AQUIFER STORAGE AND RECOVERY MYRTLE BEACH, SOUTH CAROLINA

PHASE III: RESULTS OF THE MYRTLE BEACH INJECTION TEST OF 1994

By

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ABSTRACT

A second and final long-term injection test was completed at the Myrtle Beach Aquifer Storage and Recovery site. About 16 million gallons of potable water were injected into deep Cretaceous aquifers of the Coastal Plain in 1994. The injected water, which was obtained from the Atlantic Intracoastal Waterway and treated, has low concentrations of dissolved solids, sodium, and chloride. The native ground water, typical of Black Creek aquifers, is soft, alkaline, and low in iron, but it has objectionable concentrations of fluoride, sodium, and dissolved solids.

Air clogging of the test well and aquifer, after 11 million gallons were injected, forced suspension of the injection test. Air, introduced through faulty valves and vents, lodged in pore spaces of the aquifer and reduced its transmissivity and storage capacity. A short pumping cycle, instituted as a remedial procedure, immediately rehabilitated the well and restored the storage capacity of the aquifer. An additional 5 million gallons of treated water were stored in the aquifer after the test well was rehabilitated.

Gas chromatography of water samples collected during the recovery period showed that the gas is mostly nitrogen and dissolved carbon dioxide. Possible sources of these gases are air entrainment for the nitrogen and bacterial activity for the carbon dioxide. Nitrogen, more than carbon dioxide, dominates the gas phase observed in water samples. A solution to the air-entrainment problem could be the injection of water under positive pressure. A flow-control valve, installed along the pump column, would generate enough energy loss to create a positive pressure during injection, thus avoiding air entrainment.

Analysis of the data suggests that geochemical processes affecting the quality of the recovered water are sufficiently replicable to allow the use of observed trends in geochemical modeling. These processes, although important in the understanding of the chemical evolution of the water, were of limited scope. Mixing, however, had a much larger effect on the quality of the recovered water. Biological processes, moreover, appeared to have successfully reduced the concentration and formation potential of trihalomethane. On the basis of chloride concentration, a recovery efficiency of 70 percent was obtained at this site. At this efficiency, recovered water could be returned to the distribution system without additional treatment, because all concentrations were below the National Secondary Drinking Water Standards and the State of South Carolina drinking water rules.

KEYWORDS: Aquifer Storage and Recovery, well artificial recharge, geochemical modeling, geochemical processes.

INTRODUCTION

The purpose of this phase III report is to summarize the findings and conclusions of the aquifer storage and recovery (ASR) test completed at the Myrtle Beach injection site in 1994. The report primarily addresses two pending issues from phase II: (1) backflushing procedures and (2) chemical composition of the gas phase found in the recovered water during pumping cycles. This report also reviews other important issues such as replicability of results, validation of data, air-clogging problems, and deterioration of aquifer properties because of injection.

In 1986, the former South Carolina Water Resources Commission—presently the Water Resources Division of the Department of Natural Resources—initiated a program to study the applicability of aquifer storage and recovery in the Coastal Plain of South Carolina. Owing to the complexity of the endeavor and the uncertainty of expected results, the project was divided into several phases. Each phase addressed a separate aspect of the study, and only a successful culmination of a previous phase warranted the continuation of the investigation into the next phase. This stepwise approach permitted the concentration of efforts and resources in resolving critical facets of the project.

During phase I, an ASR methodology was devised (Castro, 1987; Castro and Hockensmith, 1988); a preliminary hydrologic study of the confined aquifers of the region was completed (Castro and Hockensmith, 1987); and a core hole was drilled and the Black Creek aquifer selected for the ASR injection tests (Castro and others, 1995). During phase II, several short-term injection tests and one long-term test were made between 1991 and 1992 (Castro 1994, 1995); a solute-transport model (Pettewich, 1992) and a geochemical model were developed (Castro, 1994, 1995). To address some additional concerns, which developed during phase II, a second year-long test was completed in 1994 (phase III). The work completed during this third phase is the subject of the present report.

Simultaneous with the work completed at the Myrtle Beach site in 1994, a second ASR injection test was carried out at another site (phase IV). At this new ASR site, located 20 miles southwest of Myrtle Beach, more than 52 million gallons of water from the Bull Creek treatment plant were injected into the Black Creek aquifers (Castro and others, in preparation).

Funds for the aquifer storage and recovery investigation were provided by the State of South Carolina Division of Local Governments, the City of Myrtle Beach, and the South Carolina Department of Natural Resources, Water Resources Division.

The author expresses his gratitude to Dr. L.R. Gardner, University of South Carolina, and Dr. Susan Libes, Coastal Carolina University, for their insightful comments and suggestions.

TESTING SITE

SITE HYDROGEOLOGIC SETTING

During 1994, the field injection tests were carried out at the 38th Avenue North well site in Myrtle Beach. This is the same site where the 1991 and 1992 injection tests (Castro, 1995) were completed. As in previous tests, a 10-inch, 670-ft (foot), former public supply well in the Black Creek Formation was retrofitted for injection of treated water into a confined aquifer.

Fully treated water (drinking-water quality) was injected into the unconsolidated sand and clayey sand of the Cretaceous-age Black Creek Formation. This geologic unit underlies most of the Coastal Plain of South Carolina. The aquifers of this formation are characterized by moderate to low hydraulic conductivities that range from 560 gpd/ft^2 (gallons per day per square foot) in Florence and Darlington Counties (updip) to 80 gpd/ft^2 in Horry and Georgetown Counties (downdip). A comprehensive description of the site and regional hydrology is given by Castro and Hockensmith, 1987; Castro and others, 1995; and Castro, 1995.

The quality of the native ground water deteriorates, in general, in a downdip direction (toward the coast). At the recharge area (updip) the ground water is low in dissolved solids, but it becomes moderately mineralized near the shoreline (downdip). The Black Creek Formation ground water in Horry County is described as soft and alkaline, with a low concentration of iron and objectionable concentrations of fluoride, sodium, and total dissolved solids (Castro and others, 1995).

The water used for injection is treated surface water from the Atlantic Intracoastal Waterway. This treated water is characterized by lower concentrations of dissolved solids, sodium, and chloride than those found in the native ground water (Castro, 1995).

WELLHEAD INSTALLATION AND EQUIPMENT

The wellhead design used for the 1991 and 1992 injection and recovery tests limited injection rates to 100 gpm (gallons per minute) or less. In 1994, the wellhead was modified again to test higher injection rates. Figure 1 is a schematic representation of the wellhead after modifications were made. This wellhead design is similar to one normally used for water production wells (pumping). During injection, water was delivered from

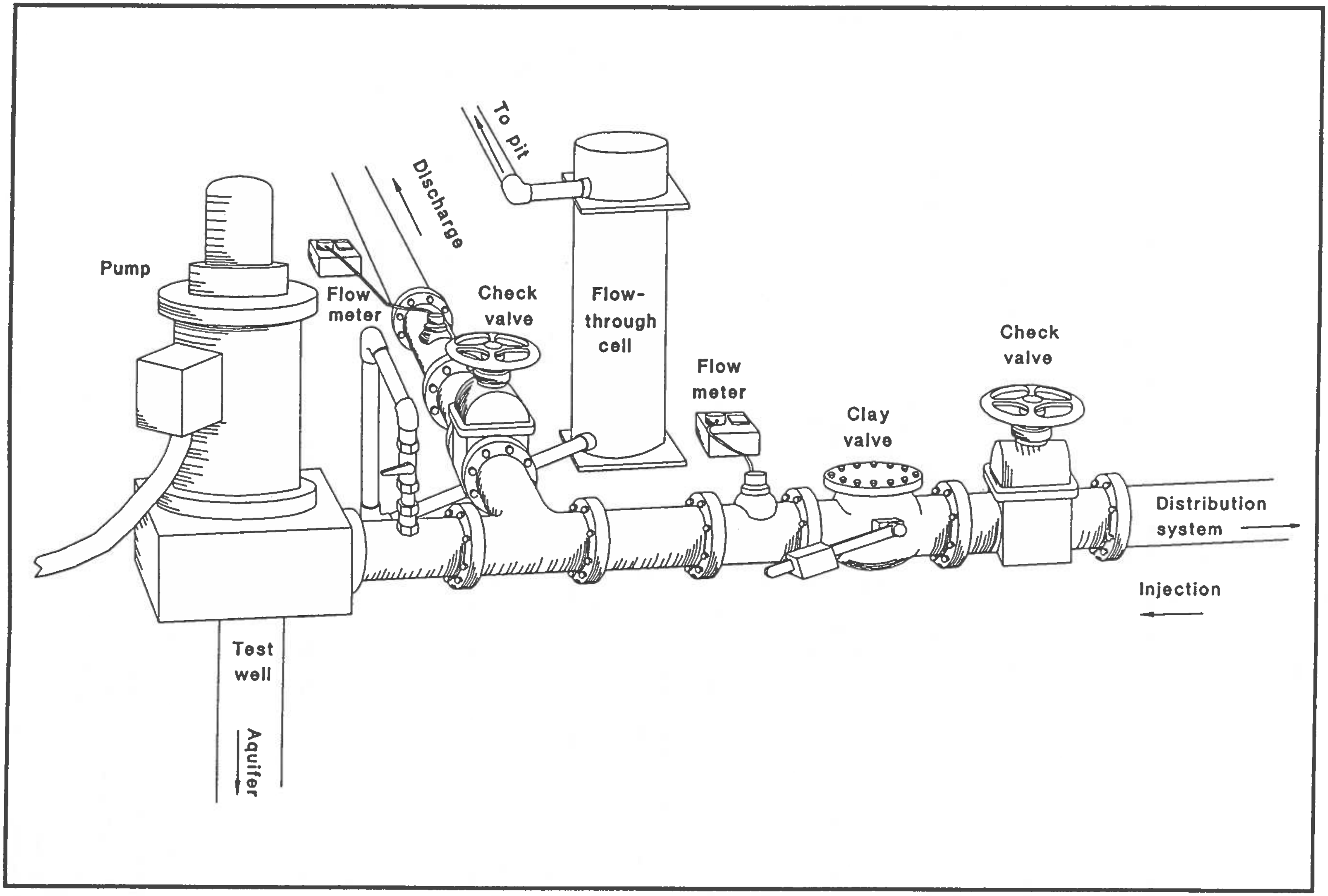

Figure 1. Wellhead design during the 1994 ASR test.

the city's distribution system to the test well by the normal line pressure. During recovery, stored water was removed from the aquifer by pumping.

The wellhead, to comply with the Underground Injection Control permit, was retrofitted with the necessary gate valves and check valves to prevent accidental discharge of recovered water into the distribution system, since the test well has been permitted only for testing and not for production. Wellhead modifications in this former public supply well were few, inexpensive, and easily implemented.

The ASR site was equipped to monitor various hydraulic parameters and water quality characteristics. The test well and observation well were fitted with pressure transducers to record water levels. A digital flow meter was used to monitor rates on injection and discharge. A flow-through cell was installed for monitoring water quality properties such as dissolved oxygen, specific conductance, redox potential, alkalinity, pH, and temperature. The cell allowed the regular measurement of dissolved oxygen and pH before the sample was exposed to the atmosphere (Fig 1.). Thus, the risk of contamination by atmospheric gasses was greatly reduced. The pH and temperature were read and logged automatically into a computer. Other characteristics were manually recorded several times a day.

Water quality samples were regularly collected and analyzed for primary and secondary chemical constituents, trihalomethane, trihalomethane potential, total organic carbon, fecal bacteria, stable carbon isotopes, tritium, and residual chlorine. Wet-chemistry analyses were made at the Coastal Carolina Environmental Laboratory, Conway, S.C. Total organic carbon, trihalomethane, and trihalomethane potential were analyzed at the Oxford Laboratories, Inc., Wilmington, N.C. The stable isotopic composition of the dissolved inorganic carbon of the water ($\delta^{13}C$) was analyzed at the Center for Applied Isotope Studies at the University of Georgia, Athens, Ga. Low-level tritium analysis was made at the Alberta Environmental Centre, Alberta, Canada. Bacteriological analysis for fecal coliform was made at the Grand Strand Water and Sewer Authority treatment plant, Conway, S.C. Residual chlorine analysis was made on the site.

FIELD TESTING SCHEDULES

During phase III, a year-long injection and recovery test was completed. Table 1 summarizes the 1994 ASR activities, which started on March 1 and ended on November 30. Constant-discharge aquifer tests were made in January and December 1994, to evaluate the hydraulic properties of the aquifers. Results of the two tests were compared with the results of previous-year aquifer tests for this well to ascertain the effects of injection and recovery on the hydraulic properties of the aquifer.

Nearly 16 million gallons of treated water, twice as much as in the previous long-term test of 1992, were injected and stored in the Black Creek aquifers during the phase III test. Various injection rates and backflushing procedures were tested to improve the performance of the ASR system. Because of unexpected plugging problems in the test well, previous field testing schedules were modified. The customary injection-storage-recovery scenario had to be altered to: injection-recovery-injection-storage-recovery. An additional recovery period was included in the middle of the injection period. This short recovery period was necessary to rehabilitate the test well after it lost most of its injection capacity. The clogging problem and subsequent remedial procedures are discussed later. In

Table 1. Schedule of field activities at the ASR site, Myrtle Beach, 1994

PERIOD	DATE	VOLUME (MILLION GALLONS) INJECTED	PUMPED	AVERAGE RATE (GPM)
FIRST INJECTION	3/1-6/1	10.72	0.04	140 (INJ)
FIRST RECOVERY	6/13-6/20		3.25	314 (PUM)
SECOND INJECTION	6/30-8/11	5.15	0.09	128 (INJ)
STORAGE	8/12-10/17		1.32	333 (PUM)
SECOND RECOVERY	10/17-11/30		21.27	333 (PUM)

GPM, gallons per minute
INJ, injection
PUM, pumping

Table 1, time discontinuities among the injection, storage, and recovery periods represent periods when the test well was shut down while preparations were underway to shift from injection to recovery and vice versa.

FIRST INJECTION PERIOD AND BACKFLUSHING

During the first injection period, March 1 to June 1, 10.72 million gallons were injected into the aquifer. Injection rates varied from 120 to 160 gpm, with the average being 140 gpm (Fig. 2).

Throughout the injection test, injection rates varied daily by as much as 8 percent. These fluctuations, induced by pressure variations, resulted from the water-demand changes in the city. During weekdays, daily-demand increased first between 7 and 9 a.m. and then between 5 and 9 p.m. Correspondingly, the pressure, and therefore, the injection rates increased during the off periods: first between 9 p.m. and 7 a.m. and then between 9 a.m. and 5 p.m. These trends are easily identified in the water level graphs, because high injection rates produced high water levels.

During this first injection period, the test well was first backflushed once a week and later twice a week, and often the test well was shut down during weekends and holidays. A total of 42,000 gallons—an average of 14,000 gallons per month—were pumped to waste during the first injection period. This was a significant improvement from backflushing volumes used in 1992, when, on average, more than 100,000 gallons were pumped per month.

To obtain a representative chemical composition of the treated water, eight samples were collected during the injection period. Samples were collected over a sufficient period, several months, to document small but discernible chemical fluctuations in the composition

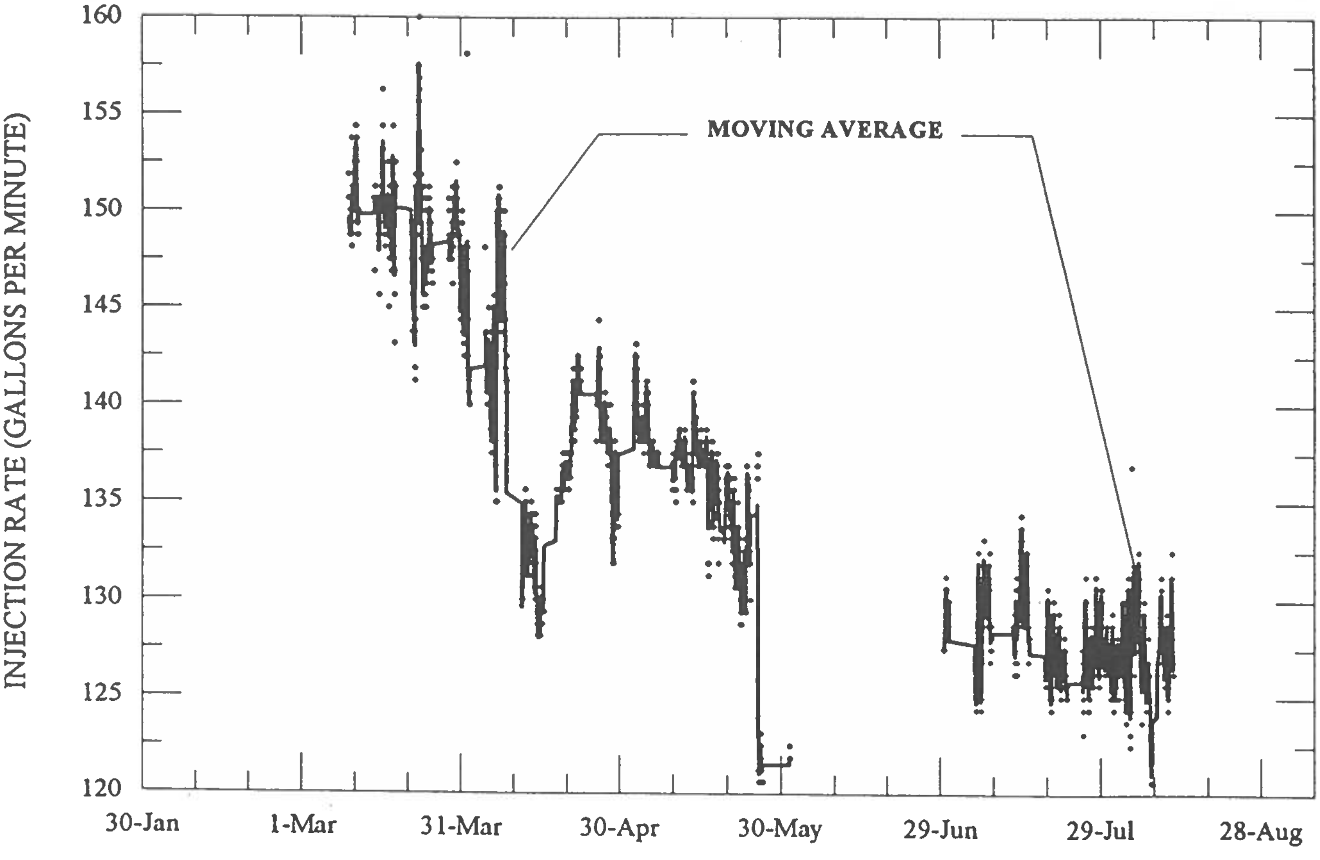

Figure 2. Injection rates during the 1994 test. Solid line is 21-term moving average.

of the water, most likely due to changes in the chemical makeup of the raw water.

WELL CLOGGING

After 84 days of injection, on May 24 the test well started developing injection problems. Water levels in the test well rose significantly, to a depth of less than 5 ft bls (below land surface). Moreover, subsequent injection attempts at lower injection rates yielded equally high water levels. It appeared that the well had lost its specific-recharge capacity and was clogged. Consequently, injection was halted and the well shut down. To correct the problem, the well was pumped (water withdrawn).

Figure 3 shows three graphs for the injection period during May 1994: (a) water levels for the test well; (b) injection rates; and (c) injected-water temperature. For most of the injection period, water levels were between 15 and 10 ft bls; injection rates gradually declined from 142 to 133 gpm; and injected-water temperatures fluctuated between 22°C (degrees Celsius) and 24°C. Starting on May 24, conditions changed in the test well and aquifer. Although not apparent in the graph, water level rates of change were large. Pressure, even during short injection intervals, reached unexpectedly high levels. The high levels persisted after the injection rate was reduced to less than 125 gpm. Temperature fluctuations, on the other hand, appear not to have affected the injection process. Injected-water temperature was 23°C, which was near the native ground water temperature of 24°C. Therefore, changes in viscosity and hydraulic conductivity, due to temperature differences, probably were small or negligible (Castro, 1995).

Injection experience at this site suggested that chemical clogging, although possible, was doubtful. Thus, the other reasonable explanation for the problem was mechanical clogging, air entrainment in particular. The wellhead installation was not airtight, and it is conceivable that vents and partially closed or faulty valves allowed air to be driven into the system. A fraction of the air entrained in the injected water may have been in solution and the remaining fraction in suspension. The latter fraction, which is suspected to be made up of tiny air bubbles, could have lodged in pore spaces of the aquifer, thus reducing the effective porosity of the formation and, consequently, raising the water level in the test well.

FIRST RECOVERY PERIOD

The test well was pumped from June 13 to June 20 to rehabilitate the aquifer. It was anticipated that, by pumping the test well, some of the air bubbles locked in the gravel pack and aquifer would be removed, thus allowing the aquifer to recover some of its lost porosity and specific-recharge potential. Starting on June 13 and for the next 9 days, the well was pumped and 3.25 million gallons were recovered. During this short recovery period, although not evident at the discharge pit, a considerable volume of the gas phase might have been removed, because injection was successfully restarted afterwards.

Fourteen samples of the recovered water were obtained during this short pumping period. Although, this pumping period was not originally planned, it provided an excellent opportunity to study chemical processes that developed near the well bore. Results from this pumping period were helpful in corroborating findings from the other recovery period.

SECOND INJECTION PERIOD

Between June 30 and August 11, 5.15 million gallons were injected at an average rate of 128 gpm. The lower injection rate selected for this second injection period reflected the initial uncertainty about the effectiveness of the remedial procedure. Later, however, water levels in the test well confirmed the success of the procedure. Water levels started at 40 ft bls and progressively rose to 20 ft bls, after 37 days of injection.

During this second injection period, four water samples of the treated water were obtained. The samples normally were collected every other week. Because sampling of the treated water extended from spring to summer, during the two injection periods, most of the possible changes in chemical composition of the product water were observed. It had been found that ambient temperature and hydrologic regimes had a strong influence on the quality of the raw water that feeds the treatment plant (Castro, 1995).

STORAGE PERIOD

Water remained stored in the aquifer from August 12 to October 16. During this period, which lasted for 62 days, the test well was pumped occasionally and 1.32 million gallons of treated water were recovered. A total of 18 water samples were collected.

The sampling schedule for this period was designed to collect information on geochemical processes taking place near the well bore and to permit analysis of the spatial variability of geochemical reactions. Water-quality analyses from previous tests indicated that samples from the storage period provided more information on geochemical processes than samples from the recovery period (Castro, 1995). The objectives of

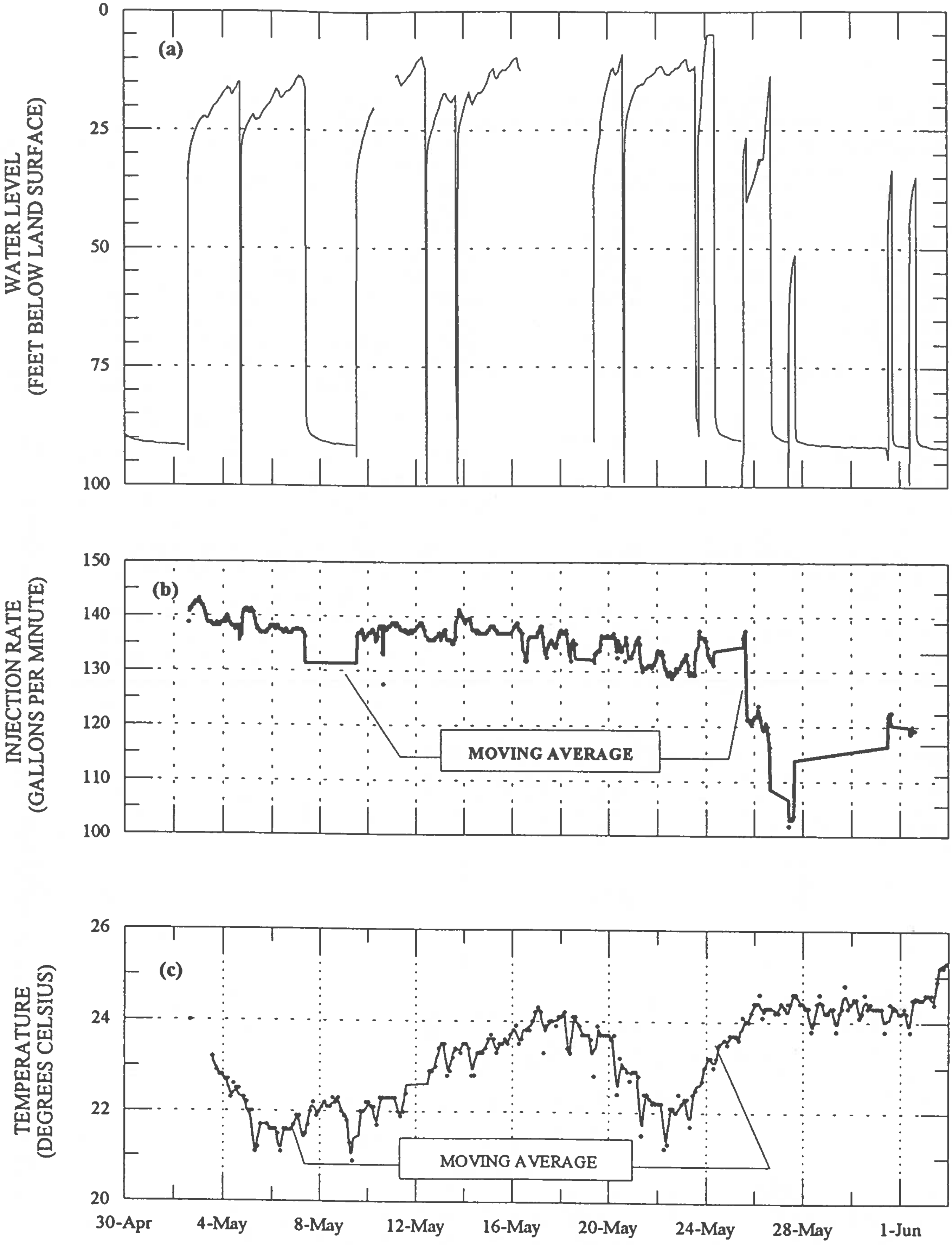

Figure 3. Test well (a) water level, (b) injection rate, and (c) temperature fluctuations before becoming air-clogged.

this sampling were to: (a) ascertain the kinetic behavior (rate of reaction) of chemical reactions (b) study the chemical evolution of the injected water.

SECOND RECOVERY PERIOD

Between October 17 and November 30, the well was pumped continuously at an average discharge rate of 333 gpm, producing 21.27 million gallons of water. For both recovery periods, in aggregate, 61 percent more water was pumped from the aquifer than had been injected into it.

During recovery, 17 samples were collected for chemical analysis. The sampling schedule for this period emphasized the early part of the recovery. Previous tests have shown that chemical reactions, more than mixing, controlled the makeup of the recovered water during the early part of the recovery period (Castro, 1995). When the chemical composition of water samples is governed by mixing, as it is during most of the recovery period, the makeup of the sample is easily determined if the chloride concentrations or specific conductivities are known (Castro, 1995).

DATA ANALYSIS

WATER LEVELS

The water level in the Black Creek test well has recovered more than 17.5 ft since 1992 and nearly 100 ft since 1988, when Myrtle Beach ceased using wells for public supply. Water levels rose 1.8 ft in 1994, from 94 ft bls in January to 92.2 ft bls in December. The water-level rise was due to natural regional recovery of the aquifer (Castro, 1995). Figure 4 shows that water levels had a net rise of 1.2 ft between January 6 and February 20. Smaller-scale fluctuations were also observed at the ASR site. These changes, which represent a semimonthly fall-and-rise of the water level, seem to be related to the neap-and- spring tidal cycle. Inferences of Black Creek regional recovery, consequently, must be based on long-term and not short-term observations, which might be misleading.

Today, recovery of water levels in the Black Creek aquifers appears to be continuing at a rate of less than 2 ft per year.

Figure 5 shows water levels for (a) the test well and (b) the observation-well zone 2 in 1994. The graphs show water levels: BACKGROUND, before the test; INJECTION, during the injection of treated water and backflushing events; RECOVERY, during recovery of the injected water; STORAGE, during the storage period, which included the sampling intervals. After the last recovery period, November 30, the graph also shows water levels for a 24-hour pumping-and-recovery test.

Buildup is a parameter that has been introduced to simplify the injection-test analysis. It is defined as the gain in head, expressed in feet, due to injection. It gives an indication of the required force to drive the water into the aquifer.

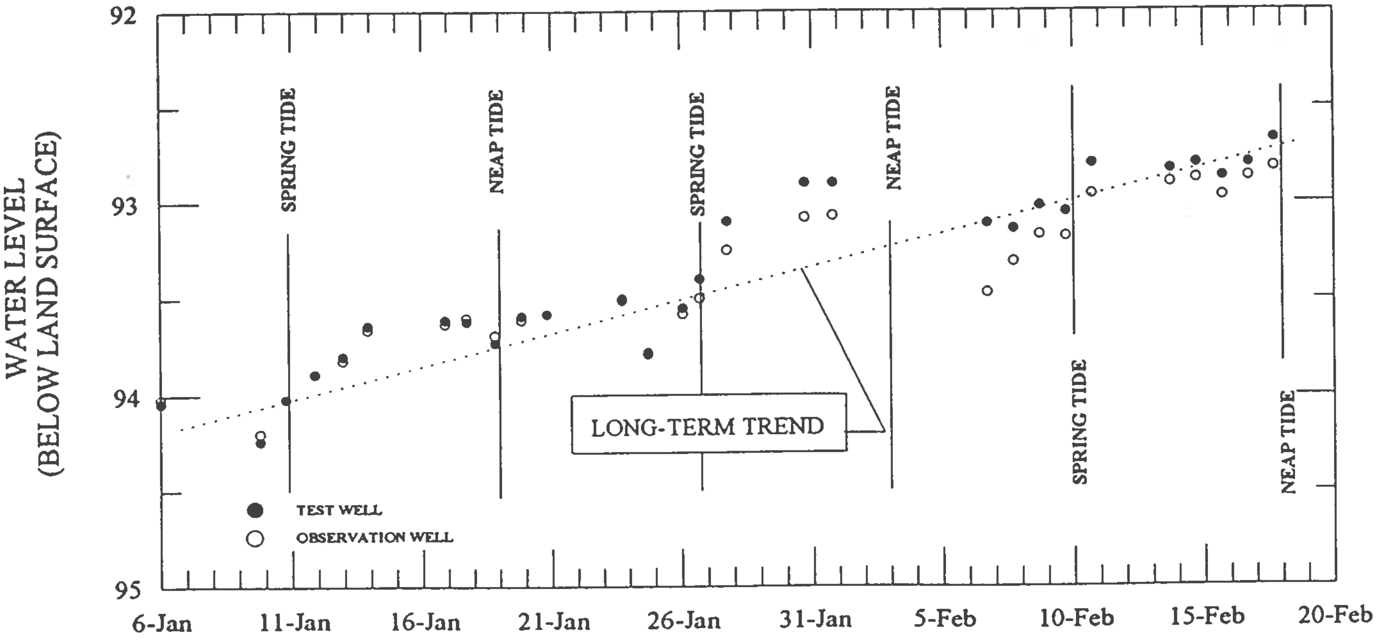

Figure 4. Spring and neap tide effects on water levels at the test site.

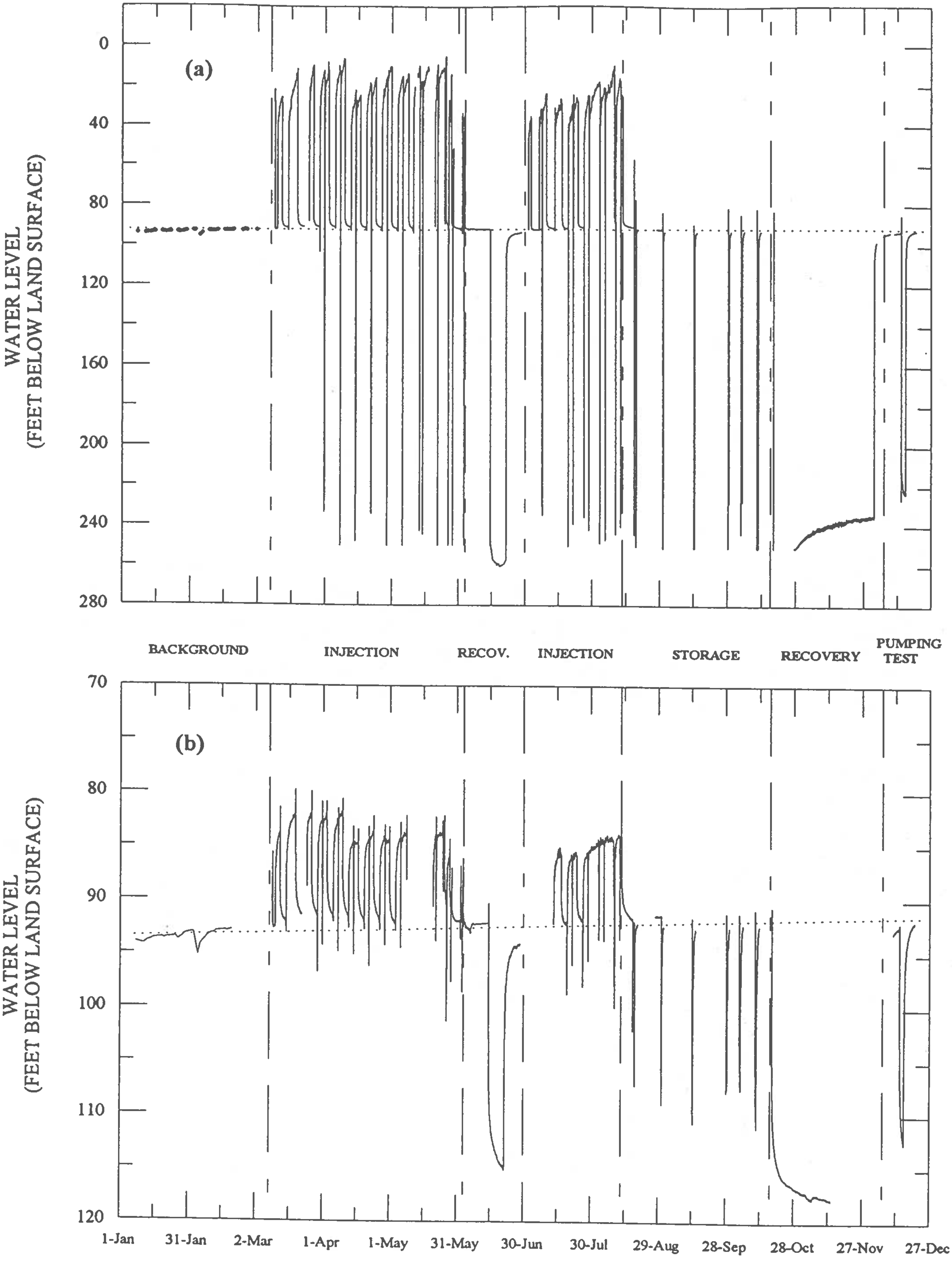

Figure 5. Water level fluctuations (a) in the test well and (b) observation well-zone 2 during the ASR test, 1994.

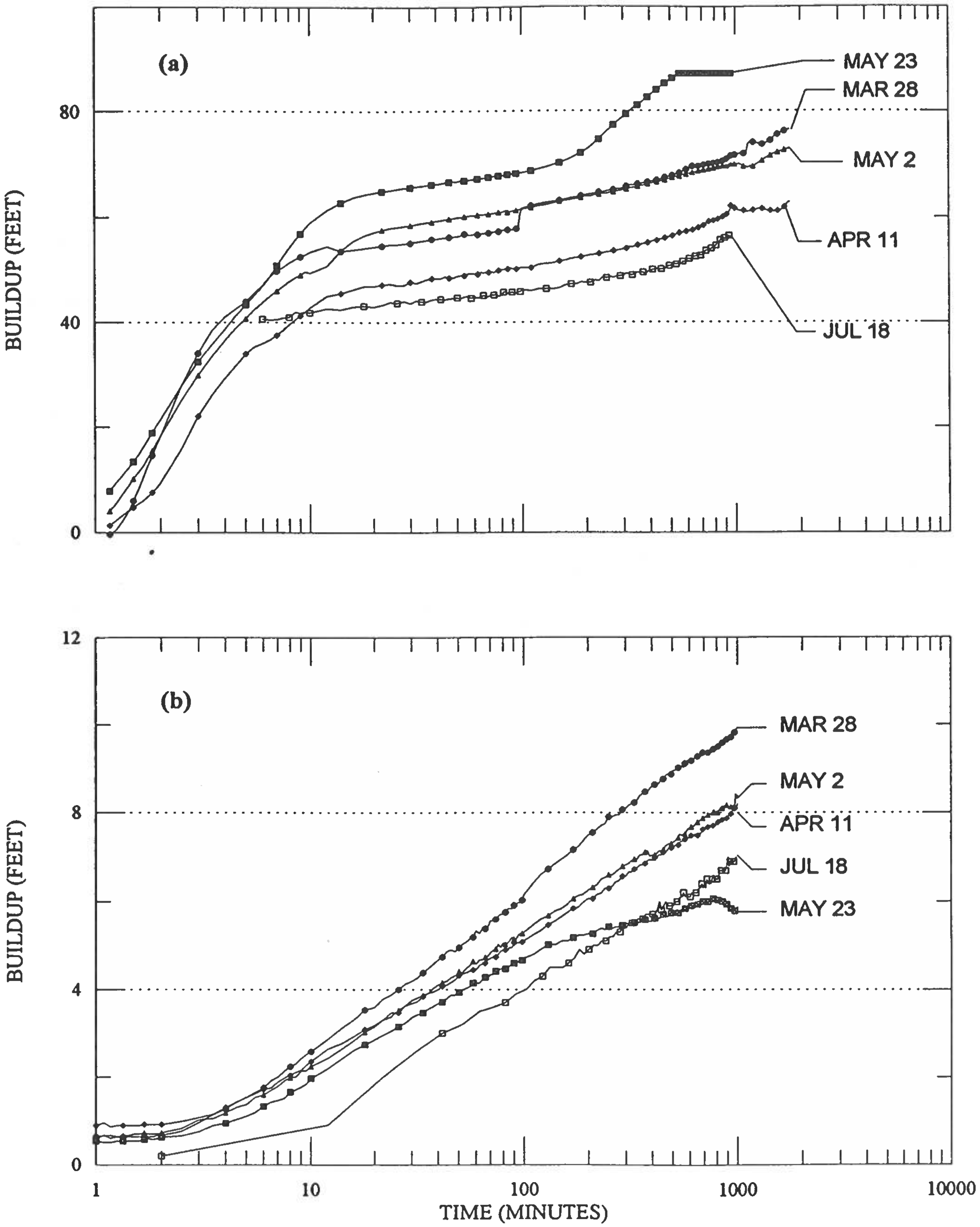

Figure 6. Buildup in (a) test well and (b) observation well-zone 2 before and after the plugging of the well.

AIR PLUGGING AND HIGH WATER LEVELS

Figure 6 shows (a) buildup curves for the test well and (b) observation-well zone 2 during five different injection days. The date indicated in the graphs is the beginning day of the injection test, which normally lasted for at least 900 minutes. In the graphs, the ordinate represents buildup, which was computed by subtracting an arbitrary static level from the injection water levels. Because water levels in the aquifer were constantly changing in response to injection, it was difficult to define a "static level" to compute buildup. Therefore, position of the curves along the Y-axis does not have an important meaning. The slopes, however, are extremely important, they are related to the performance of the well and aquifer. The steeper the slope of the curve, the higher the rate of buildup and the poorer the performance. Four of the five dates chosen for these graphs were arbitrarily selected. The fifth date, May 23, was chosen to illustrate an undesirable performance of the system due to excessive head buildup in the well. This particular test started in the afternoon of May 23, lasted for 950 minutes, and was suspended in the morning of May 24 (refer to RECOVERY section).

A review of these curves reveals that:

- buildup in the test well was larger than buildup in the observation well, as anticipated.

- initial buildup—first 10 minutes—was rapid in the test well and slower in the observation well, as expected.

- for each well, buildup rates (slopes) appeared to be similar for all tests, except for May 23. The similarity of the slopes suggests a consistency and predictability of the system. On May 23, a different behavior of the system was observed. In the test well, after the first 200 minutes, the slope of the buildup curve increased, indicating a faster rate of buildup. At the observation well during the same time interval, the buildup rate decreased. The system behaved as if a hydraulic discontinuity (barrier) partially separated the two wells. It is possible that an air barrier developed around the test well, restricting the flow of water farther into the aquifer. Consequently, continued injection resulted in higher heads at the test well and lower than expected heads at the observation well.

- the buildup curve for July 18, which shows water levels after the corrective action was implemented, has an average rate of buildup (slope) similar to that observed in previous months. Thus, pumping of the test well proved to be an effective remedial procedure to restore the transmissivity and storage capacity of the aquifer.

- for all tests in the test well, the rate of buildup was significantly larger than buildup predicted by ground-water flow equations; the rate of buildup in the observation well, however, appeared to be in good agreement with analytical computations. Figure 7 shows the measured and computed specific recharge for (a) the test well and (b) the observation-well zone 2 during the May 23 injection test. Specific recharge was computed by dividing buildup (feet) by recharge (gallons per minute) and was expressed in feet over gallons per minute. The excessive buildup, as marked in the graph, might be an artifact of the calculations and/or a real head loss due to turbulent flow. The head loss would be artificial if the static water level and the effective diameter of the well were underestimated. The head loss would be the result of turbulent flow if entrance velocities in the filter pack and well screens were greater than 1 ft/sec (Castro, 1995).

INJECTION RATES

During the first injection period, March through June, flow rates averaged 140 gpm and, in general, had a decreasing trend. During the second period, June through August, injection rates were generally smaller, averaging 128 gpm, and had a decreasing trend (Fig. 2). Injection rates normally fluctuated ±7 gpm, owing to pressure changes in the distribution system.

pH MEASUREMENTS

Figure 8 shows the pH of the injected and recovered water measured at the flow-through cell. In order to improve the appearance of the graph, one symbol has been plotted for every four measurements and a 21-term moving average curve has been fitted to the data. During injection, pH hovered around 8 but occasionally rose above 8.5 units. During the first recovery and storage periods the pH at first decreased rapidly to about 7.2 and later increased gradually to 8.5. During the second recovery, the pH decreased from 9 to 8.4, which was the background level. The pH trend during the first recovery period and the storage period are similar, suggesting that the geochemical processes controlling the chemical composition of the water were alike and, therefore, that the processes were reproducible.

WATER TEMPERATURE

Temperatures (Fig. 8) have been plotted with a frequency of four—one symbol for every four

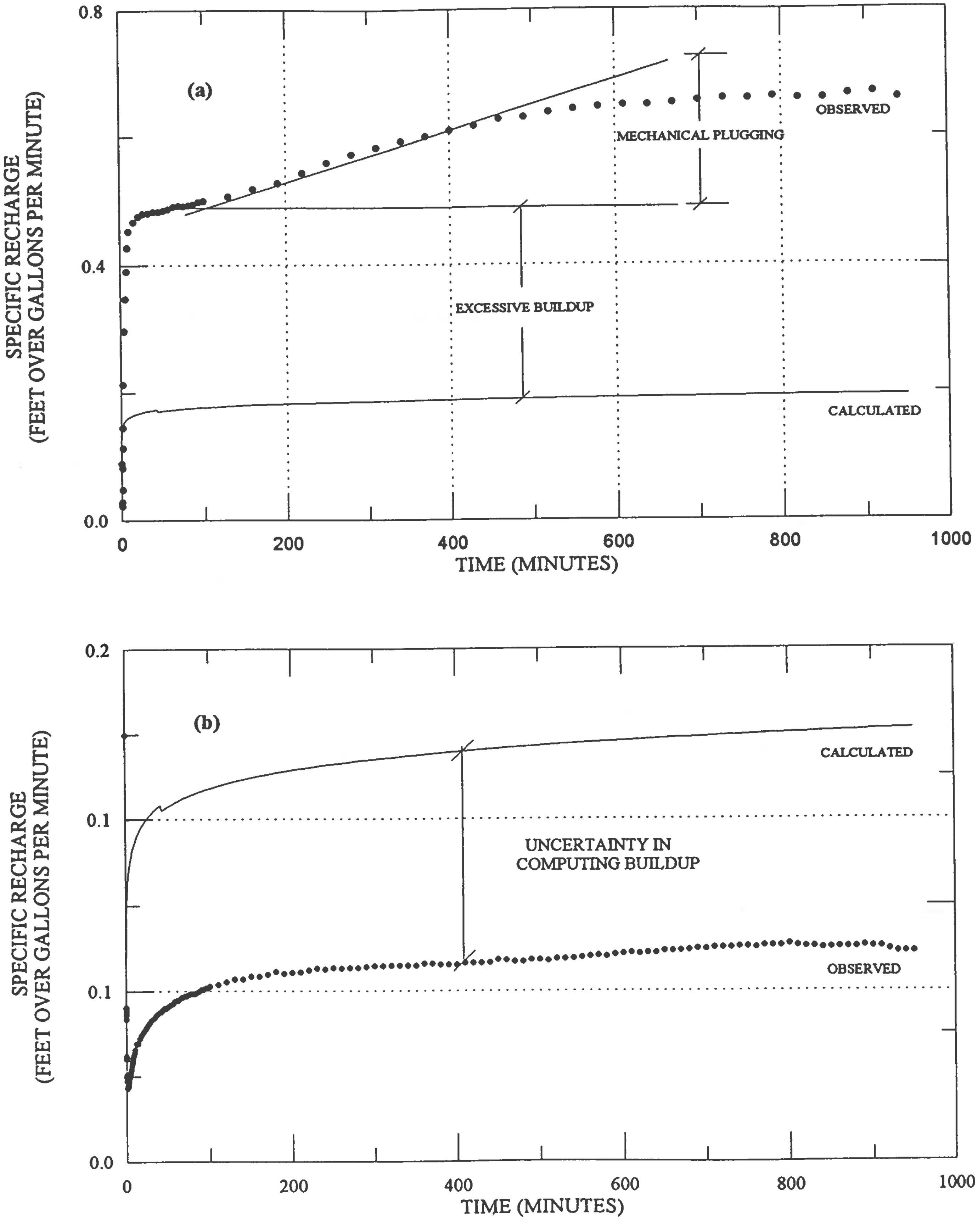

Figure 7. Specific recharge for (a) test well and (b) observation well-zone 2 during the May 23, 1994 test.

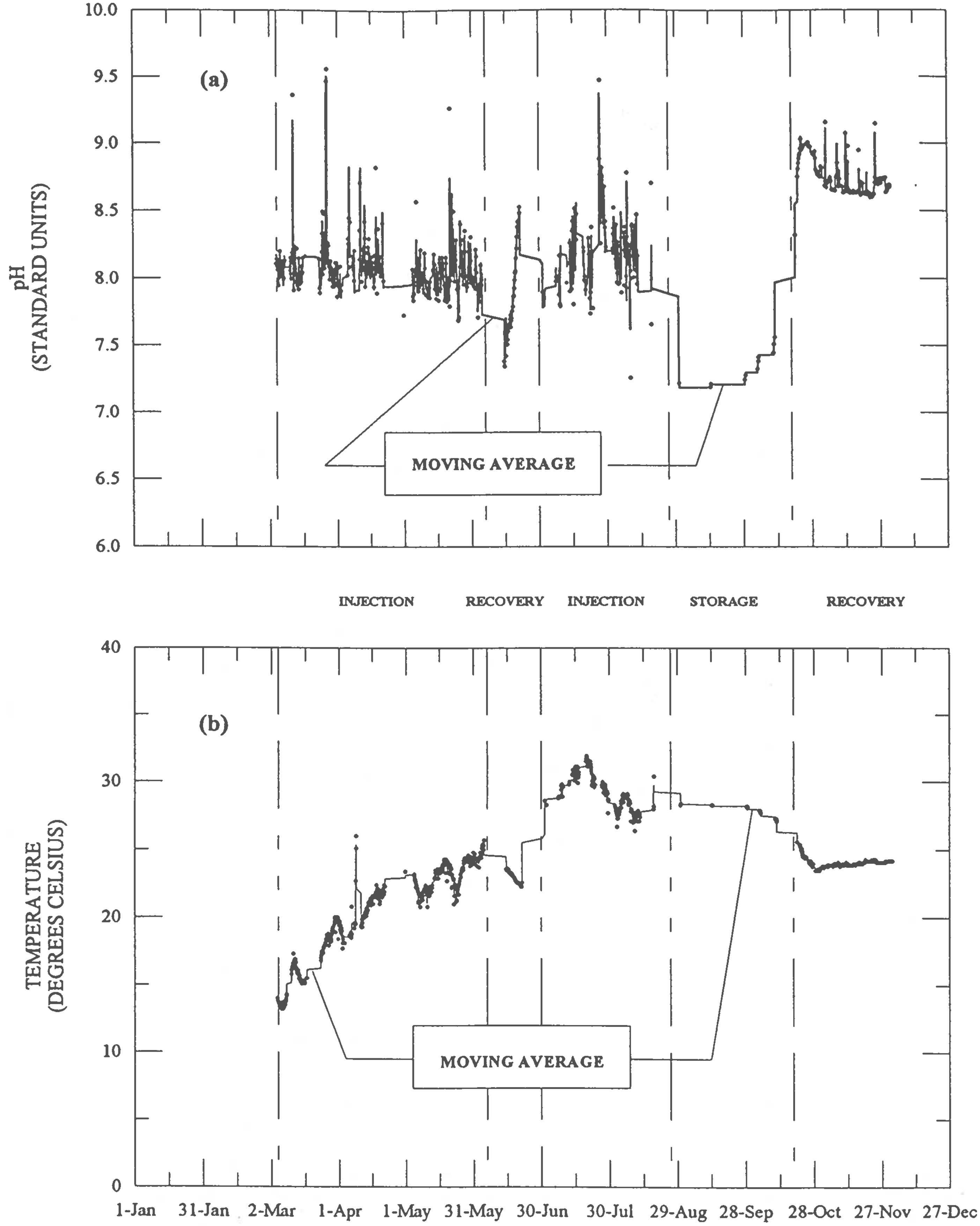

Figure 8. Fluctuations of (a) pH and (b) temperature during the ASR test, 1994. Solid line is 21-term moving average.

measurements—and fitted with a 21-term moving average curve to emphasize important trends. During the first injection period, the temperature increased from 14°C to 25°C, and during the second injection period the temperature increased to a maximum of 32°C. In general, injected-water temperature varied almost 20°C between the first days of March, the beginning of injection, and the middle of July, the end of injection. This large water temperature fluctuation had a significant impact on the aquifer properties and on the chemical composition of the water (Castro 1995). During the recovery and storage periods, temperature normally decreased, showing the effects of mixing of injected and native ground water. Recovered water, at first, had a temperature lower than the native ground water, reflecting a colder injected water (March through May). Water that was recovered during the storage period and second recovery period had a temperature greater than the ground water because of the warmer water injected during the second injection period. Throughout the last recovery period, the water temperature gradually decreased toward the ground water background temperature of 24°C (Hockensmith and Castro, 1993).

BLENDING OF ASR WATER AND SYSTEM WATER

Under production conditions, water that is recovered from an ASR site would need only disinfection before it is pumped—blended—into a distribution system. The final ionic concentration of the potable water after the ASR water is blended into the system, such as might be indicated by chloride and sodium, will depend on the chemical concentration of the two types of water and the proportional volumes of water mixed. Assuming that the ASR water is thoroughly blended with the treated water, the sodium and chloride concentrations can be estimated by using Figure 9. This figure shows concentrations of chloride and sodium in milligrams per liter (a) for different recovery efficiencies and (b) for systems with different numbers of ASR wells.

Figure 9(a) shows that the recovery rate at this site is approximately 70 percent—given by the steepest portion of the curve. At this recovery rate (efficiency) the maximum chloride and sodium concentrations would be 40 and 150 mg/L, respectively, in the recovered water. A blending model, which assumes 70-percent efficiency and a production capacity of 0.5 mgd (million gallons per day) per ASR well, was used to predict concentrations in a system with a water demand of 11.4 mgd—the Myrtle Beach demand in 1992. For example, if a 10-million gallon per day ASR system is built (20 wells), the distribution system would have a chloride concentration of 38 mg/L during September and 30 mg/L during July. Similar calculations showed that a 15-million gallon per day system (30 wells) would still have concentrations of chloride and sodium below the suggested maximum contaminant levels put forth by the National Secondary Drinking Water Standards and the State of South Carolina drinking-water rules.

According to this model, September has the highest concentrations and July the lowest ones. September is the worst-case scenario because it has the lowest demand for the recovery period and, therefore, the smallest volume of potable water in the distribution system available for blending.

The same type of model can be used, for example, to estimate that Myrtle Beach, during the summer, could lower the water temperature in the distribution system by 2°C or 4°C with ASR systems of 10 or 20 ASR wells, respectively. The 10-well ASR network would increase the capacity of the system by 5 mgd and the 20-well ASR system by 10 mgd.

CHEMICAL COMPOSITION OF THE GAS PHASE

During the pumping period of most injection tests, recovered water degassed when it was exposed to the atmosphere. Normally, the degassing lasted less than 5 minutes. The cloudiness of the water, because of the bubbles, varied randomly. On occasions the recovered water was clear, and degassing did not take place for days at a time.

Possible sources of the gas phase were deduced to be: (a) air entrained during injection and (b) geochemical processes that developed in the aquifer. To differentiate these two potential sources, gas samples were collected from the recovered water. Samples were analyzed by gas chromatography with a thermal conductivity detector.

Gas chromatography of these samples indicates that the gas is made up mainly of nitrogen and carbon dioxide. Table 2 shows volume percentages for the four major gasses found in solution. The mean chemical composition of air in the atmosphere, for the mentioned gasses, is provided for comparison. Carbon dioxide ranged from 2 to 17.1 and had a representative value of 16.6 volume percent. This gas in the samples, compared to the atmospheric concentration of 0.03 volume percent, was oversaturated and, in general, had a volume percent 550 times that in the atmosphere.

Dissolved oxygen ranged from 1.7 to 18.1 and had a representative value of 2.6 volume percent. The atmosphere has 21 volume percent. Consequently, the concentration of dissolved oxygen in the samples

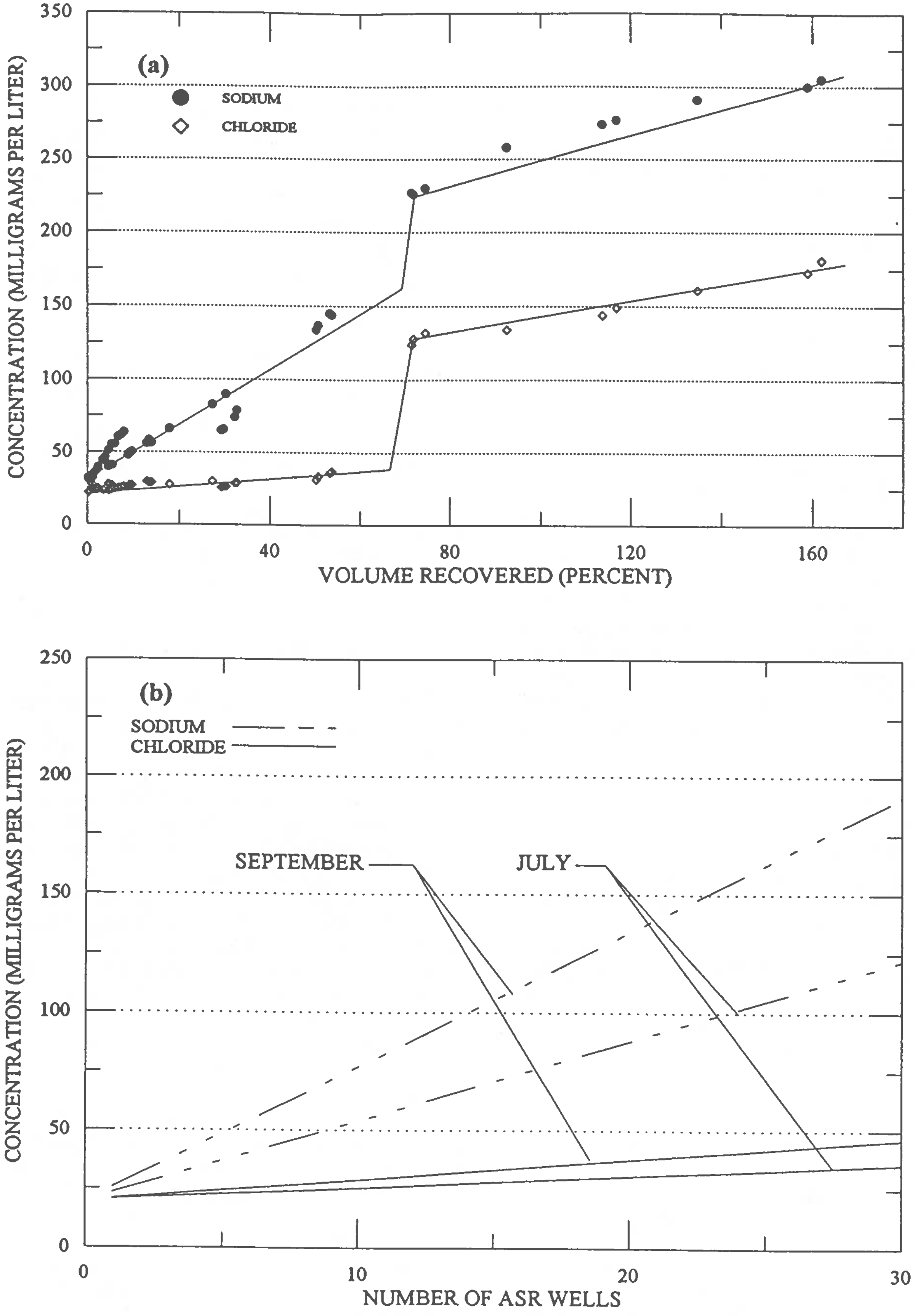

Figure 9. Concentration of sodium and chloride as a function of (a) the volume recovered and (b) number of ASR wells in a system.

Table 2. Chemical composition of gas samples (Analyses by Paul Bradley, U.S. Geological Survey, Columbia, S.C.)

DATE COLLECTED	CARBON DIOXIDE	OXYGEN	NITROGEN	METHANE
	VOLUME PERCENT			
MB 11/14 2:38 PM	17.1	1.7	80.2	1.0
MB 11/14 2:43 PM	16.7	1.8	80.9	.6
MB 11/15 10:05 AM	16.8	2.8	79.6	.7
MB 11/15 3:05 PM	2.0	18.1	79.8	.1
MB 11/16 10:20 AM	15.9	4.1	79.2	.8
MB 11/16 10:27 AM	5.7	14.0	79.8	.5
ATMOSPHERE[1]	0.03	20.9	78.1	.00015

[1] mean composition (Hem, 1985)

appeared undersaturated. The volume percent of most samples was one-eighth the reported volume of dissolved oxygen in the atmosphere.

Nitrogen ranged from 79.2 to 80.9 and had a representative value of 79.9 percent volume, showing a conservative behavior. The atmosphere has 78 volume percent. Nitrogen in the samples was oversaturated and had a volume percent slightly greater than that in the atmosphere. Nitrogen was the largest contributor to the total gas volume in all samples.

Methane ranged from 0.1 to 1.0 and had a representative value of 0.62 volume percent. The atmosphere has a value of 0.00015 volume percent. Although volumes measured in samples are larger than those found in the atmosphere, methane contribution to the total volume of the sample is small and, therefore, not of great consequence in the analysis.

The most likely source of nitrogen gas appears to be air entrained in the system during injection. The most likely source for carbon dioxide appears to be biochemical reactions. Bacterially mediated processes, such as respiration, consumed oxygen, decreasing the concentration of O_2 in solution, and produced CO_2, increasing the concentration of DIC (dissolved inorganic carbon) in solution. These two gasses, in samples collected at the Myrtle Beach site, were inversely correlated and had a correlation coefficient of -0.997. The same biological process, moreover, was independently identified by geochemical modeling of the ground water system. Air entrainment, more than the biogeochemical reaction, appeared to be the dominant source of gas in the recovered water.

The presence of nitrogen gas in the recovered water was attributed to air entrainment only, although geochemical modeling has shown that denitrification could take place in the aquifer. Nitrate reduction, via organic matter fermentation, could not account for most of the nitrogen gas in the water samples, because denitrification was constrained by the availability of organic matter in the aquifer.

AIR ENTRAINMENT

This is a common problem and very often the single most important cause for failure in ASR projects. Inasmuch as the test well was not originally designed to function as an injection well, it may be more susceptible to air entrainment problems. In the Myrtle Beach ASR well, the problem appears to originate during injection. When injection is started, after the well has been sitting idle or after a backflush cycle, air filling the pipes is driven into the aquifer. Moreover, injected water moving downward in the pump column, when under vacuum conditions, will force air through faulty valves or joints into the aquifer. The air, eventually, will lodge in the pore spaces of the aquifer, reducing its transmissivity and storage capacity.

A solution to this problem is to alter the system design to inject only under positive heads. This could be achieved by installing a flow-control valve. This valve is made of two pipes, one inside the other. The outer pipe, which has been modified to increase its rugosity, houses an air packer. The inner pipe, which has the same diameter as the pump column, has a check valve at the end of it (Baski, 1994). During injection, the packer is deflated and the check valve closed, forcing the water to flow in the outer pipe. The rugosity of the outer pipe induces high energy losses by friction, forcing the water to back up in the pump column and allowing the system to work under positive heads. During recovery, the check valve is open and the packer inflated, allowing the water to flow though the inner pipe into the pump column and up the well without interference from the packer. The packer, moreover, is used to regulate the injection rate by controlling the clearance between the packer and the outer pipe. Although the flow-control valve is one of many designs available for reducing air-entrainment problems (Pyne, 1995), this type of valve appears to be simple and effective, and therefore it is recommended by the author for the Myrtle Beach wells.

TRANSMISSIVITY VALUES AND INJECTION TESTS

Beginning in October 1990 and ending in December 1994, several pumping tests were completed at the ASR injection site. The purpose of these tests was to ascertain if changes occurred in the aquifer after the ASR tests. The analysis of an earlier test, made by the well driller in October 1982, suggests a transmissivity of 12,000 gpd/ft (gallons per day per foot). This value is in good agreement with transmissivities obtained from the tests completed between 1990 and 1994; although the values varied slightly among the tests and among pumping and recovery phases of the tests. The last pumping test, completed in December 1994 at this site, suggested a transmissivity of 11,000 gpd/ft, which is less than the average noted above. The difference is less than 10 percent, easily within the limits of accuracy in interpretation of pumping-test data. Consequently, on the basis of the pumping-test information there is no conclusive evidence that the injection tests have adversely affected the transmissivity of the aquifer.

GEOCHEMICAL PROCESSES

Laboratory measurements of major anions and cations for samples collected during the 1994 ASR test were made at the Environmental Laboratory of Coastal Carolina University, Conway, S.C. Results are presented in Table 3. It is necessary to explain that the data set compiled during 1994 does not completely agree with the data set compiled in 1992 (Castro, 1995). The difference mainly relates to background concentrations in the makeup of the native ground water. Specifically, the chloride concentration for the test well (5S-i8) was determined to be 141 mg/L in 1992 and 180 mg/L in 1994. Efforts were made to explain this difference, but no satisfactory answer was found. Field and laboratory procedures, as well as quality-control and quality-assurance programs, were rigorously implemented. It is equally important to state that, for the geochemical analyses used in the interpretation of the data, absolute values are less important than relative values; because the analysis is based on the concept that water samples evolved from two end members, the treated water and the ground water. Consequently, the data set collected in 1994 was deemed adequate for the analyses.

The geochemical analysis of this data set corroborated the findings of previous ASR tests. Near the well bore, geochemical reactions affected the quality of the water, and most of the reactions developed under aerobic conditions. Farther away from the well bore, chemical reactions and mixing controlled the quality of the water, and these reactions developed under anaerobic conditions. Beyond this zone, mixing alone determined the chemical composition of the water, and the environment in this zone was purely anaerobic. Both aerobic and anaerobic bacteria catalyzed several of the chemical reactions and produced appreciable quantities of dissolved inorganic carbon.

NUMERICAL MODELING

Modeling of the chemical evolution of the water injected, stored, and recovered in the aquifer during the ASR tests followed an "inverse" approach proposed by Plummer, 1984. A numerical model "Net Geochemical Reactions Along A Flow Path" (NETPATH) developed by the U.S. Geological Survey (Plummer and others, 1991) was used to estimate mass transfers between minerals present in the aquifer and the injected water. The purpose of the modeling effort was to identify those processes that affected the chemical composition of the stored water.

In modeling the system, it was assumed that water samples collected during the storage and recovery periods evolved from a mixture of injected surface water and native ground water and from chemical reactions with the aquifer matrix. For a given water sample, the ionic concentration that was contributed by mixing was estimated from tritium or chloride concentrations. Both constituents behaved conservatively in this system (Castro, 1995). Ionic concentrations contributed by chemical reactions were determined by an iterative mass-balance procedure using the NETPATH code. Plausible reactions were postulated, on the basis of mineralogical information, and tested in the numerical model. The procedure was repeated until the proposed set of reactions produced a mass transfer that when added to the ionic concentrations from mixing equaled the composition of the water sample being modeled. Mass transfers entering or leaving the injected water, moreover, were restricted by the water's state of saturation with respect to mineral phases present in the aquifer. Model solutions were not always unique and several models often were obtained for the same set of conditions. Further discrimination

Table 3. Water quality properties and constituents analyzed

Sample ID	Julian Days	Date	Time	Spec cond. µS/cm	Temp. deg. C	Field Alk mg/L	Field pH	Field D.O. mg/L	Lab Alk mg/L	Lab pH	Aluminum mg/L	Boron mg/L	Calcium mg/L	Chloride mg/L
M1TA0222	**53.5**	**02/22/94**	**1240**	**263**	**13.6**	**31**	**8.1**	**10.94**	**30**	**8.2**	**0.625**	**0.15**	**13.0**	**13.1**
M1TA0315	74.4	03/15/94	1035	242	15.1	34	8.1	9.89	31	8.0	1.006	0.05	15.8	20.0
M1TA0322	81.4	03/22/94	1035	253	16.7	38	8.5	9.48	34	8.0	1.171	0.08	16.0	18.9
M1TA0329	88.4	03/29/94	1030	279	18.9	39	7.9	10.07	27	7.9	0.916	0.09	21.4	20.9
M1TA0411	101.6	04/11/94	1510	269	20.3	36	8.1	12.07	27	8.1	0.866	0.10	19.6	21.1
M1TA0425	115.6	04/25/94	1505	269	22.4	38	8.0	8.40	30	7.9	0.524	0.09	19.4	21.3
M1TA0509	129.6	05/09/94	1320	258	22.1	32	7.8	8.54	31	7.9	0.555	0.10	16.1	20.5
M1TA0523	143.4	05/23/94	1035	271	22.5	33	7.9	8.43	31	8.0	0.571	0.11	16.9	21.0
M1WA0613	164.4	06/13/94	1030	361	23.5	71	7.4	<0.1	72	7.6	0.155	0.13	28.6	28.8
M2WA0613	164.6	06/13/94	1340	355	23.6	66	7.4	<0.1	66	7.6	0.162	0.14	27.0	27.2
M1WA0614	**165.4**	**06/14/94**	**0905**	**375**	**23.7**	**72**	**7.7**	**<0.1**	**78**	**7.6**	**0.190**	**0.10**	**26.4**	**27.5**
M2WA0614	165.5	06/14/94	1110	377	23.5	72	7.6	<0.1	79	7.6	0.170	0.10	26.6	26.9
M3WA0614	165.6	06/14/94	1420	380	23.5	79	7.5	<0.1	80	7.5	0.146	0.13	26.0	26.5
M1WA0615	166.4	06/15/94	0940	391	23.3	91	7.6	<0.1	89	7.6	0.172	0.18	24.9	26.0
M2WA0615	166.5	06/15/94	1120	394	23.2	90	7.6	<0.1	91	7.7	0.136	0.20	24.7	26.9
M3WA0615	166.6	06/15/94	1425	397	23.3	94	7.6	<0.1	89	7.7	0.156	0.19	25.0	26.9
M1WA0616	167.4	06/16/94	0915	414	23.1	100	7.5	<0.1	95	7.8	0.212	0.16	22.9	29.6
M2WA0616	167.5	06/16/94	1135	415	23.1	101	7.6	<0.1	98	7.8	0.147	0.16	23.4	29.1
M3WA0616	167.6	06/16/94	1435	417	23.0	99	7.7	<0.1	100	7.9	0.186	0.11	21.9	29.1
M1WA0617	168.5	06/17/94	1240	435	22.9	109	7.7	<0.1	107	7.9	0.204	0.13	18.8	27.5
M1WA0619	**170.8**	**06/19/94**	**1805**	**486**	**22.4**	**138**	**8.2**	**<0.1**	**139**	**8.4**	**0.298**	**0.15**	**13.5**	**29.9**
M1WA0620	171.5	06/20/94	1105	507	22.3	147	8.5	<0.1	148	8.6	0.388	0.14	13.1	26.2
M1TA0706	187.6	07/06/94	1440	273	28.7	39	8.1	7.68	38	8.2	0.574	0.10	12.9	22.7
M1TA0718	199.5	07/18/94	1115	269	31.5	40	8.0	7.36	37	8.0	0.493	0.13	11.0	22.9
M1TA0801	213.4	08/01/94	1040	277	27.5	38	8.3	7.87	38	8.2	0.518	0.07	17.3	18.6
M1TA0811	223.4	08/11/94	1000	272	27.6	39	8.2	7.82	37	8.1	0.491	0.10	15.3	19.4
M1WA0817	229.4	08/17/94	0950	363	28.0	72	7.6	<0.1	72	7.9	0.200	0.07	26.1	22.1
M2WA0817	229.5	08/17/94	1050	347	28.1	63	7.6	<0.1	63	7.7	0.190	0.07	25.9	21.9
M3WA0817	229.5	08/17/94	1150	340	28.1	59	7.5	<0.1	58	7.7	0.191	0.08	24.2	22.3
M1WA0829	241.5	08/29/94	1110	365	28.3	70	7.3	<0.1	74	7.6	0.182	0.12	28.3	24.3
M2WA0829	**241.5**	**08/29/94**	**1310**	**358**	**28.4**	**69**	**7.2**	**<0.1**	**70**	**7.5**	**0.166**	**0.13**	**27.0**	**24.8**
M3WA0829	241.6	08/29/94	1510	358	28.4	71	7.2	<0.1	72	7.4	0.153	0.12	26.8	25.0
M1WA0912	255.4	09/12/94	0850	379	28.3	80	7.2	<0.1	82	7.4	0.139	0.07	27.0	24.0
M2WA0912	255.5	09/12/94	1150	380	28.3	83	7.2	<0.1	83	7.5	0.118	0.04	27.1	24.4
M3WA0912	255.6	09/12/94	1450	385	28.3	84	7.2	<0.1	85	7.4	0.120	0.04	27.2	24.7
M2WA0927	270.7	09/27/94	1605	404	28.2	94	7.3	<0.1	99	7.4	0.116	0.13	24.3	23.3
M3WA0927	270.8	09/27/94	2005	415	28.1	100	7.3	<0.1	101	7.4	0.127	0.11	25.0	24.1
M1WA1003	276.2	10/03/94	0455	414	27.9	101	7.3	<0.1	105	7.6	0.115	0.12	22.8	22.9
M2WA1003	276.4	10/03/94	0950	415	27.9	103	7.4	<0.1	108	7.6	0.112	0.12	22.5	24.0
M3WA1003	276.6	10/03/94	1455	429	27.7	108	7.4	<0.1	115	7.6	0.114	0.10	22.9	24.7
M1WA1010	**283.2**	**10/10/94**	**0450**	**425**	**27.3**	**109**	**7.5**	**<0.1**	**109**	**7.7**	**0.113**	**0.12**	**21.6**	**24.9**
M2WA1010	283.4	10/10/94	0950	435	27.3	111	7.5	<0.1	114	7.7	0.120	0.11	20.8	25.4
M3WA1010	283.6	10/10/94	1450	445	27.1	116	7.6	<0.1	119	7.8	0.130	0.12	20.1	25.9
M1WA1017	290.5	10/17/94	1137	450	26.8	120	7.5	<0.1	120	7.6	0.116	0.11	17.2	25.7
M2WA1017	290.6	10/17/94	1435	440	26.8	112	7.6	<0.1	117	7.8	0.120	0.13	17.1	26.4
M1WA1018	291.5	10/18/94	1110	472	26.3	131	7.9	<0.1	133	8.1	0.150	0.19	17.0	28.6
M2WA1018	291.6	10/18/94	1410	476	26.2	132	7.9	<0.1	144	8.1	0.154	0.20	15.7	29.1
M1WA1024	297.4	10/24/94	1040	695	24.0	245	9.1	<0.1	251	9.1	0.361	0.58	11.5	31.3
M2WA1024	297.6	10/24/94	1340	699	24.0	247	9.0	<0.1	253	9.1	0.345	0.59	11.7	33.7
M1WA1025	298.4	10/25/94	1010	736	24.1	270	9.0	<0.1	268	9.1	0.330	0.61	12.2	36.1
M2WA1025	**298.5**	**10/25/94**	**1310**	**739**	**23.6**	**270**	**9.0**	**<0.1**	**272**	**9.1**	**0.342**	**0.66**	**13.0**	**37.0**
M1WA1031	304.4	10/31/94	1010	1087	23.7	374	8.8	<0.1	384	8.9	0.214	1.90	10.6	124.0
M2WA1031	304.5	10/31/94	1310	1092	23.8	383	8.8	<0.1	382	9.0	0.216	1.35	11.4	128.0
M1WA1101	305.4	11/01/94	1010	1126	23.9	391	8.7	<0.1	382	8.8	0.210	1.42	10.3	132.0
M1WA1107	311.4	11/07/94	1010	1237.0	23.8	444	9.2	<0.1	448	8.9	0.173	1.99	8.3	134.0
M1WA1114	318.4	11/14/94	1040	1301.0	24.0	462	8.6	<0.1	480	8.9	0.143	2.22	8.0	144.0
M1WA1115	319.5	11/15/94	1135	1311.0	24.0	468	8.6	<0.1	477	8.9	0.143	2.47	7.7	149.0
M1WA1121	325.4	11/21/94	1010	1337.0	24.2	491	8.6	<0.1	494	8.8	0.134	2.33	7.2	161.0
M1WA1129	333.4	11/29/94	1010	1356.0	24.2	479	8.7	<0.1	500	8.8	0.121	2.38	6.4	173.0
M1WA1130	334.4	11/30/94	1010	1357.0	24.2	477	8.7	<0.1	499	8.8	0.114	2.56	6.3	181.0

Spec cond., specific conductance in microsiemens per centimeter
D.O., dissolved oxygen
Alk, alkalinity as an equivalent concentration of calcium carbonate
PDB, Peedee Belemnites
TOC, total organic carbon
TU, tritium units
THM, trihalomethane
THMP, trihalomethane potential

for samples collected during the 1994 ASR test

Carbon-13 mil (PDB)	Fluoride mg/L	Iron mg/L	Magnesium mg/L	Manganese mg/L	Nitrate mg/L	TOC mg/L	Phosphate mg/L	Potassium mg/L	Silica mg/L	Sodium mg/L	Sulfate mg/L	Sulfide mg/L	Tritium TU	THM µg/L	THMP µg/L
---		**0.056**	**1.96**	**0.024**	**---**	**---**	**0.010**	**2.61**	**6.7**	**25.4**	**52.3**	**0.14**	**---**	**---**	**---**
---	1.2	0.089	1.51	0.020	0.30	---	0.011	2.47	4.6	25.3	47.2	0.10	---	---	---
---	0.9	0.100	1.75	0.022	0.30	---	0.022	2.42	3.7	25.4	48.5	0.10	---	---	---
---	0.9	0.108	1.81	0.026	0.35	---	0.028	2.18	3.2	25.8	55.8	0.10	---	---	---
---	0.9	0.063	1.72	0.022	0.29	7.39	0.010	2.27	3.8	25.0	51.7	0.11	---	27.9	827
---	1.3	0.043	1.84	0.025	0.40	5.92	0.012	2.73	5.4	27.8	48.4	<0.1	---	20.0	667
---	1.1	0.041	1.77	0.017	0.38	5.48	0.016	2.37	6.4	27.8	41.5	<0.1	14.7	21.8	557
-19.50	1.2	0.023	1.94	0.014	0.52	5.00	0.014	2.78	7.2	29.5	51.8	<0.1	16.2	20.5	555
-9.64	0.9	0.049	3.48	0.049	0.02	3.48	0.180	3.51	8.4	32.6	54.7	<0.1	16.9	9.6	359
---	1.0	0.046	3.16	0.047	<0.01	---	0.160	3.27	7.6	33.6	57.9	<0.1	---	---	---
-10.75	**1.3**	**0.024**	**2.72**	**0.045**	**<0.01**	**3.08**	**0.120**	**2.91**	**6.4**	**39.5**	**57.6**	**<0.1**	**16.6**	**2.2**	**317**
---	1.3	0.024	2.79	0.044	0.02	---	0.130	2.43	6.1	41.1	56.2	<0.1	---	---	---
---	1.3	0.023	2.73	0.045	0.02	---	0.130	2.42	6.1	40.7	51.3	<0.1	---	---	---
-7.27	1.4	0.024	2.37	0.038	<0.01	3.35	0.120	3.21	5.5	47.6	58.3	<0.1	15.1	1.3	351
---	1.4	0.023	2.42	0.037	<0.01	---	0.120	3.13	5.7	48.9	60.1	<0.1	---	---	---
---	1.4	0.026	2.27	0.038	<0.01	---	0.120	3.10	5.5	49.8	59.2	<0.1	---	---	---
-7.34	1.4	0.023	1.98	0.034	<0.01	3.88	0.120	3.34	5.2	55.8	59.2	<0.1	13.9	1.0	403
---	1.4	0.019	1.94	0.031	<0.01	---	0.130	3.30	5.2	57.9	60.6	<0.1	---	---	---
---	1.4	0.024	1.89	0.033	<0.01	---	0.130	3.23	5.2	56.2	57.8	<0.1	---	---	---
---	1.4	0.024	1.61	0.028	<0.01	---	0.140	3.28	5.0	65.8	59.7	<0.1	---	---	---
---	**1.5**	**0.031**	**1.23**	**0.014**	**<0.01**	**---**	**0.185**	**2.83**	**4.4**	**82.6**	**58.3**	**<0.1**	**---**	**---**	**---**
-7.69	1.6	0.036	1.87	0.019	<0.01	4.38	0.194	3.08	4.4	89.5	60.6	<0.1	13.9	1.0	406
-18.23	0.7	0.036	1.59	0.012	0.41	5.31	0.028	2.87	6.2	31.5	47.3	<0.1	16.4	27.0	540
-18.34	0.8	0.029	1.70	0.012	0.41	4.40	0.037	2.99	6.9	33.0	47.8	<0.1	19.3	24.0	543
-17.64	0.8	0.016	1.66	0.014	0.37	3.51	0.026	2.66	5.6	28.4	50.1	<0.1	12.3	23.4	433
-17.09	0.7	0.015	1.82	0.013	0.38	3.68	0.028	3.06	6.3	29.2	49.2	<0.1	19.0	21.0	421
-10.75	0.6	0.031	3.22	0.030	0.22	2.66	0.280	4.04	7.3	31.8	62.0	<0.1	19.6	15.7	280
---	0.6	0.028	3.00	0.028	0.25	---	0.265	4.08	7.3	31.0	61.1	<0.1	---	---	---
---	0.6	0.030	2.80	0.028	0.24	---	0.251	3.67	7.3	31.5	56.8	<0.1	---	---	---
-10.41	0.7	0.077	3.18	0.048	<0.01	2.82	0.262	3.65	8.3	30.9	60.6	<0.1	15.9	6.9	274
---	**0.7**	**0.050**	**2.97**	**0.046**	**<0.01**	**---**	**0.244**	**3.34**	**7.7**	**32.0**	**58.4**	**<0.1**	**---**	**---**	**---**
---	0.8	0.049	2.95	0.044	<0.01	---	0.221	3.15	7.5	31.9	58.0	<0.1	---	---	---
-8.97	1.0	0.086	3.02	0.061	<0.01	3.13	0.205	3.15	7.6	35.6	58.2	<0.1	15.5	1.7	278
---	1.0	0.079	2.95	0.053	<0.01	---	0.190	3.17	7.3	37.1	57.7	<0.1	---	---	---
---	1.1	0.067	2.98	0.050	<0.01	---	0.184	3.12	7.1	39.3	57.3	<0.1	---	---	---
-8.36	1.0	0.098	2.78	0.045	<0.01	2.44	0.186	3.12	6.5	44.1	54.3	<0.1	14.7	<0.1	---
---	1.0	0.079	2.85	0.047	<0.01	---	0.186	3.10	6.4	46.4	55.9	<0.1	---	---	---
-7.58	1.0	0.107	2.56	0.043	<0.01	2.48	0.201	3.29	6.3	50.9	57.7	<0.1	16.3	<0.1	237
---	1.1	0.087	2.55	0.041	<0.01	---	0.200	3.21	6.1	54.8	55.3	<0.1	---	---	---
---	1.1	0.093	2.45	0.038	<0.01	---	0.201	3.30	6.0	55.2	56.3	<0.1	---	---	---
-7.31	**1.1**	**0.086**	**2.02**	**0.034**	**<0.01**	**2.71**	**0.227**	**3.09**	**6.0**	**60.2**	**51.4**	**<0.1**	**15.9**	**<0.1**	**248**
---	1.1	0.064	2.02	0.033	<0.01	---	0.217	3.18	5.8	61.2	51.0	<0.1	---	---	---
---	1.1	0.055	1.92	0.031	<0.01	---	0.218	3.31	5.6	63.2	53.4	<0.1	---	---	---
-7.26	1.2	0.099	1.70	0.027	<0.01	2.39	0.266	3.73	5.7	64.9	47.6	<0.1	17.0	<0.1	249
---	1.2	0.077	1.62	0.027	<0.01	---	0.259	3.25	5.6	65.5	52.6	<0.1	---	---	---
-6.68	1.3	0.043	1.50	0.019	<0.01	2.67	0.239	3.57	5.2	73.8	56.2	<0.1	---	---	---
-6.74	1.3	0.043	1.37	0.021	<0.01	2.81	0.238	3.64	5.1	78.7	51.1	<0.1	---	---	---
-6.03	2.1	0.045	0.96	0.008	<0.01	4.72	0.209	3.81	5.8	134.0	54.3	<0.1	---	---	---
-7.67	2.1	0.036	0.96	0.007	<0.01	3.25	0.203	3.81	5.8	137.0	55.4	<0.1	10.7	<0.1	404
-6.40	2.3	0.033	0.94	0.006	<0.01	4.89	0.190	3.98	5.9	145.0	53.8	<0.1	---	---	---
-6.23	**2.3**	**0.021**	**0.92**	**0.006**	**<0.01**	**4.89**	**0.187**	**4.01**	**6.0**	**144.0**	**52.8**	**<0.1**	**9.0**	**<0.1**	**414**
-6.60	3.6	0.013	1.11	0.007	<0.01	2.79	0.120	8.60	6.6	227.0	23.2	<0.1	---	---	---
-6.60	3.5	0.013	1.19	0.008	<0.01	2.64	0.120	8.06	6.9	226.0	22.2	<0.1	4.2	<0.1	327
-6.56	3.6	0.012	1.19	0.008	<0.01	2.64	0.118	8.02	7.1	230.0	20.8	<0.1	---	---	---
-6.60	3.7	0.012	1.30	0.008	<0.01	2.03	0.103	7.12	7.3	258.0	14.0	<0.1	0.9	<0.1	323
-6.56	3.7	0.011	1.38	0.008	<0.01	1.86	0.097	7.04	8.0	274.0	9.1	<0.1	---	---	---
-6.36	3.7	0.012	1.40	0.007	<0.01	1.86	0.096	7.10	7.9	277.0	7.8	<0.1	<0.8	<0.1	323
-6.18	3.6	0.011	1.40	0.008	<0.01	1.77	0.103	6.57	9.7	291.0	6.5	<0.1	---	---	---
-6.03	3.7	0.011	1.36	0.007	<0.01	5.89	0.101	6.24	10.3	300.0	4.8	<0.1	<0.6	---	---
-7.34	3.7	0.011	1.40	0.007	<0.01	1.40	0.100	6.09	10.5	305.0	5.1	<0.1	---	<0.1	404

of models on the basis of mineralogic and isotopic information, therefore, was necessary to validate a solution.

DISSOLVED INORGANIC CARBON AND δ^{13}C

The study of the chemical composition of water samples collected throughout the test clearly indicated a considerable increase in alkalinity during the storage of treated water in the aquifer. Figure 10 shows alkalinity expressed as calcium carbonate in milligrams per liter. Alkalinity doubled in a period of 7 days from an average of 40 mg/L during injection to almost 80 mg/L during the first recovery period. None of this alkalinity was contributed by the native ground water, based on the tritium activity. The gain in alkalinity or, better, the gain in DIC (dissolved inorganic carbon), consequently, had to come from some other processes. Two possible sources for DIC are (1) respiration and fermentation processes coupled with calcium carbonate dissolution in the aquifer and (2) diffusion of DIC and organic acids from confining beds (Chapelle and McMahon, 1991). DIC isotopic composition of these possible sources—δ^{13}C in ‰ (permil) relative to the PDB (Peedee Belemnite) standard—was used to determine the possible origin of the DIC in the water samples. The δ^{13}C of the calcite cement in the Black Creek aquifer is +1.1‰ and of the DIC from confining beds is -12‰ (McMahon and Chapelle, 1991). The δ^{13}C for the injected water ranged from -19.5 to -17.09‰ and for the early water samples it ranged from -10.75 to -9.64‰.

$$CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^{+2} + 2HCO_3^- \quad (1)$$

$$\tfrac{1}{2}(+1.1\text{‰}) + \tfrac{1}{2}(-22\text{‰}) = -10.45\text{‰} \quad (2)$$

During calcium carbonate dissolution (Eq. 1) the resulting δ^{13}C of the DIC has a carbon composition that is 50 percent from calcite and 50 percent from biological CO_2. The CO_2, which is produced during respiration or fermentation of organic matter, has a δ^{13}C of -22‰, similar to the δ^{13}C of organic matter (-25‰). If calcium carbonate has a δ^{13}C of +1.1‰, the δ^{13}C of the DIC would be -10.45‰ (Eq. 2), which is similar to values measured in the water samples. This implies that extremely large quantities of calcite were dissolved to enrich the δ^{13}C of the injected water from -17.09 to -10.75‰, which rendered this scenario unlikely.

During the numerical modeling of the system, various attempts were made to simulate the production of CO_2 in the aquifer; however, no realistic results were obtained. A CO_2 phase was always necessary to achieve a feasible solution. This suggested that the source of CO_2 might not have been in the aquifer but in the confining beds, as postulated by Chapelle and McMahon, 1991. If the CO_2 from the confining beds had a δ^{13}C of -12‰ and the calcite from the aquifer had a δ^{13}C +1.1‰, then the resulting DIC would have a δ^{13}C of -5.45‰. Numerical models, under this condition, obtained isotopic mass balance by incongruently dissolving less than 0.3 millimole of calcium carbonate per kilogram of solution, which appears reasonable. Subsequent models, therefore, were developed by assuming the presence of a CO_2 phase with a δ^{13}C of -5.45‰.

Heavier isotopic DIC composition can be obtained if calcite dissolves without a CO_2 phase. Under this condition, calcite dissolution produces solutions with pH's near 10. Since the pH of water samples ranged from 7.4 to 9.1, it was concluded that calcite dissolved in the presence of CO_2.

GEOCHEMICAL RESULTS

Results of the geochemical model are presented in Figure 11. Thirteen water samples were simulated. Each water sample was modeled by considering that it evolved from the injected water rather than from a previous sample. For example, if T, 1, and 2 represent treated surface water, samples 1 and 2, then sample 2 was simulated as if it evolved from T only. The other option was to model sample 2, assuming that it evolved from sample 1 instead. The difference lies in the interpretation of results. In the first case, the overall contribution from chemical reactions of the injected water with the aquifer matrix is determined; in the second case, only the incremental contribution is determined.

For water samples collected from August 17 to October 10—sample ID between m1wa0817 and m3wa1010—mixing was not considered. For samples after October 10 (ID m3wa1010) mixing of injected water and native ground water was allowed, as indicated by tritium concentrations. For all models, the same constraints (elements) and mineral phases were selected. Figure 11 shows that the system consumed 0.4 to 0.8 mmol (millimole) of carbon dioxide per kilogram (Kg) of solution and that the rate of consumption was greater in early samples and nearly constant in later samples. As much as 0.8 mmol/Kg of calcium carbonate dissolved (positive mass transfer) during the storage period and very little during the recovery period. The sodium-calcium exchange process mimicked the latter one, suggesting that calcium from calcite dissolution was exchanged for sodium. Lignite oxidation—aerobic and anaerobic—gradually increased from near zero during early samples to 0.3 mmol/Kg during later samples.

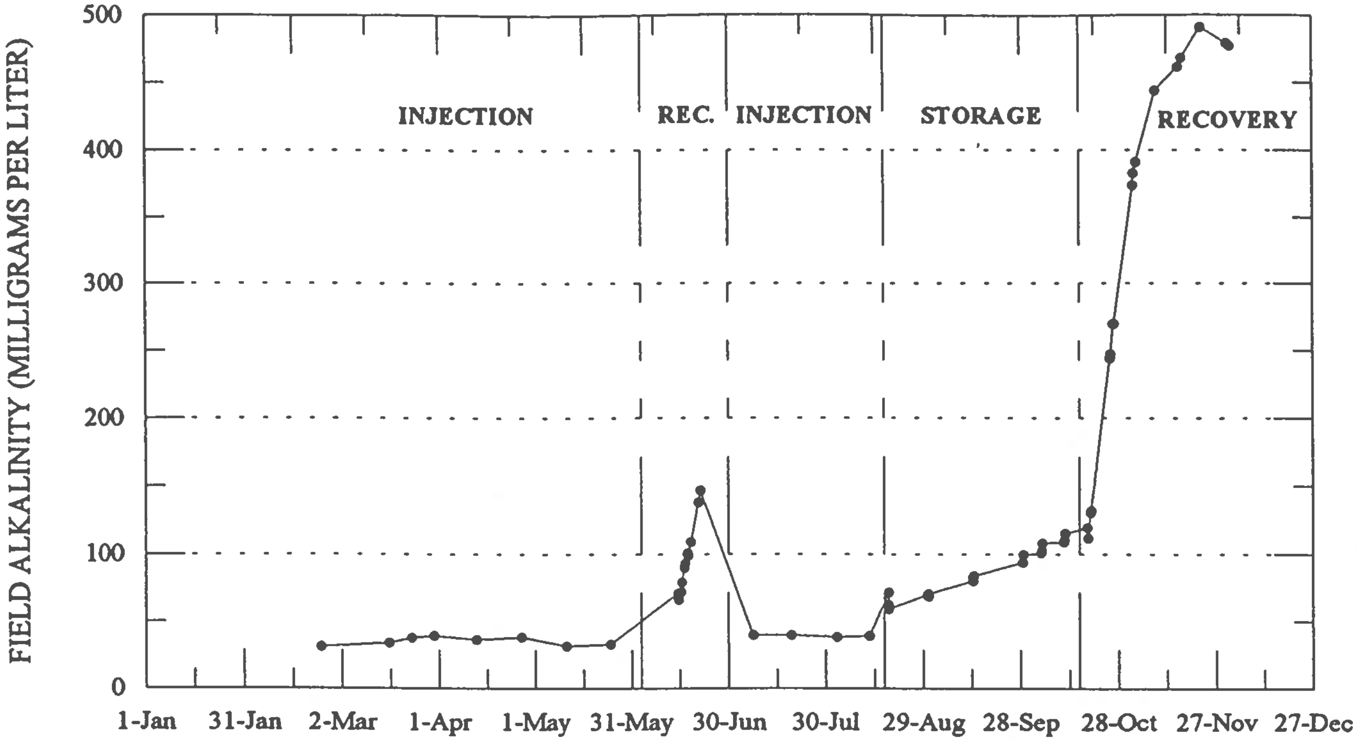

Figure 10. Field alkalinity, as $CaCO_3$,in milligrams per liter.

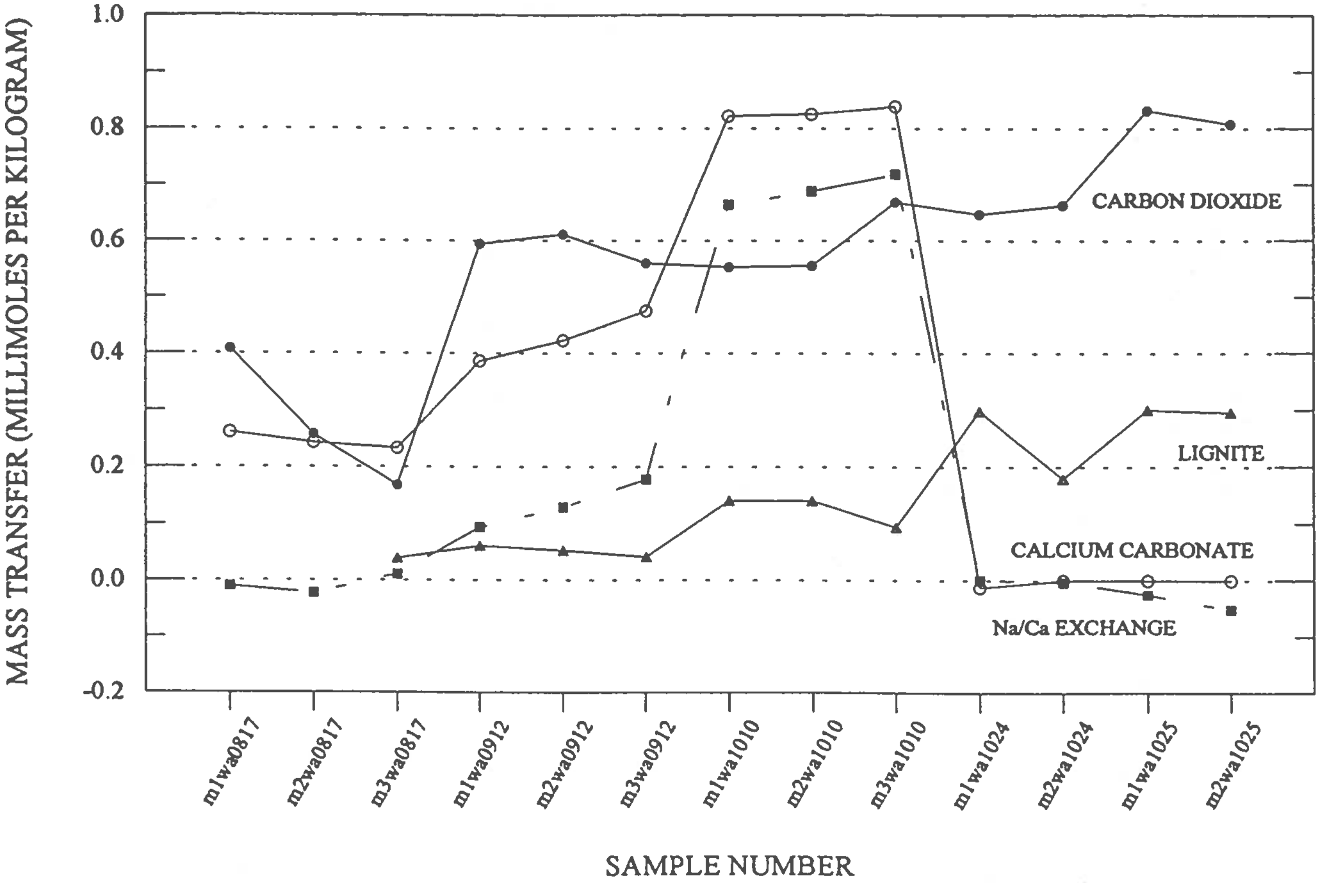

Figure 11. Results of geochemical modeling showing mass transfers between injected water and aquifer matrix.

Lignite oxidation might have increased in later samples because of the longer contact period and larger surface area of aquifer available to the samples. Other processes modeled but not included in Figure 11, because of their small mass-transfer contribution to the system, were ferrous-sodium exchange, pyrite oxidation, and sodium sulfate dissolution. The sodium contribution from the sodium sulfate phase represented about 6 percent of the sodium concentration in the sample, which is near the accuracy of analytical measurements. Thus, the addition of the phase helped the numerical model to arrive at a feasible solution within the margin of error of laboratory measurements.

CHEMICAL AND BIOLOGICAL REACTIONS

Several geochemical processes that altered the quality of the recovered water were identified. These processes are the same as those described and modeled in phase II (Castro, 1995).

Oxidation Processes

Mainly two chemical reactions, pyrite oxidation and organic-matter oxidation, were identified as the initial processes that increased the alkalinity and decreased the pH of the recovered water. The aerobic oxidation of a ferrous sulfur phase, like the pyrite that is present in the Black Creek aquifers, decreased the dissolved-oxygen concentration and increased the concentration of sulfate and ferrous iron ions in solution. Sulfate, which was between 40 and 55 mg/L during injection, increased to a maximum of 60 mg/L and then decreased to less than 2 mg/L during recovery. The iron concentration during recovery never exceeded the concentration of the treated water (0.11 mg/L) and did not violate the MCL (maximum contaminant level).

Organic matter, which is in the form of lignite in the Black Creek aquifer (Castro and others, 1995), was aerobically and anaerobically oxidized. During the aerobic process oxygen was reduced, and during the anaerobic process nitrate and sulfate were reduced. Because these processes developed rapidly, they were probably mediated by bacteria. This implies that deep aquifers, like some surficial soils, can effectively remove certain types of contaminants. In this system, for example, nitrate was reduced to nitrogen gas (denitrification). These processes might also suggest that various hosts of bacteria (aerobic) quickly become acclimated and efficiently function in new and previously unfavorable environments (anaerobic). It might also means that the bacteria become dormant when the ground water system reverts to its original anaerobic condition, assuming that the indigenous bacteria are not facultative anaerobes.

Calcite Dissolution and Sodium Exchange

The added carbon dioxide from the oxidation processes formed a weak acid that enhanced calcium carbonate dissolution. On the basis of carbon-13 isotope data, the calcium carbonate appeared to have incongruently dissolved. In this process a less stable calcium carbonate phase, such as aragonite, dissolves and at the same time a more stable calcium carbonate phase, such as calcite, precipitates. An important implication of the incongruent dissolution of calcite is a no-net-change in porosity and, therefore, of transmissivity and storage capacity of the aquifer, which was already discussed. Because not all the calcium carbonate underwent incongruent dissolution, some calcium and carbonate ions were added to the solution. The added calcium was removed from solution by exchange with sodium from the marine clay. Consequently, the concentration of sodium, and not of calcium, increased in solution. Approximately 70 percent of the recovered volume (as a percentage of the injected volume) had a sodium concentration less than 150 mg/L (Fig. 9). The sodium concentration in the recovered water increased because of exchange with clay and because of mixing with the native ground water.

Fecal Coliform

Prior to the injection tests in 1991, there was some uncertainty regarding the growth and propagation of bacteria in the recovered water, especially because the injected water would be stored in the aquifer for extended periods of time. During the injection cycles in 1994, 48 samples of the recovered water were sampled for fecal-coliform analysis. All tested negative, although the water remained in the aquifer for more than 70 days and no residual chlorine was detectable (<0.1 mg/L) in the recovered water. Similar results were obtained in the 1991 and 1992 field tests.

Trihalomethane

To study the development of disinfection byproducts in an ASR test well, a number of THM (trihalomethane) compounds were tested. Samples were analyzed for chloroform, bromoform, chlorodibromomethane, and bromodichloromethane. Additionally, the THMP (trihalomethane formation potential) of the recovered water was measured by using an incubation period of seven days at 25°C. During the 1994 test, the THM in the injected water ranged from 15 to 28 µg/L (micrograms per liter), and that in recovered water was less than 2 µg/L. It appears that the THM's are degraded by bacteria, and in particular by anaerobic bacteria. The THMP in the injected water ranged from 550 to 800 µg/L, while that in the recovered water was around 300 µg/L. Early recovered water, moreover, had lower THMP values than later recovered water. This, at least initially, would suggest that the treated water injected earlier (spring) had less of a potential for forming THM than the treated water injected later (summer). In general, the ASR systems seems to provide an ideal mechanism to reduce the THM and THMP of the treated surface water, either by bacterial degradation or by mixing.

SUMMARY AND CONCLUSIONS

The Aquifer Storage Recovery project at Myrtle Beach started with the drilling of a 1,340-ft core hole in 1988 and finished with the long-term injection tests in 1994. Owing to the complexity of the endeavor, the project was divided into four phases. Work completed during phase I, mostly a hydrologic and geologic study of the potential aquifers of the region, was summarized by Castro and others (1995); work completed during phase II, a hydrogeologic, geochemical, and economic feasibility study of the injection tests, was discussed by Castro (1995); and, phase III is addressed in this report. Simultaneous with the Myrtle ASR test of 1994, another ASR test was completed at a different site in Horry County. This work, which is phase IV, will be described by Castro and others in a forthcoming report.

The purposes of phase III were to study the chemical makeup of the gaseous phase present during the recovery of the water and to propose a more efficient backflush procedure. The unexpected plugging of the aquifer, however, changed the scope of the project somewhat, and field schedules had to be modified and a remedial procedure developed. Finally, a more effective injection system had to be proposed.

During the 1994 test, 15.87 million gallons of treated water were injected between March 1 and August 11; and 25.97 million gallons were recovered from June 13 to June 20 and from October 17 to November 30. In the 111 days of injection, the recharge rate declined from 160 to 120 gpm and the average was 140 gpm. A total of 68 samples were collected to characterize the native ground water, the treated drinking water, and the recovered water. On-site measurements, using a flow-through cell, were made for dissolved oxygen, specific conductance, redox potential, pH, and temperature. Additionally, alkalinity and residual chlorine were measured several times a day. Water samples were analyzed for primary and secondary constituents, fecal coliform, THM (trihalomethane) and THM potential, dissolved organic carbon, tritium, and isotopic carbon-13. Injection and discharge were regularly measured, and water levels were continuously recorded.

Following is a listing of the most important findings and conclusions for the ASR phase III Myrtle Beach project:

Injection Rates. Injection rates of 160 to 120 gpm were tested. A reasonable injection rate for this well is 133 gpm, although the well could accept higher rates, especially when the water temperature is above 24°C.

Backflushing Procedures. Two backflushing events every week were sufficient to maintain an adequate injection capacity in the well. During each backflush the well was first rested for 10 minutes, pumped for 20 minutes, and again rested for 10 minutes. An average of 7,000 gallons were pumped per backflush.

Treated Water. The quality of the treated injected water had changed slightly since the 1992 long-term injection test. The pH of the 1994 injected water averaged 8.2 and had a much smaller range of variability; alkalinity averaged 40 mg/L (milligrams per liter), potassium had increased to about 2.8 mg/L, and sulfate to about 43 mg/L.

Recovered-Water Concentrations. Trends and variations in concentrations for the recovered water during the first and second recovery periods in 1994 were in good agreement with those observed in tests completed in 1991 and 1992. This suggests that the results of tests are reproducible and, therefore, that the geochemical processes controlling the quality of recovered water are sufficiently replicable to permit the use of the observed trends in geochemical models.

Changes of Transmissivity. Transmissivity values obtained from pumping tests completed before and after the injection tests at the ASR site varied slightly. The average transmissivity for the aquifer, from the various tests, was calculated to be 12,000 gpd/ft. On the basis of the pumping-test information, there is no conclusive evidence that the aquifer transmissivity has declined as a result of the injection tests.

Chemical Composition of Gas Phase. During pumping periods, the recovered water often degassed when it was exposed to the atmosphere. Gas chromatography showed that the gas was made up mostly of nitrogen and carbon dioxide. Two processes have been identified as the sources for these gasses; air entrainment and chemical reactions. During injection, if air entrainment takes place the nitrogen gas is retained in suspension and also added to solution. During storage, geochemical reactions mediated by bacterial activity increased the concentration of dissolved inorganic carbon in water. Air entrainment more than geochemical reactions, however, appeared to be the dominant source of gas in the recovered water.

Air Entrainment. This is a common problem and most often the principal cause of failure in ASR projects. During previous injection tests at this site, air entrainment was not a problem. During the 1994 test, however, it was a sufficiently severe problem to prompt the halting of injection activities. Inasmuch as the well was specifically designed for pumping and not for injection, it might have been prone to air-entrainment problems. The clogging problem originated at the start of the injection cycle. Air trapped in the pump column or forced into the system through faulty valves or joints might be driven into the aquifer, decreasing its transmissivity and storage capacity. A solution to this problem is the installation of a flow control and a check valve.

Geochemical Processes. Several processes controlling the quality of the recovered water were identified. Chemical processes, although important in the understanding of the chemical evolution of the water, were of limited scope and bestowed only minor changes to the quality of the water. Mixing had a larger effect on the quality of the recovered water. Despite these changes, a significant fraction of the injected water retained its potable quality and could be returned to the distribution system without additional treatment other than disinfection.

Oxidation Processes. Mainly two chemical reactions, pyrite oxidation and organic-matter oxidation, were identified as the initial processes that increased the alkalinity and decreased the pH of the recovered water. The oxidation processes were aerobic and anaerobic, mediated by bacterial activity. Concentration increases, due to oxidation, were not substantial and did not violate the MCL (maximum contaminant level) of the recovered water.

Calcite Dissolution and Sodium Exchange. The added carbon dioxide from the oxidation processes formed a weak acid that enhanced calcium carbonate dissolution. On the basis of carbon-13 isotope data, the calcium carbonate appeared to have incongruently dissolved, which means that while aragonite dissolves, calcite precipitates. Calcium, which was added by congruent dissolution of aragonite, was quickly removed from solution by exchange with sodium from the marine clay. Consequently, the concentration of sodium increased in solution. Other important changes observed in the recovered water were the increase of bicarbonate alkalinity and pH, which neutralized the aggressiveness of the injected water and therefore improved the overall quality of the recovered water.

Fecal Coliform. Samples of the recovered water, during the ASR cycle in 1994, tested negative for fecal-coliform bacteria. Similar results were obtained in the 1991 and 1992 field tests.

Trihalomethane. During the 1994 test, the THM in the injected water ranged from 15 to 28 µg/L, whereas the recovered water had a THM of less than 2 µg/L. The THMP in the injected water ranged from nearly 550 to 800 µg/L; the recovered water had values around 300 µg/L. Consequently, the ASR system provides an ideal mechanism to reduce the THM's and THMP of the treated surface water, either by degradation or by mixing.

Temperature. Temperature of the injected water ranged from 13°C during February to as much as 32°C during July. In contrast, the temperature of the recovered water ranged only from 24°C to 28°C, and most of the water had a temperature near 24°C. An ASR system of 10 wells, capable of increasing daily flows by 5 million gallons, would lower the temperature of the water in the distribution system by 2°C; and a 20-well system, able to produce 10 million gallons per day, would lower the temperature by 4°C.

Blending Proportions. Final concentration of ions, such as chloride and sodium, in the blended water will depend on mixing ratio of the ASR-recovered water and potable water from the distribution system. During the production cycle of an ASR system in Myrtle Beach, higher ionic concentrations would be expected during September than during July. If a 10-million gallon per day ASR system is built, the distribution system would have a chloride concentration of 38 mg/L during September and 30 mg/L during July. Similar calculations showed that a 15-million gallon per day system would still have concentrations of chloride and sodium below the suggested contaminant levels as indicated by the National Secondary Drinking Water Standards and the State of South Carolina drinking water rules.

Efficiency. On the basis of chloride concentrations, the recovery efficiency of the Myrtle Beach test site is estimated at 70 percent. This recovery efficiency, moreover, is expected to increase with subsequent injection tests.

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