2/s}) \qquad \text{Equation C22}$$

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).

$$\boldsymbol{D}_{\boldsymbol{H2S},\boldsymbol{Air}} = 1.76 \cdot 10^{-5} \cdot \left(\frac{\boldsymbol{T}_{\boldsymbol{ASB}} + 273.15}{293.15} \right)^{1.5} \ (\mathrm{m^2/s}) \qquad \text{Equation C23}$$

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.

$$\ln \frac{\boldsymbol{H}_{\boldsymbol{CP}}}{(\boldsymbol{H}_{\boldsymbol{CP}})_{30}} = 2.3 \cdot 767.3886 \cdot \left(\frac{1}{30 + 249.09} - \frac{1}{\boldsymbol{T}_{\boldsymbol{ASB}} + 249.09} \right) \cdot \ln 2.7182 \qquad \text{Equation C24}$$

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 $\mathrm{m^2}$ 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.

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ATTACHMENT C
DECEMBER 2, 2021 RESPONSE TO DHEC
NEW INDY CORRECTIVE ACTION PLAN – AIR DISPERSION MODELING ANALYSIS, OCTOBER 2021 DHEC – BAQ COMMENTS
NOVEMBER 17, 2021

NEW INDY
CONTAINERBOARD

December 2, 2021

John P. Glass Jr.
Bureau of Air Quality, Modeling Section Manager
South Carolina Department of
Health and Environmental Control
2600 Bull Street
Columbia, South Carolina 29201

Re: Responses to Corrective Action Plan Air Dispersion Modeling Comments

Dear John:

New-Indy Catawba LLC (New-Indy Catawba) appreciates the South Carolina Department of Health and Environmental Control's (SCDHEC or DHEC) review of the Mill's ambient air dispersion modeling report. As requested in your email dated November 17, 2021, New-Indy Catawba has updated the ambient air dispersion modeling report Tables and is providing the below responses to each of the comments.

November 17, 2021 Comments from SCDHEC:

General –

1. Please provide a drawing or picture that shows all the locations of the sources covered in the analysis, to include: Closed Trench No. 1, Ditch 0, Splitter, Open Sump No. 4, Closed Trench No. 5, Clarifier, Ditch 1, Ditch 2 with respect to the ASB, EQ Basin, Post-Aeration, Holding Pond, and Sludge Pond. Also provide an explanation of the wastewater flow through the wastewater treatment plant.

New-Indy Catawba Response 1: The drawing is provided in Attachment 1. Wastewater flow through the treatment process is indicated by blue arrows. Wastewater flows through the wastewater treatment plant through each of the following units in the corresponding order:

1. Closed Trench No. 1
2. Primary Clarifier
3. Ditch No. 0
4. Splitter and Open Sump No. 4
5. Closed Trench No. 5
6. EQ Basin
7. Ditch No. 1
8. ASB
9. Ditch No. 2
10. Holding Pond No. 1
11. Post-Aeration Basin

Sludge from the primary clarifier enters the EQ basin for settling and dewatering. Free water from the primary clarifier sludge flows over the EQ basin into Ditch No. 1. Settled solids from the EQ basin and ASB are removed and placed in Sludge Pond No. 4.

2. The emissions estimates and modeling do not include any H2S/TRS emissions from the No. 1 and No. 2 Sludge Ponds, and the Temporary Effluent Holding Basin. Please explain whether these ponds/basins are part of the wastewater treatment process, how these units are used, why emissions were not estimated from these units, etc.

New-Indy Catawba Response 2: The No. 1 and No. 2 sludge ponds are not currently used for managing wastewater or primary clarifier sludge. The No. 1 sludge pond is filled with rainwater. The No. 2 sludge pond receives the backwash from the filter plant used to treat the incoming raw river water. The temporary effluent holding basin is used during extreme drought to store treated wastewater transferred from the No. 1 Holding Pond. The temporary effluent holding basin was last used during the extreme drought in 2008. The temporary effluent holding pond and the No. 1 and No. 2 sludge ponds do not contain any material expected to generate H2S/TRS emissions, so they are not included in the emissions estimates or the modeling.

3. Please provide a rationale/explanation for all the assumptions that were made for the data presented in the analysis (e.g., why the closed trench No. 1 will not have emissions to the air, etc.). Also, please provide a discussion of the differences in the data between the current report and the August 2021 modeling analysis report.

New-Indy Catawba Response No. 3: The emissions rates are based on site-specific data and/or stack test results used in conjunction with the United States Environmental Protection Agency (USEPA) or National Council for Air and Steam Improvement (NCASI) air emissions models. The October 5, 2021 and October 27, 2021 responses submitted by New-Indy Catawba and the footnotes to each table in the October 2021 modeling report describe the defaults used in the air emissions models and assumptions (See Appendices A and C of the October 2021 modeling report).

There are numerous differences in the data between the August 2021 modeling report and the October 2021 modeling report. The significant differences are related to the changes mandated by the South Carolina Department of Health and Environmental Control (DHEC) and USEPA regarding the numerous non-detect values in the June 2021 stack test report and the July 2021 40 CFR 63 Subpart S Initial Performance Test (IPT). New-Indy Catawba addressed these and other comments from DHEC and USEPA regarding the June stack test and July IPT on October 5, 2021. New-Indy Catawba also responded to DHEC and USEPA comments regarding the August 2021 modeling report on October 27, 2021. Please refer to the October 5 and October 27 responses submitted by New-Indy Catawba for discussion of the changes to the data in response to the DHEC and USEPA comments. Additional changes to the data between August 2021 to October 2021 are described in responses 5, 6, 7, 8, 10 and 11 of this document.

Regarding your specific example, the WATER9 air emissions results for closed trench No. 1 are zero (0 g/s). The WATER9 air emissions results for closed trench No. 5 are included in the emissions from Ditch 0 and the Splitter Box shown in Table A-8 of the October 2021 modeling report, as noted in footnote 1 to Table A-8.

4. Footnote 5, on Table A-8 provides the dimensions and area calculation for Ditch 0. This same footnote has been repeated starting with Table A-9 and thereafter and has not been corrected for the sources in those tables. Please revise to provide the correct source and dimensions for each table.

New-Indy Catawba Response 4: Footnotes have been corrected in Table A-9 through A-17 and provided in Attachment 2.

5. Regarding the SO2 modeling submitted in October 2021: Besides a slight increase in emissions for emission point FUTNCG1, are there any differences in the modeling compared to the SO2 modeling submitted in August 2021? If so, please provide a list of and reasons for the changes.

New-Indy Catawba Response 5: There are no differences in the August 2021 and October 2021 SO2 modeling other than the slight increase in SO2 emissions from source FUTNCG1.

Primary Clarifier –

6. Section 3.2 of the report narrative says "The July 2021 liquid sample results are coupled with the National Council for Air and Stream Improvement (NCASI) wastewater Hydrogen Sulfide Emissions Simulator (H2SSIM) emissions model for H2S emission [f]rom the primary clarifier and ..." Please explain why inputs to the H2SSIM model changed from the August 2021 submittal – total sulfide, flow, temperature, pH, and length and width (diameter?) of clarifier.

New-Indy Catawba Response 6: In the August 2021 submittal, individual H2SSIM models were run for each day of the July 2021 IPT (conducted July 9-11, 2021). In the October 2021 submittal, one run using the average Flow, Temperature, and pH were used to estimate H¬¬¬2¬S emissions. The length and width of the clarifier were re-calculated as equivalent lengths and widths based on the surface area due to H2SSIM's inability to accommodate circular clarifiers. The total sulfide concentration was back-calculated using the WATER9 calculated removal efficiency (e.g., ASB influent concentration/removal efficiency).

7. Please explain why the modeled emission rate has increased from 2.07E-02 lb/hr to 1.63E-01 lb hr for H2S (and a similar change for the TRS emissions).

New-Indy Catawba Response 7: See Response 6 above for an explanation of the changes to the primary clarifier H2S emissions from the August 2021 submittal to the October 2021 modeling submittal. However, the primary clarifier H2S emissions have been re-calculated based on comments 8 and 9 in this document. The revised maximum emissions rate for H2S is 1.98E-03 lb/hr and 1.44E-01 lb/hr for TRS (as H2S). Table A-9 is provided in Attachment 2.

8. A pH of 9.08 was used in the Water9 runs for DMS, DMDS, and MM, but 8.943333 was used in the H2SSIM model. Why? Also, for Ditch 0, that follows the clarifier, a pH of 9.08 was used in the Water9 run for H2S.

New-Indy Catawba Response 8: The pH of 9.08 is sourced from the average readings of the Primary Clarifier pH PI tag from July 9-11, 2021. The pH of 8.943333 is the average ASB inlet pH from July 9-11, 2021, which was used as a surrogate until source specific data was available. Substituting the pH of 9.08 in H2SSIM results in a 27% decrease of H2S emissions from the primary clarifier (15.2 lb/yr vs. 11.1 lb/yr). No source specific pH data is available for Ditch 0, so the Ditch 0 pH is assumed equal to the primary clarifier. The corrected H2SSIM model for the Primary Clarifier is provided in Attachment 3.

9. Table A-9 – It appears the H2S rate, in g/s was not calculated correctly. A conversion from minutes to seconds was missed in the denominator, based on footnote 2. This will impact the TRS as H2S rates as well other calculations in this table. Please confirm correct emission rates throughout this table.

New-Indy Catawba Response 9: The conversion from hours to minutes and minutes to seconds have been included in the conversion calculation of H2S in g/s to H2S in lb/hr in Table A-9. The revised maximum emissions rate for H2S is 1.98E-03 lb/hr and 1.44E-01 for TRS (as H2S). Footnote 2 has also been updated to include the missing conversion. Table A-9 is provided in Attachment 2.

Aerated Stabilization Basin –

10. Slightly larger areas than those in the August report were used for each of the zones in the ASB in Table A-13. Please explain.

New-Indy Catawba Response 10: The actual water surface area of each ASB zone was determined from the aerial photo taken during the July 2021 IPT. The actual water surface area of each zone was converted to an equivalent length and width to use as an input to the WATER9 emissions model. The AERMOD polygons representing the areas of each ASB zone were harmonized with the areas for each zone in the WATER9 emissions model. The polygon area of each zone in AERMOD was made slightly larger than the area in the WATER9 emissions model as a conservative assumption. When the WATER9 emissions rates in g/cm2-s are applied to the AERMOD model areas, the total mass emissions are slightly overestimated in the AERMOD model. This change was made for consistency with responses to previous comments from DHEC and EPA related to the wastewater ditches in the model.

Holding Pond –

11. A smaller area has been used for the holding pond than that used in the August report. Please explain.

New-Indy Catawba Response 11: The AERMOD area of the holding pond was harmonized with the area in the WATER9 emissions model by correcting the north and west boundaries of the holding pond to represent the surface area in the WATER9 model. This change was made for consistency with responses to previous comments from DHEC and EPA related to the wastewater ditches in the model.

Post-Aeration Basin (Tank?) –

12. Were the stack tests performed on the Post-Aeration Basin approved by BAQ? The referenced test dates in Table A-7 are different from those that supplied data for the Initial Performance Test (IPT), where testing was done at the Post-Aeration Tank. How and from where was the source test data derived for this basin? Just to make sure, the IPT refers to this source as a tank. Is this the same as the Post-Aeration Basin?

New-Indy Catawba Response 12: The post aeration basin is a concrete tank. The post-aeration unit has been described as a basin or a tank at various times during its existence. The post-aeration basin (PAB) is an open top tank which was fitted with a cover and carbon absorption system to reduce the potential for H2S/TRS emissions. DHEC approved the temporary removal of the PAB cover for the duration of the July 2021 IPT wastewater sampling effort. Following the IPT, New-Indy Catawba purchased a Scentroid portable monitor for sampling H2S concentrations. The post-aeration basin stack tests were performed using the Scentroid portable monitor described in the New-Indy Catawba submittal on September 17, 2021 responding to DHEC comments on the August 2021 modeling report. The H2S concentrations measured at the outlet of the carbon absorption system during the July 2021 IPT represented the H2S emissions from the PAB at that time. Emissions measurements taken in September 2021 using the Scentroid portable monitor are more representative of actual H2S emissions from the PAB. Measuring the H2S concentrations at the outlet of the PAB carbon absorption system using the Scentroid portable monitor was not pre-approved by BAQ.

Please feel free to contact me via phone at 803-981-8010 or email at dan.mallett@new-indycb.com if you have any additional questions.

Sincerely,

Daniel J. Mallett
Environmental Manager

Enclosures

ATTACHMENT 1 – DRAWING

Legend

→ Wastewater Flow

Figure 1
Wastewater Treatment Sources and Flow Direction

New-Indy Catawba
Catawba, SC

DRAWN BY:	CHECKED BY:	PROJECT NO.
A.K.	S.M.	00958-0010.00

ATTACHMENT 2 – CORRECTED TABLES

Table A-8

Ditch 0 + Splitter Box Water9 Model Results

New-Indy Catawba - Catawba, SC

DITCH 0 + SPLITTER BOX													
		ACTUAL								MAXIMUM			
	MW	g/s	Reference	Justification	sq meters[5]	g/s-sq meter[6]	lb/hr[7]	ODTP/day[8]	lb/ODTP[9]	ADTP/day[10]	lb/hr[11]	g/s[12]	g/s-sq meter[13]
H_2S	34.08	1.57E-05	WATER9, NCASI TB 1000[2]	WATER9 and Free Sulfide Tool	222.65	7.07E-08	1.25E-04	1553.08	1.93E-06	2700	1.95E-04	2.46E-05	1.11E-07
MM[1]	48.11	7.19E-05	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	222.65	3.23E-07	5.71E-04	1553.08	8.82E-06	2700	8.93E-04	1.12E-04	5.05E-07
DMS[1]	62.14	7.67E-03	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	222.65	3.44E-05	6.08E-02	1553.08	9.40E-04	2700	9.52E-02	1.20E-02	5.39E-05
DMDS[1]	94.20	1.47E-03	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	222.65	6.59E-06	1.16E-02	1553.08	1.80E-04	2700	1.82E-02	2.30E-03	1.03E-05
TRS (as H_2S)	34.08	5.33E-03	Summation[4]	Summation of H_2S, MM, DMS and DMDS converted to common H_2S basis based on molecular weight of sulfur in each constituent	222.65	2.40E-05	4.23E-02	1553.08	6.54E-04	2700	6.62E-02	8.34E-03	3.75E-05

[1] includes emissions from Ditch 0 (open from Primary Clarifier to Splitter Box), Splitter Box, and enclosed pipe from Splitter Box to Ditch 1

[2] H_2S emissions rate (g/s) calculated based on the site-specific liquid H_2S concentration from the July 9-11, 2021 initial performance test (IPT) under 40 CFR 63, Subpart S, adjusted for pH using the NCASI Free Sulfide Tool (as described in NCASI Technical Bulletin 1000, section 3.2), and the site-specific WATER9 program mass transfer coefficient for Ditch #0 + Splitter Box. Calculations of the fraction of H_2S and the H_2S emissions rate is provided in the attached spreadsheet Ditch #0 Calcs.xlsx. USEPA WATER9 Program, Version 3.0 is posted at: https://www3.epa.gov/ttnchie1/software/water/water9_3/index.html. The basis for the input values and the output files from the WATER9 Program are also attached.

[3] MM, DMS, and DMDS emissions rates (g/s) calculated based on site-specific MM, DMS, and DMDS liquid concentrations from the July 9-11, 2021 IPT and configuration of the Ditch #0 + Splitter Box utilizing the USEPA WATER9 Program, Version 3.0, posted at: https://www3.epa.gov/ttnchie1/software/water/water9_3/index.html. The basis for the input values and the output files from the WATER9 Program are also attached.

[4] 5.33E-03 g TRS/s = [(1.57E-05 g H2S/s x 32.07 mol S/g ÷ 34.08 mol H2S/g) + (7.19E-05 g MM/s x 32.07 mol S/g ÷ 48.11 mol MM/g) + (7.67E-03 g DMS/s x 32.07 mol S/g ÷ 62.14 mol DMS/g) + (1.47E-03 g DMDS/s x 64.14 mol S/g ÷ 94.20 mol DMDS/g)] x (34.08 mol H2S/g÷ 32.07 mol S/g)

[5] Ditch 0 is 3.65 meters wide and 61 meters long = 3.65 × 61 = 222.65 sq meters

[6] g TRS/s-sq meter = 5.33E-03 g TRS/s ÷ 222.65 sq meters = 2.40E-05 g TRS/s-sq meter

[7] lb TRS/hr = 5.33E-03 g TRS/s x 3600 s/hr ÷ 453.592 g TRS/lb TRS = 4.23E-02 lb TRS/hr

[8] average pulp production during sampling on July 9, 10 and 11 (1694.16, 1609.17, 1355.92 ODTP/day)

[9] lb TRS/ODTP = 4.23E-02 lb TRS/hr x 1 hr/1553.08 ODTP = 6.54E-04 lb TRS/ODTP

[10] maximum production from June 2019 and April 2020 Project Columbia construction permit applications (construction permit DF)

[11] lb TRS/hr = 6.54E-04 lb TRS/ODTP x 2700 ADTP/day x 1 day/24 hr x 0.9 ODTP/1.0 ADTP = 6.62E-02 lb TRS/hr

[12] g TRS/s = 6.62E-02 lb TRS/hr x 453.592 g TRS/lb TRSx 1 hr/3600 s = 8.34E-03 g TRS/s

[13] g TRS/s-sq meter = 8.34E-03 g TRS/s ÷ 222.65 sq meters = 3.75E-05 g TRS/s-sq meter

Table A-9
Primary Clarifier Water9 Model Results
New-Indy Catawba - Catawba, SC

PRIMARY CLARIFIER													
		ACTUAL								MAXIMUM			
	MW	g/s	Reference	Justification	sq meters[5]	g/s-sq meter[6]	lb/hr[7]	ODTP/day[8]	lb/ODTP[9]	ADTP/day[10]	lb/hr[11]	g/s[12]	g/s-sq meter[13]
H_2S	34.08	1.60E-04	H2SSIM[2]	National Council for Air and Stream Improvement (NCASI) model for pulp and paper biological wastewater system H_2S emissions	5542	2.88E-08	1.27E-03	1553.08	1.96E-05	2700	1.98E-03	2.50E-04	4.51E-08
MM	48.11	1.40E-04	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	5542	2.53E-08	1.11E-03	1553.08	1.72E-05	2700	1.74E-03	2.20E-04	3.96E-08
DMS	62.14	1.63E-02	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	5542	2.94E-06	1.29E-01	1553.08	2.00E-03	2700	2.02E-01	2.55E-02	4.59E-06
DMDS	94.20	3.36E-03	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	5542	6.06E-07	2.67E-02	1553.08	4.12E-04	2700	4.17E-02	5.26E-03	9.49E-07
TRS (as H_2S)	34.08	1.16E-02	Summation[4]	Summation of H_2S, MM, DMS and DMDS converted to common H_2S basis based on molecular weight of sulfur in each constituent	5542	2.10E-06	9.22E-02	1553.08	1.42E-03	2700	1.44E-01	1.82E-02	3.28E-06

[1] Reserved.

[2] H2SSIM model results for wastewater samples collected on July 9, July 10 and July 11 (11.1 lb/yr) during the 40 CFR 63, Subpart S IPT converted to grams per second [11.1 lb/yr * 453.592 grams/lb / (8760 hrs/yr * 60 min/hr * 60 s/min)]. The NCASI H2SSIM model that calculates the sulfide fate and transport in wastewater treatment basins is documented in NCASI TB 1000. Input and output files from the H2SSIM model are attached.

[3] Average of WATER9 model results for wastewater samples collected on July 9, July 10 and July 11 during the 40 CFR 63, Subpart S IPT. USEPA WATER9 Program, Version 3.0, posted at: https://www3.epa.gov/ttnchie1/software/water/water9_3/index.html. The basis for the input values and the output files from the WATER9 Program are also attached.

[4] 1.16E-02 g TRS/s = [(1.60E-04 g H2S/s x 32.07 mol S/g ÷ 34.08 mol H2S/g) + (1.40E-04 g MM/s x 32.07 mol S/g ÷ 48.11 mol MM/g) + (1.63E-02 g DMS/s x 32.07 mol S/g ÷ 62.14 mol DMS/g) + (3.36E-03 g DMDS/s x 64.14 mol S/g ÷ 94.20 mol DMDS/g)] x (34.08 mol H2S/g÷ 32.07 mol S/g)

[5] Primary Clarifier is 84 meters in diameter = 3.14 x (84/2)^2 = 5,542 sq meters

[6] g TRS/s-sq meter = 1.16E-02 g TRS/s ÷ 5542 sq meters = 2.10E-06 g TRS/s-sq meter

[7] lb TRS/hr = 1.16E-02 g TRS/s x 3600 s/hr ÷ 453.592 g TRS/lb TRS = 9.22E-02 lb TRS/hr

[8] average pulp production during sampling on July 9, 10 and 11 (1694.16, 1609.17, 1355.92 ODTP/day)

[9] lb TRS/ODTP = 9.22E-02 lb TRS/hr x 1 hr/1553.08 ODTP = 1.42E-03 lb TRS/ODTP

[10] maximum production from June 2019 and April 2020 Project Columbia construction permit applications (construction permit DF)

[11] lb TRS/hr = 1.42E-03 lb TRS/ODTP x 2700 ADTP/day x 1 day/24 hr x 0.9 ODTP/1.0 ADTP = 1.44E-01 lb TRS/hr

[12] g TRS/s = 1.44E-01 lb TRS/hr x 453.592 g TRS/lb TRSx 1 hr/3600 s = 1.82E-02 g TRS/s

[13] g TRS/s-sq meter = 1.82E-02 g TRS/s ÷ 5542 sq meters = 3.28E-06 g TRS/s-sq meter

Table A-10
Equalization Basin Water9 Model Results
New-Indy Catawba - Catawba, SC

EQUALIZATION BASIN[1]													
		ACTUAL								MAXIMUM			
	MW	g/s	Reference	Justification	sq meters[5]	g/s-sq meter[6]	lb/hr[7]	ODTP/day[8]	lb/ODTP[9]	ADTP/day[10]	lb/hr[11]	g/s[12]	g/s-sq meter[13]
H_2S	34.08	4.56E-03	NCASI Form R and TB 956 and 1000[2]	NCASI Toxics Release Inventory (TRI) Form R Guidance and Free Sulfide Tool	7616	5.99E-07	3.62E-02	1553.08	5.59E-04	2700	5.66E-02	7.14E-03	9.37E-07
MM[3]	48.11												
DMS[3]	62.14												
DMDS[3]	94.20												
TRS (as H_2S)	34.08	4.56E-03	Summation[4]	Summation of H_2S, MM, DMS and DMDS converted to common H_2S basis based on molecular weight of sulfur in each constituent	7616	5.99E-07	3.62E-02	1553.08	5.59E-04	2700	5.66E-02	7.14E-03	9.37E-07

[1] Equalization Basin area includes open channel along northern edge between open surface area on western side to Ditch 1 on eastern side

[2] NCASI Handbook of Chemical-Specific Information for Superfund Amendments and Reauthorization Act (SARA) Section 313 Form R Reporting - Pulp and Paper Facilities. Hydrogen Sulfide, Table 4 "WWTP PARTITIONING AND EMISSIONS OF HYDROGEN SULFIDE", Sludge Pond mean emissions factor of 4.2 lb/(day-Acre). H_2S emissions factor adjusted for pH using the NCASI Free Sulfide Tool (as described in NCASI Technical Bulletin 1000, section 3.2) and documentation of the emissions rate calculation is provided in the attached spreadsheet "EQ Basin and Sludge Lagoon Calcs.xlsx".

[3] There are no emissions of MM, DMS, and DMDS reported from the equalization basin. Small amounts of MM, DMS, and DMDS that are contained in the water that remains with the sludge from the primary clarifier that is deposited in the equalization basin are assumed to be emitted in the primary clarifier, ditch #0, #1, and #2, or Aerated Stabilization Basin (ASB) Zones 1-3.

[4] 4.56E-03 g TRS/s = [(4.56E-03 g H2S/s x 32.07 mol S/g ÷ 34.08 mol H2S/g) + (0.00E+00 g MM/s x 32.07 mol S/g ÷ 48.11 mol MM/g) + (0.00E+00 g DMS/s x 32.07 mol S/g ÷ 62.14 mol DMS/g) + (0.00E+00 g DMDS/s x 64.14 mol S/g ÷ 94.20 mol DMDS/g)] x (34.08 mol H2S/g÷ 32.07 mol S

[5] Equalization Basin free water surface area calculated using Geographic Information System (GIS) software.

[6] g TRS/s-sq meter = 4.56E-03 g TRS/s ÷ 7616 sq meters = 5.99E-07 g TRS/s-sq meter

[7] lb TRS/hr = 4.56E-03 g TRS/s x 3600 s/hr ÷ 453.592 g TRS/lb TRS = 3.62E-02 lb TRS/hr

[8] average pulp production during sampling on July 9, 10 and 11 (1694.16, 1609.17, 1355.92 ODTP/day)

[9] lb TRS/ODTP = 3.62E-02 lb TRS/hr x 1 hr/1553.08 ODTP = 5.59E-04 lb TRS/ODTP

[10] maximum production from June 2019 and April 2020 Project Columbia construction permit applications (construction permit DF)

[11] lb TRS/hr = 5.59E-04 lb TRS/ODTP x 2700 ADTP/day x 1 day/24 hr x 0.9 ODTP/1.0 ADTP = 5.66E-02 lb TRS/hr

[12] g TRS/s = 5.66E-02 lb TRS/hr x 453.592 g TRS/lb TRSx 1 hr/3600 s = 7.14E-03 g TRS/s

[13] g TRS/s-sq meter = 7.14E-03 g TRS/s ÷ 7616 sq meters = 9.37E-07 g TRS/s-sq meter

Table A-11
Ditch #1 Water9 Model Results
New-Indy Catawba - Catawba, SC

DITCH 1													
		ACTUAL								MAXIMUM			
	MW	g/s	Reference	Justification	sq meters[5]	g/s-sq meter[6]	lb/hr[7]	ODTP/day[8]	lb/ODTP[9]	ADTP/day[10]	lb/hr[11]	g/s[12]	g/s-sq meter[13]
H_2S	34.08	2.10E-04	WATER9, NCASI TB 1000[2]	WATER9 and Free Sulfide Tool	2190	9.57E-08	1.66E-03	1553.08	2.57E-05	2700	2.60E-03	3.28E-04	1.50E-07
MM	48.11	4.50E-04	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	2190	2.05E-07	3.57E-03	1553.08	5.51E-05	2700	5.58E-03	7.03E-04	3.21E-07
DMS	62.14	5.04E-02	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	2190	2.30E-05	4.00E-01	1553.08	6.18E-03	2700	6.26E-01	7.88E-02	3.60E-05
DMDS	94.20	1.09E-02	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	2190	4.99E-06	8.68E-02	1553.08	1.34E-03	2700	1.36E-01	1.71E-02	7.81E-06
TRS (as H_2S)	34.08	3.61E-02	Summation[4]	Summation of H_2S, MM, DMS and DMDS converted to common H_2S basis based on molecular weight of sulfur in each constituent	2190	1.65E-05	2.86E-01	1553.08	4.43E-03	2700	4.48E-01	5.65E-02	2.58E-05

[1] Reserved.

[2] H_2S emissions rate (g/s) calculated based on the site-specific liquid H_2S concentration from the July 9-11, 2021 initial performance test (IPT) under 40 CFR 63, Subpart S, adjusted for pH using the NCASI Free Sulfide Tool (as described in NCASI Technical Bulletin 1000, section 3.2), and the site-specific WATER9 program mass transfer coefficient for Ditch #1. Calculations of the fraction of H_2S and the H_2S emissions rate is provided in the attached spreadsheet Ditch #1 Calcs.xlsx. USEPA WATER9 Program, Version 3.0 is posted at: https://www3.epa.gov/ttnchie1/software/water/water9_3/index.html. The basis for the input values and the output files from the WATER9 Program are also attached.

[3] MM, DMS, and DMDS emissions rates (g/s) calculated based on site-specific MM, DMS, and DMDS liquid concentrations from the July 9-11, 2021 IPT and configuration of the Ditch #1 utilizing the USEPA WATER9 Program, Version 3.0, posted at: https://www3.epa.gov/ttnchie1/software/water/water9_3/index.html. The basis for the input values and the output files from the WATER9 Program are also attached.

[4] 3.61E-02 g TRS/s = [(2.10E-04 g H2S/s x 32.07 mol S/g ÷ 34.08 mol H2S/g) + (4.50E-04 g MM/s x 32.07 mol S/g ÷ 48.11 mol MM/g) + (5.04E-02 g DMS/s x 32.07 mol S/g ÷ 62.14 mol DMS/g) + (1.09E-02 g DMDS/s x 64.14 mol S/g ÷ 94.20 mol DMDS/g)] x (34.08 mol H2S/g÷ 32.07 mol S/g)

[5] Ditch 1 is 3.65 meters wide and 600 meters long = 3.65 × 600 = 2,190 sq meters

[6] g TRS/s-sq meter = 3.61E-02 g TRS/s ÷ 2190 sq meters = 1.65E-05 g TRS/s-sq meter

[7] lb TRS/hr = 3.61E-02 g TRS/s x 3600 s/hr ÷ 453.592 g TRS/lb TRS = 2.86E-01 lb TRS/hr

[8] average pulp production during sampling on July 9, 10 and 11 (1694.16, 1609.17, 1355.92 ODTP/day)

[9] lb TRS/ODTP = 2.86E-01 lb TRS/hr x 1 hr/1553.08 ODTP = 4.43E-03 lb TRS/ODTP

[10] maximum production from June 2019 and April 2020 Project Columbia construction permit applications (construction permit DF)

[11] lb TRS/hr = 4.43E-03 lb TRS/ODTP x 2700 ADTP/day x 1 day/24 hr x 0.9 ODTP/1.0 ADTP = 4.48E-01 lb TRS/hr

[12] g TRS/s = 4.48E-01 lb TRS/hr x 453.592 g TRS/lb TRSx 1 hr/3600 s = 5.65E-02 g TRS/s

[13] g TRS/s-sq meter = 5.65E-02 g TRS/s ÷ 2190 sq meters = 2.58E-05 g TRS/s-sq meter

Table A-12

Aerated Stabilization Basin - Zone 1 - Water9 Model Results

New-Indy Catawba - Catawba, SC

AERATED STABILIZATION BASIN - ZONE 1													
		ACTUAL								MAXIMUM			
	MW	g/s	Reference	Justification	sq meters[5]	g/s-sq meter[6]	lb/hr[7]	ODTP/day[8]	lb/ODTP[9]	ADTP/day[10]	lb/hr[11]	g/s[12]	g/s-sq meter[13]
H_2S	34.08	5.20E-02	H2SSIM[2]	National Council for Air and Stream Improvement (NCASI) model for pulp and paper biological wastewater system H_2S emissions	50625	1.03E-06	4.13E-01	1553.08	6.38E-03	2700	6.46E-01	8.14E-02	1.61E-06
MM	48.11	4.44E-02	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	50625	8.77E-07	3.52E-01	1553.08	5.44E-03	2700	5.51E-01	6.94E-02	1.37E-06
DMS	62.14	8.00E-02	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	50625	1.58E-06	6.35E-01	1553.08	9.81E-03	2700	9.93E-01	1.25E-01	2.47E-06
DMDS	94.20	3.96E-02	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	50625	7.82E-07	3.14E-01	1553.08	4.85E-03	2700	4.91E-01	6.19E-02	1.22E-06
TRS (as H_2S)	34.08	1.56E-01	Summation[4]	Summation of H_2S, MM, DMS and DMDS converted to common H_2S basis based on molecular weight of sulfur in each constituent	50625	3.08E-06	1.24E+00	1553.08	1.91E-02	2700	1.94E+00	2.44E-01	4.82E-06

[1] Reserved.

[2] Average of H2SSIM model results for Zone 1 ASB wastewater samples collected on July 9, July 10 and July 11 (0.0240 g/s, 0.0770 g/s, 0.0550 g/s) during the 40 CFR 63, Subpart S IPT. The NCASI H2SSIM model that calculates the sulfide fate and transport in wastewater treatment basins is documented in NCASI TB 1000. Input and output files from the H2SSIM model are attached.

[3] Average of WATER9 model results for Zone 1 ASB wastewater samples collected on July 9, July 10 and July 11 during the 40 CFR 63, Subpart S IPT. USEPA WATER9 Program, Version 3.0, posted at: https://www3.epa.gov/ttnchie1/software/water/water9_3/index.html. The basis for the input values and the output files from the WATER9 Program are also attached.

[4] 1.56E-01 g TRS/s = [(5.20E-02 g H2S/s x 32.07 mol S/g ÷ 34.08 mol H2S/g) + (4.44E-02 g MM/s x 32.07 mol S/g ÷ 48.11 mol MM/g) + (8.00E-02 g DMS/s x 32.07 mol S/g ÷ 62.14 mol DMS/g) + (3.96E-02 g DMDS/s x 64.14 mol S/g ÷ 94.20 mol DMDS/g)] x (34.08 mol H2S/g÷ 32.07 mol S/g)

[5] ASB Zone 1 is 225 meters wide and 225 meters long = 225 × 225 = 50,625 sq meters

[6] g TRS/s-sq meter = 1.56E-01 g TRS/s ÷ 50625 sq meters = 3.08E-06 g TRS/s-sq meter

[7] lb TRS/hr = 1.56E-01 g TRS/s x 3600 s/hr ÷ 453.592 g TRS/lb TRS = 1.24E+00 lb TRS/hr

[8] average pulp production during sampling on July 9, 10 and 11 (1694.16, 1609.17, 1355.92 ODTP/day)

[9] lb TRS/ODTP = 1.24E+00 lb TRS/hr x 1 hr/1553.08 ODTP = 1.91E-02 lb TRS/ODTP

[10] maximum production from June 2019 and April 2020 Project Columbia construction permit applications (construction permit DF)

[11] lb TRS/hr = 1.91E-02 lb TRS/ODTP x 2700 ADTP/day x 1 day/24 hr x 0.9 ODTP/1.0 ADTP = 1.94E+00 lb TRS/hr

[12] g TRS/s = 1.94E+00 lb TRS/hr x 453.592 g TRS/lb TRSx 1 hr/3600 s = 2.44E-01 g TRS/s

[13] g TRS/s-sq meter = 2.44E-01 g TRS/s ÷ 50625 sq meters = 4.82E-06 g TRS/s-sq meter

Table A-13

Aerated Stabilization Basin - Zone 2 - Water9 Model Results

New-Indy Catawba - Catawba, SC

AERATED STABILIZATION BASIN - ZONE 2													
		ACTUAL								MAXIMUM			
	MW	g/s	Reference	Justification	sq meters[5]	g/s-sq meter[6]	lb/hr[7]	ODTP/day[8]	lb/ODTP[9]	ADTP/day[10]	lb/hr[11]	g/s[12]	g/s-sq meter[13]
H_2S	34.08	4.00E-02	H2SSIM[2]	National Council for Air and Stream Improvement (NCASI) model for pulp and paper biological wastewater system H_2S emissions	66540	6.01E-07	3.17E-01	1553.08	4.91E-03	2700	4.97E-01	6.26E-02	9.41E-07
MM	48.11	1.26E-03	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	66540	1.90E-08	1.00E-02	1553.08	1.55E-04	2700	1.57E-02	1.98E-03	2.97E-08
DMS	62.14	2.66E-03	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	66540	4.00E-08	2.11E-02	1553.08	3.26E-04	2700	3.30E-02	4.16E-03	6.26E-08
DMDS	94.20	9.94E-04	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	66540	1.49E-08	7.89E-03	1553.08	1.22E-04	2700	1.23E-02	1.56E-03	2.34E-08
TRS (as H_2S)	34.08	4.31E-02	Summation[4]	Summation of H_2S, MM, DMS and DMDS converted to common H_2S basis based on molecular weight of sulfur in each constituent	66540	6.47E-07	3.42E-01	1553.08	5.28E-03	2700	5.35E-01	6.74E-02	1.01E-06

[1] Reserved.

[2] Average of H2SSIM model results for Zone 2 ASB wastewater samples collected on July 9, July 10 and July 11 (0.0250 g/s, 0.0430 g/s, 0.0520 g/s) during the 40 CFR 63, Subpart S IPT. The NCASI H2SSIM model that calculates the sulfide fate and transport in wastewater treatment basins is documented in NCASI TB 1000. Input and output files from the H2SSIM model are attached.

[3] Average of WATER9 model results for Zone 2 ASB wastewater samples collected on July 9, July 10 and July 11 during the 40 CFR 63, Subpart S IPT. USEPA WATER9 Program, Version 3.0, posted at: https://www3.epa.gov/ttnchie1/software/water/water9_3/index.html. The basis for the input values and the output files from the WATER9 Program are also attached.

[4] 4.31E-02 g TRS/s = [(4.00E-02 g H2S/s x 32.07 mol S/g ÷ 34.08 mol H2S/g) + (1.26E-03 g MM/s x 32.07 mol S/g ÷ 48.11 mol MM/g) + (2.66E-03 g DMS/s x 32.07 mol S/g ÷ 62.14 mol DMS/g) + (9.94E-04 g DMDS/s x 64.14 mol S/g ÷ 94.20 mol DMDS/g)] x (34.08 mol H2S/g÷ 32.07 mol S/g)

[5] ASB Zone 2 is 365 meters wide and 182.3 meters long = 365 × 182.3 = 66,540 sq meters

[6] g TRS/s-sq meter = 4.31E-02 g TRS/s ÷ 66539.5 sq meters = 6.47E-07 g TRS/s-sq meter

[7] lb TRS/hr = 4.31E-02 g TRS/s x 3600 s/hr ÷ 453.592 g TRS/lb TRS = 3.42E-01 lb TRS/hr

[8] average pulp production during sampling on July 9, 10 and 11 (1694.16, 1609.17, 1355.92 ODTP/day)

[9] lb TRS/ODTP = 3.42E-01 lb TRS/hr x 1 hr/1553.08 ODTP = 5.28E-03 lb TRS/ODTP

[10] maximum production from June 2019 and April 2020 Project Columbia construction permit applications (construction permit DF)

[11] lb TRS/hr = 5.28E-03 lb TRS/ODTP x 2700 ADTP/day x 1 day/24 hr x 0.9 ODTP/1.0 ADTP = 5.35E-01 lb TRS/hr

[12] g TRS/s = 5.35E-01 lb TRS/hr x 453.592 g TRS/lb TRSx 1 hr/3600 s = 6.74E-02 g TRS/s

[13] g TRS/s-sq meter = 6.74E-02 g TRS/s ÷ 66539.5 sq meters = 1.01E-06 g TRS/s-sq meter

Table A-14
Aerated Stabilization Basin - Zone 3 - Water9 Model Results
New-Indy Catawba - Catawba, SC

AERATED STABILIZATION BASIN - ZONE 3													
		ACTUAL								MAXIMUM			
	MW	g/s	Reference	Justification	sq meters[5]	g/s-sq meter[6]	lb/hr[7]	ODTP/day[8]	lb/ODTP[9]	ADTP/day[10]	lb/hr[11]	g/s[12]	g/s-sq meter[13]
H_2S	34.08	2.40E-02	H2SSIM[2]	National Council for Air and Stream Improvement (NCASI) model for pulp and paper biological wastewater system H_2S emissions	72352	3.32E-07	1.90E-01	1553.08	2.94E-03	2700	2.98E-01	3.76E-02	5.19E-07
MM	48.11	3.48E-05	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	72352	4.80E-10	2.76E-04	1553.08	4.26E-06	2700	4.32E-04	5.44E-05	7.51E-10
DMS	62.14	7.81E-05	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	72352	1.08E-09	6.20E-04	1553.08	9.58E-06	2700	9.70E-04	1.22E-04	1.69E-09
DMDS	94.20	1.55E-05	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	72352	2.14E-10	1.23E-04	1553.08	1.90E-06	2700	1.92E-04	2.42E-05	3.34E-10
TRS (as H_2S)	34.08	2.41E-02	Summation[4]	Summation of H_2S, MM, DMS and DMDS converted to common H_2S basis based on molecular weight of sulfur in each constituent	72352	3.33E-07	1.91E-01	1553.08	2.95E-03	2700	2.99E-01	3.77E-02	5.21E-07

[1] Reserved.

[2] Average of H2SSIM model results for Zone 3 ASB wastewater samples collected on July 9, July 10 and July 11 (0.0230 g/s, 0.0230 g/s, 0.0260 g/s) during the 40 CFR 63, Subpart S IPT. The NCASI H2SSIM model that calculates the sulfide fate and transport in wastewater treatment basins is documented in NCASI TB 1000. Input and output files from the H2SSIM model are attached.

[3] Average of WATER9 model results for Zone 3 ASB wastewater samples collected on July 9, July 10 and July 11 during the 40 CFR 63, Subpart S IPT. USEPA WATER9 Program, Version 3.0, posted at: https://www3.epa.gov/ttnchie1/software/water/water9_3/index.html. The basis for the input values and the output files from the WATER9 Program are also attached.

[4] 2.41E-02 g TRS/s = [(2.40E-02 g H2S/s x 32.07 mol S/g ÷ 34.08 mol H2S/g) + (3.48E-05 g MM/s x 32.07 mol S/g ÷ 48.11 mol MM/g) + (7.81E-05 g DMS/s x 32.07 mol S/g ÷ 62.14 mol DMS/g) + (1.55E-05 g DMDS/s x 64.14 mol S/g ÷ 94.20 mol DMDS/g)] x (34.08 mol H2S/g÷ 32.07 mol S/g)

[5] ASB Zone 3 is 380.4 meters wide and 190.2 meters long = 380.4 × 190.2 = 72,352 sq meters

[6] g TRS/s-sq meter = 2.41E-02 g TRS/s ÷ 72352.08 sq meters = 3.33E-07 g TRS/s-sq meter

[7] lb TRS/hr = 2.41E-02 g TRS/s x 3600 s/hr ÷ 453.592 g TRS/lb TRS = 1.91E-01 lb TRS/hr

[8] average pulp production during sampling on July 9, 10 and 11 (1694.16, 1609.17, 1355.92 ODTP/day)

[9] lb TRS/ODTP = 1.91E-01 lb TRS/hr x 1 hr/1553.08 ODTP = 2.95E-03 lb TRS/ODTP

[10] maximum production from June 2019 and April 2020 Project Columbia construction permit applications (construction permit DF)

[11] lb TRS/hr = 2.95E-03 lb TRS/ODTP x 2700 ADTP/day x 1 day/24 hr x 0.9 ODTP/1.0 ADTP = 2.99E-01 lb TRS/hr

[12] g TRS/s = 2.99E-01 lb TRS/hr x 453.592 g TRS/lb TRSx 1 hr/3600 s = 3.77E-02 g TRS/s

[13] g TRS/s-sq meter = 3.77E-02 g TRS/s ÷ 72352.08 sq meters = 5.21E-07 g TRS/s-sq meter

Table A-15
Ditch #2 - Water9 Model Results
New-Indy Catawba - Catawba, SC

DITCH 2													
		ACTUAL								MAXIMUM			
	MW	g/s	Reference	Justification	sq meters[5]	g/s-sq meter[6]	lb/hr[7]	ODTP/day[8]	lb/ODTP[9]	ADTP/day[10]	lb/hr[11]	g/s[12]	g/s-sq meter[13]
H_2S	34.08	1.56E-03	WATER9, NCASI TB 1000[2]	WATER9 and Free Sulfide Tool	1825	8.57E-07	1.24E-02	1553.08	1.92E-04	2700	1.94E-02	2.45E-03	1.34E-06
MM	48.11	3.69E-04	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	1825	2.02E-07	2.93E-03	1553.08	4.53E-05	2700	4.59E-03	5.78E-04	3.17E-07
DMS	62.14	1.67E-03	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	1825	9.13E-07	1.32E-02	1553.08	2.04E-04	2700	2.07E-02	2.61E-03	1.43E-06
DMDS	94.20	4.48E-04	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	1825	2.46E-07	3.56E-03	1553.08	5.50E-05	2700	5.57E-03	7.02E-04	3.84E-07
TRS (as H_2S)	34.08	3.06E-03	Summation[4]	Summation of H_2S, MM, DMS and DMDS converted to common H_2S basis based on molecular weight of sulfur in each constituent	1825	1.68E-06	2.43E-02	1553.08	3.76E-04	2700	3.80E-02	4.79E-03	2.63E-06

[1] Reserved.

[2] H_2S emissions rate (g/s) calculated based on the site-specific liquid H_2S concentration outlet calculated from Zone 3 ASB H2SSIMS, adjusted for pH using the NCASI Free Sulfide Tool (as described in NCASI Technical Bulletin 1000, section 3.2), and the site-specific WATER9 program mass transfer coefficient for Ditch #2. Calculations of the fraction of H_2S and the H_2S emissions rate is provided in the attached spreadsheet Ditch #2 Calcs.xlsx. USEPA WATER9 Program, Version 3.0 is posted at: https://www3.epa.gov/ttnchie1/software/water/water9_3/index.html. The basis for the input values and the output files from the WATER9 Program are also attached.

[3] MM, DMS, and DMDS emissions rates (g/s) calculated based on site-specific MM, DMS, and DMDS liquid concentrations from the July 9-11, 2021 IPT and configuration of the Ditch #2 utilizing the USEPA WATER9 Program, Version 3.0, posted at: https://www3.epa.gov/ttnchie1/software/water/water9_3/index.html. The basis for the input values and the output files from the WATER9 Program are also attached.

[4] 3.06E-03 g TRS/s = [(1.56E-03 g H2S/s x 32.07 mol S/g ÷ 34.08 mol H2S/g) + (3.69E-04 g MM/s x 32.07 mol S/g ÷ 48.11 mol MM/g) + (1.67E-03 g DMS/s x 32.07 mol S/g ÷ 62.14 mol DMS/g) + (4.48E-04 g DMDS/s x 64.14 mol S/g ÷ 94.20 mol DMDS/g)] x (34.08 mol H2S/g÷ 32.07 mol S/g)

[5] Ditch 2 is 3.65 meters wide and 500 meters long = 3.65 × 500 = 1,825 sq meters

[6] g TRS/s-sq meter = 3.06E-03 g TRS/s ÷ 1825 sq meters = 1.68E-06 g TRS/s-sq meter

[7] lb TRS/hr = 3.06E-03 g TRS/s x 3600 s/hr ÷ 453.592 g TRS/lb TRS = 2.43E-02 lb TRS/hr

[8] average pulp production during sampling on July 9, 10 and 11 (1694.16, 1609.17, 1355.92 ODTP/day)

[9] lb TRS/ODTP = 2.43E-02 lb TRS/hr x 1 hr/1553.08 ODTP = 3.76E-04 lb TRS/ODTP

[10] maximum production from June 2019 and April 2020 Project Columbia construction permit applications (construction permit DF)

[11] lb TRS/hr = 3.76E-04 lb TRS/ODTP x 2700 ADTP/day x 1 day/24 hr x 0.9 ODTP/1.0 ADTP = 3.80E-02 lb TRS/hr

[12] g TRS/s = 3.80E-02 lb TRS/hr x 453.592 g TRS/lb TRSx 1 hr/3600 s = 4.79E-03 g TRS/s

[13] g TRS/s-sq meter = 4.79E-03 g TRS/s ÷ 1825 sq meters = 2.63E-06 g TRS/s-sq meter

Table A-16
Holding Pond - Water9 Model Results
New-Indy Catawba - Catawba, SC

HOLDING POND													
		ACTUAL								MAXIMUM			
	MW	g/s	Reference	Justification	sq meters[5]	g/s-sq meter[6]	lb/hr[7]	ODTP/day[8]	lb/ODTP[9]	ADTP/day[10]	lb/hr[11]	g/s[12]	g/s-sq meter[13]
H_2S	34.08	4.00E-02	NCASI TB956[1]	Consistent with emissions from ASB Zones 2 and 3. See also Footnote 1.	388550	1.03E-07	3.17E-01	1553.08	4.91E-03	2700	4.97E-01	6.26E-02	1.61E-07
MM	48.11	1.54E-05	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	388550	3.96E-11	1.22E-04	1553.08	1.89E-06	2700	1.91E-04	2.41E-05	6.20E-11
DMS	62.14	4.82E-05	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	388550	1.24E-10	3.83E-04	1553.08	5.91E-06	2700	5.99E-04	7.54E-05	1.94E-10
DMDS	94.20	3.89E-06	WATER9[3]	USEPA Emissions Model for Wastewater Treatment Plants	388550	1.00E-11	3.09E-05	1553.08	4.77E-07	2700	4.83E-05	6.08E-06	1.57E-11
TRS (as H_2S)	34.08	4.00E-02	Summation[4]	Summation of H_2S, MM, DMS and DMDS converted to common H_2S basis based on molecular weight of sulfur in each constituent	388550	1.03E-07	3.18E-01	1553.08	4.91E-03	2700	4.97E-01	6.26E-02	1.61E-07

[1] The H2SSIM model was not calibrated for post-aeration basins. However, eleven post-aeration basins (i.e., holding or retention ponds) were tested as part of the NC study published in NCASI TB 956. Two of the eleven post-aeration basins resulted in reported H_2S emissions (all others were not significant based on the screening study results). Based on the stie-specific H2SSIM Model results for New-Indy, worst-case emissions are assumed to be equal to Mill B reported H_2S emissions (0.04 g/s). This H_2S rate is consistent with Zones 2 and 3 H_2S emissions rates and emissions would not expect to be higher than these rates as the Holding Pond is aerated with dissolved oxygen levels at an average of 1.1 across the holding pond during the test (Note: anoxic conditions occur when dissolved oxygen levels near zero per NCASI TB 1000).

[2] Reserved.

[3] Reserved.

[4] 4.00E-02 g TRS/s = [(4.00E-02 g H2S/s x 32.07 mol S/g ÷ 34.08 mol H2S/g) + (1.54E-05 g MM/s x 32.07 mol S/g ÷ 48.11 mol MM/g) + (4.82E-05 g DMS/s x 32.07 mol S/g ÷ 62.14 mol DMS/g) + (3.89E-06 g DMDS/s x 64.14 mol S/g ÷ 94.20 mol DMDS/g)] x (34.08 mol H2S/g÷ 32.07 mol S/g)

[5] Holding Pond is 818 meters wide and 475 meters long = 818 × 475 = 388,550 sq meters

[6] g TRS/s-sq meter = 4.00E-02 g TRS/s ÷ 388550 sq meters = 1.03E-07 g TRS/s-sq meter

[7] lb TRS/hr = 4.00E-02 g TRS/s x 3600 s/hr ÷ 453.592 g TRS/lb TRS = 3.18E-01 lb TRS/hr

[8] average pulp production during sampling on July 9, 10 and 11 (1694.16, 1609.17, 1355.92 ODTP/day)

[9] lb TRS/ODTP = 3.18E-01 lb TRS/hr x 1 hr/1553.08 ODTP = 4.91E-03 lb TRS/ODTP

[10] maximum production from June 2019 and April 2020 Project Columbia construction permit applications (construction permit DF)

[11] lb TRS/hr = 4.91E-03 lb TRS/ODTP x 2700 ADTP/day x 1 day/24 hr x 0.9 ODTP/1.0 ADTP = 4.97E-01 lb TRS/hr

[12] g TRS/s = 4.97E-01 lb TRS/hr x 453.592 g TRS/lb TRSx 1 hr/3600 s = 6.26E-02 g TRS/s

[13] g TRS/s-sq meter = 6.26E-02 g TRS/s ÷ 388550 sq meters = 1.61E-07 g TRS/s-sq meter

Table A-17
No. 4 Sludge Pond - Water9 Model Results
New-Indy Catawba - Catawba, SC

No. 4 SLUDGE POND													
		ACTUAL								MAXIMUM			
	MW	g/s	Reference	Justification	sq meters[5]	g/s-sq meter[6]	lb/hr[7]	ODTP/day[8]	lb/ODTP[9]	ADTP/day[10]	lb/hr[11]	g/s[12]	g/s-sq meter[13]
H_2S	34.08	2.65E-02	NCASI Form R and TB 956 and 1000[2]	NCASI Toxics Release Inventory (TRI) Form R Guidance and Free Sulfide Tool	44192	5.99E-07	2.10E-01	1553.08	3.25E-03	2700	3.29E-01	4.14E-02	9.37E-07
MM	48.11												
DMS	62.14												
DMDS	94.20												
TRS (as H_2S)	34.08	2.65E-02	Summation[4]	Summation of H_2S, MM, DMS and DMDS converted to common H_2S basis based on molecular weight of sulfur in each constituent	44192	5.99E-07	2.10E-01	1553.08	3.25E-03	2700	3.29E-01	4.14E-02	9.37E-07

[1] Reserved.

[2] NCASI Handbook of Chemical-Specific Information for Superfund Amendments and Reauthorization Act (SARA) Section 313 Form R Reporting - Pulp and Paper Facilities. Hydrogen Sulfide, Table 4 "WWTP PARTITIONING AND EMISSIONS OF HYDROGEN SULFIDE", Sludge Pond mean emissions factor of 4.2 lb/(day-Acre). H_2S emissions factor adjusted for pH using the NCASI Free Sulfide Tool (as described in NCASI Technical Bulletin 1000, section 3.2) and documentation of the emissions rate calculation is provided in the attached spreadsheet "EQ Basin and Sludge Lagoon Calcs.xlsx".

[3] There are no emissions of MM, DMS, and DMDS reported from the No. 4 Sludge Pond. Small amounts of MM, DMS, and DMDS that are contained in the water that remains with the sludge from the ASB are assumed to be emitted in the ditch #2 or ASB Zones 1-3.

[4] 2.65E-02 g TRS/s = [(2.65E-02 g H2S/s x 32.07 mol S/g ÷ 34.08 mol H2S/g) + (0.00E+00 g MM/s x 32.07 mol S/g ÷ 48.11 mol MM/g) + (0.00E+00 g DMS/s x 32.07 mol S/g ÷ 62.14 mol DMS/g) + (0.00E+00 g DMDS/s x 64.14 mol S/g ÷ 94.20 mol DMDS/g)] x (34.08 mol H2S/g÷ 32.07 mol S

[5] No. 4 Sludge Pond free water surface area was calculated using Geographic Information System (GIS) software.

[6] g TRS/s-sq meter = 2.65E-02 g TRS/s ÷ 44192 sq meters = 5.99E-07 g TRS/s-sq meter

[7] lb TRS/hr = 2.65E-02 g TRS/s x 3600 s/hr ÷ 453.592 g TRS/lb TRS = 2.10E-01 lb TRS/hr

[8] average pulp production during sampling on July 9, 10 and 11 (1694.16, 1609.17, 1355.92 ODTP/day)

[9] lb TRS/ODTP = 2.10E-01 lb TRS/hr x 1 hr/1553.08 ODTP = 3.25E-03 lb TRS/ODTP

[10] maximum production from June 2019 and April 2020 Project Columbia construction permit applications (construction permit DF)

[11] lb TRS/hr = 3.25E-03 lb TRS/ODTP x 2700 ADTP/day x 1 day/24 hr x 0.9 ODTP/1.0 ADTP = 3.29E-01 lb TRS/hr

[12] g TRS/s = 3.29E-01 lb TRS/hr x 453.592 g TRS/lb TRSx 1 hr/3600 s = 4.14E-02 g TRS/s

[13] g TRS/s-sq meter = 4.14E-02 g TRS/s ÷ 44192 sq meters = 9.37E-07 g TRS/s-sq meter

ATTACHMENT 3 – PRIMARY CLARIFIER H2SSIM MODEL

NCASI WASTEWATER HYDROGEN SULFIDE EMISSIONS SIMULATOR (H2SSIM)

Version 1.3

Data Type 1. Site Identification

Company Name	New-Indy
Facility Name	Catawba SC
Basin Name	Primary Clarifier

Data Type 2. Model Zone Information

Number of Zones	1
Zone Location of Hardpipe	None
Type of Basin	PC

Data Type 3. Load Characteristics

Loading Characteristics	Main Influent	Hardpipe	Units
Flow	21.35	0	MGD
Total Sulfide	0.02003706	0	mg/L
Sulfate	390	0	mg/L

Data Type 4. Atmospheric Conditions

Windspeed	3.79	mph
Ambient Temperature	79	F

Data Type 5. Zone Physical and Chemical Conditions

Zone Condition	Zone 1	Zone 2	Zone 3	Zone 4	Units
Dissolved Oxygen	0				mg/L
Temperature	111.9				F
pH	9.08				s.u.
Redox Condition	Anoxic	Aerobic	Aerobic	Aerobic	
Length	243.7				feet
Width	243.7				feet
Depth	5.41				meters
Mixing	Moderat	Moderat	Moderat		
Number of Aerators	0				
Total Horsepower	0				HP
Impellor Size	1.625				feet
Impellor RPM	1200				RPM
Diffused Air Flow	0				cms
Weir Height	0.38				meters

7/9/2021 - 7/11/2021 Average

Model Controls

Run H2SSIM

View Parameters

Clear Input Sheet

H2SSIM Results

7/9/2021 - 7/11/2021 Average

Basin Emissions		Units
Total Emissions (H_2S)	0.000	gms/s
Total Emissions (H_2S)	11.1	lbs/yr
Total Emissions (H_2S)	0.0	tons/yr
Total Emissions (H_2S)	0.0	tonnes/yr
Emission Flux (H_2S)	0.9	gms/m^2 yr

Zone Emissions	Zone 1	Zone 2	Zone 3	Zone 4	Units
Zone Emissions (H_2S)	0.00				gms/s
Zone Emissions (H_2S)	11.1				lbs/yr
Emission Flux (H_2S)	0.9				gms/m^2 yr
Liquid Conc. (Total Sulfide)	0.452				mg/L
Liquid Sulfide Load (lbs/yr)	4637.300				lbs/yr

Percent Inlet Sulfide Removed	-257.0%

Current Parameters	
kgen	0.25
ThetaGen	1.06
KDO	0.05
KSO4	10
kanox	0.006
ThetaOx	1.05
m	1
n	0.2
MLVSS	2500
O_2 Transfer Coeff.	2
alpha 1	0.83
alpha 2	0.6

ATTACHMENT D
SCENTROID PORTABLE MONITOR
OPERATION AND MAINTENANCE MANUAL

SCENTROID
Future of Sensory Technology

IDES CANADA INC.

TR8+ PollutrackerAir Quality Mobile Laboratory
Operation and Maintenance Manual

Version 4.0
December 9, 2020

IMPORTANT

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1 Introduction

1.1 Welcome

Thank you for purchasing a Scentroid PolluTracker!

The Scentroid PolluTracker is a field-deployable multi-sensor device capable of measuring airborne contaminants such as Hydrogen Sulfide, Ammonia, Volatile organic compounds (VOCs), and others in real-time according to customer's configurations.
The instrument logs the chemical measurements as well as the temperature and humidity of the sample. It also measures the GPS location of each measurement and continuously records for remote and local monitoring via Bluetooth and microSD card inserted in the instrument respectively.
Depending on the type of sensor installed, the TR8+ Pollutracker is capable of monitoring the following:

- **Volatile Organic compounds** (See annex 1)
  Photoionization (PID) Sensor using 10.6 eV UV lamp.
- **Inorganic compounds** (See annex 1)
  Substance Specific Electrochemical Sensor(s).
- **Combustible gases** (See annex 1)
  0-100 LEL range.
- **Oxygen Concentration** (See annex 1)
  Electrochemical Sensor.

1.2 Package Contents

Check your Pollutracker for the following items

1. Charger for TR8+.
2. Micro USB to USB cable (Tablet charging cable).
3. Tablet Charging adapter.
4. Android Tablet.

5. Carbon Filter.
6. PTFE tube For carbon Filter.

If any of these items is damaged or missing, please contact your distributor.

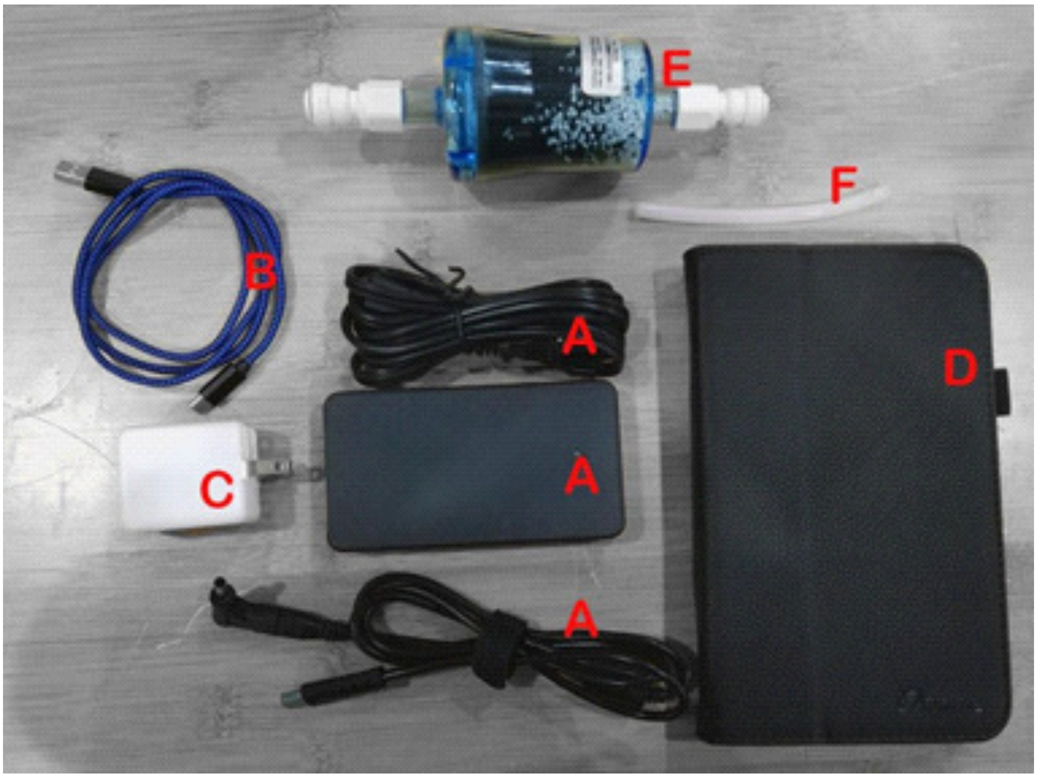


Figure 1: Package Contents

1.3 Device Overview

Figure 2: Device Overview

Table 1: List of Device Parts

A	Pollutracker On/Off Switch	**F**	Charging Port
B	Firmware Update Port	**G**	Temperature/Humidity Sensor Port
C	MicroSD Slot	**H**	Fan
D	Power Lights	**I**	Exhaust
E	Calibration Sticker	**J**	Inlet Sampling Port

1.4 General Specifications

Table 2: TR8+ General Specifications

Feature	Specifications
Dimensions	16.54" L x 13.03" W x 6.84"H (42cm L x 33.10cm W x 17.4cm H)
Weight	Less than 10 Lbs
Detectors	Up to 10 sensors
Battery	High capacity of 8000 mAh Li-Ion battery
Display	10" Android® Tablet
Direct Readout	Up to 10 instantaneous values Sensor name
Data Transmission	Bluetooth®
Sampling Pump	Built-in sampling pump
Data Storage	8 GB
Data Log Interval	Automatic Mode: User programmable (2 & up) seconds Manual Mode: 1 seconds
Operating Temperature	0^o C to 45^oC
Relative Humidity	0% *to* 90% Non-condensable

2 Operating the PolluTracker

The Scentroid Pollutracker is a compact, portable instrument that provides real-time airborne pollutants measurements. Prior to factory shipment, the TR8+ is present with default calibration.

2.1 Preparing Pollutracker for Sampling

2.1.1 Charging the Battery

Before using the battery, It is recommended that the Pollutracker battery is fully charged before using.

To charge the battery:

1. Connect the provided charger to a power outlet.
2. Connect the provided charger to the charging port on the rear of the PolluTracker.

2.1.2 Turning on the PolluTracker

1. Flip the power switch to ON position.
2. The power LED will illuminate.

2.1.3 The Installation of the Pollutracker Application

The Pollutracker uses an Android application as the user interface. This application is pre-installed before shipment. If the tablet is reset to factory settings, please contact Scentroid Support for the application and its installation procedures.

2.1.4 Pairing the Android Device with the PolluTracker

The Pollutracker and the Android device are paired during shipment. If the android device is factory reset please use the following steps to pair the two devices:

1. Turn on the PolluTracker.
2. Open the Android device **Settings Menu**.
3. Under **Wireless & Networks**, touch Bluetooth.
4. Make sure Bluetooth is turned on and the Android device is set to visible.
5. The Android device will scan for and display all available Bluetooth devices in range under **Available Devices**.
6. If the Pollutracker is not found
    - Android 4.4 and lower: If your Android device stops scanning before your Bluetooth device is ready, touch **Search** at the bottom of the screen.
    - Android 5.0 or higher: If your Bluetooth device is not showing in the list, touch the **Menu** icon, then touch **Refresh**.

7. From the list, select and tap **ptxxxxxx-** the 6 digits corresponds to the device Serial Number.

8. Follow the on-screen instructions to complete the pairing.

9. When you're prompted to enter a passcode, enter **1234**. If the pairing is successful, your Android device will connect to the PolluTracker.

2.1.5 Connecting the Android Device to the Pollutracker

The TR8+ Pollutracker uses an Android application as the user interface. This user application should be connected with the TR8+ to manage the settings and the functions in the TR8+.
To pair the 10" Android Tablet with the TR8+, please follow these procedures

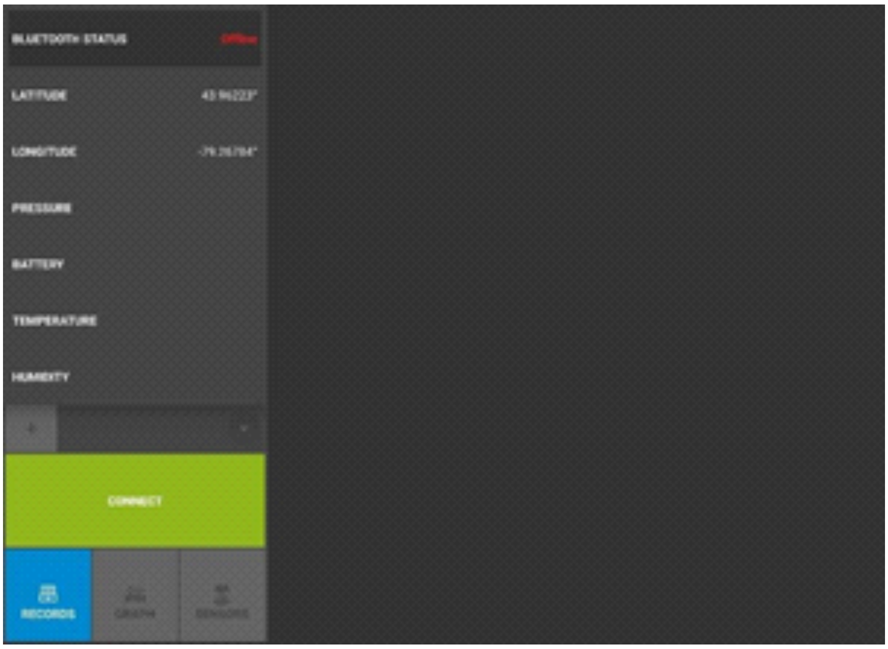
1. Turn on the Pollutracker.

2. Enable the Bluetooth option in your Android Device (please follow the manufacturer's instructions to do so).

3. Open the Pollutracker Android application. You will find that the application indicates **Connect** on the home page.

Figure 3: Android Device Home Page

4. Tap the **Connect** option.



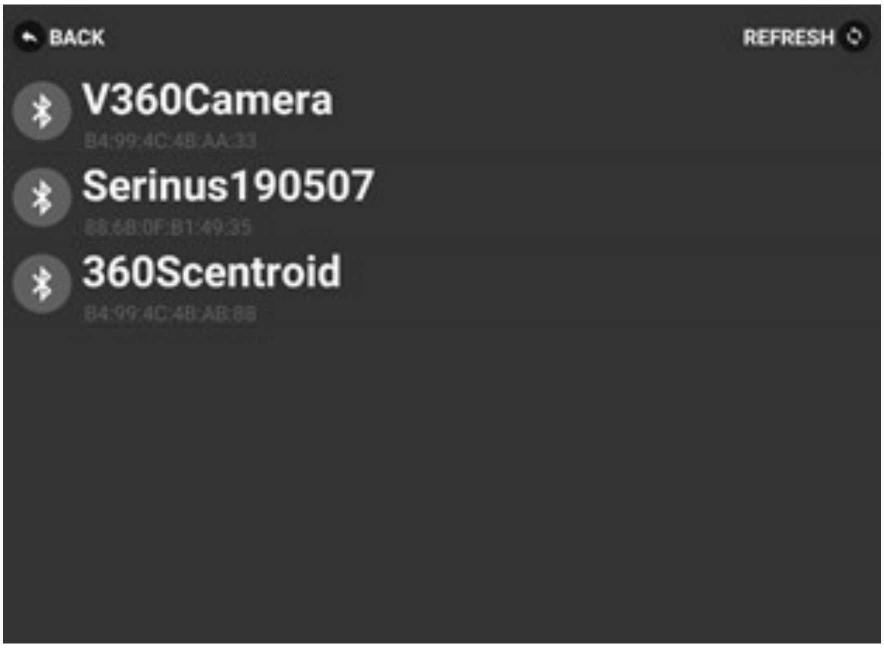
BLUETOOTH STATUS Offline

LATITUDE 43.96223°

LONGITUDE -79.26784°

Figure 4: Application Home Screen

5. The Android device will list all the Bluetooth devices you have paired with. If you are not able to see the device, tap on the refresh button to see all paired devices.



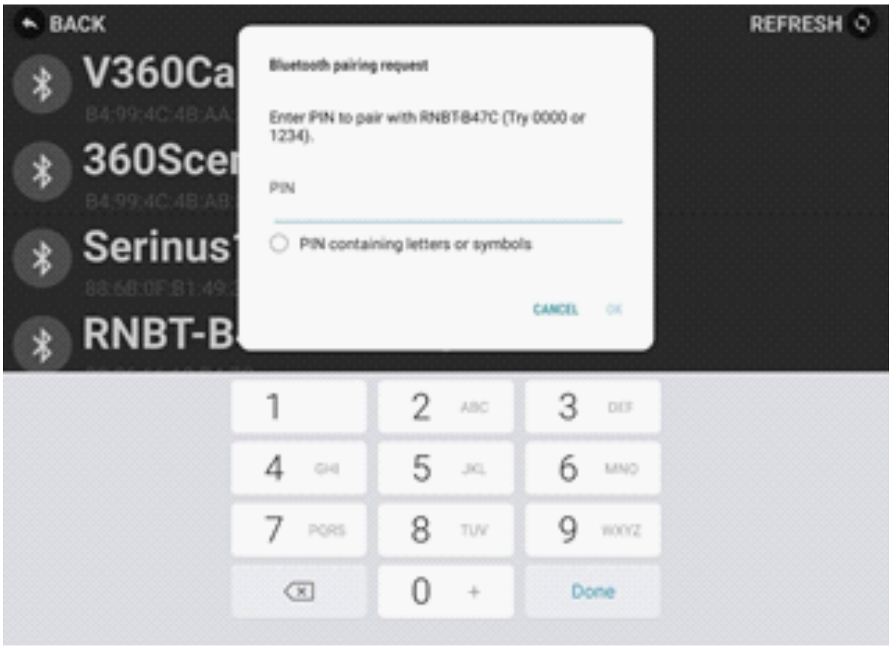
V360Camera
B4:99:4C:4B:AA:33

Serinus190507
88:6B:0F:B1:49:35

360Scentroid
B4:99:4C:4B:AB:88

Figure 5: List of Bluetooth-Paired Devices

6. From the list,select and tap **ptxxxxxx-** the 6 digits corresponds to the device Serial Number.



Bluetooth pairing request

Enter PIN to pair with RNBT-B47C (Try 0000 or 1234).

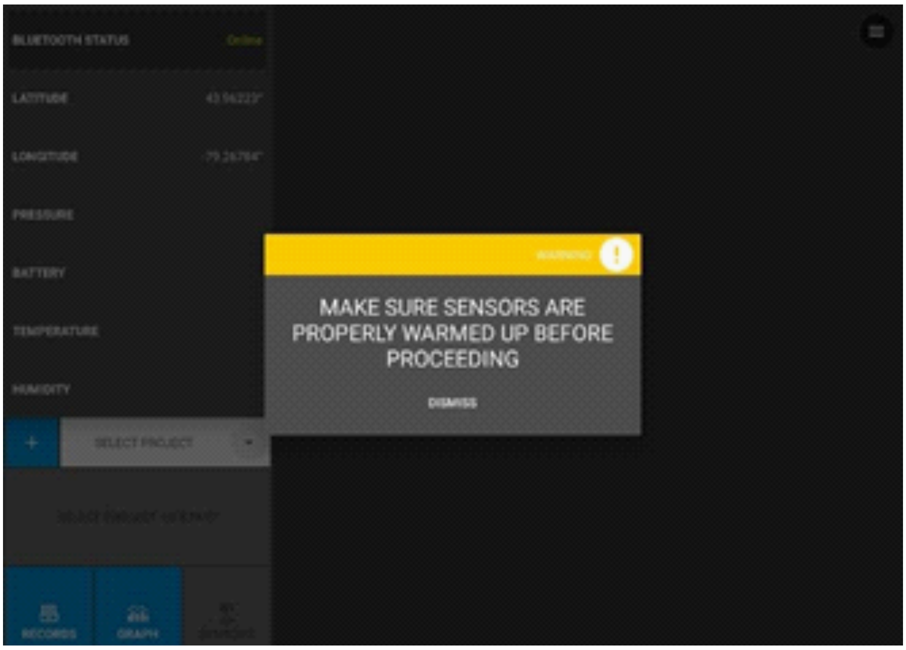
PIN

○ PIN containing letters or symbols

Figure 6: Bluetooth Pairing Request Screen

2.1.6 Sampling with Pollutracker

Once the application is connected to the TR8+hardware, it will be **Online** and paired with the TR8+Pollutracker, and the device is ready to be configured for sampling. The application will display a warning to ensure that the sensors are properly warmed up as per sensor warm up time (See Appendix A).



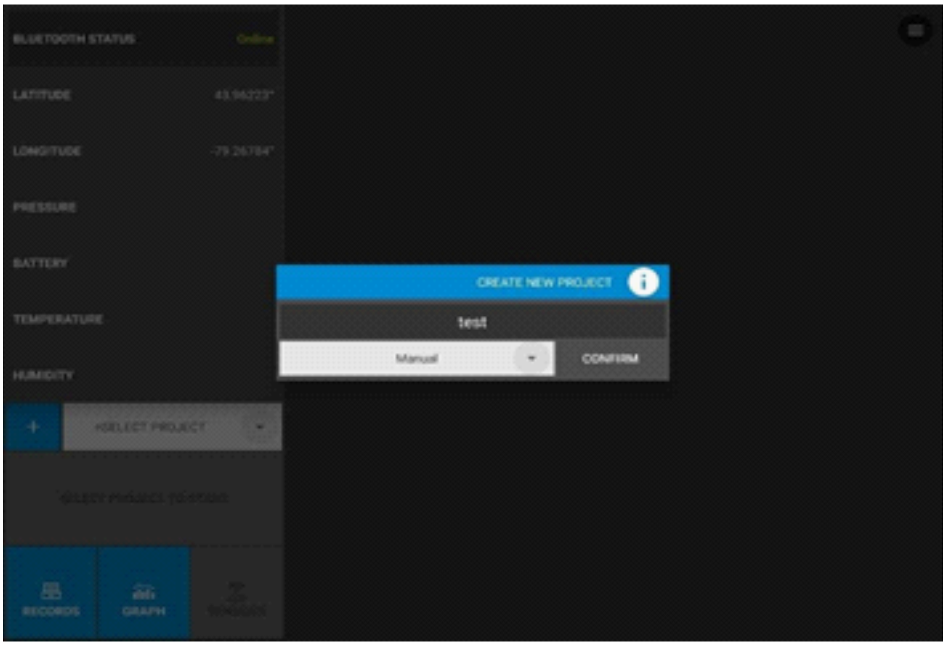
BLUETOOTH STATUS Online
LATITUDE 43.96223°
LONGITUDE -79.26784°
PRESSURE
BATTERY
TEMPERATURE
HUMIDITY

WARNING

MAKE SURE SENSORS ARE PROPERLY WARMED UP BEFORE PROCEEDING

Figure 7: Warn- up Sensor Warning Screen

The Pollutracker can be used to assess sample sunder a variety of settings. By only attaching a 1/4" tubing or a sample bag into the 1/4" inlet sampling port push-in fitting (To release the tubing or the sample bag, just push the fitting collar and tug the tubing).
After then the application will prompt you to either select a project from project list or to create a new one. In this screen, you will be able to create different projects according to your testing plan.



BLUETOOTH STATUS Online
LATITUDE 43.96223°
LONGITUDE -79.26784°
PRESSURE
BATTERY
TEMPERATURE
HUMIDITY

test
Manual

Figure 8: Create a New Project Screen

Once you select a project or you create a new one, tap the start button and the application will begin reporting the data that is collected from the Pollutracker.

The Pollutracker has the capability of collecting samples in a continuous mode by intervals. The application will automatically log other parameters such as latitude, longitude, temperature, humidity, barometric pressure and Pollutracker battery status.

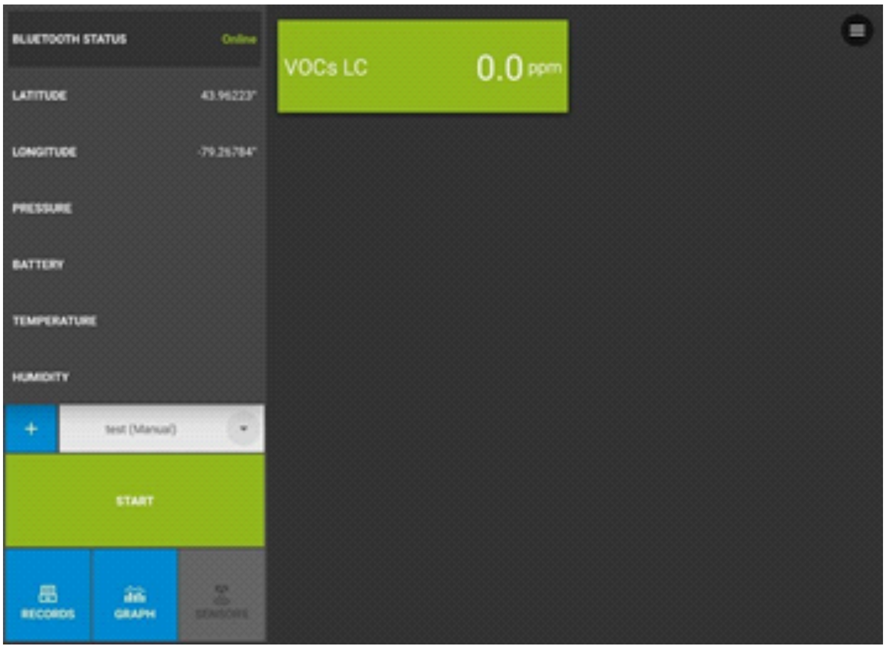
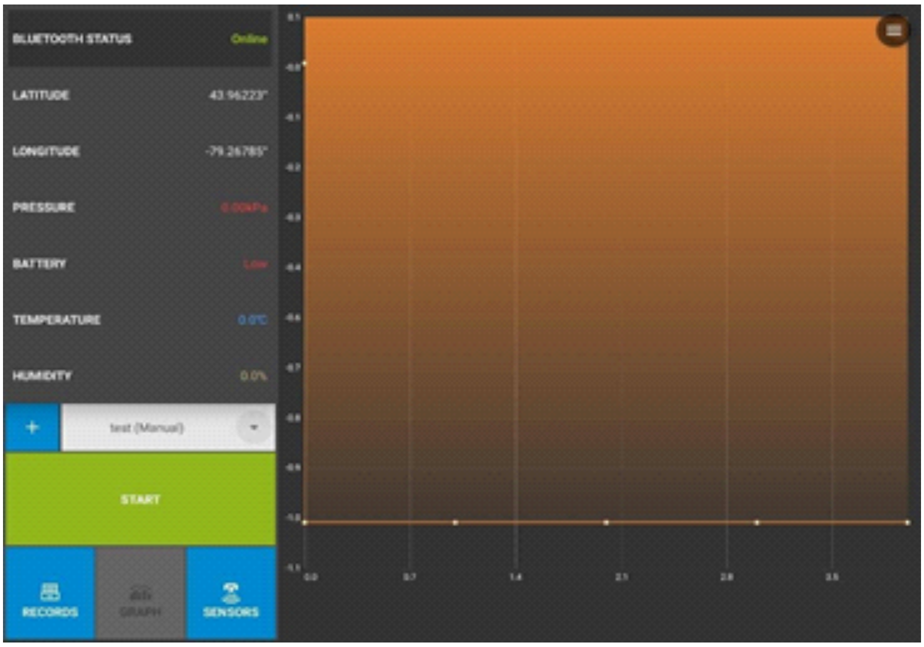

BLUETOOTH STATUS Online
LATITUDE 43.96223°
LONGITUDE -79.26784°
PRESSURE
BATTERY
TEMPERATURE
HUMIDITY
test (Manual)
VOCs LC 0.0 ppm

Figure 9: Samples Collection

When running a test, the user will be able to see the values of the chemicals detected by the Pollutracker. The user will be able to see these values in graph mode by only tapping the **Show Graph** button located at the top right of the screen (see previous Fig.). The application will show all data points in a graph mode for comprehensive data analysis.



BLUETOOTH STATUS Online
LATITUDE 43.96223°
LONGITUDE -79.26785°
PRESSURE 0.00kPa
BATTERY Low
TEMPERATURE 0.0°C
HUMIDITY 0.0%
test (Manual)

Figure 10: Graph Mode Analysis

To see the sensor readings again, tap **Show Sensor Reading**.
The Sensor reading can be configured to send visual alarms (changing from green to red) when specific concentration thresholds are surpassed.
To configure visual alarms, tap on the **Setting** button located at the bottom left corner of the main screen.On **setting** screen, a list of all available sensors will be displayed, enter the desired AQ limit according to your requirements and tap on **Save**.

SENSOR	SCALE	AUTO CAL.	OFFSET	SENSITIVITY	AQ LIMIT
VOCs LC	ppm		0.0	1.0	5.0
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				

Figure 11: Sensor Configuration Screen

If a sensor detects concentrations above the selected AQ limit while sampling, the sensor box will change from green to red.

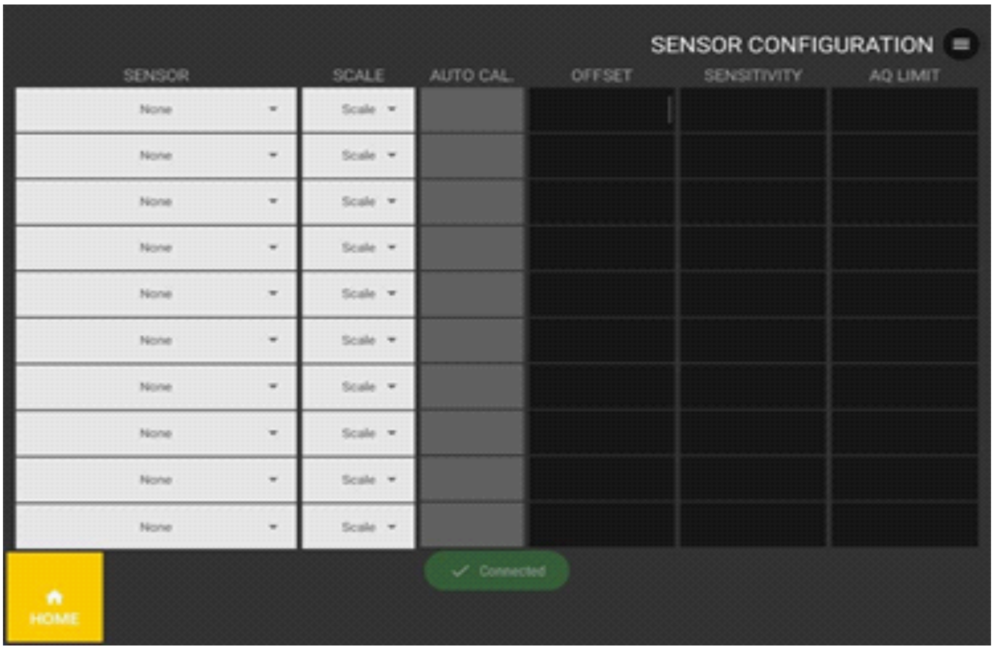
2.1.7 Selecting Sensors and Filling Calibration Factors

The Pollutracker is factory calibrated and the calibration parameters are shown on the Calibration sticker. In case of further calibration is required, please follow the following steps

1. Select the **Settings three lines icon** on the top right corner of the Pollutracker application main page.

2. From the drop down list, refer to your calibration sticker and select the associated sensors, which comes with your Pollutracker in the same order.

3. After selecting the sensors, input the **Zero Offset** and **Sensitivity** and the desired scale either parameters accordingly. (See Appendix B for TR8+calibration procedure)

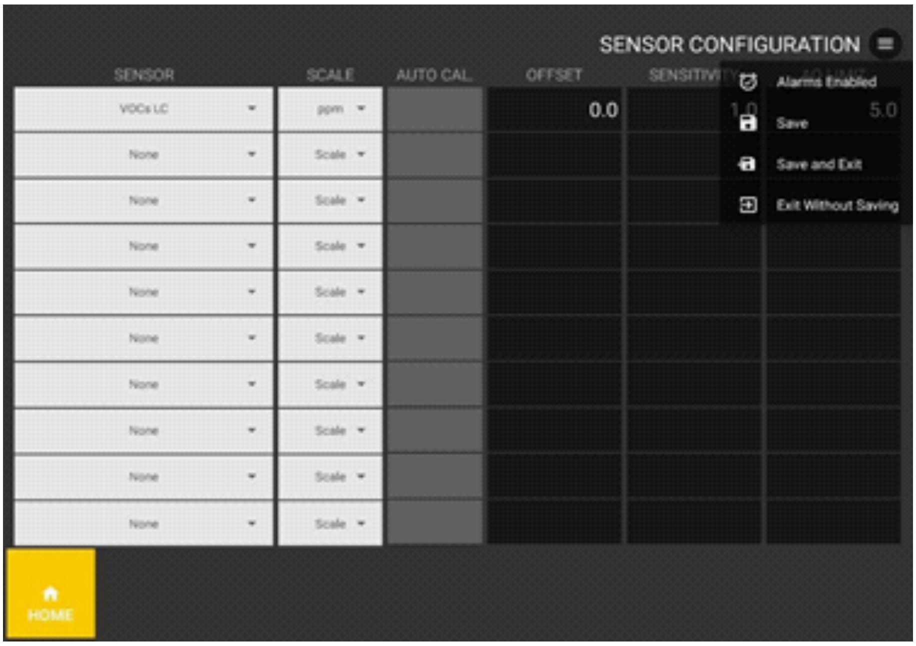


SENSOR	SCALE	AUTO CAL.	OFFSET	SENSITIVITY	AQ LIMIT
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				

Figure 12: Filling Calibration Factors Screen

2.1.8 Saving the Configuration settings

After the user set up all the desired settings for the test, it is necessary to save the configuration by tapping on the **Save** button.

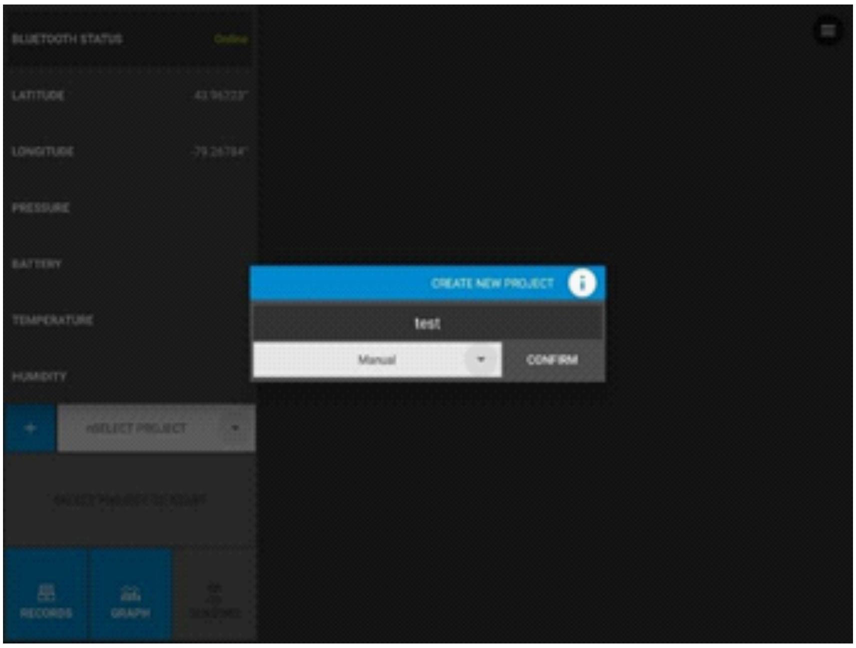


SENSOR	SCALE	AUTO CAL.	OFFSET	SENSITIVITY	
VOCs LC	ppm		0.0	1.0	5.0
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				

Figure 13: Saving the Configuration Screen

2.2 Operation Modes

The user may change the configurations based on their needs. When creating a new project, the Pollutracker application will display the option for **Manual** or **Automatic** sampling.



BLUETOOTH STATUS Online

LATITUDE 43.96223°

LONGITUDE -79.26784°

test

Manual

Figure 14: Operation Mode Screen

2.2.1 Manual Sampling

In manual sampling, the user manually decides when to start and stop the sampling process. The user starts this sampling process by pressing the **Start** button on the application home screen.

When this button is pressed, the built-in pump is activated and the sampling process begins.The Pollutracker will read the sensor data every 2 seconds and record it in a CSV file. The user can press the stop sampling button at any time to end the sample testing.

2.2.2 Automatic Sampling

In automatic sampling the user can specify the interval at which the sensor reading is recorded.

To accomplish that, the user must select **Pump Work Duration** and **Pump Work Frequency**. The **Pump Work Duration** is a time period in which the pump will be turned on and the Pollutracker will log sample recordings. To decide on **Pump Work Duration** it is important to consider the sensor response time (see Appendix A). The new pump cycle will start after the time period selected in the **Pump Work Frequency**.

To change sampling parameters, tap on **Change** and select the desired sampling time and pump cycle frequency. Tap on **Save** to record all settings parameters.

3 Sampling

You can begin sampling once sampling settings are selected. To start sampling

1. Turn on the Pollutracker TR8+ by flipping the ON/OFF switch.
2. Open the Pollutracker TR8+ application on your Android Device.
3. Connect the Pollutracker to the Android Device.
4. Select a project or create a new one. (If automatic mode is desired, enter the sampling parameters as desired.
5. For accurate results leave the Pollutracker ON according to warm up time sensors, see Appendix A.
6. Enable GPS and Android location access on the Android device.
7. To measure the gases from sample bag, connect the sample bag into the inlet port.
8. Press the **Start Sampling** button to begin the sampling process.

Figure 15: Sample bag connected into TR8+

3.1 Recording your Sensor Readings

Once you press the **start sampling button** your data will be saved into a CSV file which is accessible from the android device application as follows

3.1.1 Select your Project

On the main page, tap on **Records** then the application will display all projects created by the user on the left side of the screen.

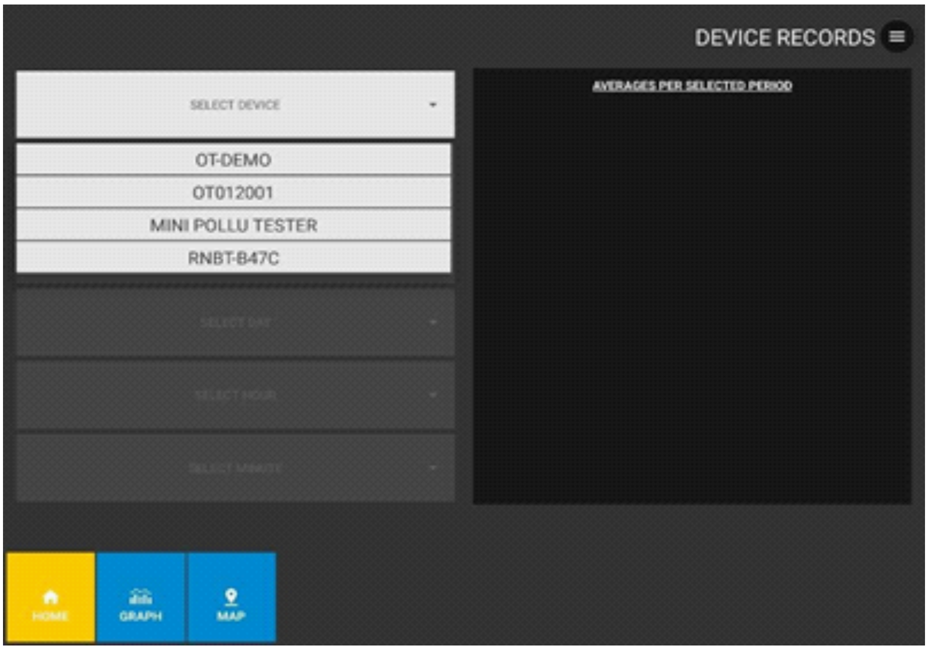
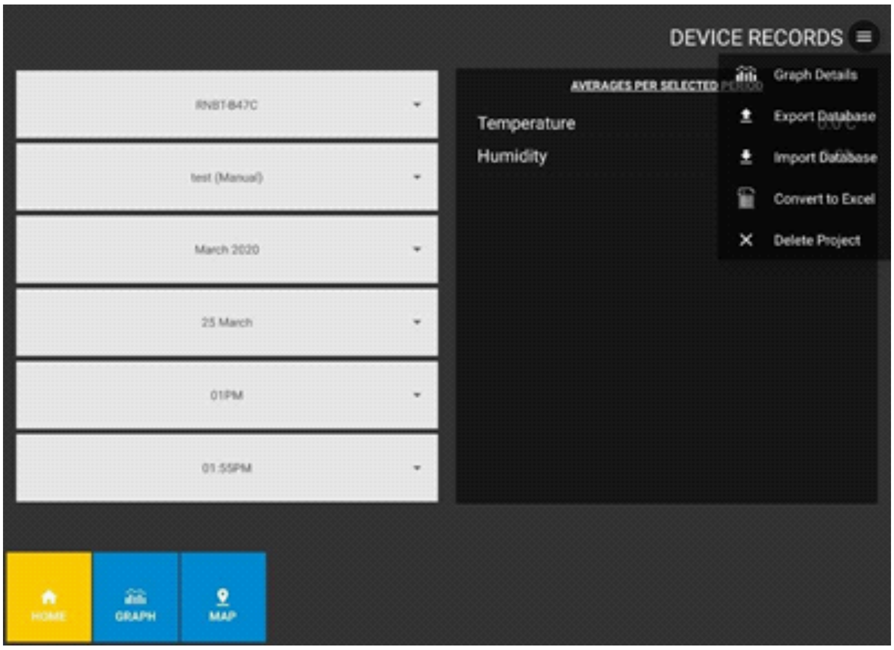


Figure 16: Project Selection Screen

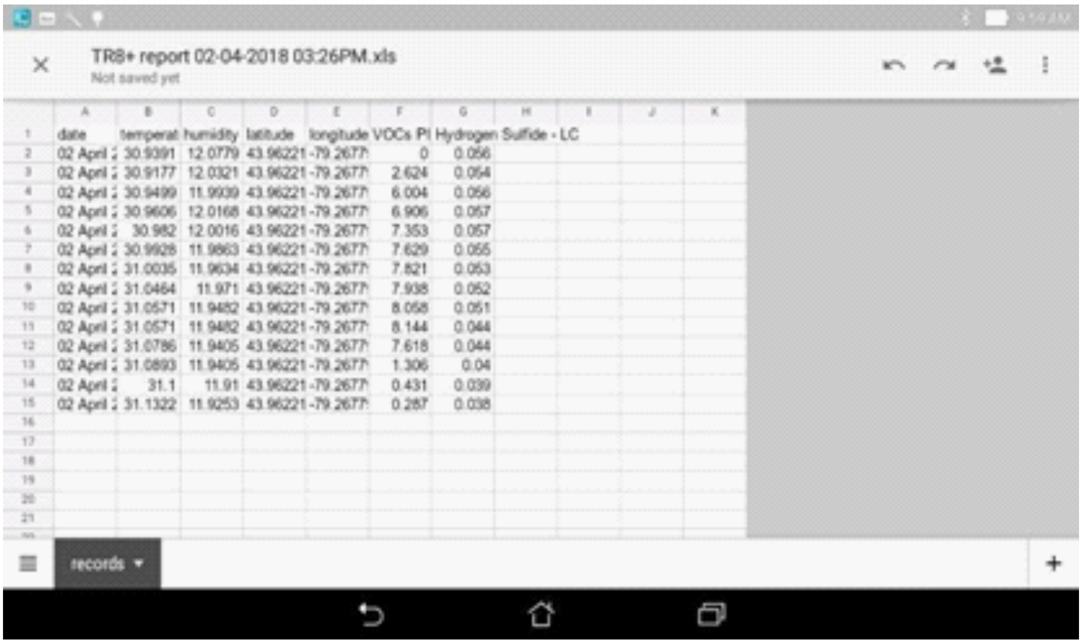
Once you tap on the desired project, you will be able to see the records created under that specific project where the data is sorted by months, days, hours or minutes. Tap on the desired parameters to display the desired data.



RNBT-B47C
test (Manual)
March 2020
25 March
01PM
01:55PM

Figure 17: Device Records Screen

All project records can be converted into an Excel file by tapping **Convert to Excel** button located at the bottom right of the screen. The Excel file will be saved on the Android device under **File Manager/Internal Storage**.



TR8+ report 02-04-2018 03:26PM.xls

Not saved yet

	A	B	C	D	E	F	G
1	date	temperat	humidity	latitude	longitude	VOCs PI	Hydrogen Sulfide - LC
2	02 April	30.9391	12.0779	43.96221	-79.2677	0	0.056
3	02 April	30.9177	12.0321	43.96221	-79.2677	2.624	0.054
4	02 April	30.9499	11.9939	43.96221	-79.2677	6.004	0.056
5	02 April	30.9606	12.0168	43.96221	-79.2677	6.906	0.057
6	02 April	30.982	12.0016	43.96221	-79.2677	7.353	0.057
7	02 April	30.9928	11.9863	43.96221	-79.2677	7.629	0.055
8	02 April	31.0035	11.9634	43.96221	-79.2677	7.821	0.053
9	02 April	31.0464	11.971	43.96221	-79.2677	7.938	0.052
10	02 April	31.0571	11.9482	43.96221	-79.2677	8.058	0.051
11	02 April	31.0571	11.9482	43.96221	-79.2677	8.144	0.044
12	02 April	31.0786	11.9405	43.96221	-79.2677	7.618	0.044
13	02 April	31.0893	11.9405	43.96221	-79.2677	1.306	0.04
14	02 April	31.1	11.91	43.96221	-79.2677	0.431	0.039
15	02 April	31.1322	11.9253	43.96221	-79.2677	0.287	0.038

Figure 18: Importing Data into Excel File

3.1.2 On Board SD Card Archives

If a microSD card is inserted in the Pollutracker, the continuous recording archives will also be saved to this card. We recommend that you have a microSD card inserted for archive back-up purposes.

4 High Concentration Sensors

If you purchased a Pollutracker with one or more High Concentration sensors, your Pollutracker will be installed with a HC/LC switch. If you are testing samples with a high concentration of chemical, it is very important you have this switch set to HC.
Sampling high concentration gases with low concentration sensors can permanently damage your sensors. If you are sampling low concentration samples,please set the switch to LC.

Figure 19: HC/LC Switch

5 Maintenance and Storage

If you have not used your Pollutracker for a long period of time, we recommend that you plug in the charger and keep it turned on for 12 hours before using it again. This ensures all the sensors are properly warmed up so that accurate measurements can be taken. Furthermore, for accurate measurements we highly recommend to send the Pollutrackerfor a yearly factory maintenance that includes replacement of the internal tubes and re-calibration of all sensors.

Appendix A: Sensor Warm up and Response Time

#	**Type**	**Formula**	**Chemical**	**Maximum Detection Limit**	**Lowest Detection Threshold**	**Resolution (ppm)**	**Expected Life (year)**	**Warm up Time (Sec)**	**Response Time (Sec)**
1	NDIR	CO_2	Carbon Dioxide-HC	5%	100 ppm	20	1	120	120
2	NDIR	CO_2	Carbon Dioxide-LC	2000 ppm	1 ppm	0.6 ppm	2	12	120
3	EC	CO	Carbon Monoxide-LC	100 ppm	0.03 ppm	0.01 ppm	2	40	40
4	EC	CO	Carbon Monoxide-MC	1000 ppm	1 ppm	1 ppm	5	40	20
5	EC	CO	Carbon Monoxide-HC	10000 ppm	30 ppm	3 ppm	2	45	40
6	EC	Cl_2	Chlorine-HC	2000 ppm	1 ppm	1 ppm	2	45	40
7	EC	Cl_2	Chlorine-LC	10 ppm	0.05 ppm	0.01 ppm	2	120	60
8	EC	H_2	Hydrogen	10000 ppm	100 ppm	10 ppm	2	120	40
9	EC	HCl	Hydrogen Chlorine	20 ppm	0.5 ppm	0.2 ppm	2	120	60
10	EC	HCN	Hydrogen Cyanide	50 ppm	0.1 ppm	0.1 ppm	2	120	30
11	EC	PH_3	Phosphine-LC	5 ppm	50 ppb	30 ppb	2	60	20
12	EC	PH_3	Phosphine-HC	2000 ppm	5 ppm	2 ppm	2	60	25
13	EC	H_2S	Hydrogen Sulfide (LC/ppb)	3 ppm	7 ppb	1 ppb	2	180	35
14	EC	H_2S	Hydrogen Sulfide (HC/ppm)	2000 ppm	15 ppm	2 ppm	2	180	25
15	EC	H_2S	Hydrogen Sulfide (MC/ppm)	200 ppm	2 ppm	0.2 ppm	2	180	60
16	MOS	C_2H_6O, H_2, C_4H_{10}	Organic solvents (Ethanol, Isobutane, H_2)	500 ppm	25 ppm	1 ppm	1	30	10
17	NDIR	CH_4	Methane (LEL)	20,000 ppm	10 ppm	10 ppm	$>$ 3 years	45	12
18	EC	NO	Nitric Oxide-LC	1 ppm	0.01 ppm	0.001 ppm	2	120	60
19	EC	NO	Nitric Oxide-MC	25 ppm	0.2 ppm	0.1 ppm	2	120	60
20	EC	NO	Nitric Oxide-HC	5000 ppm	2 ppm	2 ppm	3	120	10
21	EC	NO_2	Nitrogen Dioxide-LC	1 ppm	0.01 ppm	0.001 ppm	$>$ 5 Years	120	60
22	EC	NO_2	Nitrogen Dioxide-MC	20 ppm	0.1 ppm	0.1 ppm	$>$ 5 Years	120	60
23	EC	NO_2	Nitrogen Dioxide-HC	1000 ppm	2 ppm	1 ppm	2	120	60
24	NDIR	$N2O$	Nitrous Oxide	10,000 ppm	100 ppm	1 ppm	5	30	30
25	EC	O_2	Oxygen-HC	250,000 ppm	5000 ppm	200 ppm	1	60	15
26	PID	$VOCs$	Total VOCS PID 10.0eV	100 ppm	5 ppb	5 ppb%	5	5	3
27	PID	$VOCs$	Total VOCS-LC PID 10.7eV	50 ppm (iso-butylene)	1 ppb	1 ppb	5	5	3
28	PID	$VOCs$	Total VOCS-HC PID 10.7eV	300 ppm (iso-butylene)	1 ppb	50 ppb	5	5	3
29	EC	SO_2	Sulfar Dioxide-HC	2000 ppm	2 ppm	1 ppm	2	120	25

#	Type	Formula	Chemical	Maximum Detection Limit	Lowest Detection Threshold	Resolution (ppm)	Expected Life (year)	Warm up Time (Sec)	Response Time (Sec)
30	EC	SO_2	Sulfar Dioxide-LC	1 ppm	0.01 ppm	0.001 ppm	2	120	20
31	EC	SO_2	Sulfar Dioxide-MC	100 ppm	0.4 ppm	0.2 ppm	2	120	20
32	EC	CH_2O	Formaldehyde	5 ppm	10 ppb	10 ppb	2	180	60
33	Laser Scattered	PM	Particulate PM 2.5, 10 (simultanous)	1000 $\mu g/m^3$	1 $\mu g/m^3$	1 $\mu g/m^3$	$>$ 5 Years	NA	NA
34	Laser Scattered	TSP	TSP-PM Required	20,000 $\mu g/m^3$	1 $\mu g/m^3$	1 $\mu g/m^3$	$>$ 5 Years	NA	NA
35	EC	NMHC	Non-methane Hydrocarbon	25 ppm	0.1 ppm	0.1 ppm	2	180	55
36	MOS	TRS	TRS and Amines	10 ppm	10 ppb	2 ppb	1	30	10
37	MOS	NH_3- C_2H_6O- C_7H_8	Air Contaminants (Ammonia, Ethanol, Toulene)	30 ppm	1 ppm	4 ppb	1	30	10
38	EC	NH_3	Ammonia-HC	100 ppm	3 ppm	1 ppm	2	30	40
39	EC	NH_3	Ammonia-LC	10 ppm	0.005 ppm	0.001 ppm	2	30	50
40	EC	O_3	Ozone-LC	0.5 ppm	1 ppb	1 ppb	>5 Years	60	30
41	EC	O_3	Ozone-HC	5 ppm	20 ppb	20 ppb	>5 Years	60	30
42	Geiger Counter	$\alpha-, \beta-,$ Υ, X	Radiation Monitor ($\alpha-, \beta-, \Upsilon-$and $X-$ radiation)	0.01 $\mu Sv/h$	0.01 μSv/h	0.01 μSv/h	>3 Years	0	0
43	EC	ClO_2	Chlorine Dioxide	50 ppm	0.01 ppm	0.05 ppm	2 Years	180	60
44	TDLS	CH_4	Methane-ppb	100 ppm	0.4 ppm	0.01 ppm	+10	20	1

Appendix B: TR8+ Calibration procedure

Scentroid TR8+ Pollutracker portable gas detection device will require periodical and routine calibration of gas sensors. This section describes the Standard Operating Procedure to calibrate the TR8+ with standardized reference materials. This section does not contain other maintenance procedures.

Gas sensor calibration

Before start calibrating the Scentroid Pollutracker TR8+, you should read this read this section entirely in order to perform a detailed and accurate calibration procedure. It is also recommended that an experienced technician perform the calibration procedure.

TR8+Calibration Requirements

The frequency of calibration will be highly dependent on the TR8+ Usage, testing conditions, the quality criteria established for the data set, cost and instrument stability. For further information you may review the US EPA Quality Assurance Handbook that will help you to define the calibration protocols based on the requirements of the monitoring efforts. Check the link below
https://www3.epa.gov/ttnamti1/files/ambient/qaqc/r94-038a.pdf

Calibration Highlights

A series of calibration highlights are to be understood before starting the calibration procedure. These are:

- The described calibration procedure is applicable for the following type of sensors:

TYPE OF SENSOR	**DESCRIPTION**	**CALIBRATIONNDIRN**
NDIR	Non-dispersive Infrared	User Calibration
PID	Photoionization Detector	User Calibration
EC	Electrochemical	User Calibration
MOS	Metal Oxide Sensor	Auto Calibration
LS	Laser Scattered	Auto Calibration

- TR8+ sensor calibration will require Zero and Span adjustments for some sensors and has to be performed by adjusting the Zero Offset and the Sensor Sensitivity values which are located in **Settings** screen on the TR8+ application.

- PTFE 20L purged sampling bags should be used to avoid cross contamination and false positives.

- PTFE tubing should be used for gas calibration train. If applicable PTFE or stainless-steel fitting should be used.

- The calibration procedure should be performed with the TR8+ enclosure door closed to ensure stable internal temperature. It is recommended to calibrate the TR8+at temperatures 22 $\pm 2^{o}$C.

- Certified reference materials should be used to reach maximum sensor accuracy.

- TR8+ uses electrochemical sensors, which are specified to operate in the humidity range of 15 to 90% RH. Short-term excursions into a low of 0% RH are permissible only for calibration proposes. Exposing sensors for a long period of time below the recommended relative humidity range will affect either its sensitivity or response time.

- It is expected that the calibration procedure takes place in an office or laboratory settings.

  The recommended calibration set up is shown below. The sampling inlet pipe should be removed for calibration and zero air. The calibration gas should be delivered to the instrument via 20L sampling bag as follows:

- TR8+ must be powered for at least 8 hours before starting the calibration procedure.

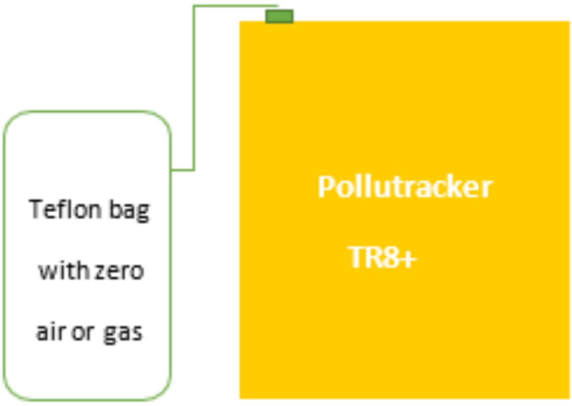


Figure 20: Illustration of the Recommended Calibration

- Verify in TR8+ android device that the temperature shows 22 ±2°C. Note the enclosure lid must be closed to ensure a stable internal temperature.
- Log into the TR8+ application. Panel screen will show the **Settings** button where you can view the operating settings of the TR8+.

SENSOR CONFIGURATION

SENSOR	SCALE	AUTO CAL.	OFFSET	SENSITIVITY	AQ LIMIT
VOCs LC	ppm		0.0	1.0	5.0
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				
None	Scale				

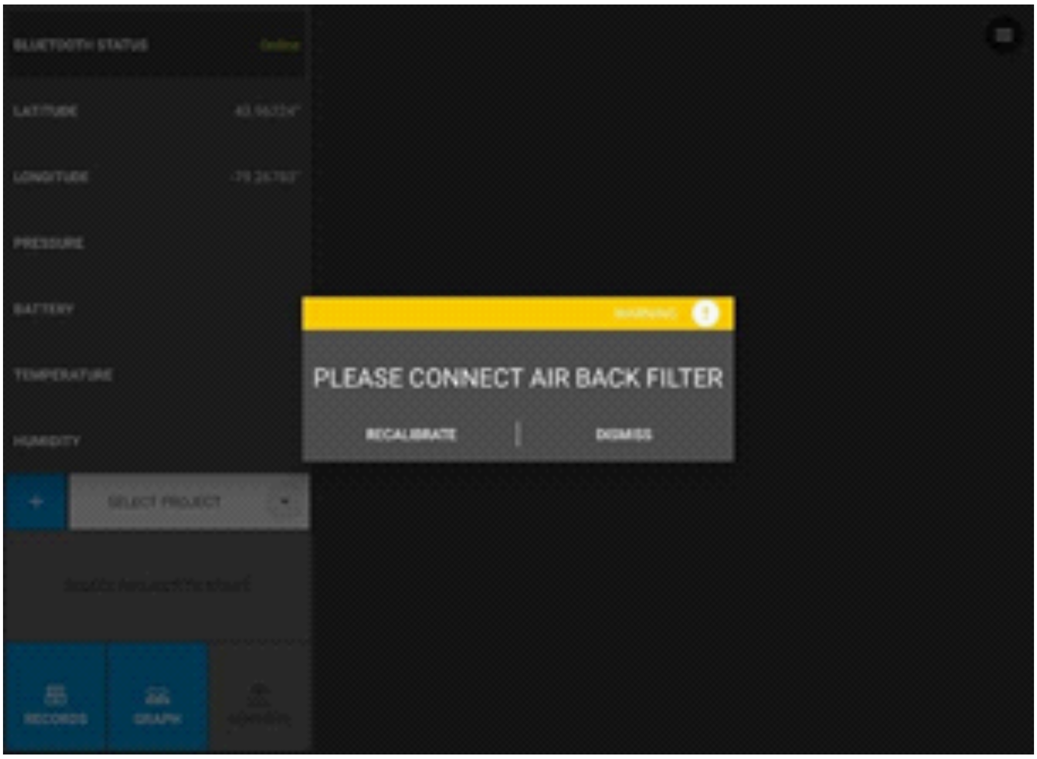
Figure 21: Sensor Configuration Screen

- Record the operating setting in the calibration logbook. The **operating settings** are the configuration values in which your Pollutracker is working before the calibration procedure.
- Change the operating setting values to the calibration setting values and save the calibration values.
- Verify the sampling intake rate by using a 1/4” Teflon® tube attached to the sampling inlet port in combination with a acrylic flow meter (0.4-5 LPM). The sampling intake rate should be between 2.0 to 4.0 LPM. If the inlet flow rate is less than specified, check for leaks, otherwise, adjust the pump flow rate.

Zero Calibration Procedure

Before using your TR8+, it is important to zero the sensors to correct for any baseline shifts. Scentroid has included a carbon filter to your product for this reason. Please note that before zeroing the sensors, ensure the unit has been powered on for at least 20 minutes. For best results, please zero your sensors right before sampling.
The steps for auto zeroing the sensors are as follows

1. Selecting the sensors to zero calibrate By default, the sensors that should have their reading zero calibrated are selected by Scentroid during the time of manufacturing. If you have not updated your application since receiving your unit or have not recently installed the application on a new tablet, you can skip this step. To select a sensor to auto calibrate, go to the **Sensor Settings** page of the TR8+ application, then check mark the auto-calibration box.
2. Run the auto calibration First, connect the carbon air filter. Please ensure the arrow on the filter is pointing towards the TR8+. Firmly press into the filter to ensure the 1/4” Teflon® tube is fully inserted into both ports.



PLEASE CONNECT AIR BACK FILTER

Figure 22: Connecting Air Back Filter Screen

Now begin the zero-air calibration process by going to the setting menu in the top right of the app and selecting re-calibration. Follow the prompts and the unit will start the auto zero process. The software will tell the user when the auto calibration function is complete.

Multipoint Calibration Procedure

When doing the multipoint calibration procedure, the following steps should be followed

- Allow the system to be stabilized for 3-5 minutes.
- Plug the calibration gas into the inlet port of the Pollutracker. The results gathered within the gas calibration will be used to setup the sensors span value.
- Allow the system to take several samples from the calibration gas air bag until stable readings are reached.

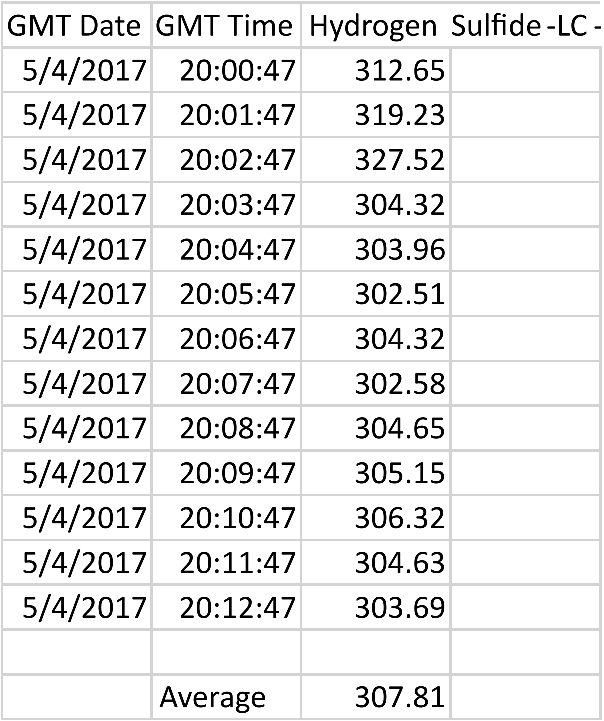
- you unplug the calibration gas bag from the Pollutracker.
- Allow the system to be stabilized for 3-5 minutes.
- Repeat calibration gas procedure for all required sensors.
- You may use a 3-point calibration system by measuring 3 different concentrations of the calibration gas.
- Once you have finished the calibration process, it is time to calculate the calibration settings. Calibration settings are defined by **Zero Offset** and **Sensor Sensitivity**.
- Extract the project file from the Android device or from the Pollutracker miniSD card. Insert the miniSD card in the supplied SD adaptor to be inserted in a computer slot.
- Data recorded is showed in a .XLS file for further analysis.
- Locate the readings taken during the calibration process for zero air and for all calibration gases.
- For zero air readings calculate the average value of the data showed per sensor for the time in which the Zero Air bag was plugged into the Pollutracker.

GMT Date	GMT Time	Hydrogen	Sulfide -LC -
5/4/2017	19:32:47	101.5400	
5/4/2017	19:33:47	102.35	
5/4/2017	19:34:47	101.98	
5/4/2017	19:35:47	106.44	
5/4/2017	19:36:47	103.96	
5/4/2017	19:37:47	112.02	
5/4/2017	19:38:47	109.07	
5/4/2017	19:39:47	106.35	
5/4/2017	19:40:47	103.89	
5/4/2017	19:41:47	103.67	
5/4/2017	19:42:47	102.38	
5/4/2017	19:43:47	102.02	
5/4/2017	19:44:47	101.9	
	Average	104.4285	

The average value of each sensor will be the Zero Offset value for that specific sensor in mVolt. If the value is close to the initial Zero Offset value recorded in the calibration log book (<15% drift), no further action is required, and you will be done with the calibration process. If the value shows a drift higher than 15%, then a new sensor sensitivity must be calculated as follows

– To obtain sensor sensitivity value, use the same data file recorded in the SD card and locate the values obtained during gas calibration for the specific sensor. You will be able to identify the gas calibration readings using the time at which the calibration gas was attached to the inlet sampling port of the TR8+. The example below shows the results obtained for the Hydrogen sulfide.

– Identify the column with the response readings and calculate the arithmetic average of these values. This will be used to calculate the new sensor sensitivity as described below.



GMT Date	GMT Time	Hydrogen	Sulfide -LC -
5/4/2017	20:00:47	312.65	
5/4/2017	20:01:47	319.23	
5/4/2017	20:02:47	327.52	
5/4/2017	20:03:47	304.32	
5/4/2017	20:04:47	303.96	
5/4/2017	20:05:47	302.51	
5/4/2017	20:06:47	304.32	
5/4/2017	20:07:47	302.58	
5/4/2017	20:08:47	304.65	
5/4/2017	20:09:47	305.15	
5/4/2017	20:10:47	306.32	
5/4/2017	20:11:47	304.63	
5/4/2017	20:12:47	303.69	
	Average	307.81	

Sensor sensitivity must be calculated by subtracting the sensor Zero Offset value from the sensor reading when the calibration gas was delivered as follows:

$$Sensor\ Sensitivity = \frac{(Gas\ calibration\ reult - Sensor\ zero\ offset\ value)}{Gas\ calibration\ concentration}$$

From the example:

$$\begin{aligned} Sensor\ Sensitivity &= \frac{307.81 - 104.4285}{20} \\ Sensor\ Sensitivity &= 10.169 \end{aligned}$$

Once the zero offset voltage value and the sensor sensitivity are obtained, enter the new values in the **Settings** screen. Once the new offset, sensor sensitivity, maximum sensitivity and minimum sensitivity values are entered, tap on the **save** button to save the new calibration settings.

ATTACHMENT E
CORRECTIVE ACTION PLAN AIR DISPERSION MODELING ANALYSIS
OCTOBER 2021

Table A-35
Water9 Inputs - Clarifier to Ditch #1
New-Indy Catawba - Catawba, SC

Sources	Variable	Value	Unit	Source
Closed Trench No. 1	Underflow Temperature	44.4	C	Average ASB Influent Temperature during IPT (7/9-11/2021)
	Total water added at the unit		l/s	
	Area of openings at unit	50	cm^2	Water9 Default
	Radius of drop pipe	5	cm	Water9 Default
	Drop length to conduit	61	cm	Water9 Default
	width of trench	1.2	m	Estimated based on Google Earth and drone footage (when available)
	Distance to next unit	500	cm	Water9 Default
	slope of underflow conduit	0.015		Water9 Default
	depth of trench	1.2	m	Estimated based on site-specific data
	velocity air at opening	84	ft/min	
	pH	9.08		Site Specific Average from Primary Clarifier Pi Tag between 7/9-11/2021

Table A-35
Water9 Inputs - Clarifier to Ditch #1
New-Indy Catawba - Catawba, SC

Sources	Variable	Value	Unit	Source
Primary Municipal Clarifier (no. 2)	Wastewater Temperature	44.4	C	Average ASB Influent Temperature during IPT (7/9-11/2021)
	Primary Clarifier Diameter	84	m	Estimated based on Google Earth and drone footage (when available)
	Primary clarifier depth	5.41	m	Assumption
	Clarifier solids removal efficiency	0.7		Water9 Default
	waterfall drop height	38	cm	Visual estimate
	Clarifier weir/circumference	1		
	Number of identical units in parallel	1		Water9 Default
	cover vent rate	0.0005	m^3/s per m^2 surface	Water9 Default
	pH	9.08		Site Specific Average from Primary Clarifier Pi Tag between 7/9-11/2021

Table A-35
Water9 Inputs - Clarifier to Ditch #1
New-Indy Catawba - Catawba, SC

Sources	Variable	Value	Unit	Source
Open Trench No. 3 (Ditch #0)	Underflow Temperature	44.4	C	Average ASB Influent Temperature during IPT (7/9-11/2021)
	width of trench	3.65	m	Estimated based on Google Earth and drone footage (when available)
	Distance to next unit	6100	cm	Estimated based on Google Earth and drone footage (when available)
	Slope of underflow conduit	0.015		Water9 Default
	depth of trench	3	m	Water9 Default
	pH	9.08		Site Specific Average from Primary Clarifier Pi Tag between 7/9-11/2021

Table A-35

Water9 Inputs - Clarifier to Ditch #1

New-Indy Catawba - Catawba, SC

Sources	Variable	Value	Unit	Source
Open Sump No. 4	Underflow Temperature	44.4	C	Average ASB Influent Temperature during IPT (7/9-11/2021)
	Area of openings at unit	50	cm^2	Water9 Default
	Radius of drop pipe	5	cm	Water9 Default
	Drop length to conduit	61	cm	Water9 Default
	Radius of underflow conduit	12	cm	Water9 Default
	Distance to next unit	500	cm	Water9 Default
	slope of underflow conduit	0.015		Water9 Default
	open surface of liquid at the unit	1000	cm^2	Water9 Default
	flow entrance depth under surface	10	cm	Water9 Default
	depth of liquid in sump	50	cm	Water9 Default
	velocity air at opening	88	ft/min	Water9 Default
	pH	9.08		Site Specific Average from Primary Clarifier Pi Tag between 7/9-11/2021

Table A-35
Water9 Inputs - Clarifier to Ditch #1
New-Indy Catawba - Catawba, SC

Sources	Variable	Value	Unit	Source
Closed Trench No. 5	Underflow Temperature	44.4	C	Average ASB Influent Temperature during IPT (7/9-11/2021)
	Total water added at the unit		l/s	
	Area of openings at unit	50	cm^2	Water9 Default
	Radius of drop pipe	5	cm	Water9 Default
	Drop length to conduit	61	cm	Water9 Default
	width of trench	1.2	m	Estimated based on Google Earth and drone footage (when available)
	Distance to next unit	42614	cm	Estimated based on Google Earth and drone footage (when available)
	slope of underflow conduit	0.015		Water9 Default
	depth of trench	3	m	Water9 Default
	velocity air at opening	84	ft/min	
	pH			
Open Trench No. 6 (Ditch #1)	Underflow Temperature	44.4	C	Average ASB Influent Temperature during IPT (7/9-11/2021)
	width of trench	3.65	m	Assumption based on aerial view
	Distance to next unit	60000	cm	Assumption based on aerial view
	Slope of underflow conduit	0.015		Water9 Default
	depth of trench	3	m	Water9 Default
	pH	8.94		Average ASB Influent pH during IPT (7/9-11/2021)