AQUIFER STORAGE AND RECOVERY HORRY COUNTY, SOUTH CAROLINA

PHASE IV: RESULTS OF THE BAY ROAD WELL AND HIGHWAY 501 POTTERY WELL INJECTION TESTS

By

Joffre E. Castro
South Carolina Department of Natural Resources,
Water Resources Division

Susan Libes
Coastal Carolina University,
Center for Marine and Wetlands Studies

Sharon Garrell
Grand Strand Water and Sewer Authority

SOUTH CAROLINA DEPARTMENT OF NATURAL RESOURCES

WATER RESOURCES DIVISION

REPORT 11

1996

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ABSTRACT

An injection storage-recovery test of several months duration was completed in 1994 as part of a program to develop Aquifer Storage and Recovery sites in the Grand Strand area of Horry County, S.C. For this test, a former public-supply well on Bay Road was modified to permit injection of treated surface water into Coastal Plain sediments of Cretaceous age. More than 52 million gallons of treated surface water were injected, using the line pressure of the distribution system. After 2½ months of storage, the water was recovered. Significant quality changes were observed in the chemical composition of the recovered water.

An intensive monitoring program was implemented at the ASR site to explain the chemical evolution of the recovered water. The ratio of mixing between the treated water and the native ground water was estimated from measurements of two conservative tracers, chloride and tritium. Specific chemical reactions were identified from calculations of equilibrium speciation and mineral saturation, using WATEQ4F, and by mass-balance calculations using NETPATH. Both WATEQ4F and NETPATH are computer programs developed by the U.S. Geological Survey.

Although most changes in chemical composition of the recovered water were caused by the mixing of treated water with ground water, a small fraction was due to geochemical reactions. The four most important reactions (mass-wise) were pyrite and organic matter oxidation, calcium dissolution, and calcium-sodium exchange.

At the Bay Road well, extensive mixing of the treated water with the ground water is attributed to partial clogging of the well screens. Clogging probably was caused by chemical precipitation and/or by mechanical conditions such as air locking due to gas entrainment during injection. During the recovery period, continuous pumping probably caused progressive unclogging of the screens. This led to mixing of the treated water stored in the aquifer with native ground water. The native ground water came from the aquifers that had clogged screens, and therefore, did not accept treated water during the injection period.

At a well on Highway 501, seven short-term injection tests were completed. Chemical quality of the recovered water showed significant improvement with each successive test. This confirmed that flushing of the aquifer and appropriate management of the injected plume can significantly improve the recovery efficiency of the system.

During these tests and others in the region, the following field practices were found to be essential in developing and operating a successful ASR program: (1) Optimizing of injection rates to increase storage capacity without risking well overflow and aquifer compaction or fracturing. Initial rates of approximately one-third of the well's pumping capacity are recommended; (2) Using of injection techniques that will minimize air entrainment, such as maintaining full pump columns with positive heads throughout the injection period; (3) Backflushing regularly to remove solids from the well screens and gravel pack; (4) Developing and maintaining of a buffer zone to improve the isolation of treated water from native ground water; (5) Monitoring water quality to assess mixing and chemical reactions during storage and recovery, information that can be used to improve the management of water quality; and (6) Implementing of management practices appropriate to specific project objectives to ensure an optimum rate of recovery and also produce consistent quality in the recovered water.

INTRODUCTION

Starting in 1991, a series of well injection tests was made in Horry County to study the hydrologic, geochemical, and economic feasibility of storing treated water in an aquifer, for later recovery (Fig. 1). This report describes, mostly, the results obtained from testing the Bay Road Well (HOR-936), a former public-supply production well. At this site, a single injection-storage-recovery test was completed between March and December, 1994, during which approximately 52 million gallons of treated surface water were stored in the aquifer and then recovered.

During the preparation of this report, data from another ASR site—Highway 501 Pottery Well (HOR-934)—became available. A series of seven injection tests, each involving approximately 1 million gallons, was made at this site between September 1995 and March 1996. The data show a well-developed buffer zone and a significant improvement in the quality of the recovered water with each successive test. Hence, a brief section discussing the results from the Hwy 501 Pottery well injection test has been included.

The Grand Strand Water and Sewer Authority (GSWSA) and the South Carolina Department of Natural Resources (DNR), with the support of the Office of Local Governments, financed the project. Sample collection was coordinated by the Authority. Data analysis and geochemical modeling were done by DNR and the Center for Marine and Wetlands Studies at Coastal Carolina University.

A major goal of this project was to gain an understanding of the geochemical processes controlling the quality of the recovered water. These processes were identified by constructing geochemical models using NETPATH, a program developed by the U.S. Geological Survey (Plummer and others, 1991). Ground-water flow and solute transport were modeled by using SUTRA, also a program developed by the U.S. Geological Survey (Voss, 1984).

This investigation, in conjunction with the work completed in Myrtle Beach (Castro and others, 1995; Castro, 1995 and 1996), represents pioneering efforts to introduce Aquifer Storage and Recovery (ASR) technology to South Carolina. The use of ASR for management of the water resources is presently being tested at several sites in the coastal region of South Carolina. The GSWSA is testing two additional Black Creek aquifer wells in Horry County, the Mount Pleasant Waterworks and Sewer Commission is testing the

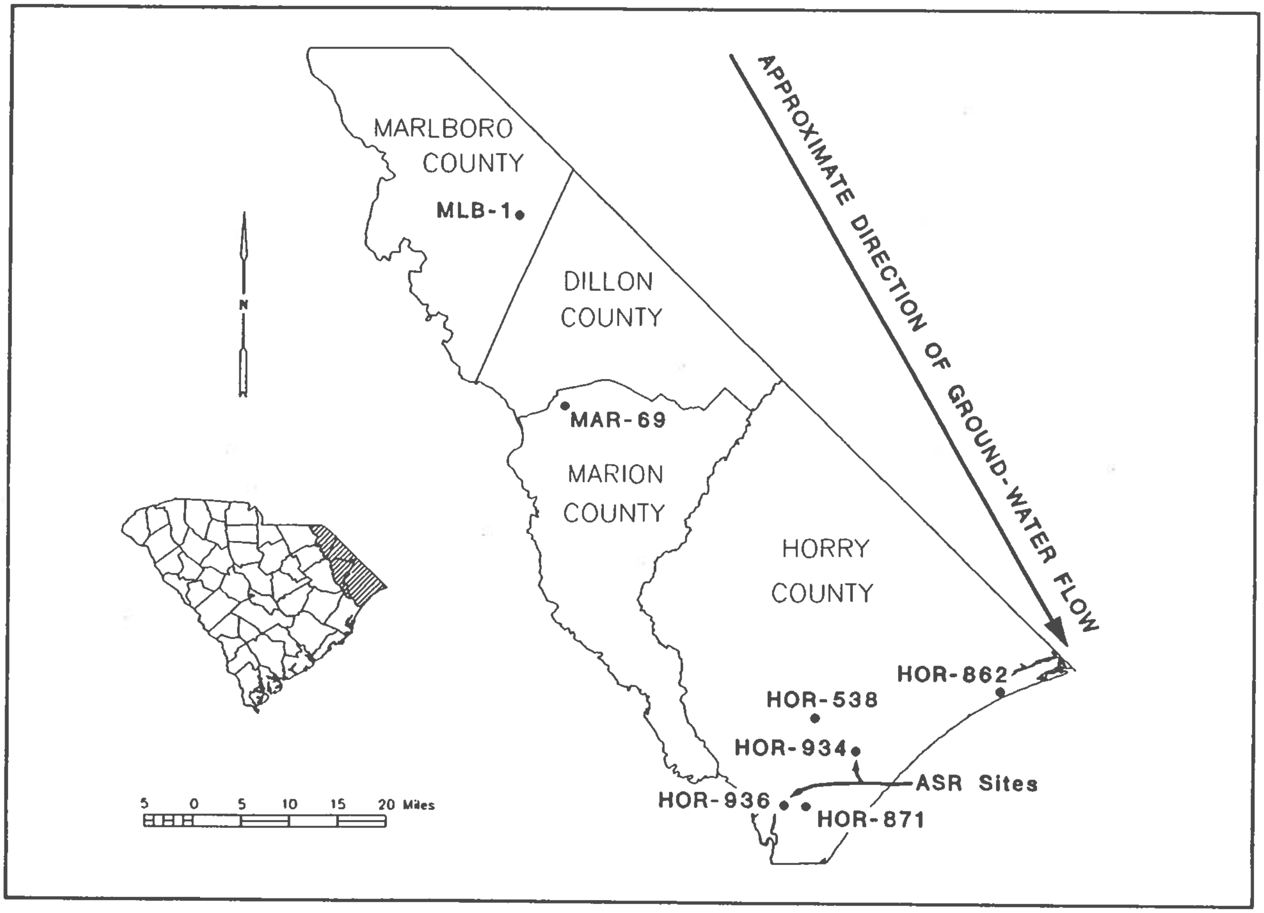


Figure 1. Location of the ASR sites and selected wells in the vicinity.

Tertiary Formations in Charleston County, and the city of Charleston is experimenting with some Floridan aquifer wells. These tests have brought a new awareness and a better understanding of ASR in South Carolina.

HYDROGEOLOGIC FRAMEWORK

The sediments overlying the crystalline bedrock in Horry County are classified into five geological units: the Cape Fear, Middendorf, Black Creek, and Peedee Formations and the shallow deposits. The first four are of Cretaceous age and the last comprises sediments of Tertiary and Quaternary ages. A brief description of these sediments is provided in Table 1.

SHALLOW DEPOSITS

These deposits consist of thin beds of fine clayey sand, fine calcareous sand, and limestone of Tertiary and Quaternary ages. Water-table and artesian conditions occur in these sediments. The aquifers are discontinuous, subject to water-level fluctuations, and dependent on local rainfall for recharge. The quality of the water is variable and generally inferior to that of deeper aquifers, especially where a free exchange of water between these sediments and surface-water bodies is present. Shallow artesian aquifers of the Tertiary formations yield good water. This water is soft, has very low concentrations of fluoride and chloride, and is nearly devoid of iron, sulfate, and hydrogen sulfide.

PEEDEE FORMATION

These open-shelf deposits consist of dark-gray, fine-grained clayey sand. The formation is characterized by various zones of coarse and loose, shelly limestone that probably were deposited on shallow marine continental shelves. In general, the aquifers are under artesian (confined) conditions; but they are not tapped by municipal water-supply wells because of their unsatisfactory water quality and low yield. The ground water is characterized by objectionably high concentrations of iron, hydrogen sulfide, manganese, and calcium. High chloride concentrations are common in areas where the aquifer is hydraulically connected to saline water bodies. Many of these water-quality problems are geographically localized with no apparent pattern to their occurrence.

BLACK CREEK FORMATION

This Late Cretaceous formation consists of dark-gray clay interbedded with gray or white, fine to very fine, glauconitic and micaceous quartz sand. Water levels in these aquifers have been rising since the late 1980's, when most of the water utilities changed their water supply source from ground water to surface water (Castro, 1995). The aquifer has recovered almost 90 ft of head in the past 7 years, although the rate of recovery is progressively decreasing. Today the aquifer water levels around Myrtle Beach are near 90 ft bls (below land surface).

These aquifers were, until 1988, the major public water supply in the region. Even today, in areas where the fluoride and sodium are not excessively high—for example in the western portions of Horry and Georgetown Counties—ground water is often the sole public water supply source. Production of potable water from these aquifers usually is less expensive than that from surface-water bodies, because ground water requires little or no treatment. Closer to the ocean, the ground water is more mineralized and would require treatment to meet today's drinking water standards.

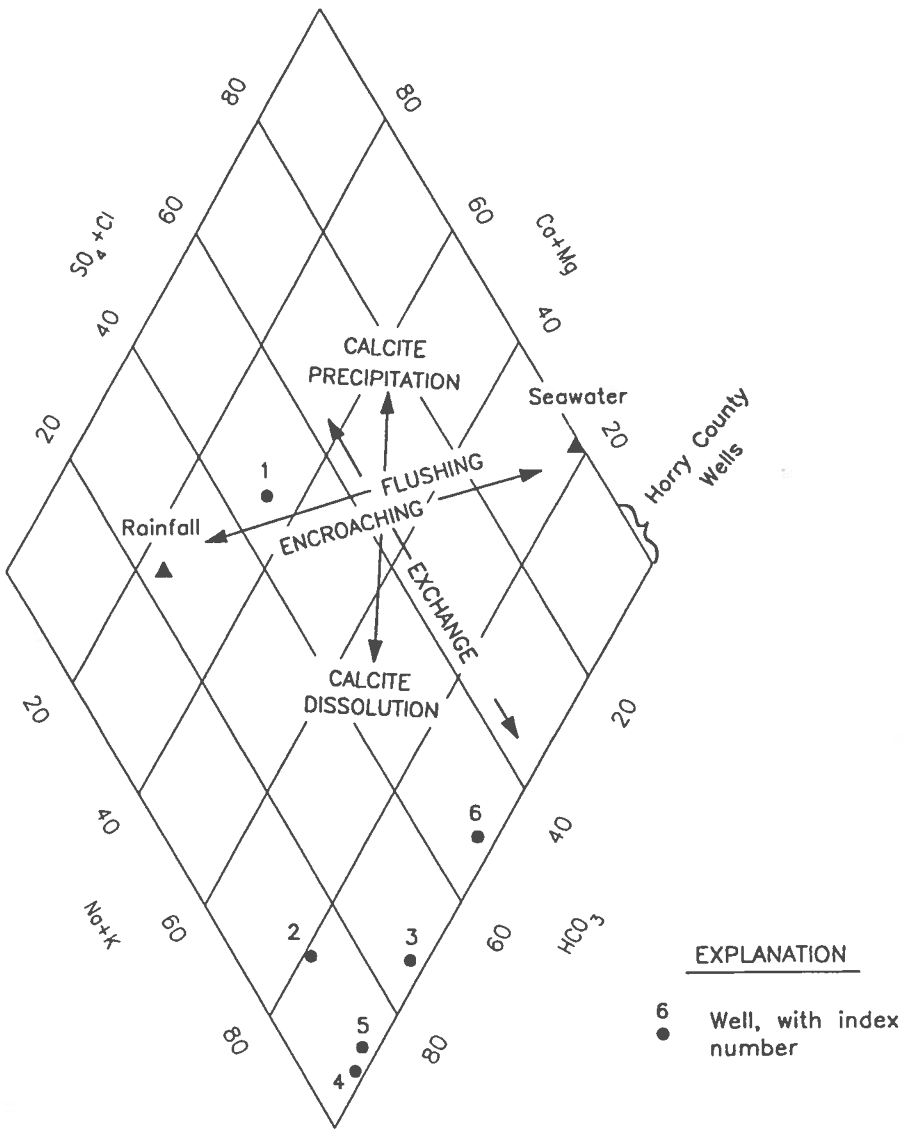
Figure 2, a trilinear (Piper) diagram, illustrates how ground water in the Black Creek aquifers has been evolving in composition from a sodium chloride type to a sodium bicarbonate type. After the last regression of the sea during the Miocene Epoch, freshwater derived from rainfall started recharging the Coastal Plain aquifers. This flushing of the aquifers replaced seawater with freshwater, thereby decreasing chloride concentrations. This process is depicted in the Piper diagram as a trend which connects diluted seawater to freshwater derived from rainfall.

As the recharging water has moved downgradient to the coast, calcite dissolution, enhanced by acid derived from organic-matter decomposition, has caused alkalinities to increase (Chapelle and McMahon, 1991). Calcium concentrations do not increase, because of ion exchange with sodium adsorbed on the surfaces of clay minerals (Zack and Roberts, 1988). Thus, sodium concentrations rise. This change in ground-water composition, from a chloride type to a bicarbonate type, is represented in Figure 2 by the wells that plot in the lowest corner of the Piper diagram.

As shown in Figure 2, flushing of the aquifers occurs as ground water moves from the recharge areas downslope toward the coastal areas. Owing to its lower density, the freshwater moves as a wedge. At the top of the aquifer, this freshwater wedge displaces the more saline ground water. At the bottom of the aquifer, the freshwater wedge overrides the denser ground water. The upper end of the freshwater front (defined as water containing <1,000 mg/L TDS) lies in sedimentary strata several miles offshore. The lower end of the front is presently located several miles west of Horry County (Newcome, 1989). The movement of this freshwater front is somewhat constrained by the Cape Fear Arch, a structural feature north of Myrtle Beach (along the state

TABLE 1. Lithology of sediments in the ASR study area

SYSTEM	SERIES	GEOLOGIC FORMATION	FORMATION DESCRIPTION
QUATERNARY	PLEISTOCENE	SHALLOW DEPOSITS	Blue, gray,yellow, and brown sandy marl; gray to buff, fine-grained quartz sand.
TERTIARY	EOCENE AND PALEOCENE	UNDIFFERENTIATED DEPOSITS AND BLACK MINGO	Greenish-gray glauconitic sand with thick beds of coquina (loose, fossiliferous limestone)
CRETACEOUS	UPPER CRETACEOUS	PEEDEE	Gray, calcareous, fossiliferous clay; gray, glauconitic, calcareous, fine- to medium-grained, muddy sand; and coquina.
		BLACK CREEK	Well-sorted, calcareous, fine-to medium-grained quartz sand; calcareous silty clay; and glauconitic, calcareous, muddy, fine- to medium-grained quartz sand.
		MIDDENDORF	Multicolored clay and olive-gray, clayey, coarse, feldspathic sand.
		CAPE FEAR	Fining-upward sequences of multicolored, silty,clayey, coarse feldspathic sand to multicolored clay.
CRYSTALLINE ROCK			SAPROLITE Yellow-brown to yellow-orange, sandy silt.
			BEDROCK Quartz-biotite schist.



INDEX NUMBER	WELL NAME	WELL NUMBER
1	Clio	MLB–1
2	Sellers	MRN–69
3	Conway	HOR–538
4	Bay Road	HOR–936
5	Tern Hall	HOR–871
6	Crescent Beach	HOR–862

Figure 2. Trilinear diagram showing the chemical evolution of Black Creek aquifer water.

line), as the Arch restricts the flow of freshwater in nearby aquifers (Zack, 1977). Thus, wells close to the North Carolina-South Carolina boundary have higher chloride concentrations than wells in the southern part of Horry County. As a result, chloride concentrations are geographically variable throughout the Black Creek aquifers in the county.

In general, chloride concentrations increase with depth and with proximity to the Cape Fear Arch and Atlantic Ocean. For example, well MRN-69, which is in Marion County (Fig. 1) nearly 70 miles from the coast, had a chloride concentration of 3.6 mg/L (low concentration). Well HOR-862, which is less than a mile from the ocean and near the state line, had a chloride concentration of 369 mg/L (high concentration). Most other Black Creek wells have intermediate chloride concentrations. Well HOR-538, in Conway, had a concentration of 116 mg/L and well HOR-936 (the ASR test well) had a concentration of 28 mg/L. Chloride concentrations also vary with depth at the same location. Aquifers near the top of the formation have chloride concentrations of 100 mg/L or less, and those at the bottom have concentrations of 500 mg/L or more (Castro and Hockensmith, 1987). Upconing of brackish water, because of ground-water pumping, may be the reason for variations in chloride concentration among neighboring wells. For example, well HOR-871, located a mile from the ASR well, had a chloride concentration nearly 60 percent higher (54 mg/L). Upconing can also cause chloride concentrations to be seasonally variable.

MIDDENDORF AND CAPE FEAR FORMATIONS

The sediments of the Middendorf Formation are medium-to-coarse, white or gray sand with thin layers of multicolored silty clay. Along the east edge of the Coastal Plain, the aquifers of the Middendorf Formation contain brackish water, although freshwater has been obtained at some sites in the extreme western portion of Horry County. The water levels in these aquifers are estimated to be about 110 ft above land surface. The difference in hydrostatic pressure between the Middendorf and Black Creek aquifers is nearly 200 ft. Thus, the Middendorf Formation is most probably recharging the Black Creek Formation, which may explain the high chloride concentrations in the lower units of the latter formation.

The Cape Fear Formation is characterized by fining-upward sequences, grading from silty or clayey coarse sand to clay. Neither the Middendorf nor the Cape Fear is presently tapped for public or industrial water supplies. This is primarily due to the high salinity of the water and depth of drilling required. The water level in the Cape Fear Formation is not known, but is assumed to be at least equal to that in the Middendorf Formation.

BAY ROAD WELL INJECTION TEST

INJECTION SITE

The field injection and recovery test was completed at a site in southern Horry County, 4 miles southwest of Socastee, S.C., and near Enterprise Landing on Bay Road 1¾ miles west of S.C. Hwy 707 (Fig. 1). The two wells used in the test tap the Black Creek Formation. The production well (test well) was formerly used as a public supply well, and the observation well was drilled specifically for this injection project. The test well (HOR-936) is 710 ft (feet) deep and 8 inches in diameter. It has 12 screened intervals totaling 150 ft between the depths of 385 and 698 ft. The observation well (HOR-1164), which is located 100 ft from the test well, is a 700-ft, 4-inch diameter well. The screens in the observation well are 3 ft in length and were placed at depths corresponding to the middle points of the screened intervals in the test well.

In the test well, only minor modifications were necessary to convert the former public supply well into an ASR test well. A 4-inch line was added to the wellhead to route the potable water from the distribution system to the well's riser pipe (pump column). Control and backflow-preventer valves were installed to control the direction of flow, enabling the modified well to function as either an injection or extraction well (dual-purpose well). Digital flowmeters were installed to measure flow rates as well as total injected and discharged volumes (Fig. 3). A flowthrough cell was used to continuously monitor pH, temperature, and specific conductance (Fig. 3). Pressure transducers, installed in both wells, continuously recorded water levels.

Site Hydrogeology

At the testing site, shallow deposits extend from land surface to about 60 ft bls. This aquifer is used locally for landscape irrigation. Underlying this unit is the Peedee Formation, which lies between the depths of 60 and 240 ft bls (below land surface). No wells have been drilled into the Peedee Formation in this part of Horry County. The Black Creek Formation, which underlies the Peedee, extends from 240 ft to more than 900 ft bls.

The geology of the Black Creek Formation in the vicinity of the test site is summarized in Figure 4.

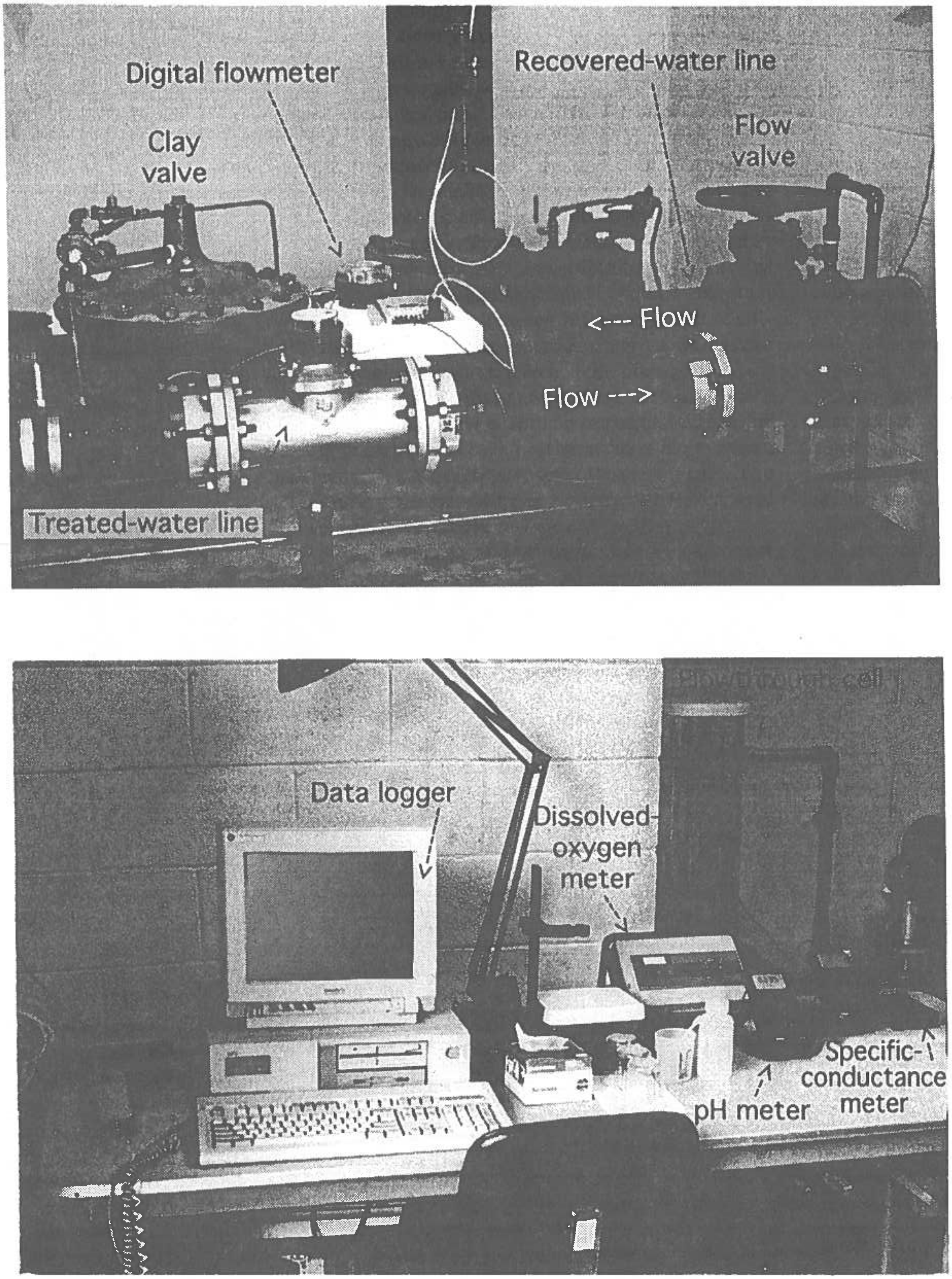


Figure 3 Bay Road wellhead installation and monitoring equipment.

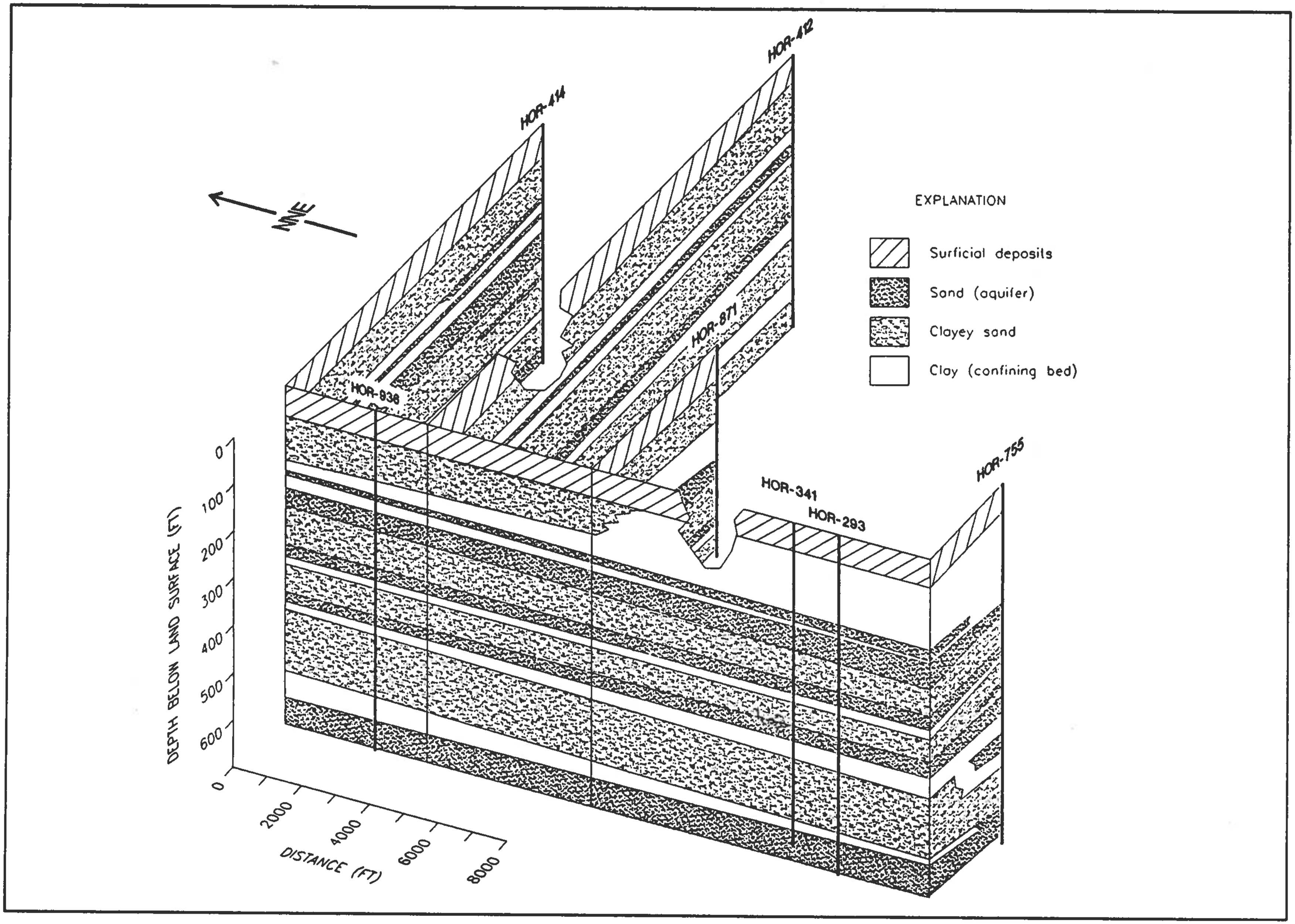


Figure 4. Geologic fence diagram of aquifers near the ASR site.

Considering the differences in artesian pressure between the Black Creek Formation and the more brackish Middendorf Formation, there would be the potential for upward movement of the deeper mineralized water were it not for the apparently continuous confining beds between the two units. At the testing site, this appears to be the reason why the chloride concentration is less than half that observed at other Black Creek wells.

The Middendorf and Cape Fear Formations underlie the Black Creek Formation and are thought to extend to about 1,400 ft bls, the top of bedrock.

Aquifer Characteristics

To characterize the transmissivity of the Black Creek aquifers at the ASR testing site, several constant-discharge pumping tests were made. Prior to injection (March 1994) four tests were carried out at the test well. Following construction of the observation well, an additional three pumping tests were made at both wells. From these tests, the average transmissivity for the site was estimated at 22,000 gpd/ft (gallons per day per foot). After recovery of the treated water (December 1994), two pumping tests were made (both wells). The pre- and post-test data indicate that the transmissivity of the aquifer had not been altered by the months-long ASR test.

FIELD ACTIVITIES

Following procedures developed at other ASR sites (Castro, 1995), treated water from Bull Creek was injected into the Black Creek aquifers. An equivalent volume of water was recovered following a two-month storage period. Table 2 is a summary of activities during the 1994 test.

Injection Period

Between April 25 and August 1, 1994, nearly 52.5 million gallons of treated surface water were injected into the Black Creek aquifers. Injection proceeded almost continuously during these months, except for a weekly backflushing. Backflushing was performed in three 10-minute steps: (a) injection was stopped and the well allowed to rest, (b) the well was then pumped, and (c) pumping was halted and the well was allowed to rest before injection was continued.

The average injection rate was 376 gpm (gallons per minute). Daily rates varied from less than 300 to more than 450 gpm. These fluctuations were caused by variations in water pressure within the distribution system, which normally ranged from 40 to 65 psi (pounds per squared inch). Because the line pressure at the wellhead was sufficient, pumping was not necessary to force the treated water through the well screens and gravel pack and into the confined aquifer. Samples of treated surface water were collected regularly at the wellhead. A total of 17 water samples were obtained, about one per week, to monitor seasonal variations in the quality of the injected water prior to its injection.

Storage Period

Between August 1 and October 17, 1994, the well was pumped only occasionally, for collection of water samples. Nearly 6.2 million gallons of treated water were removed during this period. Prior to each sampling event, the well was pumped for at least 1 hour to obtain stable readings of specific conductance.

The sampling schedule, three samples every other week, was designed to investigate the chemical processes occurring in the aquifer during the storage period. By pumping for 1 to 15 hours between the collection of successive samples, information was obtained about geochemical processes occurring through the injection and storage periods. Thus, the first water sampled reflected conditions near the well. The geochemical

Table 2. Summary of field activities during the 1994 ASR test

DATE	WATER LEVEL (FEET BLS)		VOLUME (MILLION GALLONS)	
	TW	OW	INJECTED	RECOVERED
INJECTION 04/25 - 08/01/94				
04/25	81	82.7		
08/01	49.1	77.1	52.48	0.089
STORAGE 08/01 - 10/17/94				
08/03	77.2	78.4		
10/12	100.7	95.3		
10/17	80	80.8		6.221
RECOVERY 10/17 - 12/20/94				
10/17	80	80.8		
12/20	126.1	120.2		57.914

TW test well
OW observation well

Table 3. Drinking-water standards and average composition, as measured at the ASR site, of Bull Creek treated water and Black Creek Formation water

CONSTITUENT/ PROPERTY	MCL	SML	TREATED WATER	GROUND WATER	
				HOR-936	HOR-934
Temperature (°C)	NS		18	23.6	23.6
Total dissolved solids	500		92	478	605
Sp. cond. (µS/cm)	NS		168	887	1091
pH (standard units)	6.5-8.5		8.2	8.8	8.8
Alkalinity as $CaCO_3$	NS		19	446	466
Aluminum		.05-.2	.44	.03	--
Calcium	NS		8.6	1.7	1.2
Chloride		250	16	28	57
Dissolved oxygen	NS		7.8	<0.1	<0.1
Fluoride	4	2.0	1	2.2	4.2
Iron		.3	.04	.02	0.01
Magnesium	NS		1.9	.4	0.6
Nitrate as N	10		2.2	.3	--
Phosphate as P	NS		.02	.07	--
Potassium	NS		3	2	4.5
Silica as SiO_2	NS		7.8	16.2	14.1
Sodium	250	20	17.5	210.4	244
Sulfate as SO_4^{2-}		250	29	3.5	--
Total organic carbon	NS		2.7	1.3	--

Units are mg/L, except where noted otherwise
MCL, maximum contaminant level
SML, suggested maximum level
NS, no standard

changes that had occurred in this water were probably the result of chemical reactions. Samples collected after several hours of pumping were representative of water stored farther out in the aquifer, and therefore, probably reflected the effects of mixing with the native ground water and of chemical reactions with the aquifer.

Recovery Period

From October 17 until November 24, the well was pumped continuously. Between November 24 and December 20, pumping was stopped several times because of problems with flowmeters and the power supply. By December 20, 1994, 57.914 million gallons had been pumped from the well. The average discharge rate during this period was 716 gpm. The total volume pumped from the well, including water recovered during the storage period, was 64.135 million gallons. This represents a volume 22 percent larger than that injected.

MONITORING REQUIREMENTS

An intensive program of sampling, monitoring, and laboratory analysis was required to document the chemical evolution of the injected water. These data were then used to determine the processes responsible for the observed changes in water quality that had occurred during the storage period. The characteristics monitored were those listed as being of concern by the Environmental Protection Agency (EPA) and the South Carolina Department of Health and Environmental Control (SCDHEC). These standards are given in Table 3, along with the average chemical composition of the treated surface water from Bull Creek (as supplied by GSWSA during this study) and the native Black Creek Formation water.

Hydraulic properties and some of the water-quality characteristics were measured on the site. The test well and observation wells were fitted with pressure transducers to record water levels. The test well also had a digital flowmeter to monitor injection and discharge rates. A flowthrough cell was used to monitor dissolved oxygen, specific conductance, redox potential, alkalinity, pH, and temperature. The cell enabled the measurement of dissolved-oxygen concentrations and pH of the recovered water without exposure to the atmosphere. This reduced the risk of contamination by atmospheric gasses. Temperature and pH readings were continuously logged into a computer. Other on-site measurements of water quality were done manually several times a day, for example, residual chlorine and alkalinity.

The primary and secondary drinking-water contaminants monitored were trihalomethanes, trihalomethane formation potential, total organic carbon, fecal coliform abundance, carbon-13 ($\delta^{13}C$), tritium, trace metals, and the major as well as minor ions. The metal and ion analyses were done by Coastal Carolina University's Environmental Quality Laboratory in Conway, S.C. Total organic carbon, trihalomethane, and trihalomethane potential were measured by the Oxford Laboratories, Inc., in Wilmington, N.C. Stable carbon isotope ratio analyses ($\delta^{13}C$) were made by the Center for Applied Isotope Studies at the University of Georgia, Athens, Ga. Low-level tritium analyses were made by the Alberta Environmental Centre, of Alberta, Canada. Bacteriological analyses for fecal coliform abundance were done by GSWSA.

Injected Water

The surface water used in this ASR test was obtained from the Bull Creek Regional Water Treatment Plant near Bucksport, S.C. The plant, which has its raw-water intake in Bull Creek, produces water with low concentrations of dissolved solids (120 mg/L), sodium (18 mg/L), and chloride (16 mg/L). The water is soft and has an alkaline pH (8.3). Sulfate and sodium are the dominant ions. Some seasonal variation in temperature, dissolved oxygen, and total organic carbon occurs as a result of variations in raw-water quality and treatment.

Native Ground Water

Water in the Black Creek aquifers is of a sodium bicarbonate type (Table 3 and Fig. 2). The water is soft, alkaline, and low in iron, but it has objectionably high concentrations of sodium. In Horry County, the chemical composition of the ground water is related to distance from the ocean and depth in the aquifer. For example, chloride and sodium concentrations increase with depth. Thus, concentrations in water samples collected at the ASR test well represent an aggregate chemical composition because the well taps several aquifers through 12 screens.

The volumetric contribution per foot of screen, in a multiscreened well, is determined by the aquifer transmissivity, the hydrostatic pressure in each aquifer, and the screen efficiency. Hence, the chemical composition of ground water may vary with pumping time. The longer the well is pumped, however, the more stable is the chemical composition. In recognition of such phenomena, as well as of chemical interference from the well casing and gravel pack, Driscoll (1986) has recommended the removal of the equivalent of 3 to 10 well volumes before a water sample is collected. At this ASR site, removal of this quantity did not result in stable conductivity readings and, hence, appears to be too conservative for this location.

The lateral variability in ground water composition probably is the result of several phenomena. Many water types apparently are present in the well bore. The aquifer system is made up of numerous, thin aquifers interbedded with equally numerous, thin confining layers. Thus, extensive mixing occurs, in the well bore, among the different water types whenever the well is pumped. This mixing varies over time as a result of changes in the hydrostatic pressure within any of the aquifers. Such changes can result if a nearby well is pumped. Usually these changes are not large enough to produce a noticeable alteration in taste or appearance of the ground water, but they are geochemically significant and therefore had an impact on the geochemical modeling efforts of this ASR test.

WATER QUALITY DATA

The water quality data are presented in Table 4. Pre-injection ground water samples are labeled G1RA*(month)(day)*. Samples of treated water supplied to the well head are labeled G1TA*(month)(day)*. Samples withdrawn from the well during the storage and recovery periods are labeled G#WA*(month)(day)*. Sampling was evenly divided between the storage and recovery periods. As mentioned earlier, three sets of samples were collected during the recovery period over short pumping periods to evaluate chemical gradients. These are identified as G(1,2, or 3)WA*(month)(day)*.

Methods and Quality Control

The EPA methods used for analysis of the chemical composition of the treated water, ground water, and stored water are listed in Table 5. All but the pH and alkalinity measurements were made on filtered water. Thus, all the concentrations are measurements of the dissolved fraction of the constituent present in the water.

Table 5 contains estimates of precision as well as upper and lower detection limits for each of the methods. Analytical quality control was also monitored by ensuring that ion balance was achieved to within 5 percent of the true value. Ion balance was computed as:

$$\frac{\Sigma(cations)-\Sigma(anions)}{\Sigma(cations)+\Sigma(anions)}\bullet 100$$

Table 4. Chemical analyses of water samples

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
G1RA0215	46.4	02/15/94	09:30	808	23.6	---	8.9	0.32	451	8.9	0.031	1.69	1.9	20.1
G1TA0215	46.4	02/15/94	09:30	149	12.4	---	8.5	8.58	18	7.8	0.280	0.01	10.8	12.3
G1RA0221	52.4	02/21/94	10:45	884	23.6	452	8.9	0.32	454	9.4	0.035	2.05	1.6	20.1
G1TA0221	52.5	02/21/94	11:55	167	12.8	17	8.5	9.75	17	8.5	0.341	0.15	9.1	12.3
G1RA0316	75.6	03/16/94	14:15	882	23.5	450	8.9	0.32	462	8.8	0.022	2.06	1.8	25.9
G1TA0316	75.5	03/16/94	11:00	149	14.5	22	8.6	9.75	18	8.5	0.653	0.06	8.2	13.4
G1RA0322	81.3	03/22/94	08:20	887	23.1	440	8.9	0.32	455	8.9	0.023	2.05	1.5	27.7
G1TA0322	81.4	03/22/94	09:00	146	15.4	23	8.0	8.83	15	7.7	0.484	0.05	7.8	12.3
G1RA0328	87.4	03/28/94	09:30	888	23.6	441	8.8	0.32	451	8.9	0.030	2.06	2.0	29.8
G1TA0328	87.4	03/28/94	10:10	164	17.5	23	8.7	8.51	18	8.2	0.435	0.09	9.7	16.2
G1RA0411	101.6	04/11/94	13:15	885	23.7	440	8.8	0.32	448	9.0	0.027	2.11	1.5	29.5
G1TA0411	101.5	04/11/94	12:20	147	18.1	23	8.3	8.43	19	8.3	0.450	0.10	9.3	14.6
G1TA0425	115.7	04/25/94	17:25	157	19.9	22	8.4	8.96	19	8.1	0.473	0.09	9.0	16.0
G1TA0509	129.4	05/09/94	10:45	175	20.2	20	8.2	7.26	20	8.1	0.505	0.09	9.6	15.5
G1TA0523	143.4	05/23/94	09:45	170	21.4	18	7.7	6.91	16	7.8	0.318	0.07	8.6	16.7
G1TA0606	157.4	06/06/94	09:30	200	26.9	31	8.4	6.32	27	8.4	0.065	0.08	8.3	21.2
G1TA0620	171.6	06/20/94	13:20	162	27.4	21	8.2	5.77	19	7.9	0.291	0.01	8.5	20.0
G1TA0706	187.4	07/06/94	09:30	173	27.5	26	8.5	6.22	21	8.3	1.023	0.10	7.7	17.6
G1TA0718	199.4	07/18/94	09:15	157	30.2	23	8.9	5.48	21	9.0	0.415	0.10	7.7	15.0
G1WA0803	215.5	08/03/94	11:30	197	27.6	40	8.3	0.20	36	8.3	0.261	0.12	13.4	17.3
G2WA080	215.5	08/03/94	12:30	210	27.9	44	8.3	0.08	43	8.3	0.241	0.11	14.6	17.3
G3WA0803	215.6	08/03/94	13:30	222	27.9	56	8.4	0.03	50	8.4	0.198	0.09	14.8	17.6
G1WA0817	229.4	08/17/94	10:35	240	27.5	60	8.6	0.46	61	8.7	0.190	0.16	13.7	19.3
G2WA0817	229.5	08/17/94	12:35	267	27.3	80	8.9	0.40	77	9.1	0.210	0.14	13.3	18.7
G3WA0817	229.6	08/17/94	14:35	284	27.1	88	9.1	0.22	88	9.1	0.197	0.17	13.5	18.8
G1WA0829	241.4	08/29/94	10:15	339	26.3	119	9.2	0.18	120	9.4	0.241	0.30	12.6	19.4
G2WA0829	241.7	08/29/94	16:15	378	25.9	143	9.3	0.06	142	9.5	0.229	0.41	10.8	20.6
G3WA0829	241.8	08/29/94	20:15	414	25.3	169	9.3	0.03	164	9.6	0.174	0.43	9.2	26.0
G1WA0912	255.4	09/12/94	10:00	478	24.9	202	9.4	0.03	206	9.5	0.166	0.39	7.1	20.6
G2WA0912	255.8	09/12/94	20:00	539	24.6	242	9.4	<0.02	244	9.5	0.164	0.51	6.9	21.1
G3WA091	256.3	09/13/94	06:00	607	24.3	281	9.4	<0.02	289	9.4	0.160	0.72	6.2	22.3
G1WA0927	271.0	09/27/94	23:15	652	24.2	327	9.2	<0.02	336	9.3	0.104	0.61	5.9	23.0
G2WA0928	271.6	09/28/94	13:30	713	24.2	370	9.2	<0.02	383	9.2	0.073	0.74	5.5	24.8
G3WA0929	272.1	09/29/94	03:15	749	23.9	398	9.1	<0.02	410	9.1	0.064	0.94	4.9	25.7
G1WA1011	284.2	10/11/94	04:00	763	23.8	408	9.1	<0.02	419	9.2	0.064	1.47	4.2	26.9
G2WA1011	284.9	10/11/94	21:00	786	23.7	420	9.0	<0.02	433	9.1	0.052	1.61	3.7	27.4
G3WA1012	285.4	10/12/94	10:00	794	23.6	426	9.0	<0.02	439	9.1	0.050	1.71	3.7	27.7
G1WA1017	290.4	10/17/94	09:00	764	23.6	426	8.9	<0.02	430	9.2	0.058	1.76	6.0	27.7
G2WA1017	290.5	10/17/94	12:00	776	23.8	433	8.9	<0.02	433	9.2	0.053	1.85	3.6	28.3
G1WA1018	291.4	10/18/94	09:00	800	23.4	443	9.0	<0.02	440	9.2	0.043	1.86	4.1	29.1
G2WA101	291.5	10/18/94	12:00	802	23.6	443	9.0	<0.02	446	9.2	0.031	1.87	4.5	34.2
G1WA1024	297.4	10/24/94	09:00	814	23.6	443	8.8	<0.02	454	9.0	0.056	2.10	2.6	25.6
G2WA1024	297.5	10/24/94	12:00	813	23.8	444	8.8	<0.02	457	9.0	0.071	2.24	2.5	26.3
G1WA1025	298.4	10/25/94	09:00	810	23.8	445	8.8	<0.02	457	8.9	0.051	2.32	3.0	26.1
G2WA1025	298.5	10/25/94	12:00	813	23.9	446	8.8	<0.02	458	9.0	0.065	2.32	2.6	26.1
G1WA1031	304.3	10/31/94	08:00	814	24.0	466	8.8	<0.02	454	9.0	0.011	2.41	2.3	25.6
G2WA1031	304.5	10/31/94	11:00	821	24.0	445	8.8	<0.02	459	9.0	0.017	2.30	2.3	26.6
G1WA1101	305.3	11/01/94	07:00	813	24.0	446	8.8	<0.02	443	8.9	0.020	2.22	2.3	26.8
G2WA1101	305.4	11/01/94	10:00	813	24.0	448	8.8	<0.02	444	9.0	0.017	2.16	2.3	26.8
G1WA1107	311.4	11/07/94	08:30	811	24.1	441	8.7	<0.02	452	9.0	0.019	2.22	2.2	24.7
G2WA110	311.5	11/07/94	11:30	813	24.2	442	8.7	<0.02	451	9.0	0.018	2.23	2.1	26.4
G1WA1114	318.4	11/14/94	08:30	812	24.1	435	8.8	<0.02	458	9.1	0.019	2.18	2.1	26.4
G2WA1114	318.5	11/14/94	11:30	810	24.3	435	8.8	<0.02	456	9.1	0.018	2.25	2.1	26.9
G1WA1121	325.4	11/21/94	08:30	813	24.3	447	8.8	<0.02	461	8.9	0.020	2.13	2.1	25.7
G1WA1129	333.4	11/29/94	08:30	813.0	24.5	444	8.8	<0.02	463	8.9	0.018	2.12	2.0	27.0
G1WA1130	334.7	11/30/94	16:00	813.0	24.3	443	8.8	<0.02	465	8.9	0.018	2.12	2.1	27.5
G1RA0111	11.0	01/11/95	07:30	---	---	---	---	---	467	8.8	0.026	1.39	1.8	26.3
G3RA0111	11.0	01/11/95	09:30	---	---	---	---	---	465	8.8	0.025	1.47	1.6	27.5

Spec. Cond., specific conductance in microsiemens per centimeter
mg/L, milligram per liter
µg/L, microgram per liter
Alkalinity as calcium carbonate
D.O., dissolved oxygen
PDB, Peedee Belemnites
TOC, total organic carbon
TU, tritium units
THM, trihalomethane
THMP, trihalomethane potential

collected during the 1994 ASR test

Carbon-13 permil (PDB)	Fluoride mg/L	Iron mg/L	Magnesium mg/L	Manganese mg/L	Nitrogen 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
---	**2.3**	**0.027**	**0.38**	**0.007**	**---**	**---**	**---**	**3.69**	**16.5**	**214.7**	**0.0**	**---**	**---**	**---**	**---**
---	0.0	0.033	2.14	0.042	---	---	---	5.39	7.5	22.8	29.1	---	---	---	---
---	2.3	0.020	0.30	0.002	0.03	---	0.071	1.94	15.9	204.6	3.3	0.14	---	---	---
---	---	0.014	1.73	0.028	0.65	---	0.028	3.16	7.2	15.8	29.9	0.16	---	---	---
---	2.2	0.027	0.37	0.002	0.12	---	0.068	2.04	15.8	209.1	2.4	0.10	---	---	---
---	1.0	0.296	1.74	0.024	0.42	---	0.021	2.88	7.1	13.0	25.2	0.10	---	---	---
---	2.2	0.010	0.38	0.001	0.11	---	0.066	2.12	16.8	220.2	4.6	0.10	---	---	---
---	1.0	0.087	1.80	0.021	0.44	---	0.014	2.90	7.3	12.8	22.1	0.10	---	---	---
---	2.1	0.014	0.38	0.001	0.06	---	0.071	1.97	15.9	215.8	4.4	0.11	---	---	---
---	1.0	0.031	1.97	0.023	0.45	---	0.026	2.91	6.9	15.3	24.7	0.10	---	---	---
---	**2.1**	**0.018**	**0.39**	**0.002**	**0.02**	**1.33**	**0.059**	**1.79**	**16.5**	**201.9**	**2.9**	**0.15**	**---**	**<1**	**166**
---	0.9	0.134	1.83	0.026	0.36	3.20	0.010	2.94	8.7	13.6	21.0	0.11	---	42.4	373
---	1.0	0.012	1.84	0.037	0.54	3.26	0.015	2.92	7.2	14.9	27.3	<0.1	---	31.2	336
---	1.1	0.006	1.93	0.018	0.53	2.03	0.013	2.84	8.9	17.3	29.0	<0.1	18.4	21.3	192
-11.44	1.1	0.028	2.04	0.011	0.58	1.67	0.010	2.93	9.1	16.9	30.4	<0.1	19.4	20.8	159
---	1.0	0.022	2.14	0.010	0.61	2.03	0.017	3.27	7.8	27.2	38.3	<0.1	22.2	24.7	184
-21.66	1.2	0.035	1.84	0.026	0.51	3.52	0.014	3.50	7.8	21.6	32.2	<0.1	20.5	32.7	344
-16.03	1.2	0.043	1.70	0.020	0.40	3.22	0.012	3.06	7.5	21.5	32.8	<0.1	21.2	31.4	299
-21.61	1.1	0.032	1.74	0.021	0.34	2.63	0.016	3.01	8.5	20.0	31.6	<0.1	22.8	30.2	306
-8.15	1.2	0.051	2.28	0.032	0.78	2.31	0.193	3.04	5.9	19.9	33.5	<0.1	22.5	12.3	272
---	**1.2**	**0.046**	**2.27**	**0.028**	**0.72**	**---**	**0.197**	**3.16**	**5.9**	**22.4**	**33.8**	**<0.1**	**---**	**---**	**---**
---	1.2	0.039	2.22	0.024	0.73	---	0.203	3.15	5.9	25.1	34.0	<0.1	---	---	---
-6.41	1.3	0.043	1.82	0.022	5.61	2.94	0.280	3.37	8.0	33.2	33.4	<0.1	22.4	3.6	270
---	1.3	0.026	1.78	0.018	5.34	---	0.259	3.22	8.0	40.0	32.5	<0.1	---	---	---
---	1.3	0.016	1.73	0.016	5.27	---	0.242	3.30	8.1	45.2	35.7	<0.1	---	---	---
-5.30	1.6	0.028	1.36	0.015	0.16	3.14	0.217	3.08	6.6	58.9	33.9	<0.1	19.7	<1	306
---	1.8	0.041	1.23	0.012	0.10	---	0.174	2.87	6.9	70.9	34.8	<0.1	---	---	---
---	1.9	0.041	1.07	0.009	0.05	---	0.148	2.92	7.2	88.2	34.3	<0.1	---	---	---
-5.65	2.3	0.029	0.83	0.011	0.03	3.74	0.143	2.85	7.8	103.6	33.0	<0.1	16.3	<1	467
---	2.6	0.036	0.75	0.010	0.02	---	0.118	2.80	8.3	119.5	31.7	<0.1	---	---	---
---	**2.8**	**0.034**	**0.72**	**0.009**	**0.03**	**---**	**0.110**	**2.87**	**9.1**	**136.3**	**25.1**	**<0.1**	**---**	**---**	**---**
---	2.5	0.029	0.72	0.010	<0.01	---	0.120	2.90	9.7	157.4	19.1	<0.1	---	---	---
-6.20	2.6	0.022	0.68	0.008	<0.01	1.78	0.102	2.94	10.9	172.7	13.3	<0.1	7.0	<1	190
---	2.7	0.010	0.66	0.007	<0.01	---	0.092	2.91	11.7	187.0	9.3	<0.1	---	---	---
-5.98	2.4	0.021	0.60	0.007	<0.01	1.53	0.098	3.48	10.9	193.0	8.0	<0.1	2.5	<1	176
---	2.5	0.020	0.59	0.006	<0.01	---	0.089	3.45	11.7	198.0	6.1	<0.1	---	---	---
---	2.5	0.019	0.60	0.007	<0.01	---	0.085	3.38	11.9	202.0	4.6	<0.1	---	---	---
-5.86	2.4	0.028	0.56	0.006	<0.01	1.42	0.112	3.29	12.8	189.0	6.0	<0.1	2.3	<1	190
---	2.5	0.024	0.55	0.006	<0.01	---	0.100	3.31	12.8	193.0	5.4	<0.1	---	---	---
-6.40	2.5	0.017	0.58	0.004	<0.01	1.42	0.082	3.62	13.6	176.0	4.3	<0.1	1.7	<1	193
-6.23	**2.5**	**0.016**	**0.58**	**0.004**	**<0.01**	**1.28**	**0.081**	**3.81**	**13.7**	**172.0**	**3.6**	**<0.1**	**---**	**---**	**---**
-6.60	2.5	0.017	0.50	0.002	<0.01	1.61	0.072	2.77	16.5	209.0	3.5	<0.1	<0.7	<1	198
-6.09	2.6	0.018	0.51	0.002	<0.01	1.61	0.074	2.72	16.6	212.0	3.8	<0.1	---	---	---
-6.56	2.6	0.023	0.48	0.002	<0.01	1.61	0.076	2.69	16.4	205.0	3.3	<0.1	<0.8	<1	188
-6.36	2.6	0.020	0.51	0.002	<0.01	1.61	0.075	2.64	16.5	212.0	3.5	<0.1	---	---	---
-6.68	2.6	0.013	0.50	0.002	<0.01	1.60	0.066	2.60	15.3	202.0	3.7	<0.1	<0.5	<1	186
-6.74	2.7	0.011	0.50	0.002	<0.01	1.45	0.067	2.68	15.4	204.0	3.2	<0.1	---	---	---
-6.09	2.6	0.013	0.51	0.002	<0.01	1.60	0.067	2.50	15.7	209.0	3.6	<0.1	<0.5	<1	186
-6.03	2.6	0.013	0.49	0.002	<0.01	1.60	0.068	2.63	15.6	198.0	3.7	<0.1	---	---	---
-6.36	2.7	0.015	0.49	0.001	<0.01	1.23	0.055	2.44	14.1	207.0	3.1	<0.1	<0.7	<1	179
-6.60	**2.7**	**0.018**	**0.49**	**0.001**	**<0.01**	**1.39**	**0.056**	**2.52**	**14.3**	**211.0**	**2.6**	**<0.1**	**---**	**---**	**---**
-6.09	2.7	0.023	0.45	0.001	<0.01	1.41	0.057	2.48	14.2	206.0	2.6	<0.1	<0.7	<1	153
-6.03	2.7	0.025	0.46	0.001	<0.01	1.27	0.056	2.50	14.2	203.0	2.3	<0.1	---	---	---
-6.09	2.6	0.022	0.45	0.002	<0.01	1.39	0.072	2.49	16.3	205.0	3.2	<0.1	<0.7	<1	153
-5.73	2.6	0.026	0.44	0.001	<0.01	5.13?	0.089	2.50	16.4	206.0	3.3	<0.1	---	---	---
-6.31	2.6	0.025	0.47	0.002	<0.01	0.98	0.061	2.44	16.6	208.0	3.1	<0.1	<0.6	<1	179
---	2.7	0.021	0.38	0.001	<0.01	1.09	0.063	2.24	15.6	209.0	2.1	<0.1	<0.6	---	---
---	2.7	0.021	0.40	0.001	<0.01	1.09	0.058	2.18	15.8	211.0	2.3	<0.1	<0.6	---	---

TABLE 5. Description of laboratory analytical methods

CHARACTERISTIC	DETECTION LIMIT µg/L	PRECISION AT DETECTION LIMIT (2SD) µg/L	UPPER END OF ANALYTICAL RANGE µg/L	PRECISION AT THE UPPER END (+10%) µg/L	EPA METHOD NUMBER
Aluminum	3	2	100	10	202.2 GFAA
Calcium	120	90	5,000	500	215.1 FAA
Iron	0.4	0.3	20	2	236.2 GFAA
Sodium	1,800	1,200	2,000	200	273.1 FAA
Boron	14	9	140,000	1,400	212.3 (colorimetric)
Magnesium	6	5	500	50	242.1 FAA
Potassium	15	11	2,000	200	258.1 FAA
Manganese	0.2	0.12	10	1	243.1 GFAA
pH	0	0.1	14	0.1	ISE
Silica	20	14	25,000	2,500	370.1 (colorimetric)
Nitrite	4	3	1,000	100	353.3 (colorimetric)
Fluoride	15	10	—	—	340.2 ISE
Sulfate	1,500	990	300	4,500	375.3 (turbidimetric)
Chloride	600	200	—	—	325.3 ISE
Nitrate	3	1	1,000	100	353.3 (colorimetric)
Alkalinity	5,000	2,000	—	—	ISE
Sulfide	100	20	20,000	200	376.2 (colorimetric)
Phosphate	10	8	500	10	365.2 (colorimetric)

SD, Standard Deviation
ISE, Ion Selective Electrode
FAA, Flame Atomic Absorption Spectrometer
GFAA, Graphite Furnace Spectrophotometer
colorimetric, Fiber Optic Colorimeter
turbidimetric, Digital Turbimeter

Concentration Changes

By graphing concentrations with respect to time, common patterns are discernible because gains and/or losses are easily visualized. This type of data presentation, however, does not provide any clear information as to the cause of these concentration changes. For example, water quality changes effected by simple mixing are not distinguished from changes caused by chemical reaction. This can only be assessed by plotting the ion concentrations as a function of the chloride concentration.

Chloride concentration provides information on the degree of mixing that has occurred between the injected water and the native ground water. This is possible because chloride does not undergo any chemical reactions in the aquifer and therefore is conservative. Mixing information is critical because it can be used to assess the magnitude and kinds of chemical changes affecting the chemically reactive or nonconservative chemicals.

If the behavior of an ion is conservative or *nonreactive*, its concentration must be proportional to that of the chloride, and a straight line will result when the ion is plotted against chloride. This line represents the results of mixing of the treated water and native ground water. If chemical processes, such as mineral precipitation, decrease the concentration of an ion in solution, resulting data points will fall below the mixing line. Concentrations will lie above the mixing line if the ion is added to the water as a result of a chemical process such as mineral dissolution.

The chemical composition of all the samples is shown in Figures 5 through 13. The left-hand graphs (a and c) illustrate concentration changes with chloride; while the right-hand graphs (b and d) illustrate concentration changes with time. In the latter, pre-injection ground water samples are plotted on the right-hand side of the graph, although chronologically the ground water samples were collected before the beginning of injection (April 24). This has been done to facilitate comparison of the chemical composition of the recovered water with that of the native ground water.

Chloride (Cl^-). The conservative behavior of this ion is demonstrated by its linear relationship to another conservative tracer, tritium. As shown in Figure 5(a), the tritium-chloride relation describes a straight line. Some horizontal scattering of the data is present at either end of the mixing line as a result of temporal fluctuations in the chloride concentration of the injected and native ground water. These data were used to obtain an estimate of the mixing ratios of these two water masses over time, as described later in this report.

Chloride concentration in the treated surface water seems to follow a seasonal trend, with lower values in winter and higher ones in spring. During the injection period, Figure 5(b), chloride concentrations in the treated water ranged from 15 to 21 mg/L with a mean of 16 mg/L. The ground water concentration ranged from 20 to 30 mg/L with a mean of 28 mg/L. During the storage period, chloride increased gradually to 28 mg/L, and during the recovery period the first three samples had a chloride concentration greater than 28 mg/L. Thereafter, samples had lower concentrations that averaged 26 mg/L. The initially high values during recovery were unexpected, as several exceeded the maximum concentrations of the ground water and treated water. This suggests that the mixing that occurred in the well during recovery was more complicated than a two-end-member mixing of pre-test ground water and treated water.

Unlike other ASR tests in the region (Castro, 1995), the chloride data suggest that mixing was a dominant process throughout storage and recovery. Indeed, by the end of the storage period, when 10 percent of the injected volume (6.2 million gallons) had been recovered, the chloride concentration of the well water was nearly equal to the pre-test level in the aquifer.

Alkalinity (as $CaCO_3$). The field alkalinity measurements are expressed as an equivalent concentration of calcium carbonate in milligrams of calcium carbonate per liter of water (mg $CaCO_3$/L). Alkalinities were lowest in the treated water (17 to 31 mg/L) and highest in the ground water (440 to 452 mg/L) (Fig. 6). The alkalinity of the recovered water increased during the storage period until pre-test ground water levels were reached by the beginning of recovery. The alkalinity increase probably was due to mixing, as well as to calcium carbonate dissolution.

pH. The field measurements of pH were lowest in the treated water (7.7 to 8.9) during injection and highest during the midpoint of storage (9.4)(Fig. 6). Field pH of the pre-test ground water ranged only from 8.8 to 8.9. The increase in pH during the storage period probably was the result of calcite dissolution. Mixing during the latter half of storage and throughout recovery probably caused the pH to decline to native ground water levels by the beginning of recovery.

Sodium (Na^+). Sodium concentrations ranged from 13 to 27 mg/L in the treated water and from 202 to 220 mg/L in the ground water (Fig. 7). During the storage period, sodium concentrations increased from 20 to 210 mg/L (Fig. 7). As shown in Figure 7(a), mixing alone cannot explain all of the increase in sodium concentration

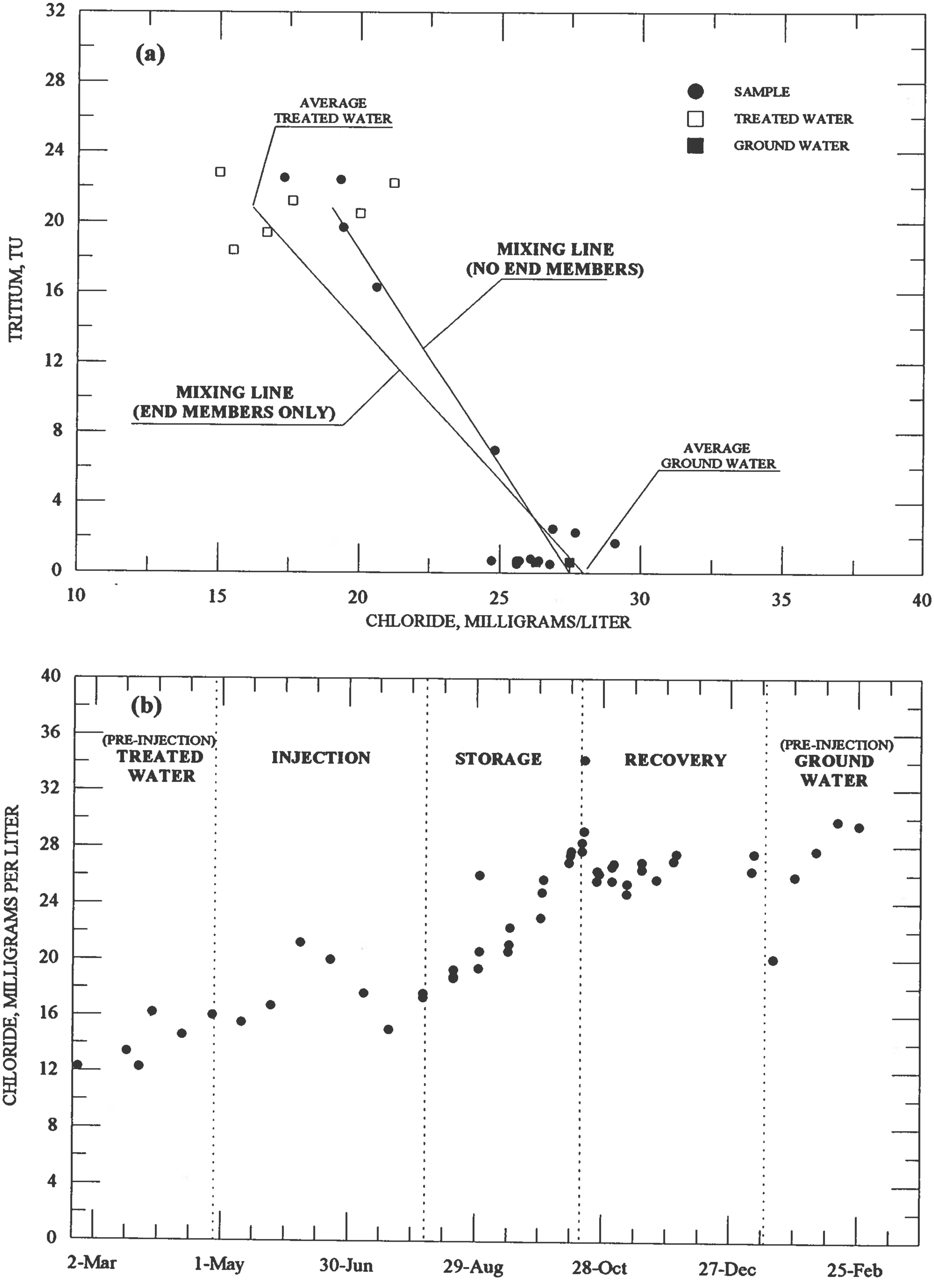


Figure 5. Variation of chloride concentration with tritum activity (a) and with time (b).

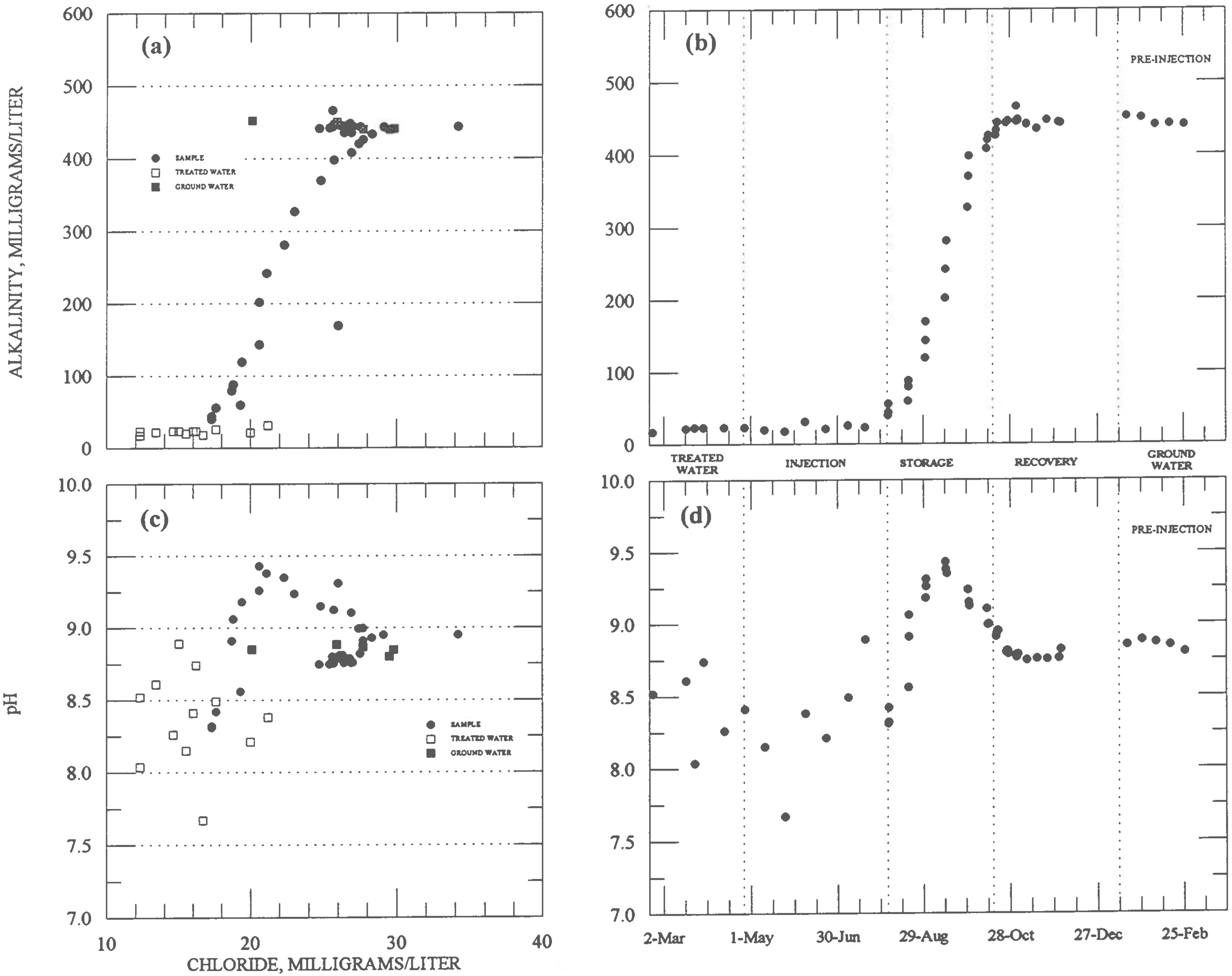


Figure 6. Variation of alkalinity and pH with chloride (a) and (c), and with time (b) and (d).

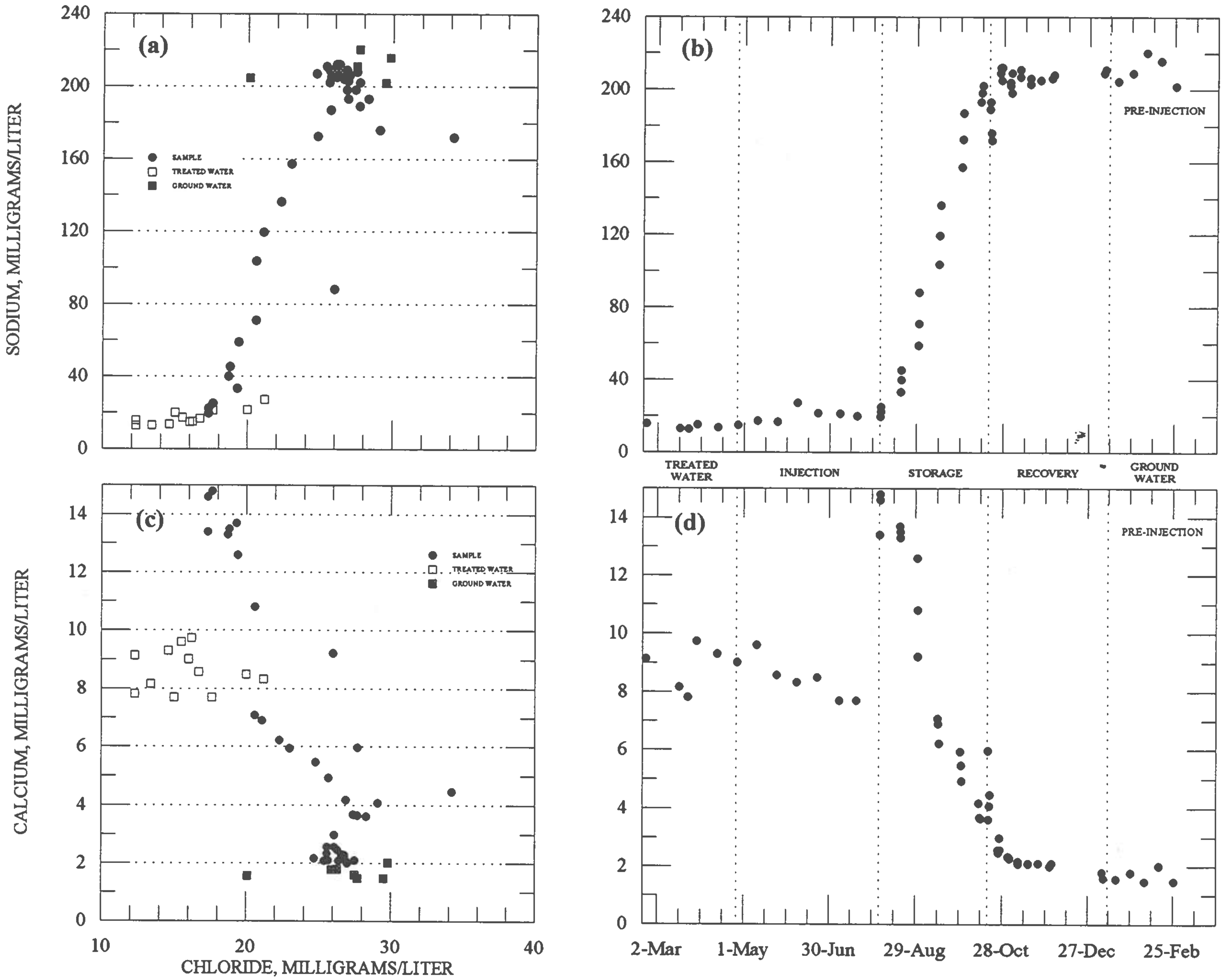


Figure 7. Variation of sodium and calcium with chloride (a) and (c), and with time (b) and (d).

observed during storage. The additional sodium was probably supplied by exchange with calcium. The calcium from calcite dissolution exchanged with sodium adsorbed on marine clay. Although the Suggested Maximum Level of 20 mg/L was exceeded, sodium concentrations were below the Maximum Contaminant Level (250 mg/L).

Calcium (Ca^{2+}). Calcium concentrations ranged from 7.7 to 9.7 mg/L in the treated water and from 1.5 to 2.0 mg/L in the native ground water (Fig. 7). Calcium, during the storage and recovery periods, exhibited a behavior similar to that observed at other ASR sites (Castro, 1995). At the start of storage, concentrations had already exceeded that found in either the treated or native ground water. In this ASR test, the calcium concentrations reached a maximum of 14.8 mg/L. The concentration increase was followed by a monotonic decrease until native ground water levels were reached during early recovery.

Calcite dissolution was the probable source of the elevated calcium concentrations. This process was enhanced by acid produced from the oxidation of organic matter to carbon dioxide and from the oxidation of pyrite to sulfate. Throughout storage and recovery, calcium concentrations declined over the three samples collected during each weekly sampling cycle, suggesting that most of the calcite dissolution had occurred close to the well bore. The overall decline in concentration observed throughout the storage period was probably caused by the loss of calcium by sodium exchange, as well as by mixing with the native ground water.

Sulfate (SO_4^{2-}). Sulfate concentrations in the treated water ranged from 21 to 38 mg/L (Fig. 8). These fluctuations are probably related to variations in the water quality of Bull Creek. During the early part of the storage period, sulfate increased slightly to a maximum of 35.7 mg/L and then decreased. By the beginning of the recovery period, concentrations had declined to native ground water levels (2.4 to 4.6 mg/L) (Fig. 8).

The chloride data suggest that a net addition of sulfate occurred during early storage. This probably was the result of pyrite oxidation. The monotonic decrease in sulfate through the remainder of the storage period was largely the result of mixing with the native ground water, although some removal by sulfate reduction could have occurred. Although sulfide levels were below the detection limit, this does not preclude sulfate reduction, as pyrite precipitation would have removed most of the sulfide from the water.

Iron (Fe^{2+}). Ferrous ion concentrations ranged from 0.060 to 0.296 mg/L in the treated water and from 0.010 to 0.027 mg/L in the ground water (Fig.8). Concentrations were highest at the start of storage (0.051 mg/L) and declined until native ground water levels were reached by the beginning of recovery. Thus, concentrations were well below the Suggested Maximum Level (0.3 mg/L). The great variability in the data is probably due to corrosion of the well casing; for example, iron was solubilized from various parts of the casing at rates determined by such factors as the degree of rusting and structural integrity of the cast-iron pipe.

The chloride data suggest that a net addition of iron occurred during early storage. This increase in ferrous iron is attributed to pyrite oxidation supported by the dissolved oxygen present in the treated water. The subsequent decline in concentrations to native ground water levels is probably the result of mixing, although removal by precipitation as pyrite could have occurred following the depletion of dissolved oxygen from the treated water.

Nitrate (NO_3^-). The concentration of nitrate plus nitrite is expressed as dissolved inorganic nitrogen (mg N/L). Nitrate concentrations are several orders of magnitude greater than those of nitrite, so the dissolved inorganic nitrogen concentration is effectively equal to the nitrate concentration. Concentrations ranged from 0.36 to 0.65 mg N/L in the treated water and from 0.02 to 0.12 mg N/L in the native ground water (Fig 9). Concentrations were highest at the start of storage (0.78 mg/L) but were below the Maximum Contamination Level (10 mg/L). Following this maximum, concentrations declined rapidly until the detection limit was reached. Thus, nitrate concentrations were below detection from the midpoint of storage through recovery. The chloride data indicate that a net removal of nitrate occurred. This is probably the result of denitrification (Chapelle, 1993) in which anaerobic bacterial respiration reduces nitrate to nitrogen gas by oxidizing organic matter to carbon dioxide.

Dissolved Oxygen (O_2). In the treated water, oxygen concentrations ranged from 5.5 to 9.8 mg/L (Fig. 9). This variation can be attributed to seasonal temperature changes, as gas solubility is inversely proportional to temperature. Thus, colder water has a higher concentration of dissolved gasses, such as oxygen, than does warmer water. Freshwater in equilibrium with the atmosphere at 5°C has a dissolved-oxygen concentration of 12.8 mg/L. This equilibrium concentration declines to 7.6 mg/L at 30°C.

The dissolved-oxygen concentration of the native ground water was 0.32 mg/L. Since the probe's detection limit was 0.1 mg/L, the ground water concentrations suggest that gas exchange with the atmosphere had probably introduced a small amount of dissolved oxygen into the bottom of the flowthrough cell. During the entire

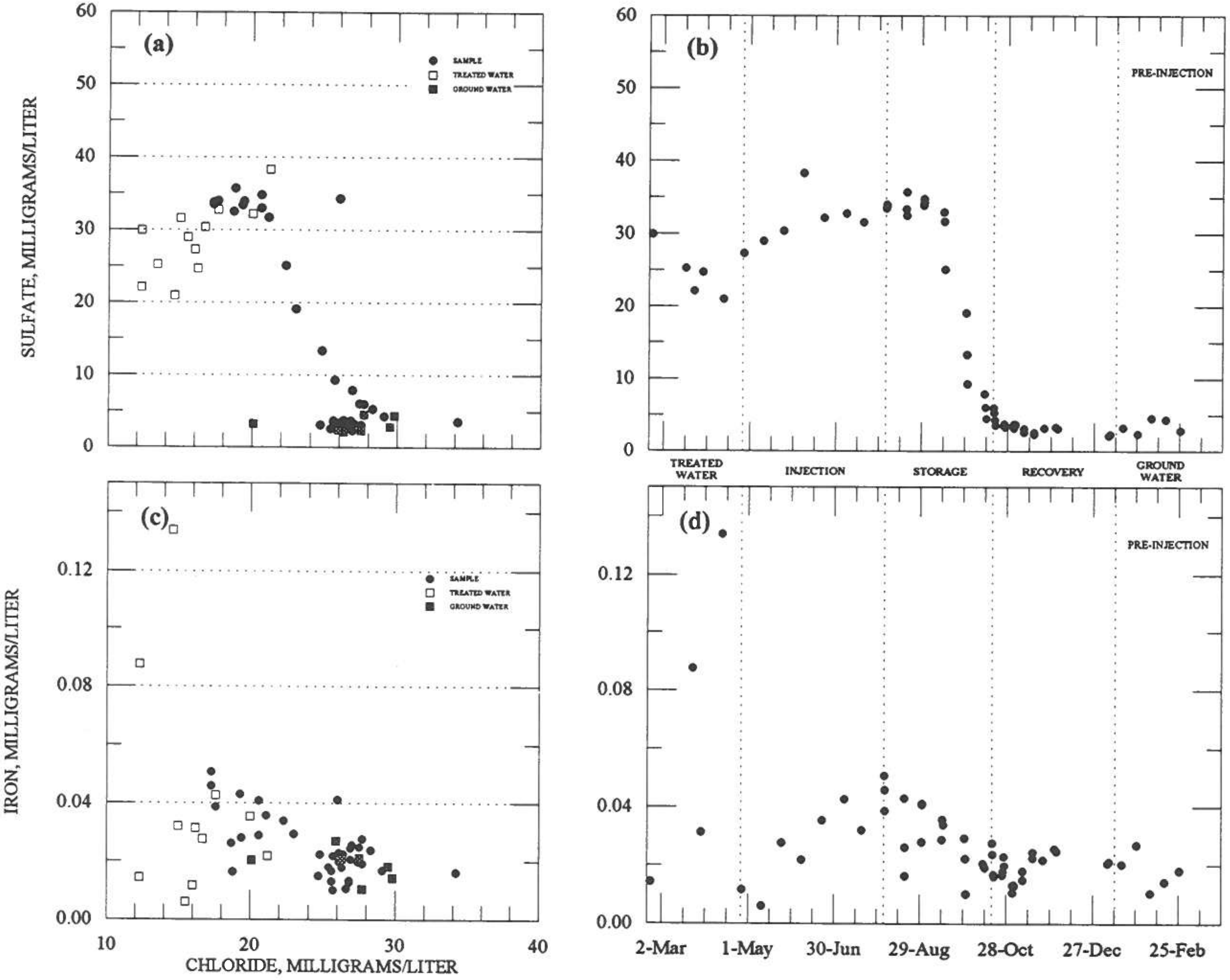


Figure 8. Variation of sulfate and iron with chloride (a) and (c), and with time (b) and (d).

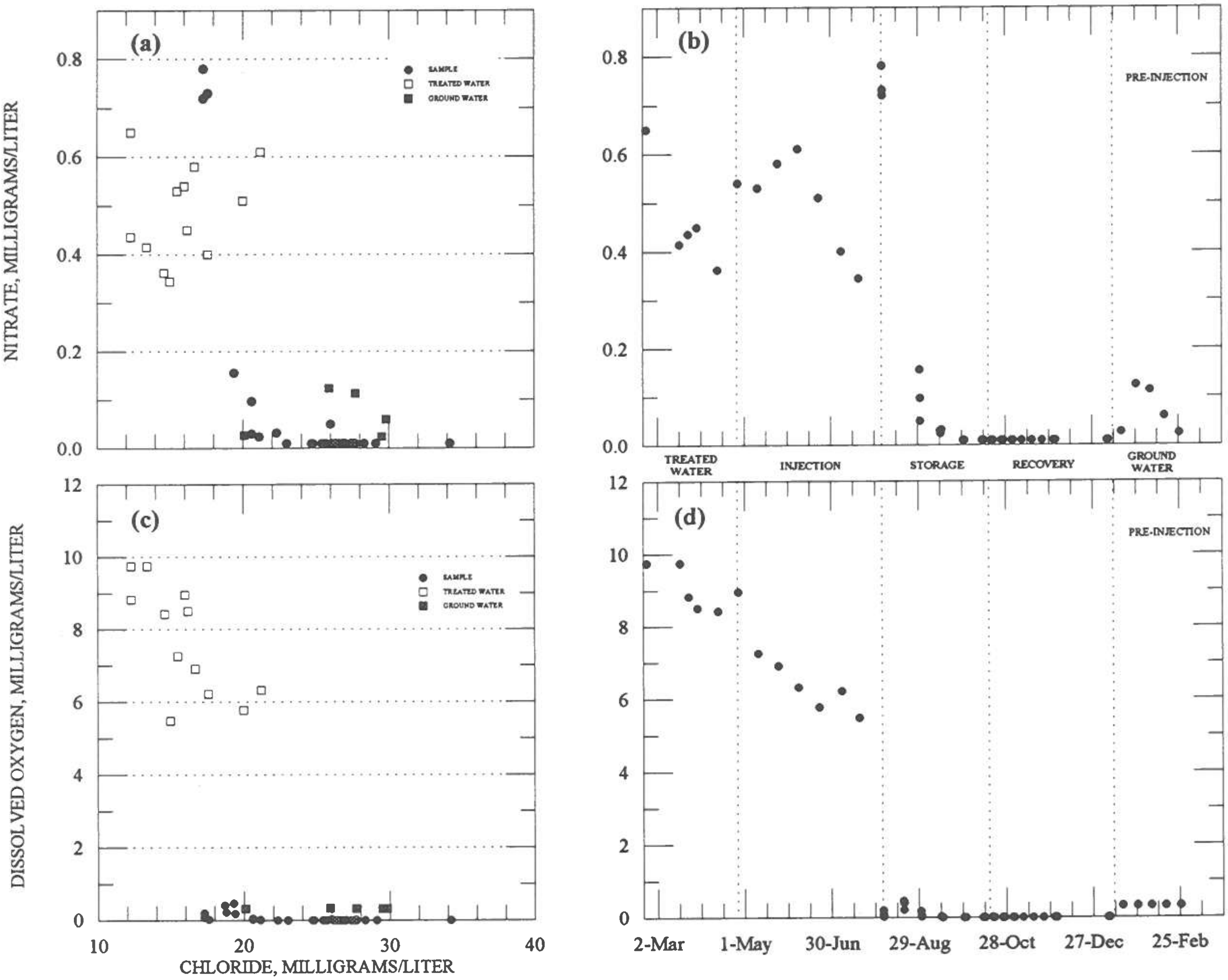


Figure 9. Variation of nitrate and dissolved oxygen with chloride (a) and (c), and with time (b) and (d).

storage and recovery period, dissolved-oxygen concentrations were less than or equal to that of the native ground water. This represents a net removal of oxygen from the treated water that was probably the result of bacterially mediated aerobic respiration of organic matter.

Fluoride (F^-). Fluoride concentrations ranged from 0.9 to 1.2 mg/L in the treated water and from 2.1 to 2.3 mg/L in the native ground water (Fig 10). In the recovered water, fluoride ranged from 1.2 to 2.8 mg/L. Fluoride concentrations reached a maximum during the midpoint of storage, declined until recovery began, and then increased to native ground water levels.

The chloride data suggest that, in addition to mixing, fluoride was supplied to the stored water as a result of some chemical process. Because fluorapatite, the most common fluoride-containing mineral in the Black Creek aquifers, is insoluble at pH's greater than 8 (Zack, 1980), congruent dissolution cannot explain the net addition of fluoride to the recovered water. Hence, anion exchange of hydroxide for fluoride from the surface of fluorapatite is postulated to have occurred (Castro, 1995). The Maximum Contaminant Level for fluoride is 4.0 mg/L and the Suggested Maximum Level is 2.0 mg/L. Thus this process, along with mixing, appears to have elevated fluoride concentrations above the Suggested Maximum Level by the midpoint of the storage period.

Phosphate (PO_4^{3-}). Phosphate concentrations are expressed as milligrams of phosphorous per liter of water (mg P/L). Phosphate concentrations ranged from 0.010 to 0.017 mg P/L in the treated water and from 0.06 to 0.07 mg P/L in the native ground water (Fig. 10). Early in the storage period, phosphate reached a maximum of 0.28 mg P/L, exceeding the concentrations in both the treated and native ground water. Concentrations then monotonically declined until, by the midpoint of recovery, they reached those of the native ground water.

The chloride data suggest that a net removal of phosphate occurred early during the storage period, probably as a result of hydroxyapatite precipitation. As discussed above, fluorapatite may not be the source of the phosphate increase observed in the early storage period.

Magnesium (Mg^{2+}). Magnesium concentrations ranged from 1.7 to 2.1 mg/L in the treated water and from 0.3 to 0.4 mg/L in the native ground water (Fig 11). The behavior of this ion was similar to that of calcium; concentrations were highest at the start of storage (2.3 mg/L) and, by the end of recovery, they monotonically declined to those of the native ground water. The chloride data indicate that, as with calcium, the initial increase in concentration was the result of calcite dissolution. Magnesium is present in small amounts in the calcite minerals typical of the Black Creek aquifers, for example, in aragonite (McMahon and Chapelle, 1991). The decline in magnesium through the recovery and storage periods was largely the result of mixing, although some exchange with sodium could have occurred.

Potassium (K^+). Concentrations ranged from 2.8 to 3.5 mg/L in the treated water and from 1.8 to 2.1 mg/L in the native ground water (Fig 11). In general, potassium concentrations declined throughout the storage and recovery periods, although native ground water levels were not reached by the end of recovery. This decline was interrupted twice, once in early storage when concentrations reached a maximum of 3.4 mg/L and then during early recovery (3.8 mg/L). They exceeded the average concentration in the treated water and ground water. Thus, these high values represent net additions probably caused by the dissolution of potassium-rich silicate minerals, such as glauconite, which is a common silicate mineral in the sediments of the Black Creek Formation (Castro and others, 1995). The overall decline in potassium concentrations is largely the result of mixing with the low-potassium ground water, although some exchange with sodium could have occurred during recovery.

Silica (SiO_2). Silica concentrations ranged from 6.9 to 9.1 mg/L in the treated water and from 15.8 to 16.8 mg/L in the native ground water (Fig 12). Silica concentrations increased during the storage period until native ground water levels were reached in early recovery. The chloride data suggest that mixing controlled the silica concentrations although some net addition probably occurred as a result of the dissolution of silicate minerals such as illite and/or glauconite.

Aluminum (Al^{3+}). Aluminum concentrations ranged from 0.065 to 1.023 mg/L in the treated water and from 0.022 to 0.035 mg/L in the native ground water (Fig 12). The Suggested Maximum Limit for aluminum is 0.20 mg/L and the Minimum Limit is 0.05 mg/L. Although the treated water exceeded the Suggested Maximum Limit, concentrations in the recovered water were less than the upper limit by the midpoint of the storage period, and by the beginning of recovery they had declined to those of the native ground water. The chloride data and the geochemical models indicate that aluminum concentrations were reduced by mixing and by

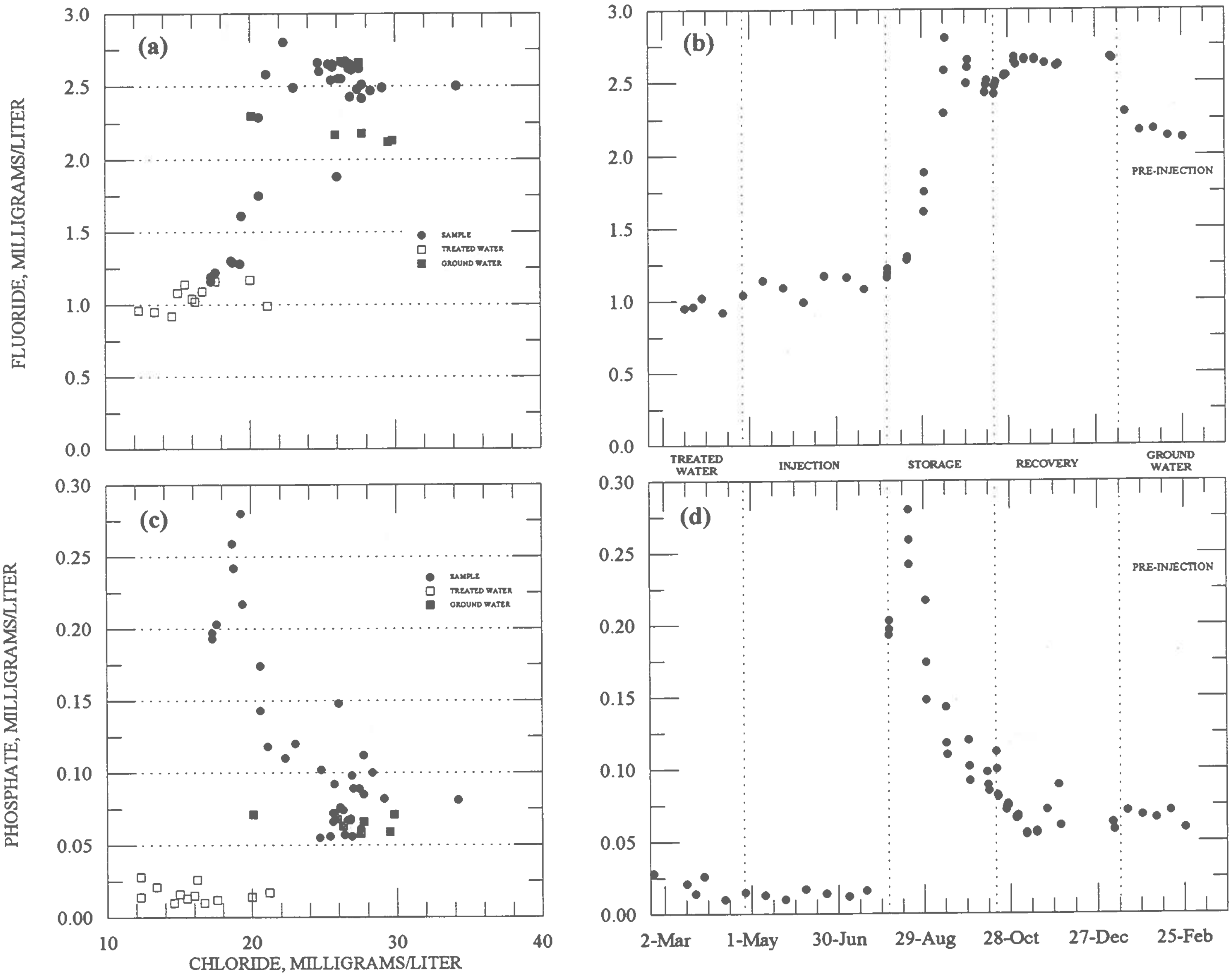


Figure 10. Variation of fluoride and phosphate with chloride (a) and (c), and with time (b) and (d).

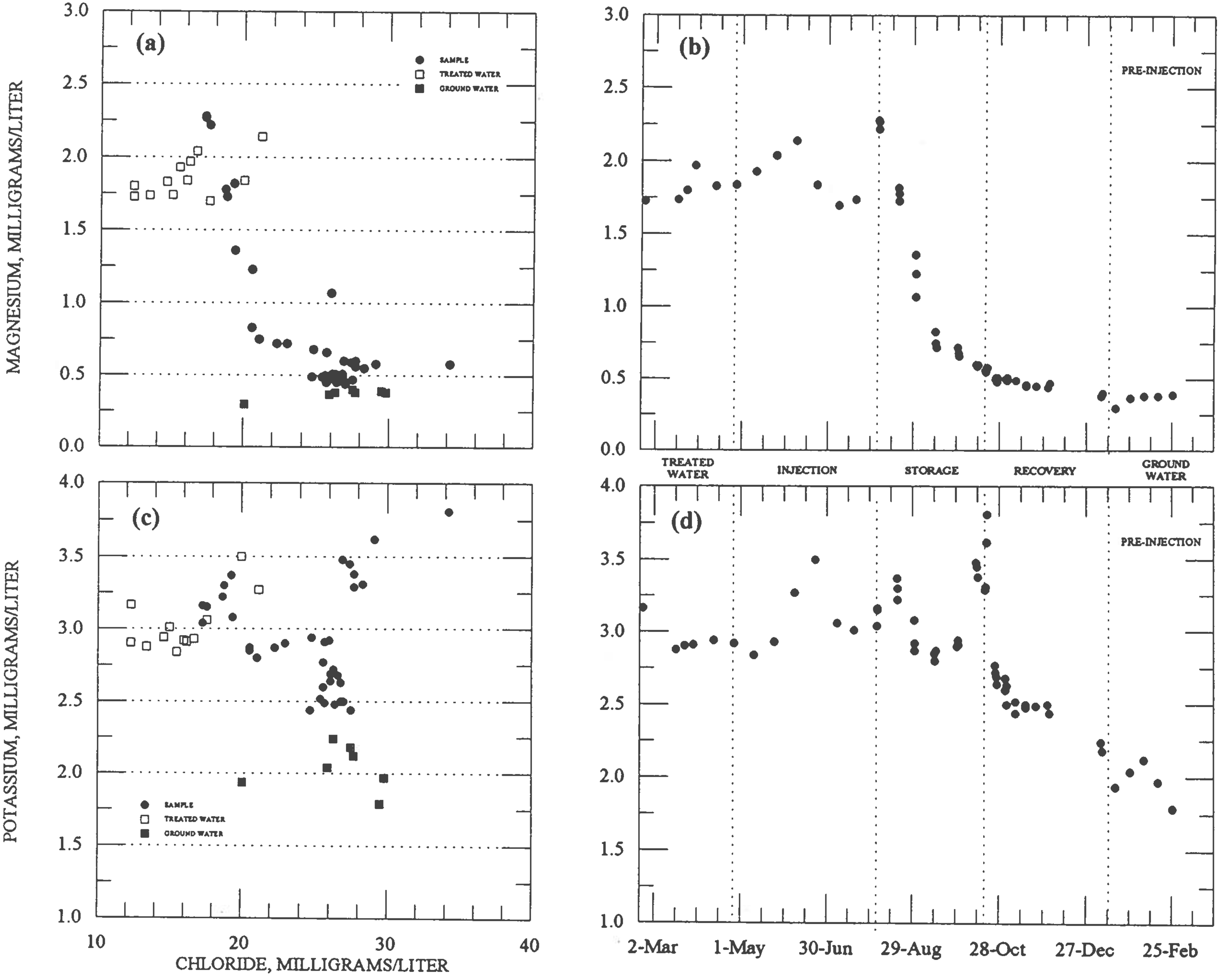


Figure 11. Variation of magnesium and potassium with chloride (a) and (c), and with time (b) and (d).

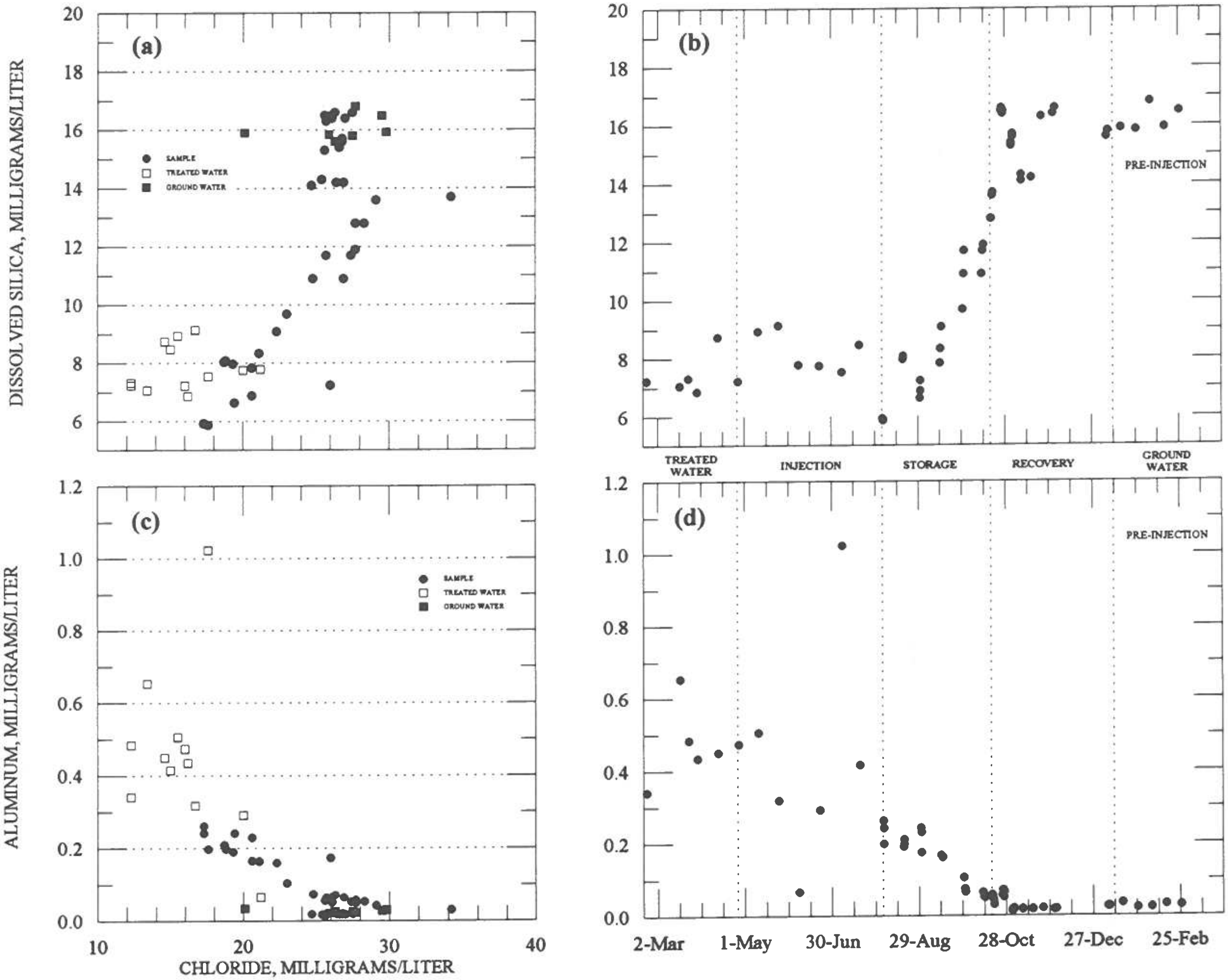


Figure 12. Variation of dissolved silica and aluminum with chloride (a) and (c), and with time (b) and (d).

incongruent dissolution of cation-rich minerals to yield kaolinite.

Total Organic Carbon (TOC). The total organic carbon is expressed as milligrams of carbon per liter of water (mg C/L). The TOC ranged from 1.7 to 3.5 mg C/L in the treated water and was 1.3 mg C/L in the native ground water (Fig 13). At the start of storage, TOC concentrations were less than that of the last treated water injected, but by the midpoint of the storage period the concentrations had increased to a maximum of 3.7 mg C/L. By the end of the storage period, the TOC had declined to values typical of the native ground water. The initial TOC increase was probably the result of an increase in the bacterially mediated oxidation of organic matter to carbon dioxide stimulated by the injection of oxygenated treated water. Mixing is the likely cause of the subsequent decline toward native ground water concentrations.

Total trihalomethane (THM). Trihalomethane (THM) concentrations ranged from 0.021 to 0.042 mg/L in the treated water and were below the detection limit of 0.001 mg/L in the native ground water (Fig 13). During storage, THM's decreased to less than the detection limits and remained there for the rest of the ASR test. The THM interim drinking water standard is 0.100 mg/L and the proposed standard is 0.080 mg/L. Thus, the THM concentrations were well below these standards throughout the ASR test.

The chloride data suggest that a chemical process caused some net removal of THM's, although mixing was also responsible for lowering concentrations. THM reduction has been associated with bacterially mediated processes (Singer and others, 1993). The potential for forming trihalomethane (THMP) also decreased during the storage and recovery periods.

Carbon-13 ($\delta^{13}C$). The relative proportions of ^{13}C and ^{12}C in the dissolved inorganic carbon are given as $\delta^{13}C$ in parts per thousand (per mil) relative to the PDB (Peedee Belemnite) standard. Owing to the cost of the analysis, only a limited number of measurements were made.

During the injection period, the $\delta^{13}C$ of the treated water ranged from -11.4 to -21.6 per mil. The $\delta^{13}C$ of dissolved inorganic carbon in the native ground water is approximately -5.4 per mil (Castro, 1996). By the midpoint of the storage period, the $\delta^{13}C$ had increased to -6.2 per mil, and by beginning of recovery, the $\delta^{13}C$ had increased to values similar to that of the native ground water. The increase probably was the result of the dissolution of calcite, as its $\delta^{13}C$ is approximately +1 per mil (McMahon and Chapelle, 1991).

MIXING FROM CONSERVATIVE TRACERS

Conservative mixing was the cause of most of the chemical changes observed during the storage and recovery periods. Two conservative tracers, chloride and tritium, were used to determine the proportions of treated and ground water present in each recovered water sample.

The conservative behavior of these tracers was evaluated by checking that the chloride (Cl) and tritium (^3H) concentrations were linearly related as shown in Figure 5 ($r^2 = 0.87$). Because chloride and tritium do not undergo chemical reactions in the aquifer, deviations from the mixing line could be caused by the presence of additional end members. Alternatively, the composition of the end members may not have been well estimated. Indeed, significant temporal variability in the treated water composition was observed.

To obtain a representative composition of the ground water, a simple average of the four pre-injection samples was calculated. The composition of the treated water varied significantly over time. Probably this was the result of changes in treatment protocols at the treatment plant and of fluctuations in the chemical composition of Bull Creek water. Instead of averaging the values, one sample was selected as most representative of the entire data set (G1TA04025) and three others as representative of extremes (G1TA0322, G1TA0606, G1TA07018). The extremes were identified as treated water samples that had the greatest number of outlier constituents. The treated water sample identified as most representative had the fewest outliers. Constituents were identified as outliers if they were greater or smaller than the mean ± 1 standard deviation. As discussed in the next section, successful geochemical models required the use of these extremes to simulate temporal changes in the composition of the treated water.

The analytical error associated with measuring tritium compounded with temporal variability yielded significant uncertainties in the mixing ratios. Since tritium's half-life is 12.4 years, its concentration in the native ground water is 0 TU (tritium units). The only uncertainty in this end member is caused by analytical error. The lowest tritium activities observed were reported as <0.5 to <0.8 TU, where these values represent 2 standard deviations (s). Standard deviations are a function of concentration or, in the case of tritium, activity. When measured near the detection limit, they can be used to compute a Practical Quantitation Limit, for example 5 TU to 6 standard deviations, which yields tritium activities ranging from 1.2 to 2.4 TU. The average treated water activity was 20.8 TU (1s is 1.5 TU for six samples). This suggests that the lowest detectable fraction of treated water was approximately 10 percent.

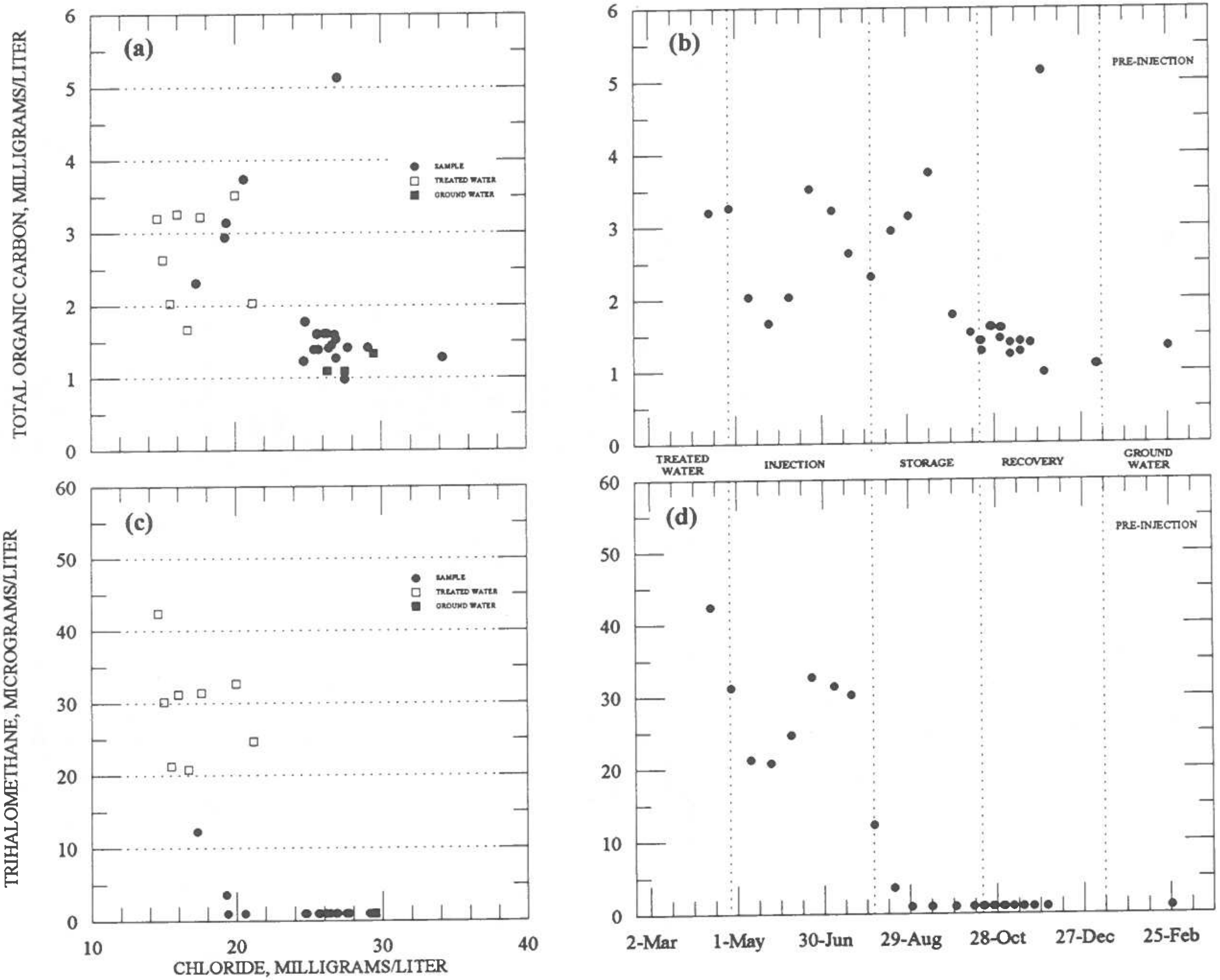


Figure 13. Variation of total organic carbon and trihalomethane with chloride (a) and (c), and with time (b) and (d).

Variability in the chloride concentrations of the end members also caused some uncertainty in the mixing ratios computed from this tracer. Thus, when employed independently, the chloride and tritium predicted somewhat different mixing ratios (Fig. 14(a)). Regardless, both tracers indicate that considerable proportions of ground water were present by the midpoint of the storage period. By the beginning of the recovery period, the water samples contained less than 20 percent treated water. This suggests that a buffer zone was not properly developed.

During the first two days of the recovery period, October 17 and 18, chloride concentrations as high as 34 mg/L were observed. This exceeded the levels of the native ground water. As shown in Figure 14(b), the relative ionic composition of the recovered water also shifted. Both observations suggest that another ground water of slightly different chemical composition to that of the pre-injection ground water was present at these dates.

The continued presence of the above-mentioned ground water (third end member) was evaluated by checking for a significant difference between the mean composition of the water recovered from October 31 to November 30 and the mean composition of the native ground water (pre-ASR). Differences at the 95-percent confidence level were observed in approximately half of the characteristics measured: Ca^{2+}, Mg^{2+}, K^+, Al^{3+}, B, SiO_2, NO^-_3, and F^-. This suggests that even at the end of the recovery period some of the other ground water (third end member) was still present.

Because the third end member (other ground water) had a higher chloride concentration than the treated water and the pre-injection ground water, its source is assumed to be ground water derived from lower units in the aquifer. Although the mean chloride and temperature of the recovered water were not significantly different at the 95-percent confidence level from those of the native ground water, they were higher in the recovered water. This supports the hypothesis that the third end member was ground water derived from lower levels of the aquifer.

Geochemical-reaction models for the samples collected at the beginning of recovery (October 17 and 18) could be constructed only if three end members were assumed to be present. The chemical composition of the third end member was simulated from concentrations reported for the Highway 501 Pottery well (HOR-934) on 6/31/87 (Table 3). The well is near the Bay Road well. The water, which represents a composite ground water sample from depths ranging from 350 to 690 ft, had a chloride concentration of 56.6 mg/L.

To determine the time periods over which mixing of three end members occurred, tritium and chloride data were simultaneously used to develop some mixing models. The results shown in Table 6 demonstrate that a three-end-member mixing situation is plausible for almost all dates after September 12. The two-end-member models constructed from chloride and tritium are also shown to illustrate the dates where these models fail and three-end-member mixing is most likely to have occurred. Plausible results from the three-end-member model required that:

a) the tritium concentration of the treated-water end member be equal to the lower limit of the 95-percent confidence interval (2s below the mean),
b) the chloride concentration of the pre-injection ground water be 1s below its mean, and
c) the detection limit of tritium in the recovered samples be approximately 1.5 TU.

At the mixing ratios predicted from the three-end-member model, only 16 percent of the treated water injected into the well was recovered by October 30. This low recovery rate (small volume of surface water) seemed to be caused by mixing between the treated water and the native ground water.

This mixing is thought to be the result of screen clogging. If during the injection period the lower screens became clogged, these aquifers would have stored a relatively small volume of treated water. Intensive pumping during recovery could have unclogged these screens. The lower aquifers would have then yielded ground water with relatively higher chloride concentrations (refer to Site Hydrogeology). As the pumping continued, more screens could have become unclogged and thereby caused the lower aquifers to contribute proportionally more to the overall well flow and therefore to the chemical composition of the recovered water. The initially greater influence of the lower aquifers (high chloride) on the water quality of the recovered water would have progressively been replaced by that from the upper aquifers (lower chloride). Thus, most of the mixing between the injected treated water and the ground water probably took place in the well casing and only some in the aquifer.

Clogging during injection could have been caused by particulate aluminum in the injected water, as aluminum concentrations in the treated water were very high during the injection phase. Alum is a byproduct of GSWSA's treatment process. The concentration of alum in the treated water varies over time and was relatively high during the injection period (Bill Bell, GSWSA, personal communication). Since screen clogging was not anticipated, no effort was made to measure the alum content of the treated water prior to injection. Although some suspended solids were collected on the 0.45-micron

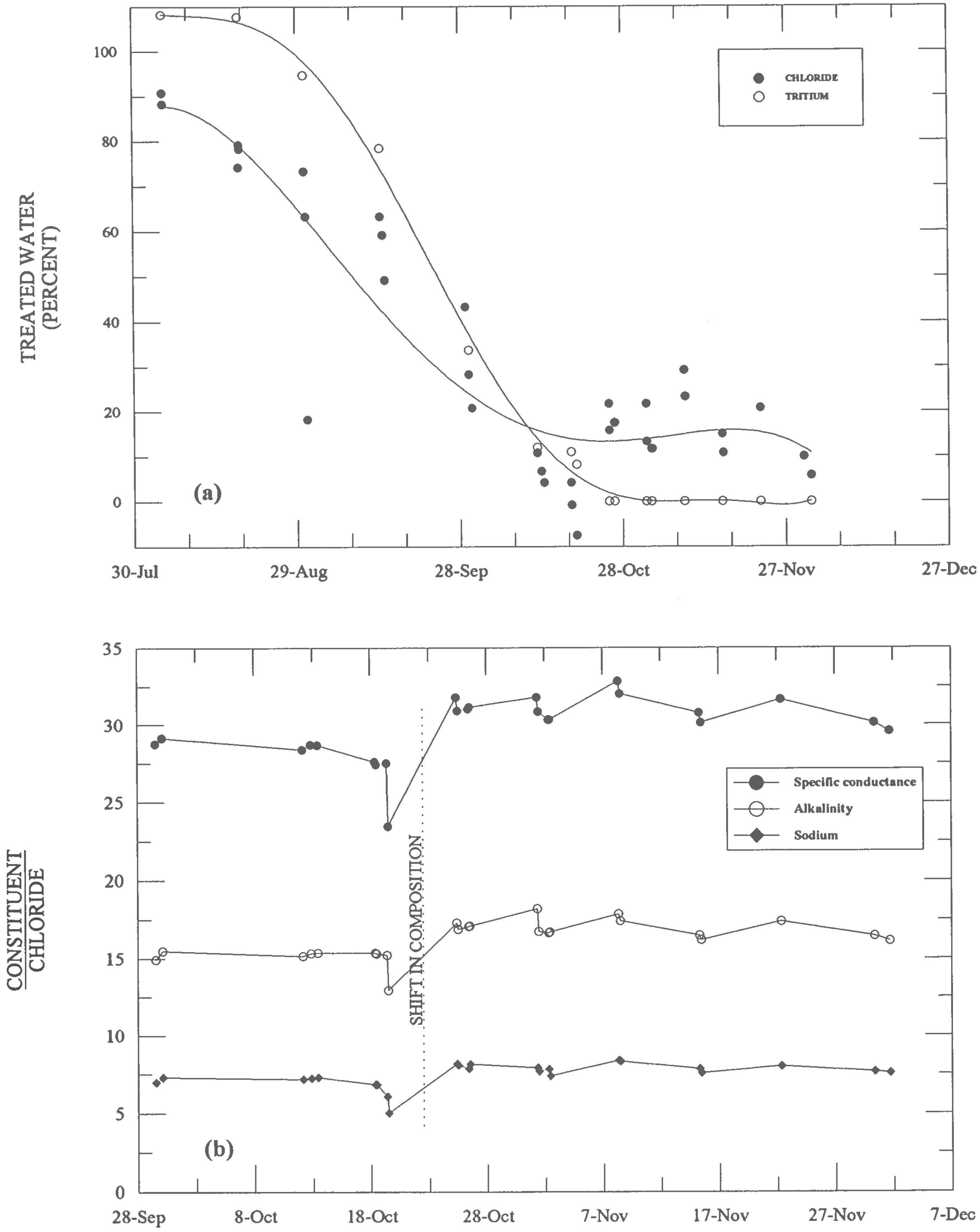


Figure 14. Mixing computed from chloride and tritium (a). Ion ratios with time during the recovery period (b).

Table 6. Two- and three-end-member mixing results

SAMPLE ID	PERCENT COMPOSITION								
	TRITIUM AND CHLORIDE			CHLORIDE		CHLORIDE		TRITIUM	
	TW	GW1	GW2	TW	GW1	TW	GW2	TW	GW1
G1WA0803	135	51	16	89	11	97	3	126	-26
G1WA0817	134	-56	22	70	30	92	8	126	-26
G1WA0829	121	-39	18	69	31	92	8	111	-11
G1WA0912	97	-11	14	57	43	89	11	92	8
G2WA0928	45	45	10	17	83	79	21	39	61
G2WA1011	20	72	8	-4	104	74	26	14	86
G2WA1017	17	73	10	-12	112	72	28	13	87
G1WA1018	13	74	13	-25	125	68	32	10	90
G2WA1018	15	54	31	-75	175	55	45	10	90
G1WA1024	10	90	0	9	91	77	23	4	96
G2WA1024	11	87	3	2	98	75	25	4	96
G1WA1025	11	86	3	4	96	75	25	4	96
G2WA1025	9	89	2	4	96	75	25	4	96
G1WA1031	7	94	-1	9	91	77	23	3	97
G2WA1031	7	90	3	-1	101	74	26	3	97
G1WA1101	7	90	3	-3	103	74	26	3	97
G2WA1102	8	88	4	-3	103	74	26	3	97
G1WA1107	10	93	-3	17	83	79	21	4	96
G2WA1107	10	90	0	11	89	77	23	4	96
G1WA1114	10	87	3	1	99	75	25	4	96
G2WA1114	10	85	5	-4	104	74	26	4	96
G1WA1121	10	89	1	8	92	76	24	4	96
G1WA1129	9	86	5	-5	105	73	27	4	96
G1WA1130	8	85	6	-10	110	72	28	3	97

TW, TREATED WATER (Cl 16.2 mg/L, T 17.8 TU)
GW1, NATIVE GROUND WATER (Cl 26.5 mg/L, T 0 TU)
GW2, OTHER GROUND WATER (Cl 56.6 mg/L, T 0 TU)

filters used to prepare the water samples, the amounts recovered were insufficient for analysis. Alternatively, clogging could have been caused by particles from the well casing and gravel pack. The filtered residue appeared to be a fine-grained sediment (clay-size).

High-turbidity water was sometimes observed, especially during the storage period when short pumping cycles were used to collect samples. As shown in Figure 15, these turbidities were very high at the beginning of each pumping cycle and then declined until pumping was terminated. The highest turbidity was observed at the initiation of continuous pumping that marked the start of the recovery period. This suggests that particulate matter was mobilized from screens, tail pipe, and gravel pack each time the pump was turned on or off. Apparently, complete particle removal was not achieved as a result of the short pumping cycles made during the storage period.

GAS ENTRAINMENT

Gas bubbles were observed in the recovered water. Samples were analyzed in an effort to determine which gases were contributing to bubble formation as well as to determine their sources. The former was accomplished by determining which of the gases were supersaturated and thereby had the potential to form bubbles.

The water samples were collected without exposure to air and then injected into an evacuated vial. The headspace concentrations of methane, carbon dioxide, nitrogen, and oxygen gas were measured by gas chromatography (Paul Bradley, U.S. Geological Survey) and the sample concentrations computed from the Henry's Law constants which describe the solubility of these gases. Blanks were used to correct for air leakage during sampling. The percent saturation of each gas was computed as a ratio of the corrected gas concentration to that which would be present if equilibrium had been achieved with air at the in situ temperature. The latter was assumed to be 25°C as the recovered water samples ranged in temperature from 20.2 to 30.2°C. The results are shown in Figure 16.

If the percent saturation exceeds 100, the gas has the potential to form bubbles. All samples were supersaturated with respect to CO_2 and N_2 gas and some with O_2. Although these supersaturations are large, the total amount of gas in the sampling vials was reasonably small; the total pressure in the vials ranged from 0.007 to 0.100 atmosphere.

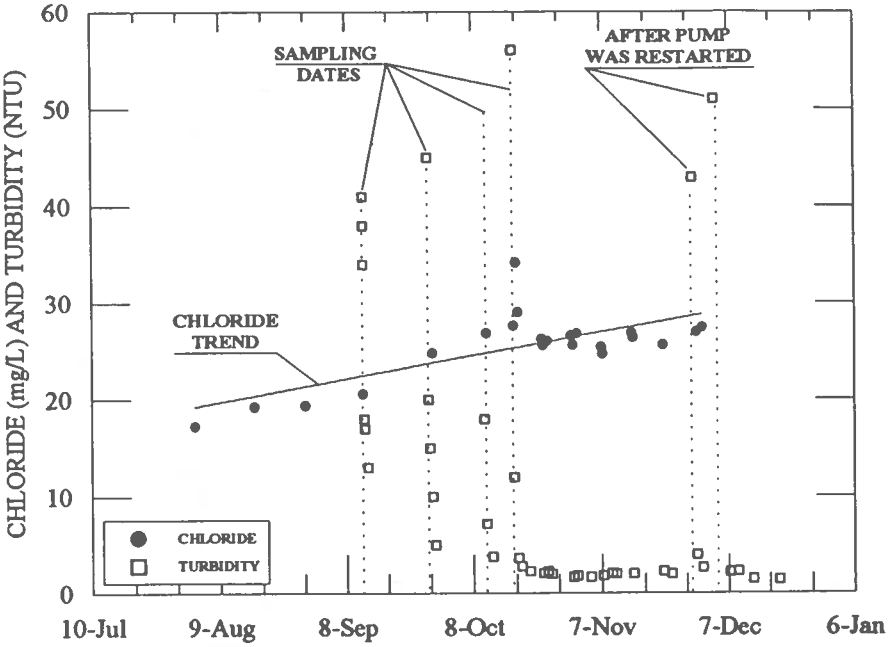


Figure 15. Turbidity variation in water samples during the storage and recovery periods.

As shown in Figure 16, the gas composition varied over time. Variations in percent saturation of nitrogen suggest differences in how much air was forced into the aquifer during injection. The observed supersaturations were unlikely to be contamination artifacts, as the gas concentrations in the blanks were so much smaller (and reasonably consistent) than the corrected gas concentrations.

To determine whether air injection was the source of gas in the samples, the headspace concentrations were compared to the gas composition of air (Fig. 16). This was done by computing the percentage of each gas relative to the total corrected gas concentration in the headspace. Using the headspace as a reflection of gas composition eliminates the need to correct for differences in solubility among the gases. Since nitrogen represents approximately 80 percent of the gas present in these water samples, the major source of the gas bubbles is probably air entrained in the well. This may have occurred when the treated water was injected into the aquifer.

None of the gases was expected to demonstrate perfect conservative behavior. Denitrification is a source of nitrogen. Aerobic respiration and pyrite oxidation are a sink for oxygen. Methane is produced by methanogenesis. Denitrification and aerobic respiration, moreover, are sources of carbon dioxide, as is the oxidation of methane. Carbon dioxide can also be lost by reaction with calcite, bicarbonate, and water. Hence, the relative abundance of dissolved oxygen was less than that predicted by the observed nitrogen, while that of carbon dioxide and methane were higher.

To determine the relative impact of aerobic respiration on the carbon dioxide and dissolved-oxygen concentrations, an estimate was made of how much carbon dioxide would have been produced if all the missing dissolved oxygen were consumed by aerobic respiration. Approximately 40 percent of the excess carbon dioxide was supplied by aerobic respiration. This is an upper estimate, as some of the dissolved oxygen was undoubtedly removed by pyrite oxidation. The rest of the carbon dioxide presumably was supplied by anaerobic respiration.

The concentration of TOC (dissolved organic carbon), which had to be oxidized to carbon dioxide in excess of the concentration supported by nitrogen, ranged from 0.3 to 2.5 mg/L. As discussed earlier, TOC concentrations declined from 3.7 to 1.0 mg/L from the middle

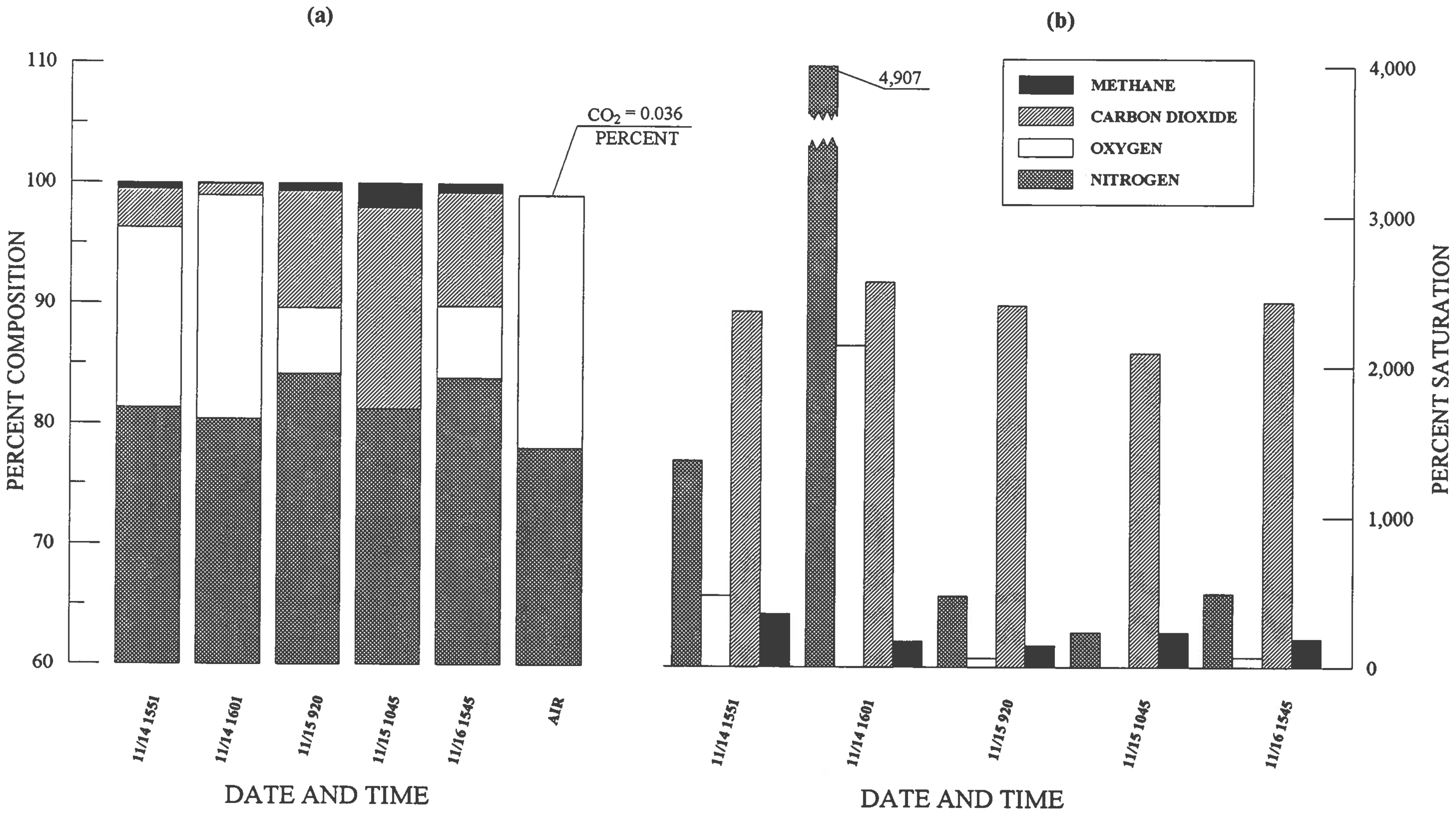


Figure 16. Percent composition and saturation of gas samples collected during the recovery period.

of storage to the end of the recovery period. Thus, TOC remineralization could have accounted for the observed excess carbon dioxide.

In conclusion, air seems to be the source of the gas causing bubbles in the recovered water. The amount of air forced into the aquifer appears to have varied significantly over time, although this could have been the result of variable amounts of degassing during sampling. The pervasive presence of relatively high concentrations of carbon dioxide and low concentrations of oxygen compared to water equilibrated with air probably is the result of organic matter respiration and pyrite oxidation.

EFFECT OF CO_2 DEGASSING ON THE pH OF THE RECOVERED WATER

Because the recovered water was supersaturated with respect to carbon dioxide, degassing could have occurred during sampling and prior to analysis. If significant, this degassing could have raised the sample's pH. This was of concern, as the degree of calcite saturation is pH dependent.

The degree of saturation and the change in pH resulting from degassing were evaluated in sample G3WA1012, as shown in Figure 17. This was done by using the carbonate speciation equations of Stumm and Morgan (1996).

Figure 17 shows how the degree of calcite saturation increases if the sample undergoes a significant amount of degassing. Sample G3WA1012 was supersaturated with respect to calcite at the time of pH measurement in the flowthrough cell. Had the sample continued to degas and been allowed to come to atmospheric equilibrium with respect to carbon dioxide, the sample pH would have increased to 9.15, and it would have become even more supersaturated with respect to calcite.

The carbon dioxide concentrations calculated from the sample pH and alkalinity are considerably lower than those measured directly as a gas under gastight conditions. Had the carbon dioxide concentrations been similar to those measured directly as a gas (log P_{CO2}=-2.23), the pH would have been slightly less than 8 and the sample would have been undersaturated with respect to calcite. Thus, degassing could have caused this sample's pH to increase from 8 to 9.

This suggests that ground water supersaturated with respect to carbon dioxide has the potential to undergo a post-sampling pH increase by as much as 1 pH unit. Much evidence exists to support this conclusion. First, direct gas measurements demonstrate that carbon dioxide was supersaturated in the ground water at concentrations higher than those computed from the post-sampling pH's. Second, the geochemical-model results indicate that calcite dissolution was one of the most important (mass-wise) chemical reactions that occurred between the treated water and ground water. To produce water undersaturated with respect to calcite the in situ pH's had to be approximately 8. Third, as shown in Figure 18, the pH's measured in the laboratory were approximately 0.2 pH unit higher than those measured in the field. This suggests that degassing continued as the samples were transported from the field to the laboratory. Finally, on the basis of the geochemical-model results, the carbon-stable isotope data indicate that incongruent dissolution of calcium carbonate occurred. This dissolution probably resulted in the production of calcite from the partial dissolution of aragonite, with the remainder of the aragonite dissolution producing dissolved inorganic carbonate, for example, carbonate and bicarbonate ions.

Field pH's were measured with a probe located at the bottom of a flowthrough cell (Fig. 2) that had a height of about 4 ft. Recovered water flowed into the cell from the bottom, where the sensor was located, and exited from the top of the tank. Evidently, this was not sufficient to prevent degassing prior to pH measurement. Thus, the pH's of the samples used to construct geochemical models had to be corrected. The pH of all the recovered water and ground water samples was lowered until calcite undersaturation was achieved. In most cases, this required lowering the pH to 8.2, in a few cases to 8.0.

GEOCHEMICAL MODELING

Conservative and Nonconservative Processes

NETPATH, a geochemical modeling program developed by the U.S. Geological Survey (Plummer and others, 1991), was used to identify the physical and chemical processes responsible for changes observed in the chemical composition of the treated water during its storage in the aquifer. The model results demonstrate that most of the geochemical changes were the result of simple mixing between the treated water and the ground water.

The models created with NETPATH simulate two phenomena: (1) the conservative mixing of water masses and (2) nonconservative processes which occurred in the aquifer. The latter are chemical reactions, such as the dissolution of calcite and ion exchange on the surface of clay minerals. The model uses conservative tracers, such as chloride and tritium, to estimate the contribution of mixing between the treated water and the native ground water. The model estimates the nonconservative contributions by using a series of mass-action equations.

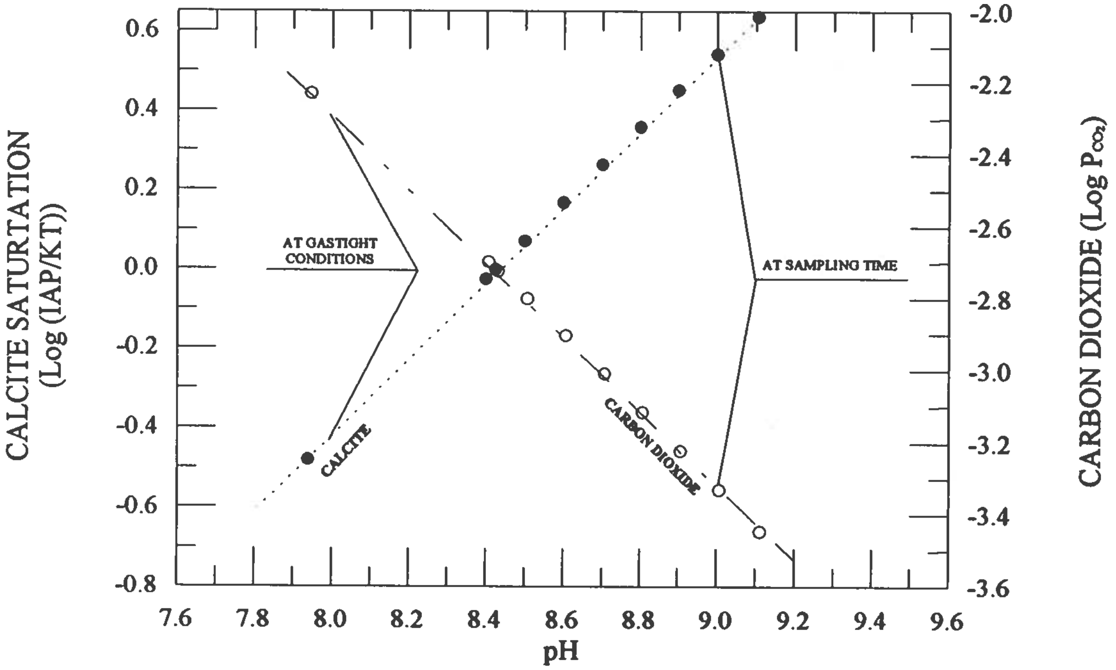


Figure 17. Effect of degassing on pH and calcite saturation for sample G3WA1012 .

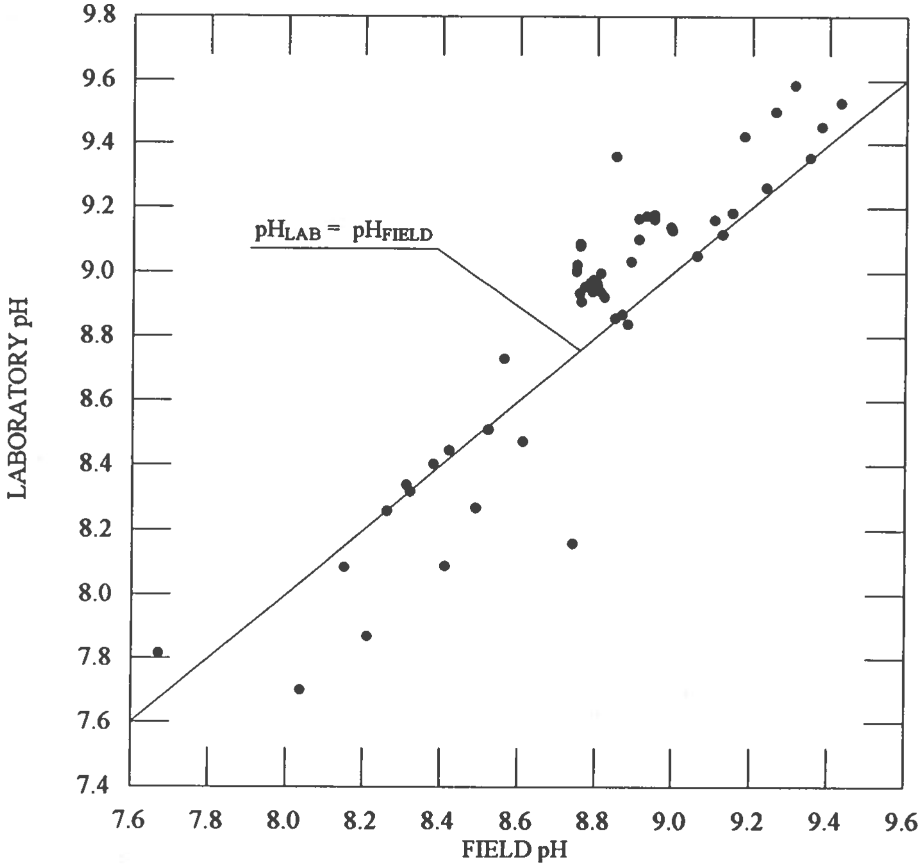


Figure 18. Graph showing comparison of laboratory and field pH.

For example, the average chloride concentration of treated water was 16.2 mg/L and that of the ground water was 28.2 mg/L. The water sample recovered on September 13 (G3WA0913) had a chloride concentration of 22.3 mg/L. It was composed of nearly equal proportions of treated and ground water—49 percent treated water and 51 percent ground water. These ratios were then used to predict the rest of the chemical composition of the water sample. The average sodium concentrations of the treated and ground water were 17.5 and 210.4 mg/L, respectively. The sodium concentration produced by admixture of 49 percent treated water with 51 percent ground water is 115.9 mg/L. The sodium concentration measured in the September 13 sample was 136.3 mg/L. This suggests that some chemical reaction between the aquifer and the treated water supplied sodium to this sample, increasing its concentration to 20.4 mg/L.

Chemical changes resulting from nonconservative behavior—chemical reactions—can be estimated by subtracting the mixing contributions from the sample's concentration. When supplied with a variety of possible chemical reactions, NETPATH distributes the observed concentration changes so as to insure that an elemental mass balance is achieved. The elements modeled were aluminum, calcium, carbon, fluoride, iron, magnesium, nitrogen, phosphorus, potassium, silica, sodium, and sulfur.

A typical model is shown in Table 7. In this example, the processes used to simulate the observed chemical-reaction effect include: (1) addition of carbon dioxide from the oxidation of organic matter in the confining beds of the aquifer, (2) dissolution of a calcite phase, (3) ion exchange, (4) incongruent dissolution and precipitation of illite and kaolinite, respectively, (5) dissolution of gibbsite and hydroxyapatite, (6) oxidation of pyrite, and (7) denitrification.

These processes are typical of the ones used to simulate most of the samples collected during storage and recovery. The amount of each mineral or ion that undergoes the specified process is reported in millimoles. This amount supplies enough of each mineral to account for the changes in elemental concentration observed per kilogram of water. A positive value for the minerals denotes dissolution and a negative value precipitation. In the case of ion exchange, a positive value indicates that the second ion is produced, for example, Na for Ca/Na, K/Na, Mg/Na, and Fe/Na exchange. In the case of fluoride, a negative value for F/OH exchange indicates that F is solubilized as a result of exchange with hydroxide.

The processes used to simulate the chemical reactions were selected on the basis of two criteria. First, the mineral's presence must have been reported in the stratigraphic analysis of the formation. Second, the direction of the process had to be thermodynamically justified. A speciation code, WATEQ4F (Ball and Nordstrom, 1991), was employed to predict the spontaneous direction of the postulated chemical reactions, using thermodynamic principles. The ion speciation of the water at equilibrium was computed for the environmental conditions in the aquifer and then used to determine mineral solubility. In the case of cation exchange, it was assumed that most of the exchange sites on the clay minerals were occupied by sodium and, therefore, exchange would proceed as:

$$\text{Na-clay} + X^{+} \dashrightarrow \text{Na}^{+} + \text{X-clay}$$

where X is Ca^{+2}, Mg^{+2}, K^{+}, or Fe^{+2}. Because of the elevated pH observed in the water samples, F/OH exchange was assumed to proceed as:

$$\text{F-apatite} + OH^{-} \dashrightarrow F^{-} + \text{OH-apatite}$$

This process can be viewed as a type of incongruent dissolution in which the fluoride content of the fluorapatite is decreased. Such reactions are probably limited to mineral surfaces in direct contact with the ground water. Similar types of surface reactions were invoked for two clay minerals, illite and kaolinite.

Incongruent dissolution of illite was used as a source of potassium, yielding a secondary clay mineral relatively depleted in this element. The *precipitation* of kaolinite was also invoked as a sink for aluminum and silica. Since kaolinite is cation poor, its formation is probably the result of incongruent dissolution of some other cation-rich mineral.

Other postulated incongruent dissolutions include the formation of calcite from partial dissolution of aragonite. Both phases are assumed to contain approximately 5 percent magnesium by mass. This is referred to simply as calcite dissolution, representing a net gain of magnesium, calcium, and carbonate in the water as a result of this chemical reaction. Other possible processes include the dissolution of gibbsite and glauconite.

As dissolved oxygen was present in the treated water, aerobic respiration or organic matter and pyrite oxidation proceeded until the oxygen was completely removed. The former is a source of carbon dioxide and the latter a source of ferrous iron and sulfate. In the absence of oxygen, organic matter can be respired by microbial dissimilatory nitrate reduction (denitrification) in which nitrate accepts electrons from organic matter and thereby is reduced to nitrogen gas. The carbon is oxidized to carbon dioxide. Denitrification was modeled as a nitrogen gas sink. Once nitrate is depleted, microbes

Table 7. NETPATH model including mass-balance results

EVOLUTION MODEL	SAMPLE	MIXING RATIO	CONCENTRATION (mmol/kg)												
			Carbon	Calcium	Sodium	Magnesium	Potassium	Sulfate	Iron	Aluminum	Silica	Fluoride	Phosphate	Chloride	Nitrate
End Member 1	G1TA0718	0.71491	0.56430	0.19210	0.87010	0.07160	0.07700	0.32900	0.00060	0.01540	0.14080	0.05690	0.00020	0.42320	0.02460
End Member 2	Ground Water	0.28509	9.17080	0.04170	9.15950	0.01490	0.05050	0.04040	0.00030	0.00100	0.26970	0.11330	0.00220	0.79680	0.00490
Resultant Water	G1WA0912		4.34360	0.17670	4.50830	0.03420	0.07290	0.34680	0.00050	0.00620	0.13050	0.12060	0.00150	0.58130	0.00210

Conservative mixing	3.01793	0.14922	3.23333	0.05544	0.06945	0.24672	0.00051	0.01129	0.17755	0.07298	0.00077	0.52971	0.01898
PERCENT	69%	84%	72%	162%	95%	71%	103%	182%	136%	61%	51%	91%	904%
Chemical reaction contribution (nonconservative)	1.32567	0.02748	1.27497	-0.02124	0.00345	0.10008	-0.00001	-0.00509	-0.04705	0.04762	0.00073	0.05159	-0.01688
PERCENT	31%	16%	28%	-62%	5%	29%	-3%	-82%	-36%	39%	49%	9%	-804%

PHASE / PROCESS	NETPATH PREDICTION	PHASE CHANGE (mmol/kg)	NONCONSERVATIVE CONTRIBUTION (mmol/kg)												
			Carbon	Calcium	Sodium	Magnesium	Potassium	Sulfate	Iron	Aluminum	Silica	Fluoride	Phosphate	Chloride	Nitrate
CO2 (g)	ingassing	0.73469	0.73469												
Calcite	dissolution	0.59093	0.59093	0.56138		0.02955									
Ca/Na Exchange	Ca -> Na	0.53522		-0.53522	1.07044										
Mg/Na Exchange	Mg -> Na	0.05228			0.10456	-0.05228									
Fe/Na Exchange	Fe -> Na	0.05000			0.10000				-0.05000						
F/OH Exchange	F -> OH	0.04766										0.04766			
Gibbsite	dissolution	0.04888								0.04888					
Illite	dissolution	0.00582				0.00146	0.00349			0.01339	0.02037				
Kaolinite	precipitation	-0.03369								-0.06738	-0.06738				
Hydroxyapatite	dissolution	0.00026		0.00130									0.00078		
Pyrite	dissolution	0.05002						0.10004	0.05002						
N2 (g)	degassing	-0.00840													-0.01680

can continue to oxidize organic matter, using sulfate as an electron acceptor. The resulting sulfide will precipitate iron as pyrite (FeS_2). This phase is so insoluble that sulfide concentrations would always be predicted to be below the analytical detection limits.

The impact of these processes on the elemental balances is also shown in Table 7. For example, 84 percent of the sodium increase resulting from chemical reaction was supplied by exchange with calcium, 8 percent from exchange with magnesium, and 8 percent from exchange with ferrous iron. Thus, most of the sodium supplied to the water by chemical reaction was the result of exchange with calcium. This was a direct consequence of the dissolution of calcite. Calcite dissolution was promoted by the relatively low alkalinity of the treated water and the in situ addition of carbon dioxide from the respiration of organic matter.

$$CO_2 + (Ca, Mg)\,CO_3 + H_2O \dashrightarrow Ca^{2+}, Mg^{2+} + 2HCO_3^-$$

Model Results

A summary of the geochemical models used to explain the chemical changes observed during the storage and recovery periods is given in Table 8. Successful models were characterized by small mass exchanges—less than 1 mmol/kg (millimole per kilogram)—and chemical processes similar to those observed in other samples. These chemical processes had to be thermodynamically spontaneous under the physical and chemical conditions present in the aquifer at the time of sampling.

Table 8 also indicates which tracer was used to develop the model and the resulting mixing ratios. Tritium was used when its concentration was significantly above its detection limit. Chloride was used as the tracer in most of the models. To correct for CO_2 degassing, pH's were lowered to values that resulted in calcite undersaturation. The treated-water end member was varied to simulate changes in the composition of this water mass through the injection period. Hence, the water injected into the well first (March 22) was recovered last (October 31 to the end of recovery). In most cases, successful models could be constructed only from the treated-water end member that followed this temporal sequence.

The most important chemical reactions are dissolution of calcite and remineralization of organic matter. The former elevates the calcium and magnesium concentrations to the point that exchange with sodium is favored, and thereby sodium is added to the solution. Under oxygenic conditions, pyrite is solubilized, adding dissolved iron and sulfate to solution. After depletion of oxygen, denitrification supported by organic matter from the confining beds removes nitrate as nitrogen; and sulfate reduction converts sulfate to sulfide, which precipitates pyrite.

As indicated, most of the chemical reactions occurred during the storage period when a significant amount of treated water was still present. The fluctuations in mass exchange during the recovery period probably reflect changes in the mixing ratios of the two ground-water end members. The relatively small impact of the third end member (other ground water) on the nonconservative behavior of the resultant water is suggested by the existence of simple two-end-member models for all but two of the sampling dates (October 17 and 18). These models are notable for their relatively large mass exchanges, which suggests that the actual chemical composition of the third end member was somewhat different from that of Hwy 501 Pottery well (HOR-934). As shown in Table 9, three-end-member models were also found for other dates, demonstrating that this third end member could have been present in samples from other dates.

The impact of these chemical reactions on the elemental mass balances are also given in Table 8 as the concentration that had to be added to (+) or removed from (-) the combined end members to produce the resultant water. The nonconservative changes in concentration are plotted, in units of milliequivalents of charge per liter, with time in Figure 19.

Most of the nonconservative behavior occurred by the middle of the storage phase, when a significant proportion of treated water was still present. This behavior is summarized in Table 9.

HIGHWAY 501 POTTERY WELL INJECTION TESTS

Owing to the promising results from this project, the GSWSA made another ASR test, this one at the Hwy 501 Pottery well (HOR-936) in the period September through December 1995. The results are briefly described below and were used to support a request for an Underground Injection Control (UIC) permit from the South Carolina Department of Health and Environmental Control in January 1996.

The goal of this application of ASR is to increase water supply availability during summer weekends when demand is the highest. During the summer of 1995, the Bull Creek Surface Water Treatment Facility had to operate at its peak limit of 18.7 mgd (million gallons per day). In contrast, offseason flows average only 11 mgd. Thus, ample unused capacity is available during off-peak periods for injection. GSWSA plans to inject

Table 8. Summary of model results

SAMPLE ID	END MEMBERS			Tr	MIXTURE (PERCENT)			PHASE CHANGES (mmol/kg)														
	TREATED WATER	GROUND WATER			Treated	GW1	GW2	Ca/Na Exch	Calcite	CO2(g)	Pyrite	Fe/Na Exch	Mg/Na Exch	K/Na Exch	Illite	Glau-conite	Gibb-site	Hydroxy-apatite	F/OH Exch	Kao-linite	N2 gas	SiO2
G1WA0803	7/18	1		T	98.68	1.32		-0.052	0.094	0.163	0.013	0.013	-0.018		0.002			0.001	-0.003	-0.005	0.016	-0.040
G1WA0817	7/18	1		T	98.25	1.75		0.184	0.349	0.337	0.013	0.013	0.017		0.016		-0.045	0.001	-0.010			-0.067
G1WA0829	7/18	1		T	86.40	13.60		0.220	0.379	0.494	0.033	0.033	0.029		0.009		0.054	0.001	-0.020	-0.040	-0.005	
G1WA0912	7/18	1		T	71.49	28.51		0.535	0.591	0.735	0.050	0.050	0.052		0.006		0.049	0.000	-0.048	-0.034	-0.008	
G1WA0927	7/18	1		Cl	39.51	60.49		0.397	0.467	0.320	0.024	0.037	0.031			0.007	0.095	0.000	-0.040	-0.069	-0.006	
G2WA0928	7/18	1		Cl	25.90	74.10		0.191	0.261	0.373	0.013	0.031	0.015			0.009	0.106	0.000	-0.038	-0.081	-0.005	
G3WA0929	7/18	1		Cl	19.10	80.90		0.236	0.305	0.159	0.002	0.021	0.014			0.009	0.106	0.000	-0.037	-0.082	-0.004	
G1WA1011	6/6	1		Cl	18.85	81.15		0.318	0.369	0.314	-0.011	0.021	0.022			0.016	0.160	0.000	-0.026	-0.128	-0.006	
G1WA1017	6/6	1	2	Cl	21.04	75.60	3.36	0.320	0.414	0.902	-0.024		0.028			0.012	0.096	0.000	-0.024	-0.085	-0.006	
G1WA1018	6/6	1	2	Cl	19.97	72.00	8.03	-0.018	0.012	1.447	-0.030		0.007			0.015	0.094	0.000	-0.022	-0.092	-0.006	
G1WA1024	4/25	1		Cl	21.46	78.55		0.827	0.854	0.776	-0.027		0.050	0.011		0.013	0.040	0.000	-0.033	-0.061	-0.006	
G1WA1025	4/25	1		Cl	17.37	82.63		0.581	0.614	0.706	-0.023		0.036	0.009		0.011	0.037	0.000	-0.031	-0.054	-0.005	
G1WA1031	3/22	1		Cl	16.47	83.53		0.495	0.514	1.199	-0.015	0.001	0.030	0.003		0.007	0.031	0.000	-0.036	-0.039	-0.004	
G1WA1101	3/22	1		Cl	8.95	91.05		0.333	0.353	0.927	-0.008	0.003	0.017			0.006	0.027	0.000	-0.030	-0.032	-0.003	
G1WA1107	3/22	1		Cl	22.13	77.87		0.819	0.842	0.836	-0.023		0.050	0.016		0.012	0.068	0.000	-0.041	-0.071	-0.005	
G1WA1114	3/22	1		Cl	11.46	88.54		0.372	0.386	0.250	-0.016		0.022	0.006		0.008	0.062	0.000	-0.034	-0.056	-0.004	
G1WA1121	3/22	1		Cl	15.85	84.15		0.528	0.543	0.716	-0.017		0.033	0.007		0.008	0.022	0.000	-0.035	-0.038	-0.004	
G1WA1129	3/22	1		Cl	7.69	92.31		0.218	0.228	0.138	-0.009	0.003	0.013			0.006	0.019	0.000	-0.029	-0.028	-0.003	
G1WA1130	4/25	1		Cl	5.93	94.07		0.165	0.176		-0.010	0.013	0.008	0.013		0.012	0.053	0.000	-0.028	-0.062	-0.003	

G3WA0929	7/18		2	Cl	30.27	64.52	5.21
G1WA1011	6/6		2	Cl	28.40	69.23	2.37

Treated, treated surface water
GW1, native ground water
GW2, second ground water
Tr, tracer (**Cl** chloride, **T** tritium)

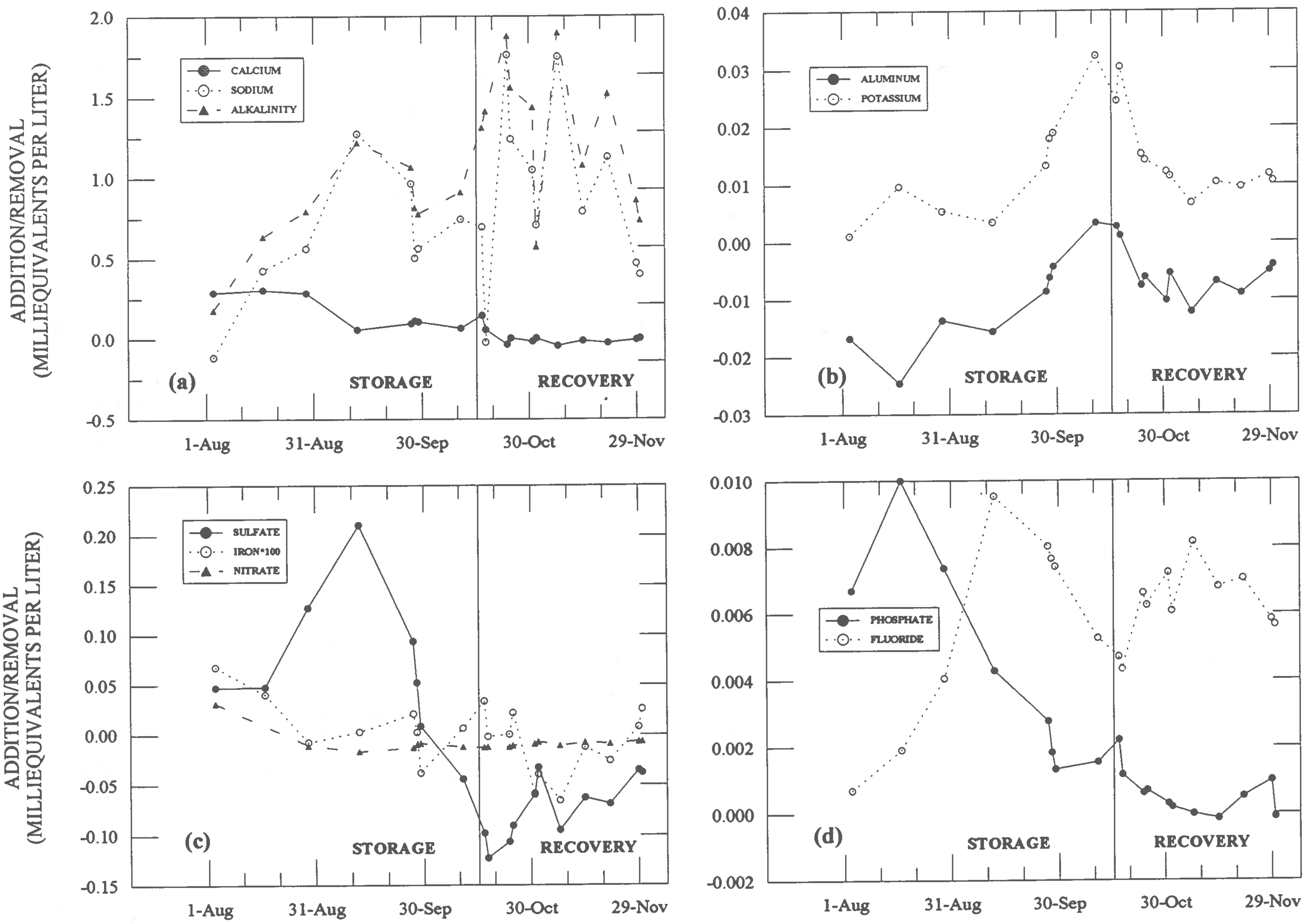


Figure 19. Mass exchanges between the injected water and mineral phases during the storage and recovery periods for: calcium, sodium, and alkalinity (a), aluminum and potassium (b), sulfate, iron, and nitrate (c), and phosphate and fluoride (d).

Table 9. Summary of chemical behavior observed during the early and middle parts of the storage periods

CHEMICAL BEHAVIOR	CONSTITUENTS AFFECTED
Conservative	None
Addition to water	calcium, potassium, sodium, iron, alkalinity, phosphate, fluoride
Removal from water	aluminum, boron, silica, nitrogen, oxygen
Addition in early storage followed by removal	magnesium (addition by calcite dissolution and removal by exchange), sulfur (addition from pyrite oxidation and removal by pyrite precipitation)

treated water during the summertime weekdays and withdraw it over the weekends.

INJECTION SITE AND SCHEDULES

The Hwy 501 Pottery well (HOR-936) is located just west of the Intracoastal Waterway on Highway 501. It has 12 screens, all of which are in the Black Creek Formation at depths ranging from 356 to 690 ft bls. Individual screens range from 5 to 22 ft in length, with a total length of 161 ft.

To simulate this injection-and-recovery scheme, the ASR test was composed of seven short injection cycles, each having an average injection volume of 1 million gallons. The injection was carried out at a rate of 140 gpm for about 5 days. Recovery at a rate of approximately 500 gpm was begun immediately after the end of injection. In an effort to establish a buffer zone, a volume equal to about half that of the injected water was recovered on each of the first seven cycles.

GEOCHEMICAL MODELING AND RESULTS

The chemical composition of treated water and native ground water was compared to that of samples collected periodically through the recovery period. Concentrations were below the Maximum and Suggested Contaminant Levels for all characteristics measured: pH, turbidity, color, fluoride, sulfate, chloride, sodium, iron, alkalinity, specific conductance, total dissolved solids, calcium hardness, total organic carbon, and total coliform. During the third cycle, concentrations of magnesium, potassium, and calcium were also measured to permit identification of possible chemical reactions, using the geochemical program NETPATH.

Chloride was used as a conservative tracer of mixing. By limiting recovery to only half of the injected water, the recovered water was composed of not more than 10 percent ground water. This suggests that mixing was well controlled (no significant mixing occurred) and that an effective buffer zone was created. Thus, chemical reaction, while resulting in small concentration changes, had a relatively larger impact than mixing on the composition of the resulting recovered water.

A sample NETPATH model is presented in Table 10 for water collected after 600,000 gallons of treated water were recovered during the third ASR cycle. As shown, half of the increase in carbon was due to chemical reactions, probably calcite dissolution and aerobic respiration of organic matter. Half of the increase in sodium was also the result of chemical reactions, probably due to exchange from clay surfaces. Thus, ion exchange was probably driven by calcium derived from calcite dissolution, causing the nonconservative contribution to be only 16 percent of the observed concentration increase in calcium.

The dissolution of glauconite accounted for 16 percent of the total increase in potassium concentration. Approximately one-third of the fluoride increase was due to exchange with hydroxide. Pyrite oxidation caused about one-third of the observed increase in sulfate. This was not seen in the iron, which appeared to exhibit nearly conservative behavior, because most of the added iron was removed by exchange with sodium. On a mass basis, the most important reactions were calcite dissolution, calcium/sodium exchange, aerobic respiration of organic matter, iron/sodium exchange, and pyrite oxidation. The types and magnitudes of these reactions were similar to those observed at the Bay Road well.

Given the short storage period of these tests, nonconservative processes appeared to have occurred throughout the entire recovery period. This is illustrated, using specific conductance as an example (third ASR cycle), in Figure 20. It appears that chemical reactions occurred quickly following injection and during the recovery period. The repeated flushing of this well, however, decreased the nonconservative contributions. As shown in Figure 21, the increases in conductivity, alkalinity, pH, and turbidity within a cycle decreased from the first to the seventh cycle. This suggests that minerals such as calcite and pyrite were progressively removed from the active surfaces of the aquifer by dissolution and that sodium was also removed from the clay surfaces by exchange with calcium.

Table 10. Summary of model results for the Highway 501 Pottery well

EVOLUTION MODEL	SAMPLE	MIXING RATIO	CONCENTRATION (mmol/kg)								
			Carbon	Calcium	Sodium	Magnesium	Potassium	Sulfate	Iron	Fluoride	Chloride
End Member 1	Treated Water	0.93478	0.76180	0.21490	0.93970	0.08270	0.09490	0.47890	0.00040	0.05260	0.36390
End Member 2	Ground Water	0.06522	9.15150	0.18230	13.28000	0.10290	0.17150	0.00520	0.00050	0.22600	3.13410
Resultant Water	600,000 Gallons		2.73220	0.25460	3.82930	0.06830	0.11870	0.68730	0.00040	0.09690	0.54460

Conservative mixing	1.30898	0.21277	1.74453	0.08402	0.09990	0.44801	0.00041	0.06391	0.54457
PERCENT	48%	84%	46%	123%	84%	65%	102%	66%	100%
Chemical reaction contribution (nonconservative)	1.42322	0.04183	2.08477	-0.01572	0.01880	0.23929	-0.00001	0.03299	0.00003
PERCENT	52%	16%	54%	-23%	16%	35%	-2%	34%	0%

PHASE / PROCESS	NETPATH PREDICTION	PHASE CHANGE (mmol/kg)	NONCONSERVATIVE CONTRIBUTION (mmol/kg)								
			Carbon	Calcium	Sodium	Magnesium	Potassium	Sulfate	Iron	Fluoride	Chloride
CO2 (g)	ingassing	0.56244	0.56240								
Calcite	dissolution	0.86080	0.86080	0.81776		0.04304					
Ca/Na Exchange	Ca -> Na	0.77590		-0.77590	1.55180						
Mg/Na Exchange	Mg -> Na	0.05874			0.11748	-0.05874					
Fe/Na Exchange	Fe -> Na	0.13847			0.41541				-0.13847		
F/OH Exchange	F -> OH	-0.03294								0.03294	
Glauconite	dissolution	0.00941					0.01882		0.01882		
Pyrite	dissolution	0.11964						0.23928	0.11964		

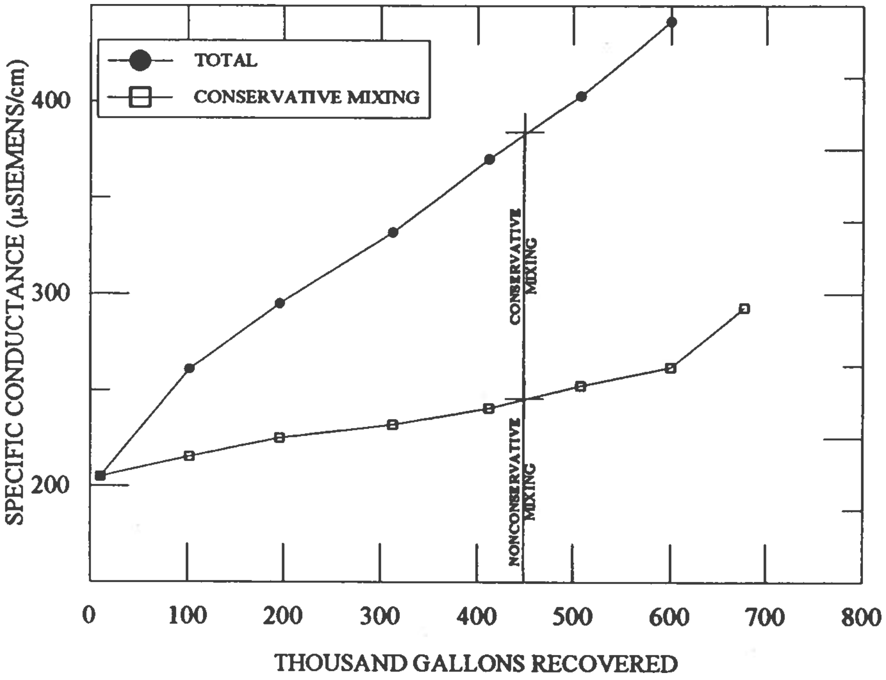


Figure 20. Conservative and nonconservative mixing as indicated by specific conductance at the 501 Pottery well.

Enhancement of supply availability is only one of several benefits of ASR. Because of its central location, ASR at this site could help maintain stable potentiometric levels throughout the Forestbrook-Socastee area distribution system as well as provide an alternative source during a line break or other emergency. Utilization of ASR to dampen peak hydraulic demands would also reduce the need to vary flow rates from the Bull Creek Surface Water Treatment Plant. This increase in stability would enable the plant operators to fine-tune the water treatment process and thereby produce the highest quality of treated water.

SUMMARY AND CONCLUSIONS

Starting in 1987, the South Carolina Water Resources Commission, in cooperation with the local government of Horry County, made an investigation of the feasibility of injecting treated surface water into the Cretaceous sediments of the Coastal Plain in South Carolina. In 1988, a deep corehole was completed and a well made in the Middendorf Formation. During 1991, 1992, and 1994, a series of ASR tests was completed at a Myrtle Beach site (Castro 1995 and 1996).

In 1994, the Water Resources Division of the South Carolina Department of Natural Resources (formerly the Water Resources Commission) and the Grand Strand Water and Sewer Authority, with support from the Center for Marine and Wetlands Studies at Coastal Carolina University, implemented an aquifer storage and recovery test project. During this several-months test, more than 52 million gallons of treated water were injected into the confined aquifers of the Black Creek Formation through a former public supply well (Bay Road). The purpose of the test was three-fold: (1) to study the chemical compatibility of the treated water, which has its raw-water source in Bull Creek, with the aquifers of the Black Creek Formation, (2) to develop injection techniques to control mixing between the treated water and the native ground water and (3) to experiment with injection rates greater than 150 gpm in an effort to store tens of millions of gallons of water during a single ASR cycle.

The test was divided into three periods: injection, storage, and recovery. During the injection period, treated water from the distribution system was delivered to the wellhead and then injected into the aquifers, using the line pressure of the system. For the storage period,

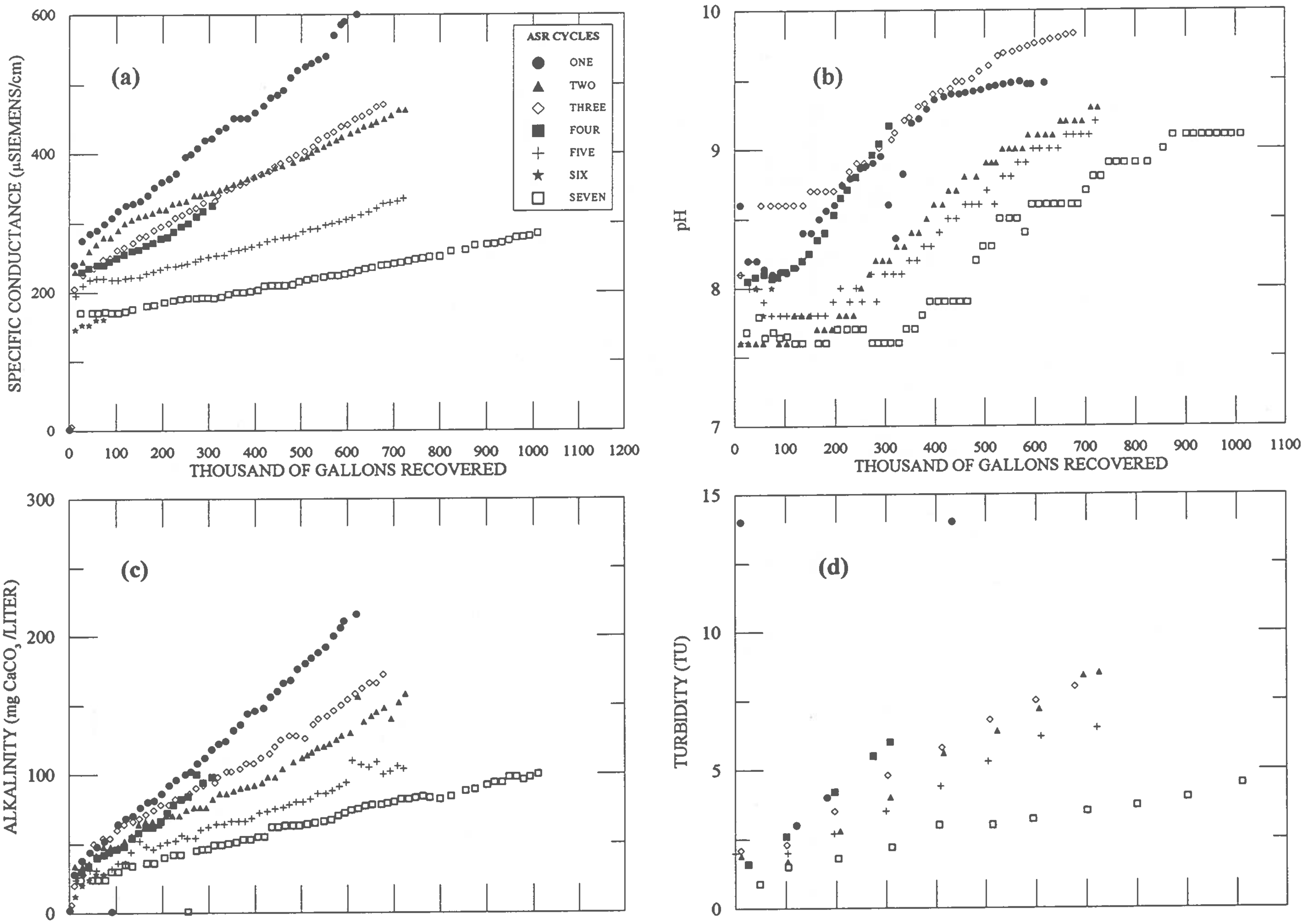


Figure 21. Trends of specific conductance (a), pH (b), alkalinity (c), and turbidity (d) with ASR cycles.

injection was suspended and the treated water was left undisturbed in the aquifer, except for weekly pumping periods to monitor changes in chemical composition of the stored water. During the recovery period, the well was continuously pumped to recover the treated water.

The initial injection rate was 100 gpm. This was soon increased to rates ranging from 250 to 450 gpm. A rapid rise in water level was observed at high injection rates, which was of significant concern, as high water levels could diminish the injection capacity of the ASR well. The closer the water level, in the annular space of the well, rose to the land surface, the smaller the injection capacity became. If the water level were high enough, the well could overflow, damaging equipment and flooding the well house. Higher injection rates also were undesirable because flow adjustments were more difficult to make when changes in the distribution line pressure were large.

The average injection rate was about one-third of the 1,000-gpm production capacity of the well. This has also been observed at the Myrtle Beach ASR test well (Castro 1996). After 3 months of continuous injection at an average rate of 376 gpm, 52.49 million gallons of treated water were stored in the aquifer. This demonstrates that even in low-yielding aquifers such as those of the Black Creek Formation, significant quantities of treated water can be stored.

The production capacity of the Bay Road ASR well is almost twice the average capacity for Black Creek wells in the region. Thus, a large volume of treated water was injected, because the well could sustain large injection rates. During tests at the Myrtle Beach site, injection rates less than 150 gpm were employed to inject up to 15 million gallons over a period of 3 or more months. At the Bay Road well, in a single month nearly 17 million gallons were injected at rates greater than 370 gpm. Consequently, during a 6-month injection period, more than 100 million gallons of treated water could, potentially, be injected.

During recovery of the stored water, larger pumping rates, greater than 1,000 gpm, could be used. This is possible because the treated water, during injection, forms a mound around the well and increases the available drawdown. These high recovery rates could be sustained for several hours or even days, depending on the stored-water volume.

During the injection period, the well was backflushed regularly to clear the screens and gravel pack of particulate matter. To do this, injection was normally stopped once a week and the well pumped for 10 minutes. Water recovered during these short pumping periods usually had a reddish tint. This colored water was flushed from the system within a few minutes of pumping, suggesting that rust was being dislodged from the well casing.

Water samples were collected throughout the test to study the impact of storage on the chemical composition of the treated water. The following characteristics were measured: major cations and ions, trace metals, total organic carbon, trihalomethane, bacterial abundance, tritium, and $\delta^{13}C$ of the dissolved inorganic carbon. On the site, specific conductance, pH, alkalinity, and dissolved oxygen were regularly monitored.

Unlike the ASR tests at the Myrtle Beach site, the Bay Road injection test seems not to have developed a buffer zone (zone of no mixing) around the injection test well. Without this zone, most of the treated water mixed with the native ground water, greatly altering the quality of the recovered water. Water recovered during the storage period—for example, the first water recovered—already had a large fraction of native ground water in its composition. By the end of the storage period, when a volume equivalent to approximately 6.2 million gallons (12 percent) of the injected water had been recovered, the chloride concentration in the recovered water was nearly as high as in the native ground water. This suggests that most of the water volume recovered was composed of ground water.

Calculations based on the chloride concentration suggest that by the end of the recovery period, when 64.1 million gallons had been pumped, less than 50 percent of the treated water had been recovered. Most water samples collected at the end of the recovery period were made up of two-thirds ground water and one-third treated water. Consequently, if this ratio persisted for subsequent samples, an additional 60 million gallons of water would have to be pumped in order to retrieve most of the treated water injected in the aquifer. The recovery efficiency at this site appeared to be less than 20 percent, less than one-third of that experienced at the Myrtle Beach site.

Two conservative tracers, chloride and tritium, were used to compute the mixing ratios of treated water and ground water in each water sample. The remainder of the concentration in each water sample was attributed to nonconservative processes. These geochemical processes were identified using NETPATH.

Although most of the chemical composition of a water sample could be explained by the mixing of treated water with ground water, a small fraction of each sample's composition was determined by geochemical processes. Chemical reaction occurred in the treated water as ions in solution sought to attain chemical equilibrium with solid and gaseous phases in the system.

Mixing between the treated water and the ground water appeared to be the dominant process controlling the quality of the recovered water. Mixing caused significant increases in bicarbonate alkalinity and sodium and moderate increases in fluoride and silica concentrations. Mixing also caused a decrease in sulfate, total organic carbon, nitrate, magnesium, calcium, aluminum, and dissolved-oxygen concentrations.

Geochemical modeling of the injected water's evolution resulted in the identification of several reactions that affected the quality of the recovered water. The four most important reactions were pyrite oxidation, organic-matter oxidation, calcite dissolution, and calcium-sodium exchange.

The oxidation reactions probably were bacterially mediated processes in which sulfide (from pyrite) was oxidized to sulfate and organic carbon (from the confining beds) was oxidized to inorganic carbon. This resulted in a decrease of dissolved oxygen and pH and an increase of sulfate and bicarbonate ions in solution.

The oxidation process, by lowering the pH and increasing the concentration of dissolved inorganic carbon in solution, enhanced the dissolution of carbonate minerals, mainly aragonite. Thus, calcium and carbon ions were added to the solution, which increased the pH and the bicarbonate alkalinity.

The lower ionic strength of the treated water, compared to that of the native ground water, promoted a cation exchange process in the aquifer. Calcium, available from calcite dissolution, exchanged with sodium that was adsorbed on the marine clay. Consequently, sodium and not calcium concentration increased in solution.

The extent to which chemical reactions occur in the aquifer is expected to decline with each successive ASR cycle. By flushing the formation, the mineral availability will decrease because the mineral phases will be eventually exhausted. Thus, chemical reactions will play a lesser role in changing the quality of the treated water. This hypothesis was supported by the tests made at the Hwy 501 Pottery well.

At the Hwy 501 Pottery well a series of seven short-term injection and recovery tests were completed in 1995. In these tests 1 million gallons of treated water were injected during weekdays and later recovered during the following weekend. This injection-and-recovery scheme simulated extremely high water demand scenarios observed in the systems during summer hours. Thus, using ASR to dampen peak-hydraulic demands would reduce the need to vary flow rates from the Bull Creek Surface Water Treatment Plant. This increase in stability would improve the treatment process and thereby maintain a high quality finished water.

The geochemical analysis of the data collected at this site confirmed the results and conclusions obtained at the Bay Road Well and the Myrtle Beach sites. Pyrite and organic-matter oxidation, calcite dissolution, and calcium-sodium exchange were the most important reactions. The contribution from this reaction, furthermore, decreased with each successive ASR cycle.

RECOMMENDATIONS

The information collected from the various ASR injection tests clearly demonstrates the applicability of this type of project in unconsolidated sediments of South Carolina's Coastal Plain. ASR wells could effectively be used as a water resources management alternative to curtail rising water-production costs. On the basis of the information collected in the ASR tests, the following recommendations are offered for the development and operation of ASR sites throughout Horry County:

The initial injection rate should be approximately one-third of the production capacity of the ASR well. This rate can then be maximized by progressively increasing the injection rate until a 1- to 1½-ft per day rise in the water level is attained. Higher rates of rise in water levels would be acceptable if the period of injection is proportionally shortened.

Injection of treated water into the aquifer should be done by using the line pressure of the distribution system. Thus, pressures could normally be maintained between 40 and 65 psi; however, the pressure should not exceed that which would cause the water level to rise to the land surface. In addition, high pressure can lead to compaction of the aquifer (by rearranging the grains) or even fracturing of the aquifer. These conditions can cause the well to produce sand and silt and thereby degrade the aquifer's capacity to transmit and store water.

Injection should always be conducted under positive heads and with a full pump column (riser pipe). Cascading of the injected water should be avoided. Injected water must be delivered at least 20 ft below the standing water level in the annular space to avoid air entrainment. Air entrainment is undesirable for at least three reasons: (1) it provides additional oxygen to the system for bacterial respiration, the byproducts of which stimulate a number of chemical reactions that alter the composition of the treated water; (2) air introduced during injection could become lodged in the pore spaces of the aquifer, reducing its hydraulic conductivity and storage coefficient; (3) air introduced during injection could be pumped out during recovery into the distribution and produce an undesirable appearance (opaque water because of air bubbles), as well as possibly obstruct the flow of water in the distribution lines.

To improve the performance of ASR wells, especially if these are wells that were originally designed for withdrawal only, an air packer should be installed inside the pump column. The packer would be deployed during injection to restrict the flow and to create a positive head in the well. This would minimize air entrainment. The packer would then be deflated during the pumping mode, offering little resistance to the ascending flow and causing only minimal head losses during the operation of the pump.

Backflushing procedures must also be field tested, because schedules may have to be tailored for each well to account for differences in well efficiency and construction. An effective backflushing method will improve the performance of the well and increase the storage capacity of the aquifer. Developing a successful schedule may require the testing, by trial and error, of various schemes.

Volumes and durations of injection schemes must be designed to satisfy the specific objectives of each project, such as short-term, emergency, or long-term demand. For all these scenarios an appropriate buffer zone must first be developed. A buffer zone is a defined volume of the aquifer, around the test well, where the native ground water has been replaced with treated water. This zone, if managed properly, will keep the bulk of the treated water separated from the native ground water. At the periphery of the injected-water zone, mixing can take place between the treated water and the water in the buffer zone. The water in the buffer zone, which is already a mixture of treated water and ground water that has reacted with the aquifer matrix, is always of a better quality than the native ground water. Thus, mixing in the periphery of the treated-water zone does not significantly impact the quality of the recovered water.

To create a permanent buffer zone, some of the treated water must be left in the aquifer. Mixing will eventually degrade the buffer zone, so it is advisable to leave some of the treated water in the aquifer at the end of each ASR cycle. Thus, the leftover water will replenish the buffer zone and improve its quality.

During any ASR injection tests, samples should be collected to permit study of the chemical evolution of the water. This information can be used to modify the injection and hence improve the quality of the recovered water. During operation of an ASR site, the specific conductance (at the very least) of the recovered water should be monitored in order to effectively manage the treated water volume stored in the aquifer.

Undesirable effects of chemical reactions in the recovered water can be controlled or eliminated by repeatedly flushing the aquifer. If possible, the flushing of the aquifer should be carried out during months when the injected-water temperature is greater than that of the ground water, for example 24°C. Higher temperatures in the injected water can increase the hydraulic conductivity of the aquifer and hence aid in the flushing of the aquifer. Furthermore, chemical reactions normally occur more rapidly at higher temperatures.

If flushing is impractical, pretreatment techniques can be considered as an option for controlling increases of sodium or bicarbonate alkalinity in the stored water. For example, pre-treating the aquifer (buffer zone) with a solution of calcium chloride would promote exchange of calcium for sodium. Thus, during injection, the treated water would be subjected to much less exchange activity, because the exchange sites on the clay would be taken. Consequently, sodium concentrations would not increase and calcium concentration will rise until the solution achieves saturation with calcite. Once saturation has been attained, calcium concentration and bicarbonate alkalinity will cease rising.

Implementation of ASR may not always be feasible at pre-existing wells. Well-construction deficiencies, prolonged periods of well inactivity, or even aquifer hydraulic or chemical idiosyncracies could render particular sites inoperable. The success of numerous tests in the Black Creek aquifers, however, categorically demonstrates the viability of ASR projects in these sediments. Attention should be focused on developing ASR implementation schemes that will encourage the joint management of surface and ground water resources. More injection sites should be tested and implemented in the Grand Strand region to fully appreciate and utilize the benefits of ASR.

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