Processes Affecting the Trihalomethane Concentrations Associated with the Third Injection, Storage, and Recovery Test at Lancaster, Antelope Valley, California, March 1998 through April 1999

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U.S. Geological Survey
Water-Resources Investigations Report 03-4062

Prepared in cooperation with the **Los Angeles County Department of Public Works** and the **Antelope Valley-East Kern Water Agency**

PWS-0210-0001

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By Miranda S. Fram[1], Brian A. Bergamaschi[1], Kelly D. Goodwin[2], Roger Fujii[1], *and* Jordan F. Clark[3]

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PWS-0210-0003

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CONVERSION FACTORS

Multiply	By	To obtain
foot (ft)	0.3048	meter
gallon per minute (gal/min)	0.06309	liter per second

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F = (1.8 \times °C) + 32$$

ACRONYMS

AODC	acridine orange direct count
AVEK	Antelope Valley–East Kern Water Agency
DBP	disinfection by-products
DOC	dissolved organic carbon
EPA	U.S. Environmental Protection Agency
LACDPW	Los Angeles County Department of Public Works
MCL	maximum contaminant level
RSD	percent relative standard deviation
STHMFP	specific trihalomethane formation potential
$SUVA_{254}$	specific ultraviolet absorbance at 254 nanometers
SWP	State Water Project
THM	trihalomethane
THMFP	trihalomethane formation potential
USGS	U.S. Geological Survey
UVA_{254}	ultraviolet absorbance at 254 nanometers

ABBREVIATIONS

µg/L	microgram per liter
µg/kg	microgram per kilogram
/cm	per centimeter
mg/L	milligram per liter
µmol/L	micromole per liter
µS/cm	microsiemens per centimeter
mL	milliliter
nm	nanometer
pmol/L	picomole per liter

$(Br/Cl)_{THM}$	the ratio of bromine to chlorine in the trihalomethane
$CHBr_3$	bromoform
$CHCl_2Br$	bromodichloromethane
$CHCl_3$	chloroform
$CHClBr_2$	dibromochloromethane
CO_2	carbon dioxide
KH_2PO_4	potassium dihydrogen phosphate
NH_4Cl	ammonium chloride
$\delta^{18}O$	delta oxygen-18
SF_6	sulfur hexafluoride

Water-Quality Information

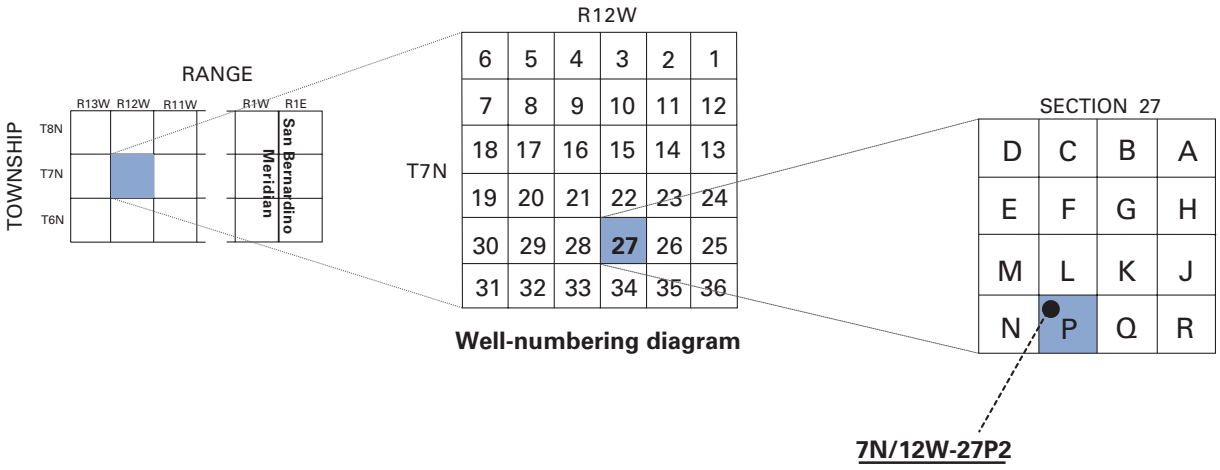
Chemical concentration is given in milligrams per liter (mg/L), micrograms per liter (µg/L), or picomoles per liter (pmol/L). Milligrams per liter is a unit expressing the mass of a solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to 1 milligram per liter, and 1,000 milligrams per liter is equivalent to 1 gram per liter. The numerical value in milligrams per liter is about the same as for concentrations in parts per million, and the numerical value in micrograms per liter is about the same as for concentrations in parts per billion. Micromoles per liter is a unit expressing the number of moles of a solute per unit volume (liter) of water. One million picomoles per liter is equivalent to 1 micromole per liter, and one million micromoles per liter is equivalent to 1 mole per liter.

Ultraviolet light absorbance is given in per centimeter (/cm). Wavelength of light is given in nanometers (nm). Specific ultraviolet absorbance is given in liters per milligram per meter [(L/mg)/m] and is equal to the ultraviolet light absorbance in per centimeter multiplied by 100 and divided by the dissolved organic carbon concentration in milligrams per liter. Specific trihalomethane formation potential is given in millimoles per mole (mmol/mol) and is equal to the trihalomethane concentration in micromoles per liter divided by the dissolved organic carbon concentration in millimoles per liter. Bacterial cell density is given in cells per milliliter (cells/mL).

Specific conductance is given in microsiemen per centimeter at 25°C (µS/cm). Microsiemen per centimeter is numerically equivalent to micromhos per centimeter. Turbidity is given in nephelometric turbidity units (NTU). Gas flow rate is given in milliliters per minute (mL/min). Volume is given in milliliters (mL) or microliters (µL). One thousand microliters is equivalent to 1 milliliter, and 1,000 milliliters is equivalent to 1 liter. Length is given in meters (m) and micrometers (µm). One thousand micrometers is equivalent to 1 millimeter, and 1,000 millimeters is equivalent to 1 meter. Mass is given in micrograms (µg), and one million micrograms is equivalent to 1 gram. Magnetic field strength is given in millitesla (mT).

WELL-NUMBERING SYSTEM

Wells are identified and numbered according to their location in the rectangular system for the subdivision of public lands. Identification consists of the township number, north or south; the range number, east or west; and the section number. Each section is divided into sixteen 40-acre tracts lettered consecutively (except I and O), beginning with "A" in the northeast corner of the section and progressing in a sinusoidal manner to "R" in the southeast corner. Within the 40-acre tract, wells are sequentially numbered in the order they are inventoried. The final letter refers to the base line and meridian. In California, there are three base lines and meridians; Humboldt (H), Mount Diablo (M), and San Bernardino (S). All wells in the study area are referenced to the San Bernardino base line and meridian (M). Well numbers consist of 15 characters and follow the format 007N012W27P002S. In this report, well numbers are abbreviated and written 7N/12W-27P2. Wells in the same township and range are referred to only by their section designation, 27P2. The following diagram shows how the number for well 7N/12W-27P2 is derived.



Well-numbering diagram

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By **Miranda S. Fram, Brian A. Bergamaschi, Kelly D. Goodwin, Roger Fujii, *and* Jordan F. Clark**

ABSTRACT

The formation and fate of trihalomethanes (THM) during the third injection, storage, and recovery test at Lancaster, Antelope Valley, California, were investigated as part of a program to assess the long-term feasibility of using injection, storage, and recovery as a water-supply method and as a way to reduce water-level declines and land-subsidence in the Antelope Valley. The program was conducted by the U.S. Geological Survey in cooperation with the Los Angeles County Department of Public Works and the Antelope Valley–East Kern Water Agency. The water used for injection, storage, and recovery must be disinfected before injection and thus contains THMs and other disinfection by-products. THMs (chloroform, $CHCl_3$, bromodichloromethane, $CHCl_2Br$, dibromochloromethane, $CHClBr_2$, and bromoform, $CHBr_3$) are formed by reaction between natural dissolved organic carbon that is present in water and chlorine that is added during the disinfection step of the drinking water treatment process. THMs are carcinogenic compounds, and their concentrations in drinking water are regulated by the U.S. Environmental Protection Agency. During previous cycles of the Lancaster program, extracted water still contained measurable concentrations of THMs long after continuous pumping had extracted a greater volume of water than had been injected. This raised concerns about the potential long-term effect of injection, storage, and recovery cycles on ground-water quality in Antelope Valley aquifers.

The primary objectives of this investigation were to determine (1) what controlled continued THM formation in the aquifer after injection, (2) what caused of the persistence of THMs in the extracted water, even after long periods of pumping, (3) what controlled the decrease of THM concentrations during the extraction period, and (4) the potential for natural attenuation of THMs in the aquifer.

Laboratory experiments on biodegradation of THMs in microcosms of aquifer materials indicate that aquifer bacteria did not degrade $CHCl_3$ or $CHBr_3$ under aerobic conditions, but did degrade $CHBr_3$ under anaerobic conditions. However, the aquifer is naturally aerobic and $CHCl_3$ is the dominant THM species; therefore, biodegradation is not considered an important attenuation mechanism for THMs in this aquifer. The alluvial-fan sediments comprising the aquifer have very low contents of organic matter; therefore, sorption is not considered to be an important attenuation mechanism for THMs in this aquifer. Laboratory experiments on formation of THMs in the injection water indicate that continued THM formation in the injection water after injection into the aquifer was limited by the amount of residual chlorine in the injection water

at the time of injection. After accounting for THMs formed by reaction of this residual chlorine, THMs behaved as conservative constituents in the aquifer, and the only process affecting the concentration of THMs was mixing of the injection water and the ground water.

The mixing process was quantified using mass balances of injected constituents, the sulfur hexafluoride (SF_6) tracer that was added to the injected water, and a simple descriptive mathematical mixing model. Mass balance calculations show that only 67 percent of the injected THMs and chloride were recovered by the time that a volume of water equivalent to 132 percent of the injection water volume was extracted. Pumping 250 percent of the injection water volume only increased recovery of injected THMs to 80 percent. THM and SF_6 concentrations in the extracted water decreased concomitantly during the extraction period, and THM concentrations predicted from SF_6 concentrations closely matched the measured THM concentrations. Because SF_6 is a conservative tracer that was initially only present in the injection water, parallel decreases in SF_6 and THM concentrations in the extracted water must be due to dilution of injection water with ground water. The simple descriptive mixing model mathematically described mixing of injection water and ground water that was displaced by injection using a single-zone mixing model. This simple model adequately predicted the concentrations of conservative constituents (SF_6, THMs, and chloride) in the extracted water during the extraction period, providing further evidence to support the conclusion that mixing injection water and ground water in the aquifer was the primary process controlling the concentration of the THMs in the extracted water.

Water-quality data and modeling results suggest that injection, storage, and recovery cycles will affect aquifer water quality. THM concentrations in water samples from piezometers located 80 horizontal feet from the injection/extraction well remained high and variable throughout the extraction period. This suggests that water entered regions of the aquifer during injection from which it was not efficiently recovered during extraction. In particular, water may have become stranded in the upper parts of the aquifer during injection and therefore could not be efficiently recovered during extraction owing to drawdown around the well. The descriptive mixing model was used to forecast the results of repeated annual cycles of injection, storage, and recovery. For the scenario of equal volumes of injected and extracted water, the model forecasts that the concentration of THMs (or of any conservative constituent in the injection water) in the ground water near the injection/extraction well would increase to nearly 100 percent of the concentration of THMs in the injection water within 10 years. This increase in THM concentration would be less if ground water from outside the region directly affected by injection also mixed with the injected water or if the volume of extracted water greatly exceeded the volume of injected water. Finally, the model results indicate that extraction of all injected constituents is difficult using existing extraction methods because the volume of water that must be extracted increases exponentially as the acceptance criteria for the concentration in the water remaining in the aquifer decreases.

I. INTRODUCTION

By Miranda S. Fram *and* Roger Fujii

Ground water is an important source of water supply in the Antelope Valley, California (fig.1). Since the late 1940s, ground-water pumpage has exceeded natural recharge, resulting in as much as 350 feet (ft) of water-level declines and more than 6 ft of land subsidence in some areas (Ikehara and Phillips, 1994). The Antelope Valley augments its ground-water supplies with imported water from the California State Water Project (SWP). The SWP is a series of storage reservoirs and aqueducts that transports surface water from northern to southern California (fig.1). Facing rapid population growth and increasing demand for water supply, water managers in the Antelope Valley are seeking ways to maximize the use of available water supplies.Using injection, storage, and recovery—injecting treated SWP water into the aquifer system during periods of greater surface-water availability to be used later during periods of surface-water deficit—is a potential water-supply method for meeting increasing water demands. This water-supply method would permit storage of additional imported water during the wet season when surface water is more available. The U.S. Geological Survey (USGS), in cooperation with the Los Angeles County Department of Public Works (LACDPW) and the Antelope Valley–East Kern Water Agency (AVEK), did research and monitoring experiments during three test cycles of injection, storage, and recovery in Lancaster, Antelope Valley, California, from September 1995 through April 1999 to assess the feasibility of using this water-supply method in the Antelope Valley.

The tests were designed to investigate how injection, storage, and recovery cycles affect water levels, land subsidence, land-surface deformation, aquifer water-quality, and regional ground-water flow patterns. A cycle consists of three periods: an injection period during which water is injected into the aquifer through a well, a storage period during which the well is idle, and a recovery period during which water is extracted from the aquifer by pumping from the same well. Surface water used for injection is treated and disinfected (usually by chlorination) prior to injection into the aquifer system to prevent biofouling and potential introduction of microbial contaminants into the aquifer.

Water-quality monitoring during the first two cycles showed high levels of trihalomethanes (THM) in the extracted water during the initial stage of pumping (Los Angeles County Department of Public Works, 2000). THMs are volatile, halogenated organic compounds and include chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$). They are carcinogenic disinfection by-products (DBP) formed by reaction between natural dissolved organic carbon (DOC) present in the water and chlorine added during the drinking-water-treatment process. The U.S. Environmental Protection Agency (EPA) regulates the concentrations of THMs and other DBPs in finished drinking water (U.S. Environmental Protection Agency, 1998). THM concentrations in the extracted water during the initial stage of pumping exceeded the EPA maximum contaminant level (MCL) of 80 micrograms per liter (µg/L). LACDPW blended the extracted water with water from other sources to lower THM levels in the water delivered to its customers to a level below the MCL. The more serious problem, however, was that the extraction water still contained measurable concentrations of THMs long after continuous pumping had presumably retrieved all of the injected water (Los Angeles County Department of Public Works, 2000). This observation raised concerns about the long-term effect of injection, storage, and recovery on aquifer water quality and thus indicates a potential problem for the feasibility of using this water-supply method in the Antelope Valley. Research and monitoring experiments during the third test cycle (March 1998 through April 1999) were expanded to include investigation of the formation and fate of THMs during the cycle.

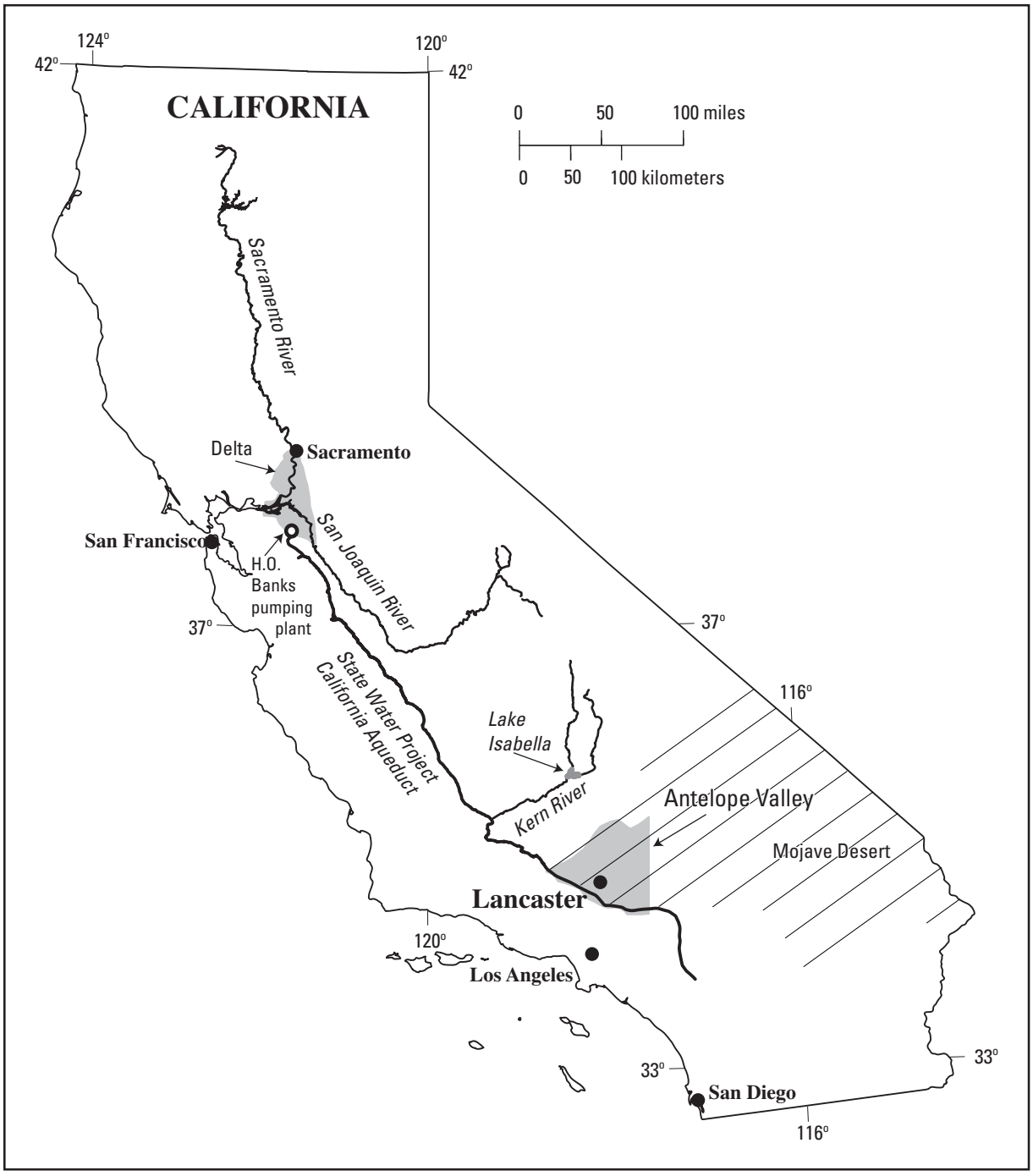

Figure 1. Locations of sites and geographic features relevant to the third injection, storage, and recovery test (March 1998 through April 1999) at Lancaster, Antelope Valley, California.

Purpose and Scope

The roles of the USGS in the injection, storage, and recovery tests were to collect and analyze hydraulic and aquifer-system deformation data, to develop a simulation/optimization model to design and manage a larger-scale injection program, and to determine the factors controlling the formation and fate of THMs in the aquifer system.

This report presents detailed discussions of the factors controlling the formation and fate of THMs in the aquifer system during the third cycle. The report is divided into five sections:

- The introductory section consists of a review of previous work and brief descriptions of the project design, the Lancaster site, and the chronology of the third cycle.
- The second section includes discussion of the results of monitoring of water quality in the injection/extraction well and a nearby set of nested piezometers and of THM formation experiments, evaluation of processes potentially controlling THM concentrations based on these results, presentation of mass-balance calculations for THMs and other constituents, and development of a conceptual model for water flow in the aquifer during the cycle.
- The third section discusses the results of the sulfur hexafluoride (SF_6) tracer experiment and presents mathematical models of mixing between ground water and injected water.
- The fourth section discusses the results of experiments that assessed the potential for biodegradation of THMs in the aquifer.
- The final section summarizes the factors controlling the formation and fate of THMs in the aquifer system during the third cycle and discusses the implications for using injection, storage, and recovery as a water-supply method in Lancaster.

A series of companion reports presents the other parts of the project. A compilation of the hydrologic data and the land-surface and aquifer deformation data, and methods for collection are reported by Metzger and others (2002). The analytical methods used and data collected for the investigation of the formation and fate of THMs are reported by Fram and others (2002). A description of the use of microgravity surveys to determine water-level changes will be presented in a forthcoming report by Howle and others (in press). Another report will present hydraulic and deformation data collected at the Lancaster site and describe a simulation/optimization model developed to evaluate the feasibility of using injection, storage, and recovery as a water-supply method in the Lancaster area (Phillips and others, in press).

Previous Studies

The formation and fate of THMs during injection, storage, and recovery cycles have been investigated in several other locations. The behavior of THMs during multiple cycles of injection, storage, and recovery has been extensively studied at a site in Las Vegas, Nevada. Treated water from Lake Mead was injected through new and existing wells into an aquifer composed of oxidized, alluvial fan sediments, and water was later extracted after a period of storage (Brothers and Katzer, 1990). THM concentrations in the extracted water at the beginning of the recovery period were higher than the concentrations in the injection water and the difference was likely due to the continued reaction of residual free chlorine that was present in the injected water (Miller and others, 1993). THM concentrations in the extracted water decreased during the recovery period. Geochemical mixing models constructed using the major-ion chemistry of the injected water, ground water, and extracted water indicated that the THM decrease observed during the extraction period of the first several cycles could be accounted for solely by mixing between injection water and ground water during extraction (Miller and others, 1993; Bernholtz and others, 1995). In subsequent cycles, the concentrations of brominated THM species ($CHCl_2Br$, $CHClBr_2$, and $CHBr_3$) decreased more than predicted for dilution by mixing between injection water and ground water. Thomas and others (2000) suggested that multiple cycles resulted in acclimation of bacteria capable of degrading brominated THMs, either under aerobic conditions or in anaerobic micro environments developed in the aquifer. However, the concentrations of $CHCl_3$ were still completely accountable by dilution due to mixing, and experiments indicated that aquifer bacteria were not capable of degrading $CHCl_3$ under any conditions (Landmeyer and others, 2000).

Singer and others (1993) also studied the fate of THMs in the Las Vegas injection, storage, and recovery program and reached a different conclusion concerning the importance of mixing between injected water and ground water. They postulated that mixing between injected water and ground water could not have occurred because the regional lateral ground water flow rates were too small to have permitted significant motion of the ground water during the time period of the cycle. Therefore, they attributed the observed decrease in THM concentrations during storage and recovery to biodegradation. However, they noted that the high dissolved oxygen and nitrate concentrations in the extracted water samples precluded widespread anoxic conditions in the aquifer (biodegradation requires anoxic conditions) and suggested that some unknown aquifer heterogeneity factor must be important for producing conditions conducive to biodegradation of THMs (Singer and others, 1993).

The fate of THMs during injection, storage, and recovery cycles at a site in Charleston, South Carolina, was different than at the Las Vegas site, primarily because the nature of the aquifer is different. The aquifer beneath Charleston is confined, anoxic, and composed of fossiliferous, sandy limestone (Campbell and others, 1997; Mirecki and others, 1998). Geochemical modeling of the major-ion chemistry of injected water, ground water, and extracted water showed that the composition of the extracted water could be accounted for by mixing between injected water and ground water and dissolution of aquifer materials (Mirecki and others, 1998). THM concentrations in the extracted water decreased during the recovery period, but no attempt was made to quantitatively account for the decrease (Campbell and others, 1997). Examination of the data indicates that the concentration of THMs decreased faster than predicted for mixing between injected water and ground water as defined by variations in the concentration of conservative constituents, suggesting that a process in addition to dilution from mixing contributed to the decrease. Based on the behavior of THMs in injection, storage, and recovery tests in other anoxic aquifers, the additional process was probably biodegradation of brominated THMs. The concentration of brominated THMs decreased during the storage periods of injection, storage, and recovery cycles in anaerobic (denitrifying) aquifers in Florida, Colorado, and London, England (Singer and others, 1993). Experimental data consistently show that biodegradation of brominated THMs does occur under anaerobic conditions (for example, Bagley and Gossett, 1995).

THM concentrations in stored water in an injection and storage pilot project at the margin of the San Francisco Bay in Palo Alto, California, showed evidence of sorption and biodegradation of THMs (Roberts and others, 1982; Roberts, 1985). Treated wastewater was injected into a shallow silty sand aquifer confined by clay units and containing ground water with low dissolved oxygen concentrations. Breakthrough curves measured at nearby observation wells yielded estimated retention capacities of 2.5 and 4.0 micrograms per kilogram (μg/kg) for $CHCl_3$ and $CHBr_3$, respectively, compared to the unretained tracer constituent, chloride (Roberts and others, 1982). Continued monitoring during the storage period showed consumption of the dissolved oxygen in the injected water and decreases in the concentrations of all the THM species, particularly of the brominated THM species. Roberts and others (1982) suggest that the decreases in THM concentrations during the storage period were due to biodegradation.

Project Design

The previous studies of the fate of THMs in injection, storage, and recovery projects identified four processes that may affect the concentration of THMs in water that has been injected, stored, and extracted from an aquifer: continued formation of THMs in the injected water after injection into the aquifer, biodegradation of THMs by bacterial communities in the aquifer, sorption of THMs to aquifer materials, and mixing between injected water containing THMs and ground water containing little or no THMs. Evaluation of these four processes would provide answers to the primary questions concerning the formation and fate of THMs during the injection, storage, and recovery cycles:

- What controls the continued formation of THMs in the aquifer after injection?
- What causes the continued presence of low concentrations of THMs in the extracted water after all the injection water presumably has been retrieved?
- What causes the decrease in THM concentrations as extraction proceeds?

- Are there natural attenuation mechanisms that can decrease the THM concentrations in the aquifer?

The continued formation of THMs in the injected water was investigated in two types of laboratory experiments. THM formation potential (THMFP) experiments were done to assess the compositional nature of the THM-forming DOC in the injection water and to determine the maximum amount of THM formation possible from the injection water. Injection water was stored for 1 to 16 weeks under controlled laboratory conditions to determine whether THM formation in the injection water was limited by the amount of DOC or the amount of residual free chlorine in the injected water.

The potential for reduction of THM concentrations by the natural attenuation process of biodegradation of THMs in the aquifer was assessed in laboratory experiments. The biodegradation experiments included several types of microcosms containing ground water or injection water with or without sediment from the aquifer, and were incubated under aerobic and anaerobic conditions. The potential for sorption of THMs to aquifer materials was evaluated using the water-quality data obtained during the injection, storage, and recovery cycle.

Mixing between injected water and ground water may also decrease THM concentrations in the aquifer and may account for the continued presence of low concentrations of THMs in the extracted water after all the injection water presumably has been retrieved. Mixing was evaluated by a tracer experiment, by mathematical modeling of mixing, and by mass balance calculations for dissolved constituents. A conservative tracer, sulfur hexafluoride (SF_6), was added to the injection water, and concentrations in the extraction water were monitored so that the proportion of injected water in the extracted water could be determined. Variations in dissolved constituents in the extraction water during the recovery period were compared with concentrations predicted using a mathematical model of a simple mixing process.

In addition, water-quality samples were collected periodically from the well used for both injection and extraction to determine the composition of the injection water and, later, the extraction water. Water-quality samples also were collected from a nearby set of nested piezometers. These samples provided a time series of water-quality data used to delineate the behavior of THMs and other chemical constituents during the cycle.

Site Description and Chronology of Third Cycle

The injection, storage, and recovery test site is located in the Antelope Valley near the city of Lancaster, California (fig.1). A detailed description of the site is given in Fram and others (2002) and Metzger and others (2002); only a brief summary will be given here.

Antelope Valley is a topographically closed basin at the western end of the Mojave Desert; it is subdivided into 12 ground-water subbasins bounded by faults and bedrock outcrops (Bloyd, 1967; Carlson and others, 1998). The three injection, storage, and recovery tests occurred in the Lancaster subbasin at the LACDPW's Avenue L and 5th Street West well field in Lancaster (fig. 2).

The Lancaster subbasin contains alluvial and lacustrine deposits, which are locally as much as 5,000 ft thick (Mabey, 1960; Dibblee, 1967; Londquist and others, 1993). The alluvial deposits consist of interbedded heterogeneous mixtures of silt, sand, and gravel (Dutcher and Worts, 1963; Bloyd, 1967); the lacustrine deposits primarily consist of thick layers of clay, interbedded with thinner sand and silty sand layers (Dibblee, 1967). Stratigraphic, hydrologic, and water-quality data were used to divide the deposits into three aquifers: an upper, a middle, and a lower aquifer (Leighton and Phillips, 2003). At the injection, storage, and recovery demonstration site, the upper aquifer extends from the water table to a depth of about 510 ft below land surface, the middle aquifer extends from about 510 to about 730 ft below land surface, and the lower aquifer extends from about 870 ft below land surface to the bedrock (fig. 2). Ground-water flow in the upper aquifer is unconfined, flow in the middle aquifer is partially confined by fine-grained sediment layers, and flow in the lower aquifer is confined by the lacustrine deposit that separates the middle and lower aquifers.

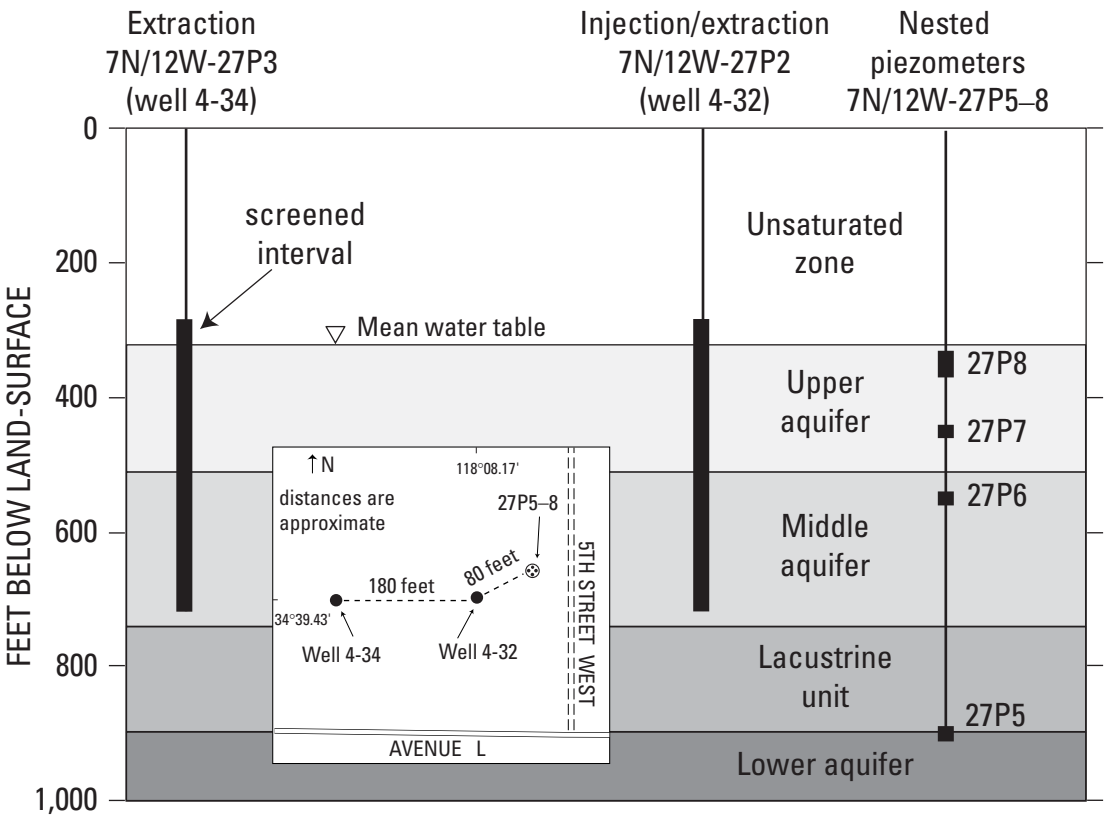

Figure 2. Generalized subsurface geology and locations of wells and nested piezometers used for the injection, storage, and recovery test (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Local well names are in parentheses.

Two wells were used during the third injection, storage, and recovery cycle: wells 7N/12W-27P2 (well 4-32) and 7N/12W-27P3 (well 4-34) (fig. 2, table 1). (The local names for the injection and extraction wells [in parentheses above] are used for the convenience of readers more familiar with these names.) Wells 4-32 and 4-34 penetrate the upper and middle aquifers and are screened from 282 to 717 ft and 280 to 710 ft below land surface, respectively (fig. 2). Well 4-34 is about 180 ft west of well 4-32.

In February 1998, a set of four nested piezometers, 7N/12W-27P5–8, was installed in a borehole about 80 ft east-northeast of well 4-32 (fig. 2, table 1). (The local names for the piezometers are not used in this report.) Borehole geophysical logs were used to determine the most suitable depth for the screened interval for each piezometer (Metzger and others, 2002). The piezometers were screened at depths of 330–370 ft (27P8), 440–460 ft (27P7), 540–560 ft (27P6), and 890–910 ft (27P5) below land surface (fig. 2). The deepest piezometer, 27P5, was placed in the lower aquifer and was not used for this project. A well-bore velocity log completed at well 4-32 under pumping conditions showed that most of the water extracted from the well came from a high flow zone in the upper aquifer at about 460 to 510 ft below land surface (Phillips and others, in press). Piezometer 27P6 was installed in the upper part of the middle aquifer, and piezometer 27P7 was installed in the lower part of the upper aquifer at the approximate depth of the maximum flow zone in well 4-32 (fig. 2). Piezometer 27P8 was installed near the water table at the time of construction. The water level fluctuated during the injection, storage, and recovery cycles; for example, the water level in piezometer 27P8 ranged from 302 ft below land surface in mid-May through mid-June 1998 (during the injection period) to 347 ft below land surface in April 1999 (during the extraction period) (fig. 3*C*). Detailed descriptions of cores collected during installation of the piezometers are given in Fram and others (2002).

Table 1. Nomenclature for wells used during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California

State well number 7N/12W-	Local well number	USGS location identification number	Aquifer zone screened	Use of well
27P5	5L-PZ1	343943118081701	Lower	Not used
27P6	5L-PZ2	343943118081702	Middle	Piezometer
27P7	5L-PZ3	343943118081703	Upper	Piezometer
27P8	5L-PZ4	343943118081704	Upper	Piezometer
27H3	4-33	344088118074701	Upper and middle	Extraction
27J4	4-13	344002118074701	Upper and middle	Extraction
27J6	4-42	344003118074901	Upper, middle, and lower	Extraction
27P2	4-32	343943118081801	Upper and middle	Injection and Extraction
27P3	4-34	343943118082101	Upper and middle	Extraction

For all three cycles, the water used for injection into the wells was imported from the SWP (fig. 1). Existing AVEK pipelines conveyed water from the SWP to the West Quartz Hill Water Treatment Plant where it was treated with chlorine. This treated water was then transported in LACDPW and AVEK pipelines to well 4-32.

During the injection periods of the first and second cycles (1996 and 1997), the water delivered by the SWP originated from the Sacramento–San Joaquin Delta and was conveyed by the H.O. Banks pumping plant and the SWP's California Aqueduct (fig. 1). However, during the injection period of the third cycle (1998), the water delivered from the SWP originated from Lake Isabella and the Kern River (fig. 1). This source water was chemically different from the Delta water used during the first two cycles and resulted in some differences in the water-quality patterns observed in the third cycle compared with the first two cycles.

Injection at well 4-32 for the third cycle began April 15, 1998, and continued through June 16, 1998. Water flow into the wellhead was maintained between 700 and 800 gallons per minute (gal/min) (fig. 3*A*). From the well, the injected water moved into the aquifer by gravity flow. The total volume injected was 58 million gallons (fig. 3*B*). The injection period was followed by 2 weeks of water storage in the aquifer during which time no pumping occurred.

The first phase of extraction from well 4-32 began June 30, 1998, and ended October 24, 1998, during which time water flow was maintained at 400–550 gal/min (fig. 3*A*). The volume of water extracted during this phase was 77 million gallons, which was 1.3 times the volume of water injected (fig. 3*B*). No extraction occurred between October 24, 1998, and February 22, 1999, due to failure and replacement of the pump. The second phase of extraction from well 4-32 began February 22, 1999, and ended April 29, 1999, during which time water flow was maintained at 750–800 gal/min and 73 million gallons of water were extracted. The total volume of water extracted from well 4-32 was 150 million gallons, which was 2.5 times the volume of water injected (fig. 3*B*). After the well 4-32 pump failed, water was extracted from nearby well 4-34 to meet water demand. Extraction from well 4-34 began December 28, 1998, and continued through April 29, 1999, and the total volume of water extracted from well 4-34 was 154 million gallons (fig. 3*B*). The extracted water was blended with other water and incorporated into the LACDPW water distribution system.

Water-quality samples were collected from well 4-32 and the nested piezometers 27P6–8 during the entire injection, storage, and recovery cycle (March 1998 through April 1999). Descriptions of sampling intervals and procedures, analytical methods, and a compilation of all of the water-quality data obtained during the third cycle are reported in Fram and others (2002). Water samples also were collected for use in the THM formation and biodegradation experiments. The methods used for these experiments and the data obtained also are reported in Fram and others (2002).

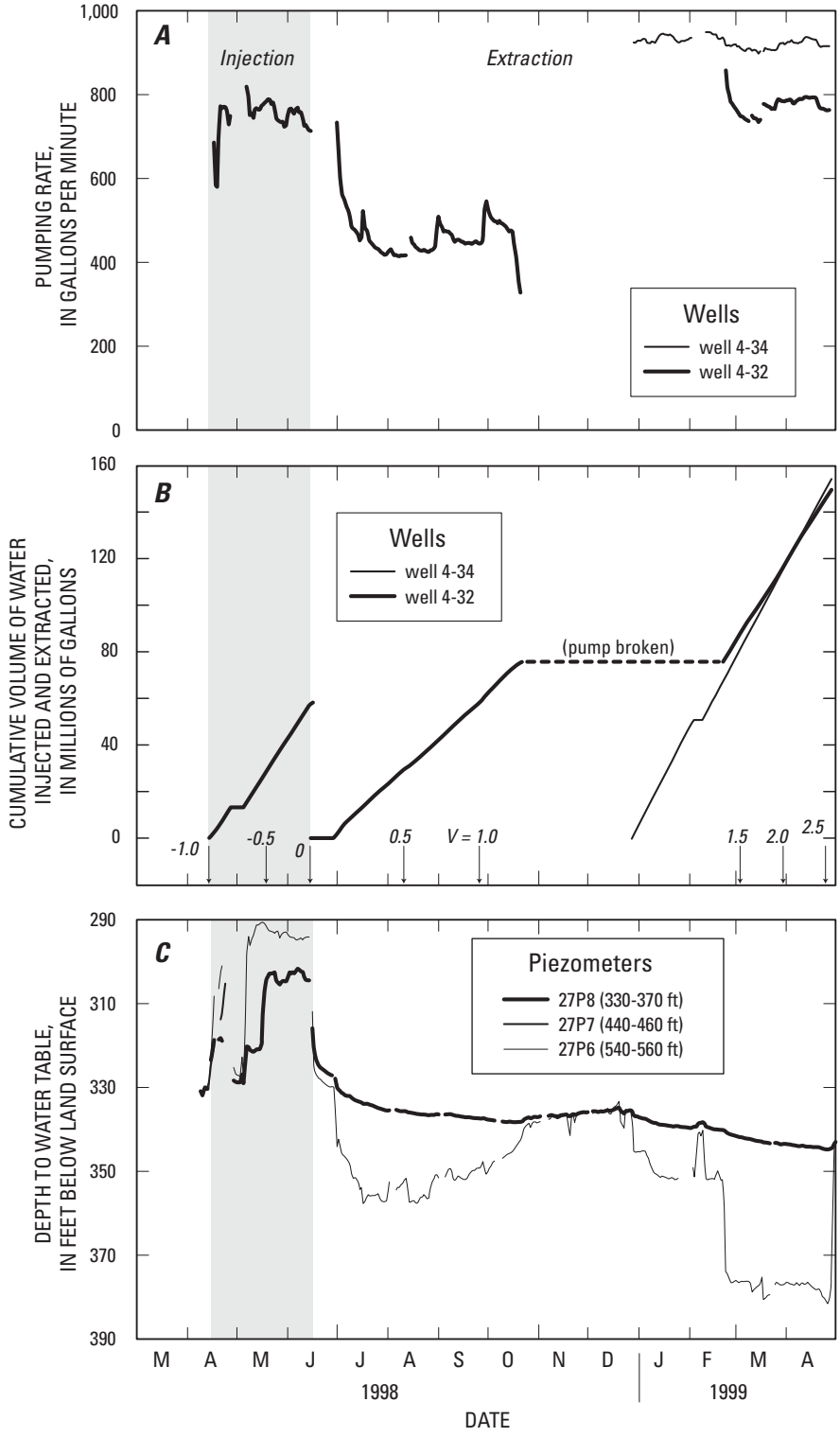

Figure 3. Average daily pumping rates ***(A)*** and cumulative volumes of water injected and extracted ***(B)*** at well 7N/12W-27P2 (well 4-32) and well 7N/12W-27P3 (well 4-34), and average daily water levels at piezometers 7N/12W-27P6–8 ***(C)*** during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

V is the cumulative volume of water extracted (positive numbers) or injected (negative numbers) relative to the total volume of water injected at well 4-32. Methods for data collection are described by Metzger and others (2002).

Acknowledgments

This study was done by the USGS in cooperation with the Los Angeles County Department of Public Works (LACDPW) and the Antelope Valley–East Kern Water Agency (AVEK). Discussions with Loren Metzger, Joshua Berghouse, and Steven Phillips during preparation of this report, reviews by Steven Phillips, James Thomas, Rick Iwatsubo and Peter Martin, and editing by Mary Gibson contributed immensely to this work.

II. FORMATION AND FATE OF TRIHALOMETHANES DURING THE INJECTION, STORAGE, AND RECOVERY CYCLE

By Miranda S. Fram

In this section of the report, concentrations of dissolved constituents in the ground water, injection water, and extraction water are used to assess the roles of mixing, biodegradation, and sorption in determining the concentrations of THMs in the extracted water. An important part of this assessment is determining factors that controlled continued formation of THMs in the aquifer after injection.

Studies of other injection, storage, and recovery programs have used the geochemistry of the ground water, injection water, and extraction waters to quantify the amount of mixing of injected water and ground water, and to constrain the importance of other processes such as biodegradation, sorption, and precipitation/dissolution. For example, Mirecki and others (1998) used inverse modeling of the major-ion concentrations in extracted water from the Charleston, South Carolina program to show that extracted water compositions represented different mixtures of the mean injected water and ground water compositions plus dissolution of evaporite and carbonate minerals in the aquifer.

The geochemistry of ground water, injection water, and extraction water was used to address the fate of THMs in the Las Vegas, Nevada program (Brothers and Katzer, 1990; Miller and others, 1993). Mass balances were constructed for THMs and the injection water during a cycle using the mean compositions of ground water and injected water, electrical conductivity as a conservative tracer, and measured compositions of the extracted water. The percentage of injected THMs recovered was similar to the percentage of the tracer of the injection water recovered, but both were lower than the percentage of the volume of the injected water recovered, indicating mixing between injected water and ground water. In addition, a THM formation experiment compared THM concentrations at three points in time: at the time of injection, after consumption of any residual chlorine in the water, and after addition of excess chlorine. The results indicated that the extracted water had the potential to form a mean of 25 μg/L additional THMs when re-chlorinated after extraction (Miller and others, 1993). Inverse modelling of the major-ion geochemistry of extracted waters showed that the compositions could be adequately explained by mixing of mean ground-water and injection-water compositions and that no significant mineral precipitation had occurred in the aquifer (Brothers and Katzer, 1990). Subsequent studies of the Las Vegas program used chloride as a conservative tracer to quantify the proportions of three components in samples of extracted water: injected water, native ground water, and injected water left over from previous cycles. Comparison between concentrations of chloride and of individual THM species indicated that $CHCl_3$ concentrations in the extracted water were consistent with conservative mixing, but that the concentrations of the brominated THM species were decreased by some additional process during residence in the aquifer (Thomas and others, 2000).

Variations in Water Quality and Water Levels during the Third Cycle

The variations in concentrations of chemical constituents throughout the cycle provide insight into processes within the aquifer during the cycle. Data discussed in this report are given by Fram and others (2002), Metzger and others (2002), and tables 2 and 3.

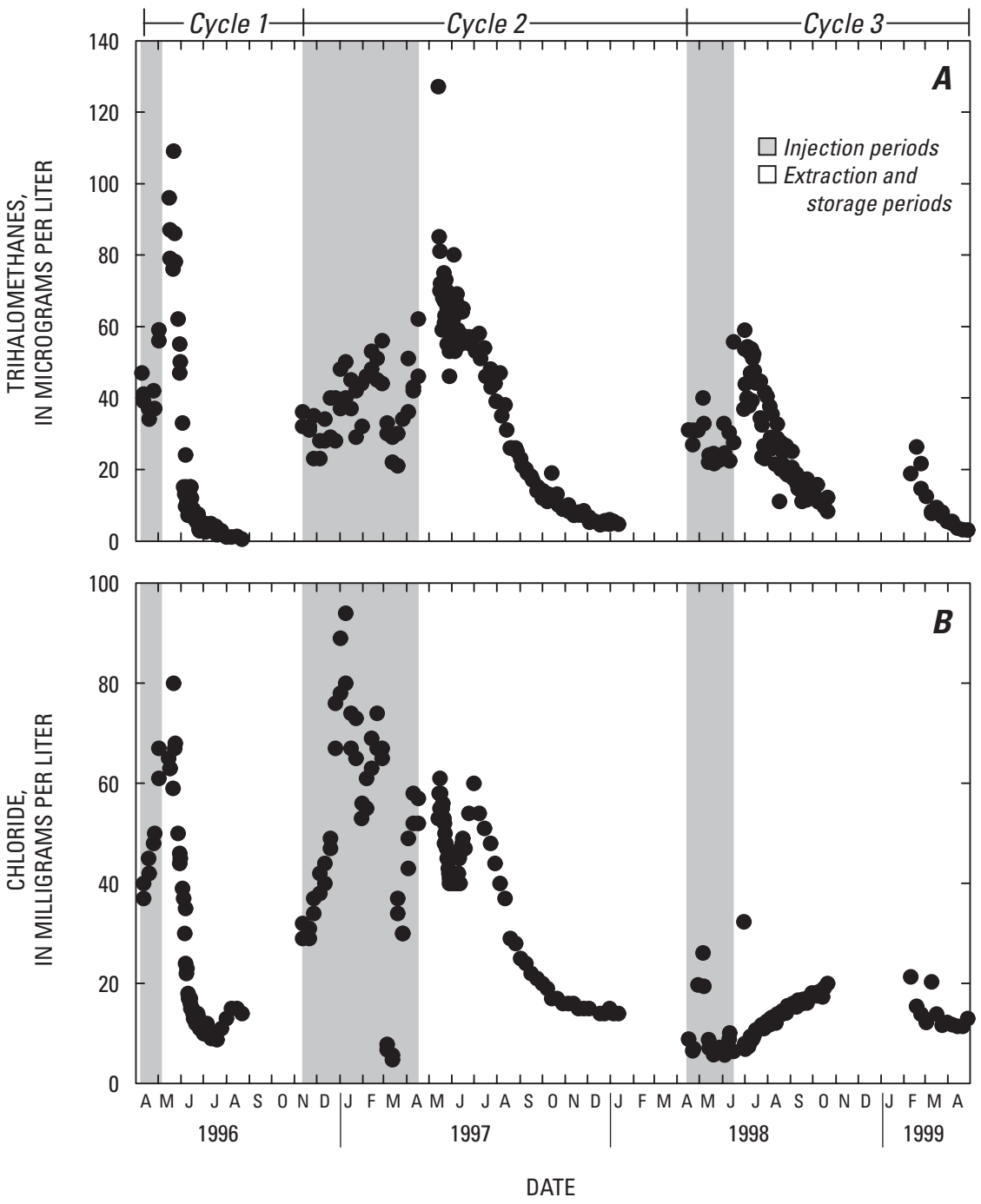

Figure 4. Trihalomethane ***(A)*** and chloride ***(B)*** concentrations in water collected from well 7N/12W-27P2 (well 4-32) during the three injection, storage, and recovery cycles (April 1996 through April 1999), Lancaster, Antelope Valley, California.

Data are from Fram and others (2002) and Metzger and others (2002).

The pattern of THM concentrations in the injected and extracted water from well 4-32 during the third injection, storage, and recovery cycle resembled those of the two previous cycles—moderate concentrations in the injection water, a large increase in concentration at the beginning of extraction, and a gradual decrease as extraction proceeded (fig. 4*A*). However, there were some important differences in water chemistry between the third cycle and the two previous cycles. THM concentrations in the injection water and in the extraction water during the early part of the extraction periods were higher in the first two cycles than in the third; the EPA MCL of 80 µg/L was exceeded in four extraction water samples in each of the first two cycles and none in the third cycle (fig. 4*A*). However, if the THM concentrations are expressed on a molar rather than a mass concentration basis, the concentrations in the three cycles were similar. The THMs in the first two cycles contained much higher proportions of brominated species ($CHCl_2Br$, $CHClBr_2$, and $CHBr_3$) than did the THMs in the third cycle. (Bromine has approximately twice the molar mass of chlorine; thus the brominated THMs are more massive than $CHCl_3$.)

SWP water used for injection during the first two cycles originated primarily from the Sacramento–San Joaquin Delta, whereas water used in the third cycle originated from the Kern River (fig. 1). The mean concentrations of DOC in the injection water in the second and third cycles were similar—1.80 and 1.76 milligrams per liter (mg/L), respectively—but the concentrations of inorganic constituents were very different (Fram and others, 2002; Metzger and others, 2002). The concentration of chloride in water injected into and extracted from well 4-32 during the three cycles is shown in figure 4*B* as an example. The median chloride concentration in the injection water in the second cycle was 52 mg/L, which was significantly higher than the concentration in the ground water, whereas the median chloride concentration in the injection water in the third cycle was 7 mg/L, which was lower than the concentration in the ground water. As a result, chloride concentrations in the extracted water decreased during extraction in the first two cycles, but increased during extraction in the third cycle (fig. 4*B*).

These differences in injection water chemistry between the first two and the third cycles are not expected to cause a significant difference in the processes affecting the formation and fate of THMs during the three cycles. Although this report only discusses the third cycle, it is expected that the results can be applied to the other cycles at the Lancaster site, with few modifications due to changes in injection water composition.

The constituents that are important for assessing the formation and fate of THMs during the third cycle are THMs, DOC, residual chlorine, bromide, the ratio of bromine to chlorine in the THM ($(Br/Cl)_{THM}$), and an appropriate conservative tracer such as chloride. The variations of these constituents in the ground water, injection water, and water extracted from well 4-32 and the nested piezometers during the third cycle are shown in figure 5 and discussed here.

Trihalomethanes

Third cycle injection water contained 22 to 40 µg/L THMs (fig. 5*A*) with a mean concentration of 27.5 µg/L. The concentration of THMs in water sampled from well 4-32 prior to the third injection was less than 2 µg/L (Los Angeles County Department of Public Works, 2000). THM concentrations in the extracted water decreased from about 59 µg/L at the beginning of extraction to about 10 µg/L on October 21, 1998 (fig. 5*A*), when extraction was halted due to failure of the pump on October 24, 1998. When extraction resumed on February 22, 1999, THM concentrations in the extracted water were 15 to 26 µg/L and then dropped steadily to 3 µg/L as extraction continued through April 28, 1999 (fig. 5*A*).

THM concentrations measured by the USGS and LACDPW in water samples from the nested piezometers showed poor agreement (table 2). Both sets of data are plotted in figure 5*A*. The differences may be due to the imperfect sampling techniques used to obtain undegassed water samples from the piezometers (see Fram and others, 2002). In that case, the highest concentration reported for each sample may be the most accurate.

On March 12, 1998, prior to the third cycle, water from piezometers 27P6 and 27P7 had no detectable concentrations of THMs, whereas water from piezometer 27P8 contained 2.4 µg/L THMs (table 2). Because THMs do not naturally occur in ground water at these concentrations, the THMs must have been residual from the previous injection, storage, and recovery cycles.

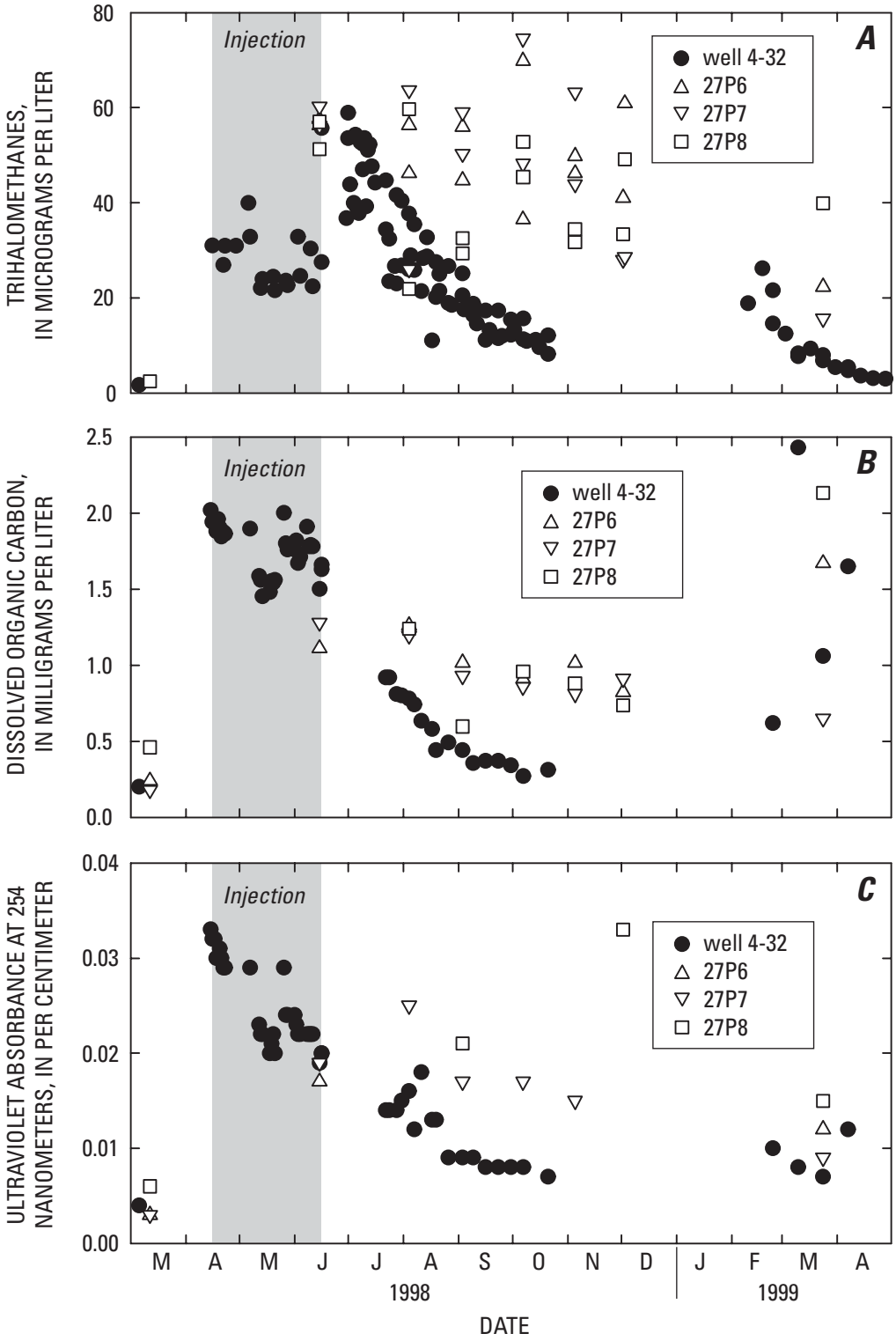

Figure 5. Trihalomethane concentrations ***(A)***, dissolved organic carbon concentrations ***(B)***, ultraviolet absorbance values at 254 nanometers ***(C)***, pH values ***(D)***, free and total residual chlorine concentrations ***(E)***, chloride concentrations ***(F)***, bromide concentrations ***(G)***, and molar bromine to chlorine ratio in trihalomethanes ***(H, I)*** in ground water, injection water, and extraction water collected from well 7N/12W-27P2 (well 4-32) and from nested piezometers 7N/12W-27P6–8 during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Data are from Fram and others (2002), Metzger and others (2002), and tables 2 and 3.

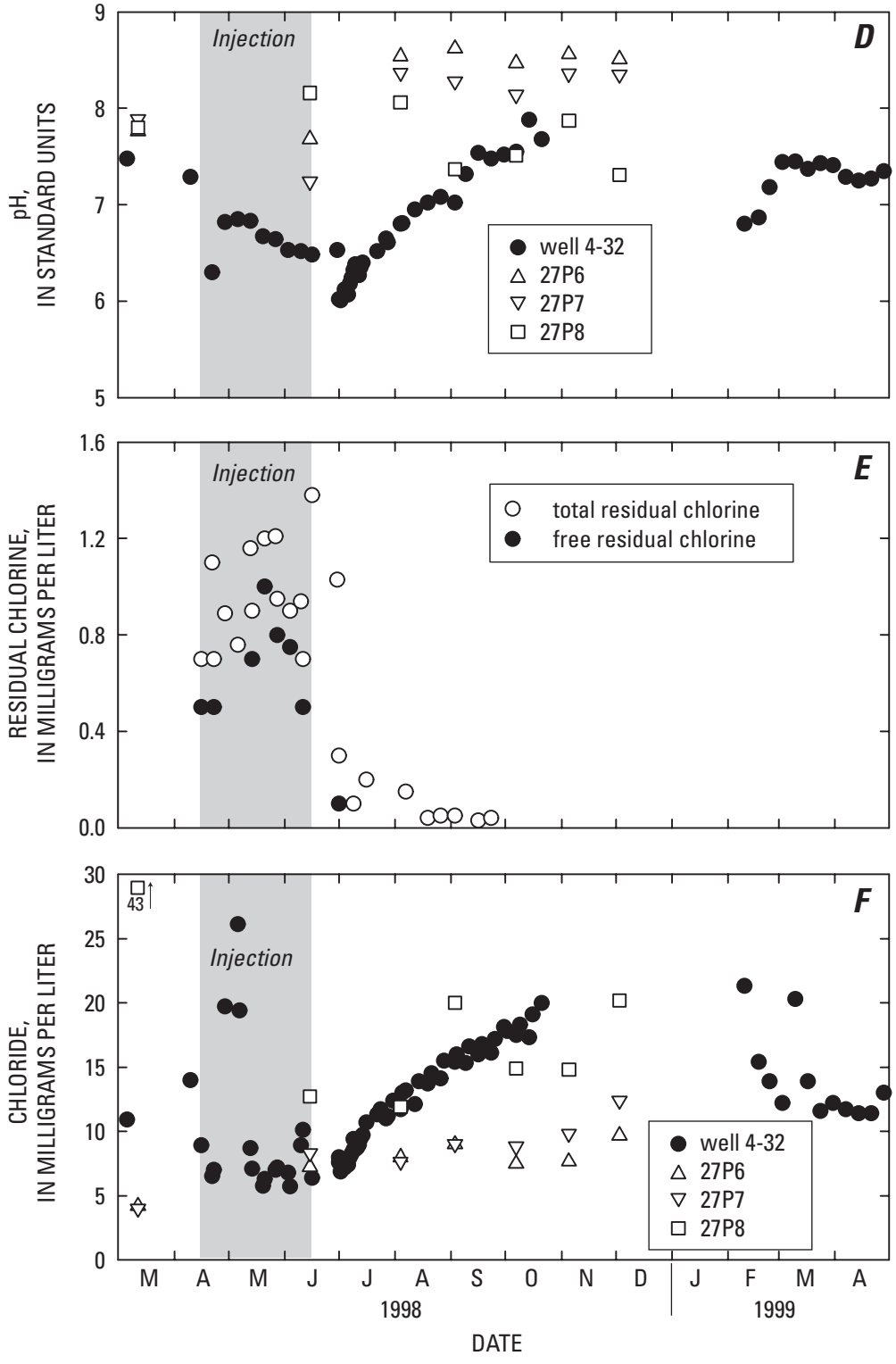

Figure 5.—Continued.

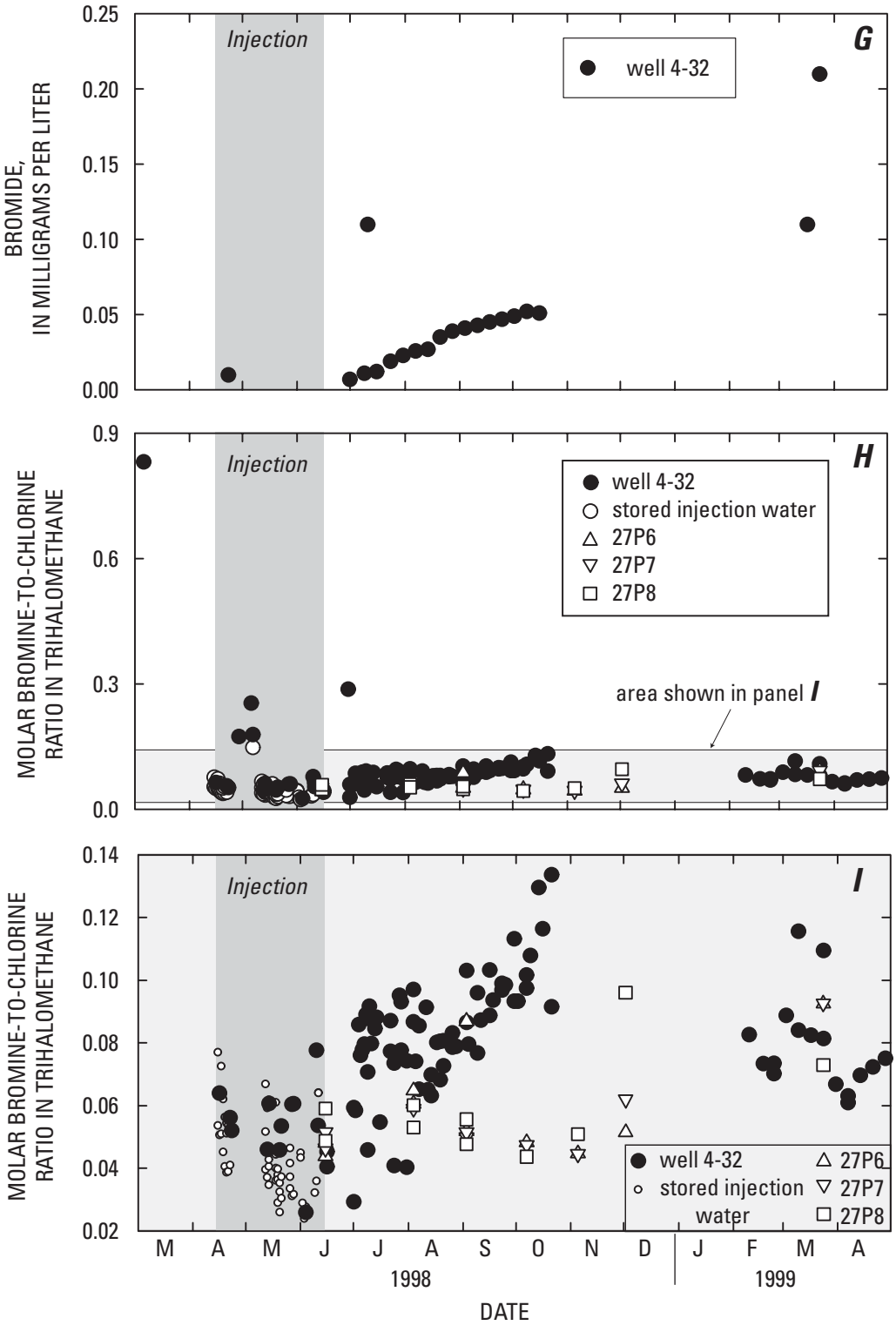

Figure 5.—Continued.

Table 2. Trihalomethane concentration data for water collected from nested piezometers 7N/12W-27P6–8 during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California

[Samples analyzed at two laboratories: U.S. Geological Survey (USGS), Sacramento District and Los Angeles County Department of Public Works (LACDPW). $CHCl_3$, chloroform; $CHCl_2Br$, bromodichloromethane; $CHClBr_2$, dibromochloromethane; $CHBr_3$, bromoform; THM, trihalomethane. µg/L, microgram per liter; nd, not detected; nr, not reported; <, less than]

Sampling date	Analyzing agency	$CHCl_3$ (µg/L)	$CHCl_2Br$ (µg/L)	$CHClBr_2$ (µg/L)	$CHBr_3$ (µg/L)	Total THM (µg/L)
Piezometer 27P6						
3/12/98	LACDPW	nd	nd	nd	nd	nd
6/15/98	USGS	47.8	8.8	1.0	<0.2	57.6
6/15/98	LACDPW	47.0	9.3	nd	nd	56.3
8/4/98	USGS	43.9	11.0	1.4	<0.2	56.3
8/4/98	LACDPW	36.9	7.7	1.6	nd	46.2
9/3/98	USGS	45.9	8.9	1.2	<0.2	56.0
9/3/98	LACDPW	32.8	9.1	2.8	nd	44.7
10/7/98	USGS	58.2	9.9	1.7	<0.2	69.8
10/7/98	LACDPW	nr	nr	nr	nr	36.5
11/5/98	USGS	39.0	6.2	1.0	<0.2	46.2
11/5/98	LACDPW	nr	nr	nr	nr	49.8
12/2/98	USGS	33.8	6.1	1.1	<0.2	41.0
12/3/98	LACDPW	nr	nr	nr	nr	60.9
3/24/99	USGS	16.0	4.9	1.4	<0.2	22.3
Piezometer 27P7						
3/12/98	LACDPW	nd	nd	nd	nd	nd
6/15/98	USGS	50.2	9.2	0.8	<0.2	60.2
6/15/98	LACDPW	46.1	9.0	1.1	nd	56.2
8/4/98	USGS	50.5	12.2	1.0	<0.2	63.7
8/4/98	LACDPW	21.1	4.9	nd	nd	26.0
9/3/98	USGS	48.6	9.4	1.0	<0.2	59.0
9/3/98	LACDPW	41.5	7.4	1.4	nd	50.3
10/7/98	USGS	62.2	10.7	1.6	<0.2	74.5
10/7/98	LACDPW	nr	nr	nr	nr	48.2
11/5/98	USGS	37.0	6.1	0.8	<0.2	43.9
11/5/98	LACDPW	nr	nr	nr	nr	63.2
12/2/98	USGS	22.2	4.9	0.9	<0.2	28.0
12/3/98	LACDPW	nr	nr	nr	nr	28.6
3/24/99	USGS	11.2	3.4	1.0	<0.2	15.6
Piezometer 27P8						
3/13/98	LACDPW	2.4	nd	nd	nd	2.4
6/15/98	USGS	47.2	8.8	1.0	<0.2	57.0
6/15/98	LACDPW	40.9	9.2	1.2	nd	51.3
8/4/98	USGS	46.6	13.1	<0.5	<0.2	59.7
8/4/98	LACDPW	17.6	4.3	nd	nd	21.9
9/3/98	USGS	26.7	5.8	<0.5	<0.2	32.5
9/3/98	LACDPW	23.3	6.0	nd	nd	29.3
10/7/98	USGS	44.1	8.7	<0.5	<0.2	52.8
10/7/98	LACDPW	nr	nr	nr	nr	45.4
11/5/98	USGS	25.7	6.0	<0.5	<0.2	31.7
11/5/98	LACDPW	nr	nr	nr	nr	34.4
12/2/98	USGS	23.8	7.2	2.4	<0.2	33.4
12/3/98	LACDPW	nr	nr	nr	nr	49.1
3/24/99	USGS	29.8	9.6	0.5	<0.2	39.9

THM concentrations in water samples collected from the nested piezometers were nearly always higher than concentrations in water collected from well 4-32 on the same date during the injection and extraction periods (fig. 5*A*). At the end of the injection period, water from all three piezometers contained about 60 μg/L THM. THM concentrations in water from piezometers 27P6 and 27P7 remained at about 60 μg/L through September and then increased to a maximum of 75 μg/L on October 4, 1998. These high THM concentrations in piezometers 27P6 and 27P7 are noteworthy because on September 26, 1998, the volume of water extracted from well 4-32—just 80 ft away—exceeded the volume of water injected (fig. 3*B*). THM concentrations in piezometers 27P6 and 26P7 then declined, reaching lows of about 20 μg/L at the end of the cycle (fig. 5*A*). THM concentrations in water from piezometer 27P8 were somewhat more variable than those in water from the other two piezometers. This difference in behavior may be due to the location of the three piezometers relative to the water table. The screened interval of piezometer 27P8 is near the pre-injection water table, and during the extraction period, the water table declined below the top of the screen, whereas the screened intervals for piezometers 27P6 and 27P7 were always significantly below the water table (figs. 2 and 3*C*). THMs are volatile compounds and may volatilize from pore waters into air in the pore spaces in the unsaturated zone above the water table.

Dissolved Organic Carbon and Ultraviolet Absorbance

DOC concentrations in the injection water ranged from 1.4 to 2.0 mg/L and had a mean value of 1.76 mg/L. The concentration in the extraction water declined from about 1.8 mg/L to about 0.3 mg/L during the first part of extraction (June 30, 1998, through October 24, 1998), but varied unsystematically between 0.5 and 2.5 mg/L during the second part (fig. 5*B*).

Water samples collected prior to the third injection, storage, and recovery cycle, in March 1998, from well 4-32 and piezometers 27P6 and 27P7 contained about 0.2 mg/L DOC and likely represent the native ground-water composition. DOC concentrations in water from piezometers 27P6 and 27P7 reached a maximum of about 1.2 mg/L near the end of the injection period (June 15, 1998) and declined gradually to about 0.8 mg/L by the end of the first phase of the extraction period (fig. 5*B*).

Ultraviolet light absorbance values at a wavelength of 254 nanometers (UVA_{254} values) (fig. 5*C*) showed patterns of variation during the cycle similar to those shown by DOC concentrations. UVA_{254} values ranged from 0.033 to 0.019 per centimeter (/cm) in the injection water and from 0.018 to 0.007/cm in the extraction water. Many of the samples from the piezometers had UVA_{254} values greater than 0.04 (not shown in fig. 5*C*), which may have been due to interference from particulate materials during analysis (Fram and others, 2002).

pH

The pH of ground-water samples collected from wells 4-32 and 4-34 prior to each of the three cycles ranged from 7.2 to 8.3 (Los Angeles County Department of Public Works, 2000; Fram and others, 2002; Metzger and others, 2002), and the pH of samples collected from the nested piezometers between August and December, 1998, ranged from 7.3 to 8.6 (fig. 5*D*). These pH values may reflect equilibration between the water and the aquifer sediments. The ground-water samples also contained 12 to 26 mg/L of calcium (Los Angeles County Department of Public Works, 2000; Metzger and others, 2002), and the aquifer sediments contained horizons of caliche, a calcium carbonate precipitate commonly formed in soils in arid environments (Fram and others, 2002). Water in equilibrium with the atmosphere and solid, pure calcium carbonate has a pH of 8.3 and a calcium concentration of 20 mg/L (Stumm and Morgan, 1996). Thus, the pH and calcium concentrations in the ground-water samples are consistent with those in pore waters in equilibrium with oxidized, calcium carbonate-bearing sediments.

In contrast, the pH of the injection water ranged from 6.3 to 6.8 (median value = 6.6) (fig. 5*D*). The pH of the extracted waters was 6.0 at the beginning of extraction (fig. 5*D*), which was lower than the pH of all of the injected water and ground-water samples. This indicates that pH behaved non-conservatively in this system and, thus, must have been affected by reactions occurring in the system. Continued reaction between DOC and free chlorine in the injected water after injection into the aquifer may account for some of the observed decrease in pH. Oxidation-reduction reactions reduce free chlorine to chloride, oxidize DOC, and produce hydrogen ions (increased acidity, lower pH) (for example, Larson and Weber, 1994). An increase in carbon dioxide (CO_2) concentration in the water upon injection also may account for some of the decrease in pH. Possible mechanisms for increasing CO_2 concentration include entrainment of air during injection and microbial respiration of DOC in the injected water.

As extraction proceeded from well 4-32, before the pumping hiatus due to pump failure, the pH of the extracted water steadily increased toward the pH values observed in the ground-water samples (fig. 5*D*). This trend could be produced by mixing between injection water and ground water, or by gradual equilibration of injection water with the carbonate-bearing aquifer sediments. It is not possible from this data alone to determine the relative importance of mixing and equilibration. However, the major-ion chemical composition of water collected from the piezometers at the end of the injection period (June 15, 1998) closely resembles that of the injection water (Fram and others, 2002; fig. 5*F*), but the pH values are significantly higher than those of the injection water, suggesting that some equilibration did occur.

Residual Chlorine

Total residual chlorine concentrations in the injection water at the time of injection ranged from 0.7 to 1.38 mg/L, while free residual chlorine concentrations ranged from 0.5 to 1.0 mg/L (fig. 5*E*). A linear regression relation calculated using the seven samples in which both total and free residual chlorine were measured was used to estimate the free residual chlorine concentrations in the remaining samples. The mean free residual chlorine concentration for all the injection water samples was 0.79 mg/L (relative standard deviation [RSD] = 28 percent). Most samples of extraction water had undetectable residual chlorine concentrations; residual chlorine was only detected in a few samples collected during the first three months of extraction (fig. 5*E*).

Chloride and Bromide

Chloride concentrations in the injection water ranged from 5.7 to 10 mg/L except during one short period when concentrations ranged from 19 to 26 mg/L (fig. 5*F*). Because only 17 samples were collected during the 2-month injection period, estimation of the average chloride concentration of the injection water is uncertain. Weighted averages were calculated by weighting the chloride concentration in the water each day by the daily volume of water injected. Daily chloride concentrations were interpolated from the measured values in several different ways, and the resulting average chloride concentration ranged between 7.5 and 9.0 mg/L. The chloride concentration in the extraction water was less than 9 mg/L during the first 10 days of extraction, suggesting that the lower end of the range estimated for the injection-water chloride concentration may be more accurate.

During the first phase of extraction from well 4-32, the chloride concentration in the extraction water increased gradually from about 7 to about 20 mg/L, and during the second phase of extraction chloride concentrations in the extraction water decreased from about 20 to about 10 mg/L (fig. 5*F*).

Chloride concentrations in the ground water of the upper and middle aquifers near well 4-32 were heterogeneous. The chloride concentrations in water collected from well 4-32 shortly before the first, second, and third cycles were 14, 19, and 11 mg/L, respectively (fig. 5*F*), and the concentration in water from well 4-34 was 21 mg/L prior to both the first and second cycles and 36 mg/L prior to the third cycle (Los Angeles County Department of Public Works, 2000; Fram and others, 2002; Metzger and others, 2002). Wells 4-32 and 4-34 are screened continuously through the upper and middle aquifers (fig. 2), and water collected from them represents a mixture of water derived from different levels in the aquifers. Ten other wells that also are screened only in the upper and middle aquifers and are within 2.5 miles of well 4-32 had chloride concentrations ranging from 3 to 28 mg/L prior to the third cycle (Los Angeles County Department of Public Works, 2000). The difference between chloride concentrations in wells 4-32 and 4-34

indicates that the ground water in the upper and middle aquifers is naturally laterally heterogeneous in composition.

The data from the piezometers indicates strong vertical heterogeneity as well. Water from piezometers 27P6 and 27P7 contained 4 mg/L chloride prior to the third cycle, whereas water from piezometer 27P8 contained 43 mg/L chloride (fig. 5*F*). However, because water from piezometer 27P8 prior to the third cycle contained THMs (fig. 5*A*), its high chloride concentration probably reflects a contribution from injection water from the previous cycle. Water from piezometer 7N/12W-27F8 contained 18 mg/L chloride (and no THMs) before the second cycle (Metzger and others, 2002). Like piezometer 27P8, it is screened from 395 to 415 ft in the upper aquifer, but is located about 2,200 ft north-northwest. The piezometer data suggest that chloride concentrations in the ground water may be greater near the top of the upper aquifer than at the base of the upper aquifer or the top of the middle aquifer where piezometers 27P7 and 27P6, respectively, are screened. No information is available about the chloride concentrations in ground water at the base of the middle aquifer.

During the injection and extraction periods of the third cycle, chloride concentrations in samples from piezometers 27P6 and 27P7 ranged from 7.5 to 12.4 mg/L, which was similar to concentrations in the injection water and always lower than concentrations in samples of extraction water collected on the same day (fig. 5*F*). Dissolved solids, nitrate, and sulfate concentrations and specific conductance values in samples from piezometers 27P6 and 27P7 also were similar to those in the injection water and lower than those in samples of extraction water collected on the same day (table 3; Fram and others, 2002). Samples from piezometer 27P8 generally contained higher concentrations of chloride (fig. 5*F*), dissolved solids, sulfate, and nitrate than samples from piezometers 27P6 and 27P7.

Bromide concentrations in the extraction water were generally well correlated with chloride concentrations (fig. 5*F*,*G*), and it is presumed that a similar correlation existed in the injection water. Accurate measurements of the bromide concentration in the injection water were not obtained because the samples were collected after chlorination, which causes incorporation of bromide into halogenated disinfection by-products.

Bromine to Chlorine Ratio in the Trihalomethanes

THMs consist of chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). The molar ratio of bromine to chlorine incorporated in trihalomethane species [$(Br/Cl)_{THM}$] reflects the mechanisms and kinetics of THM formation and the bromide content of the source water from which the THMs form. Brominated THMs are formed because the chlorine added during the water-treatment process oxidizes any bromide dissolved in the water to form the reactive species hypobromous acid. Water-treatment plants generally add chlorine by bubbling chlorine gas through the water. Free chlorine is almost completely hydrolyzed to hypochlorous acid at the chlorine concentrations used in water treatment (Larson and Weber, 1994). The bromide oxidation reaction is very rapid and scavenges bromide out of the water, converting it to hypobromous acid (Morris, 1978; Rook and others, 1978). Hypobromous acid reacts much faster with DOC to form THMs than does hypochlorous acid (Rook and others, 1978; Oliver, 1980; Amy and others, 1985; Symons and others, 1993); thus the rate of formation of brominated THMs is greater than the rate of formation of $CHCl_3$ alone.

Injection water samples collected between April 16 and April 23, 1998, and between May 12 and June 15, 1998, had $(Br/Cl)_{THM}$ values between 0.025 and 0.080, whereas samples collected between April 29 and May 8, 1998, had values between 0.175 and 0.255 (fig. 5*H*). (The $(Br/Cl)_{THM}$ values were calculated by assigning a concentration of zero to concentrations of individual species that were below the method detection limit and thus are minimum values.) The injection water samples collected between April 29 and May 7, 1998, contained higher concentrations of chloride (fig. 5*F*), sulfate, and dissolved solids than did the other injection water samples (Fram and others, 2002) and presumably also had higher bromide concentrations.

Table 3. Water quality data for water collected from nested piezometers 7N/12W-27P6–8 during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California

[Dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nanometers (UVA_{254}) were analyzed at the U.S. Geological Survey (USGS), Sacramento District. All other constituents were analyzed by the Los Angeles County Department of Public Works (LACDPW). mg/L, milligram per liter; /cm, per centimeter; μS/cm, microsiemens per centimeter; na, not analyzed]

Sampling date	DOC (mg/L)	UVA_{254} (/cm)	Specific conductance (μS/cm)	pH (standard units)	Dissolved solids (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)
Piezometer 27P6								
2/18/98	0.17	0.004	na	na	na	na	na	na
3/12/98	.24	.003	280	7.76	172	4.20	1.21	23.4
6/15/98	1.11	.017	219	7.68	142	7.24	.65	35.0
8/4/98	1.26	.191	232	8.54	144	8.00	.64	36.5
9/3/98	1.02	.160	219	8.62	138	9.00	.71	38.0
10/7/98	.91	.061	218	8.47	148	7.49	.97	29.6
11/5/98	1.01	.112	222	8.56	168	7.65	.75	29.2
12/2/98	.82	.105	225	8.51	142	9.69	1.74	32.0
3/24/99	1.67	.012	na	na	na	na	na	na
Piezometer 27P7								
2/18/98	0.11	0.003	na	na	na	na	na	na
3/12/98	.18	.003	247	7.89	152	4.00	.96	21.2
6/15/98	1.28	.019	186	7.24	120	8.30	.55	35.0
8/4/98	1.19	.025	198	8.37	120	7.63	.15	33.5
9/3/98	.93	.017	204	8.28	130	9.01	.79	33.0
10/7/98	.86	.017	208	8.14	140	8.81	.94	29.5
11/5/98	.81	.015	217	8.36	154	9.81	1.03	3.4
12/2/98	.91	na	253	8.35	162	12.40	1.03	34.0
3/24/99	.65	.009	na	na	na	na	na	na
Piezometer 27P8								
2/18/98	0.18	0.002	na	na	na	na	na	na
3/12/98	.46	.006	456	7.80	304	43.00	1.54	46.0
6/15/98	na	na	286	8.16	180	12.70	.77	42.0
8/4/98	1.24	.299	231	8.06	146	11.90	.25	39.0
9/3/98	.60	.021	262	7.37	168	20.00	1.90	41.0
10/7/98	.96	.052	237	7.51	150	14.90	1.39	34.0
11/5/98	.88	.169	251	7.87	174	14.80	1.40	38.4
12/2/98	.73	.033	274	7.31	174	20.20	1.79	41.0
3/24/99	2.13	.015	na	na	na	na	na	na

The $(Br/Cl)_{THM}$ values for water extracted from well 4-32 increased from about 0.03–0.09 to 0.09–0.14 between June 30, 1998, and October 24, 1998 (fig. 5*H*,*I*). This increase in $(Br/Cl)_{THM}$ values occurred concomitantly with the decrease in THM concentrations in the extracted water (fig. 5*A*). The $(Br/Cl)_{THM}$ values in the extracted water varied unsystematically between 0.06 and 0.12 during the second phase of extraction from well 4-32 between February 22 and April 29, 1999.

Samples from the nested piezometers 27P6–8 generally had lower $(Br/Cl)_{THM}$ values than did samples collected from well 4-32 (fig. 5*I*). The $(Br/Cl)_{THM}$ values for samples from all three piezometers were approximately 0.05 at the end of the injection period (June 16, 1998) and remained almost constant through November 5, 1998 (fig. 5*I*), while THM concentrations in the piezometer samples ranged from 35 to 75 µg/L (fig. 5*A*). Between November 5, 1998, and March 24, 1999, the $(Br/Cl)_{THM}$ values for water samples from all three piezometers rose to a maximum value of 0.09. Water from piezometers 27P6 and 27P7 always had similar $(Br/Cl)_{THM}$ values, whereas water from piezometer 27P8 had a higher $(Br/Cl)_{THM}$ value in December 1998 but a lower value in March 1999.

Water Levels

Changes in water levels in the aquifer during the injection, storage, and recovery cycle may provide information about water flow in the aquifer during different periods of the cycle. Water levels were monitored continuously in piezometers 27P6 and 27P8 and intermittently in piezometer 27P7 during the third cycle (fig. 3*C*). The depth to the water table in the piezometers decreased from 330 ft below land surface to a minimum of 290 and 302 ft below land surface in 27P6 and 27P8, respectively, during the injection period. Water levels in piezometers 27P6 and 27P8 responded to changes in the injection rate; depth to the water table increased in both piezometers during the short hiatus in injection from April 28 to May 5, 1998 (fig. 3*B*,*C*). The rapid water-level response measured in both piezometers to the injection at well 4-32 indicated that the aquifer zones screened in the piezometers were in direct hydraulic communication with the aquifer zones screened in well 4-32 during the injection period.

In contrast to the injection period, water levels in piezometers 27P6 and 27P8 responded very differently during the extraction period. After injection ceased, the depth to water measured in piezometer 27P8 increased sharply to 330 ft below land surface, then increased immediately to about 333 ft at the start of extraction at well 4-32, and then slowly increased to 347 ft below land surface over the 10 months of the extraction period (fig. 3*C*). Cessation of pumping at well 4-32 on October 24, 1998, beginning of pumping at well 4-34 on December 29, 1998, and resumption of pumping at well 4-32 on February 22, 1999, caused only minor changes in water level in piezometer 27P8. In contrast, the water level in piezometer 27P6 responded directly to changes in pumping at wells 4-32 and 4-34 (fig. 3*C*). The depth to water increased to a maximum of 357 ft below land surface during the first phase of the extraction period when water was being pumped from well 4-32, and then decreased to a level equal to that in piezometer 27P8 (335 ft below land surface) when no water was being pumped from well 4-32 or 4-34. Initiation of pumping at well 4-34 corresponded to an increase in the depth to water measured in piezometer 27P6, and then resumption of pumping at well 4-32 led to another sharp increase in the depth to water to its maximum of 380 ft below land surface. Periodic water-level measurements made at well 4-32 during the extraction period indicate that water levels declined to as much as 404 ft below land surface (K. Rosander, Los Angeles County Department of Public Works, oral commun., 2003), significantly below the screened interval of piezometer 27P8 (330–370 ft below land surface). Therefore, the aquifer zone screened by piezometer 27P8 was not in direct hydraulic communication with the aquifer zones screened by wells 4-32 and 4-34 during at least part of the extraction period, explaining the limited water-level response in piezometer 27P8 to the extraction from wells 4-32 and 4-34.

Trihalomethane Formation

This section of the report describes the factors that controlled the continued formation of THMs in the aquifer after injection and presents an estimate of the extent of THM formation in the injected water. THM concentrations in samples collected during the third injection, storage, and recovery cycle rose from a mean of 27.5 μg/L at the time of injection to about 59 μg/L at the beginning of extraction (fig. 5*A*). Similar increases occurred during the first two cycles (fig. 4*A*). THMs and other halogenated organic compounds are formed by the reaction of DOC and residual chlorine. The amount of THM formed depends on several variables including the reaction-limiting concentration of chlorine or DOC present in the water, the propensity of the DOC to form THMs (its quality with respect to THM formation), the contact time between the DOC and the chlorine, the ratio of the concentrations of bromide and DOC, and the pH (for example, Rook, 1977; Babcock and Singer, 1979; Reckhow and others, 1990). The effect of some of these variables on THM formation in the injection water was systematically investigated as part of this study.

DOC is a complex, heterogeneous material whose chemical composition and structure varies significantly, depending on its sources and the biogeochemical processing it has undergone. Chemical and structural features of DOC collectively are referred to as DOC quality. In the context of this study, DOC quality is important because the extent of THM formation during chlorination of a water sample depends on the quantity (that is, concentration) and the quality of the DOC. The quantity and quality of DOC in the injected water varied during the injection period; thus, variations in the extent of THM formation were expected. Two types of experiments were done to assess THM formation and DOC quality: trihalomethane formation potential (THMFP) experiments and a storage experiment. The THMFP experiments yielded the maximum amount of THM formation possible from samples of injection water (given fixed conditions of pH, temperature, time, and residual chlorine concentrations) and provided an indicator of DOC quality. The storage experiment tested whether THM formation in the injected water was limited by the concentration of DOC or of residual free chlorine.

Trihalomethane-Formation-Potential Experiments

Trihalomethane formation potential (THMFP) is the maximum amount of THM that will form from a water sample under controlled conditions of pH, temperature, time, and residual chlorine concentration. Because the molar yield of THMs from a given amount of DOC may vary by more than a factor of 10 (for example, see Fujii and others, 1998), no simple relation exists between DOC concentration or chlorine consumption and the extent of THM formation in natural waters. The variability in DOC quality means that THMFP is difficult to predict and thus must be measured experimentally. The THMFP experiment examines the relation between DOC quantity and quality and THM formation.

The experimental method for measuring THMFP is described in detail by Fram and others (2002). On arrival in the USGS laboratory in Sacramento, one aliquot of injection water was immediately quenched with sodium sulfite and analyzed for THM concentration. This concentration represents the concentration after one day of storage owing to transit time between the well and the laboratory. Another aliquot of injection water was quenched with sodium sulfite and purged with nitrogen to remove free chlorine and THMs. Samples were buffered to pH 8.3 with a boric acid/sodium hydroxide solution, spiked with sufficient sodium hypochlorite to ensure the presence of a chlorine residual at the end of the experiment, sealed in headspace-free amber glass serum vials with Teflon-faced septa, and stored for 7 days in the dark at 25°C. At the end of the 7 days, the THM concentration was measured by purge and trap capillary gas chromatography. This concentration represents the residual THMFP. The total THMFP for a water sample is the 1-day storage concentration plus the residual THMFP. Experimental results were tabulated by Fram and others (2002).

The total THMFP of injection-water samples ranged from 120 to 228 μg/L (fig. 6) and averaged 175 μg/L (RSD = 13 percent). These values are much higher than those for the THM concentrations at the time of injection. The ground water had a total THMFP of 21.1 μg/L, which is much lower than that of the injection-water samples. This low value primarily reflects the much lower DOC concentration in the ground water (0.2 mg/L) in comparison with that in the injection water (1.4–2.0 mg/L). The highest $(Br/Cl)_{THM}$ value was measured in the THMFP of the ground water. The THMFP of the ground-water sample was only 21 μg/L THMs, but the $(Br/Cl)_{THM}$ was equal to 0.81 (fig. 5*H*). This $(Br/Cl)_{THM}$ value was much higher than the values for all other field and experimental samples analyzed in this study and reflects the high ratio of bromide to DOC in the ground-water sample.

Results from the THMFP experiments also can be used to characterize the compositional nature, or quality, of the DOC. Specific trihalomethane formation potential (STHMFP) is defined as the total THMFP, in millimoles of THMs per liter, divided by the DOC, in moles of carbon per liter, and has units of millimoles per mole (mmol/mol). STHMFP is an indicator of DOC compositional quality and represents the molar efficiency of the DOC to form THMs. STHMFP values for the injection water ranged from 6.9 to 11.3 mmol/mol (median value was 9.9 mmol/mol) (fig. 7). In other words, approximately 10 of every 1,000 carbon atoms in the DOC formed THMs during chlorination under the experimental conditions. The STHMFP value for the ground-water sample shows that the DOC in the ground water is chemically distinct from the DOC in the injection water. The STHMFP value of the ground water was 7.3 mmol/mol (fig. 7), which is significantly lower than the STHMFP values of the injection water sample (parametric prediction interval at $\alpha = 0.05$ and nonparametric prediction interval at $\alpha = 0.1$; Helsel and Hirsch, 1995).

DOC quality also can be quantified using optical measurements. For example, aromatic moieties can absorb light of wavelengths around 254 nanometers (nm). Because light absorbance depends on DOC quantity as well as quality, ultraviolet-absorbance data are presented normalized to DOC concentration. $SUVA_{254}$ is the ultraviolet absorbance at 254 nm divided by DOC concentration and has units of liters per meter per milligram. $SUVA_{254}$ is frequently used as an indicator of the aromaticity of the DOC (Traina and others, 1990; Chin and others, 1994). Absorbance data are tabulated in Fram and others (2002). Because THMs are generally thought to form from aromatic moieties within the DOC, $SUVA_{254}$ is considered an indicator of the THM formation potential of a water sample (Rook, 1977; Reckhow and others, 1990; U.S. Environmental Protection Agency, 1998). Thus, a correlation between $SUVA_{254}$ and STHMFP is commonly expected. However, for these samples, $SUVA_{254}$ and STHMFP are poorly correlated (fig. 7) (coefficient of correlation, r^2, for $SUVA_{254}$ and STHMFP in the injection-water samples equals 0.16). This observation suggests that for these source waters, the aromatic carbon precursor model for THM formation is not sufficient.

Storage Experiment

A storage experiment was done to assess whether THM formation in the injected water was limited by DOC or chlorine. The injection water contained 0.5–1.4 mg/L of free and total residual chlorine (fig. 5*E*), and 1.4–2.0 mg/L of DOC (fig. 5*B*) at the time of injection. This water continued to form THMs (and other chlorination by-products) after injection because the residual chlorine continued to react with the DOC. THM formation over time was measured directly by storing samples of injection water and measuring THM concentrations as the residual chlorine originally present in the samples was consumed.

For the storage experiment, unopened vials of injection water were stored for different periods of time before measuring the THM concentrations. The first analysis was done after 1 day (the transit time between the well in Lancaster and the laboratory in Sacramento). The other vials then were stored in the dark at 25°C for periods of 1, 2, 4, 8, and 16 weeks. At the end of each storage period, THM concentrations were analyzed by purge and trap gas chromatography by the USGS. Fram and others (2002) present detailed descriptions of the experimental and analytical methods and give the experimental results.

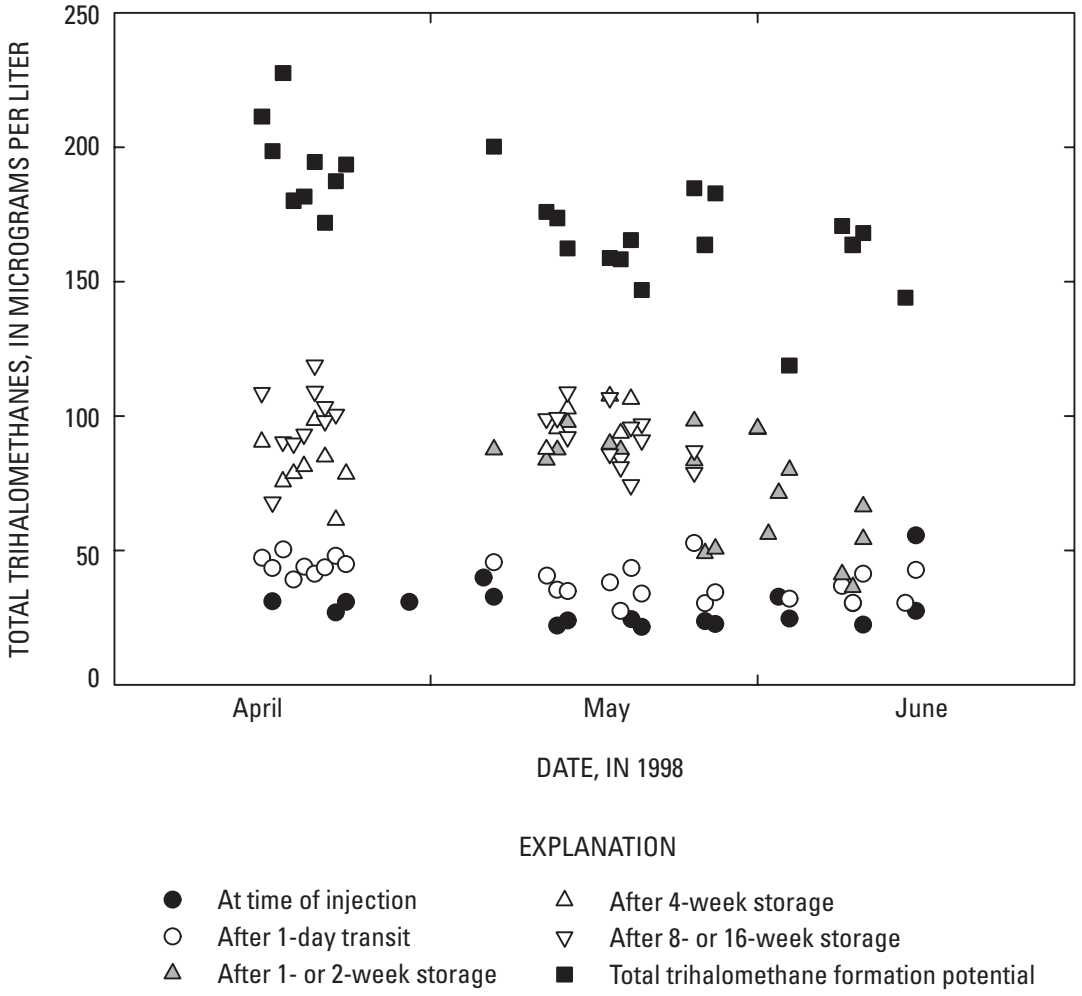

Figure 6. Trihalomethane concentrations in injection water collected from well 7/N12W-27P2 (well 4-32) during the third injection, storage, and recovers cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California

Date are from Fram and others (2002)

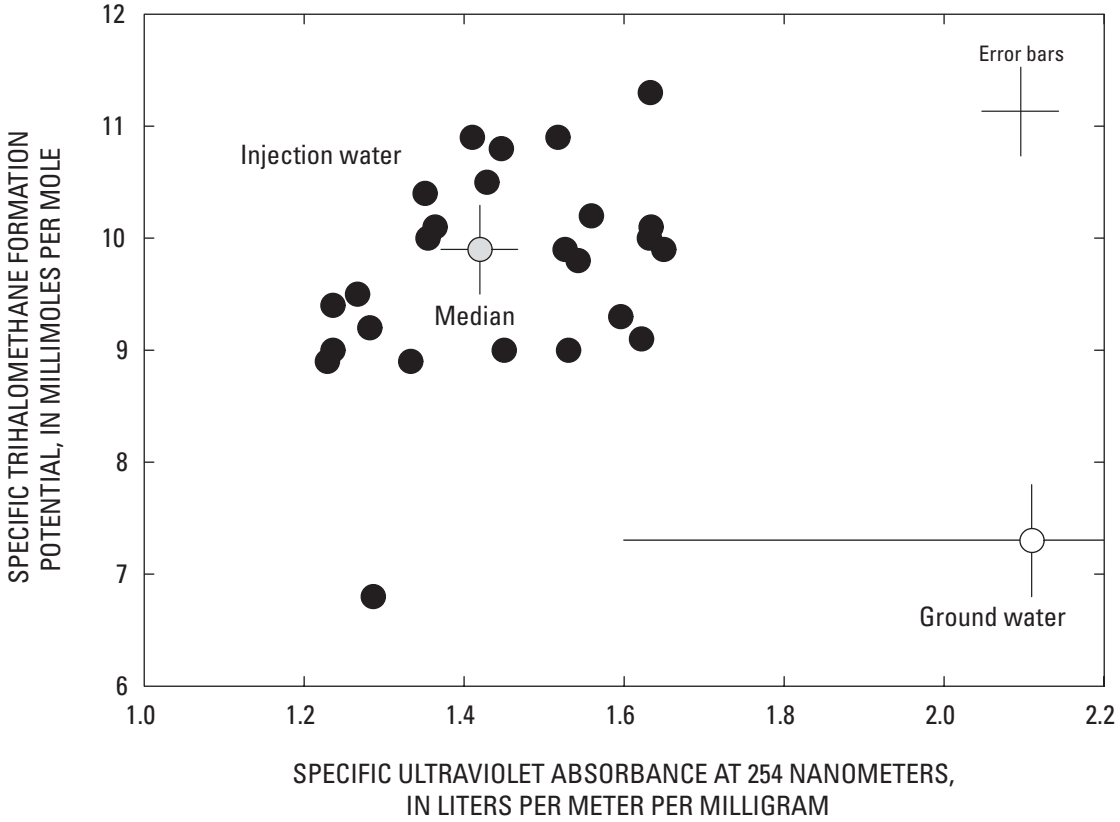

Figure 7. Values of specific trihalomethane formation potential (STHMFP) and specific ultraviolet absorbance at 254 nanometers ($SUVA_{254}$) for injection water and ground water collected from well 7N/12W-27P2 (well 4-32) during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Data are from Fram and others (2002).

The concentration of THMs in the stored samples increased during the first 4 weeks of storage and then remained relatively unchanged (fig. 8), as would be expected if one or both of the reactants (reactive DOC or free chlorine) were depleted during this time frame. Mean THM concentrations ranged from 28 μg/L at the time of injection (starting time for the storage experiment) to 40 μg/L after 1 day, to 73 μg/L after 2 weeks, to 89 μg/L after 4 weeks (fig. 8). The differences between the mean values at 4, 8, and 16 weeks were not statistically significant (the Student *t* test of difference between two means, $\alpha = 0.05$; Helsel and Hirsch, 1995).

The mean THM concentration of all of the samples stored for 1, 2, 4, 8, or 16 weeks was 86 μg/L ($\sigma = 18$ μg/L). This value is significantly less than the value determined in the THMFP experiment (175 μg/L). Because the injection period spanned 8 weeks and was followed by 2 weeks of storage before extraction began, there probably was sufficient time for the reactions to occur. Only one sample from the first few days of recovery contained traces of free residual chlorine (fig. 5*E*). Therefore, the THM formation in the injected water in the aquifer was limited by the concentration of residual free chlorine in the injection water. These results also indicate that if the water was re-chlorinated, the THM concentration would increase to 175 μg/L.

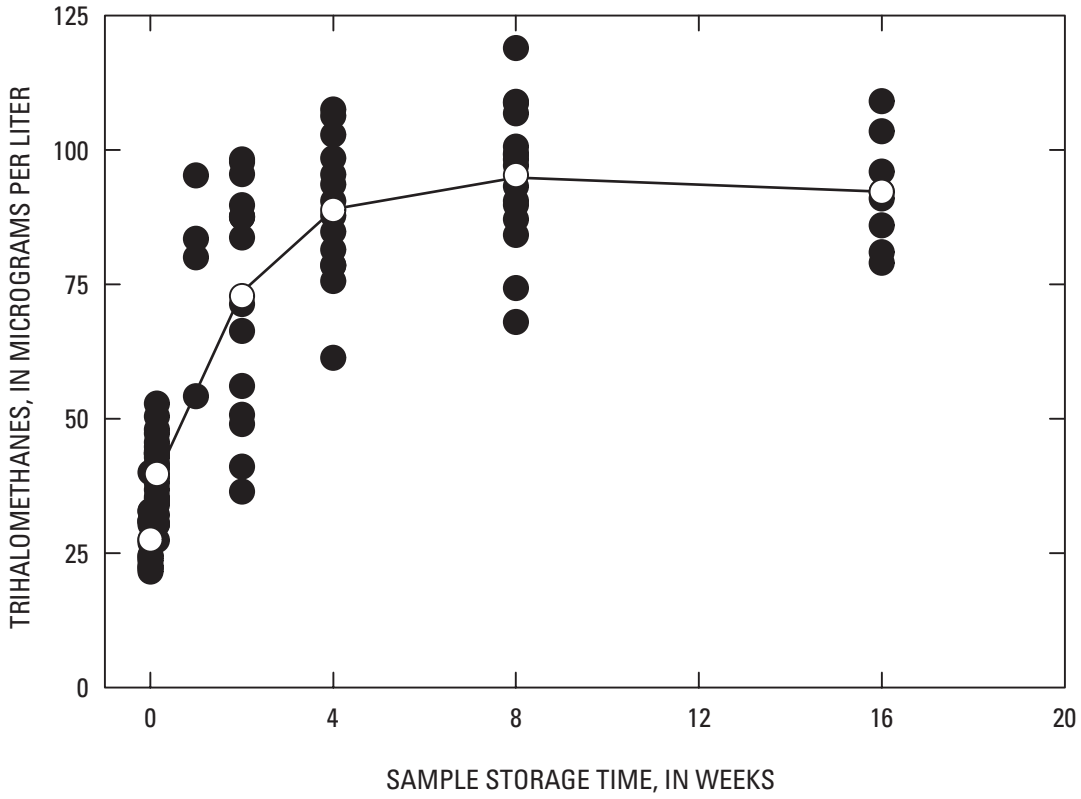

Figure 8. Trihalomethane concentrations in injection water collected from well 7N/12W-27P2 (well 4-32) dring the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Mean concentration at each time is indicated by the white points. data from Fram and others (2002).

Estimate of Trihalomethane Formation in the Injected Water

THM formation in the injected water, after injection and storage in the aquifer, was estimated using selected samples from well 4-32 and the piezometers. Interpretation of the water-quality data indicated that the water in these samples had not mixed with ground water and had not been modified by biodegradation or sorption. Samples that meet these criteria should have the chemical characteristics of the injection water. The chloride concentration and the $(Br/Cl)_{THM}$ values for the ground-water samples were used to select the set of representative samples that most closely resembled injection water. The chloride concentration of the injection water ranged between 7 and 9 mg/L; samples that had chloride concentrations within this range were selected for further review. $(Br/Cl)_{THM}$ values are very sensitive to the bromide content of water from which the THM formed and to later processes that might selectively affect the four THM species. We surmised that the injection water after storage in the aquifer and reaction of residual chlorine under aquifer conditions would contain THMs with $(Br/Cl)_{THM}$ values similar to values in the aliquots of injection water from the storage (1–16 week) experiments. Thus, samples that met the chloride criterion and had a $(Br/Cl)_{THM}$ value between 0.03 and 0.06 (fig. 5*I*) were determined to represent the THM formation in the injected water after injection into and storage in the aquifer. Mixing of injected water with ground water before consumption of residual chlorine would result in THMs with higher $(Br/Cl)_{THM}$ values, and biodegradation or sorption would result in THMs with lower $(Br/Cl)_{THM}$ values (discussed in more detail in the section "Fate of trihalomethanes"). Four samples of extraction water from well 4-32 and eight samples from piezometers 27P6 and 27P7 were selected based on these criteria. The mean THM concentration in these samples, 58 μg/L or 0.48 micromole per liter (μmol/L), is assumed to be the THM concentration of the injected water after injection and storage in the aquifer.

The mean THM concentration of the selected ground-water samples (58 μg/L) is less than the THM concentration observed in the storage experiment (86 μg/L). Possible explanations for this difference include the following:

- Water flow during injection was turbulent and may have contributed to volatilization of THMs from the injected water.
- THM formation is a function of pH; fewer THMs form when the pH is lower. The pH values of the first several samples of extracted water were lower than the pH values of the injected water (fig. 5*D*). This decrease in pH may have been due to entrainment of CO_2 during the injection process in addition to the pH decline that accompanies chlorine-consumption reactions.
- The aquifer sediments may have included material that reacted with chlorine, thus decreasing the amount of chlorine available to react with DOC to form THMs.
- DOC in the injection water may have rapidly degraded after injection into the aquifer, thus decreasing the amount of DOC available to react with chlorine to form THMs.

The THM concentration in the injected water after injection and storage in the aquifer could be reduced by dechlorination treatment of the injection water at the well-head. The residual free chlorine in the injected water could be removed by reaction with dechlorinating reagents such as sulfur dioxide, sodium bisulfite, sodium thiosulfite, sodium sulfite, ascorbic acid, or sodium ascorbate. However, depending on the dechlorination processes used, dechlorination may increase the potential for microbial growth, increase dissolved solids concentration, or decrease pH in the injected water.

Trihalomethane Fate

The $(Br/Cl)_{THM}$ values in water samples collected during the third cycle were used to help distinguish the processes that may or may not have affected the formation and fate of THMs in the aquifer. Biodegradation, sorption, and mixing would each produce predictable patterns of variation in $(Br/Cl)_{THM}$ values and THM concentrations in the extracted water. These predicted patterns can be compared to the observed patterns to infer the relative importance of the processes affecting the THM formation and fate in the aquifer. One of the most intriguing features of the data presented in figure 5*I* is the steady increase in the $(Br/Cl)_{THM}$ value in the extracted water during the first phase of extraction, concomitant with a steady decrease in THM concentrations (fig. 5*A*). Any explanation of the observed decrease in THM concentrations in the extracted water also must account for the $(Br/Cl)_{THM}$ values. Three primary processes that may affect THM concentrations and $(Br/Cl)_{THM}$ values are biodegradation of THMs by aquifer bacteria, sorption of THMs to aquifer materials, and mixing between injected water and ground water. Each of these processes will produce different patterns of variation of $(Br/Cl)_{THM}$ in the extracted water, and thus, the observed pattern of variation can be used to constrain the relative importance of these processes during the third injection, storage, and recovery cycle.

Biodegradation

Biodegradation of THMs has been observed in field and laboratory studies; however, biodegradation has been demonstrated to occur only under anoxic conditions and only brominated THMs are consumed (see the fourth section of this report for discussion). Therefore, if significant biodegradation of THMs had occurred during the third cycle, the $(Br/Cl)_{THM}$ of the remaining THMs would have decreased because the bacteria would have consumed only the brominated THM species. The data for well 4-32 show precisely the opposite trend: the $(Br/Cl)_{THM}$ of the remaining THMs increased with time, indicating that biodegradation probably had not occurred (fig. 5*I*). Furthermore, experiments designed to detect biodegradation of THMs showed that biodegradation of THMs in the aquifer at the Lancaster site was highly unlikely (see the fourth section of this report for further discussion).

Sorption

Sorption of THMs to sedimentary materials has been observed in field and experimental studies (Roberts and others, 1982; Curtis and others, 1986; Roberts and others, 1986; Walton and others, 1992; Peng and Dural, 1998). Sorption of hydrophobic organic compounds such as THMs is governed by a linear bulk partition coefficient, K_p, that is a strong function of the organic carbon content of the sedimentary material and the octanol-water partition coefficient of the organic compound (Chiou and others, 1979, 1983; Karickhoff and others, 1979; Schwarzenbach and Westall, 1981; Gschwend and Wu, 1985) (equations 1–4):

$$\log K_{oc} = a(\log K_{ow}) + b \quad (1)$$

$$K_p = K_{oc} \times f_{oc} \quad (2)$$

$$K_p = \frac{C_{sol}}{C_{wat}} \quad (3)$$

$$C_{init} = \frac{\rho C_{sol} + \varepsilon C_{wat}}{\varepsilon} \quad (4)$$

where

K_{oc} is the organic carbon/water partition coefficient,

K_{ow} is the octanol/water partition coefficient,

a and b are empirical constants,

K_p is the linear bulk sediment-water partition coefficient,

f_{oc} is the fraction of organic carbon in the sediment,

C_{sol} is the concentration of the compound in the solid at equilibrium,

C_{wat} is the concentration of the compound in the pore water at equilibrium,

C_{init} is the concentration of the compound in the injected water,

ρ is the density of the sediment, and

ε is the porosity of the sediment.

The bulk partition coefficient is defined as the ratio between the concentrations of the compound in the solid sediment material and the pore water at equilibrium. As injected water moves into the pore spaces of the aquifer sediment material, a compound present at some concentration, C_{init}, in the injected water will be partitioned between the solid sediment material and the pore water. If a large amount of sorption occurs, then the difference between C_{init} and C_{wat} will be significant.

Combining equations 1–4 and inserting appropriate values for K_{ow}, a, b, ρ, and ε yields an estimate of the minimum organic carbon content required for sorption of THMs to the aquifer sediments to result in a significant, measurable difference between C_{init} and C_{wat}. An organic carbon content of greater than about 0.05 percent would result in enough sorption of THMs to the aquifer sediment to noticeably affect the concentration of THMs in the water.

Hand-sample examination of core samples collected during drilling for installation of the nested piezometers yielded estimated organic material content of much less than 1 percent in the finer-grained layers, and organic material was not observed in the coarser-grained layers (Fram and others, 2002). Sedimentary organic material consists of approximately 60 percent (by mass) organic carbon; thus, the mean organic carbon content of the aquifer materials is estimated to be extremely small. Quantitative analysis of similar sedimentary materials yielded organic carbon content of 0.01 to 0.15 percent (Schwarzenbach and Westall, 1981; Curtis and others, 1986; MacIntyre and Stauffer, 1988). Therefore, sorption was not expected to be a significant process.

If significant sorption had occurred, it would have been apparent in the $(Br/Cl)_{THM}$ values in the extracted water. Because the log K_{ow} values of the THMs vary systematically from 1.97 for $CHCl_3$ to 2.38 for $CHBr_3$ (Mackay and others, 1993), the more brominated THMs are sorbed preferentially to sedimentary materials. Applying equations 1–4 to each of the four THM species yields an estimate of the $(Br/Cl)_{THM}$ value in the injection water after equilibration with the aquifer materials (C_{wat}) that can be compared to the $(Br/Cl)_{THM}$ value in the injection water prior to interaction with the aquifer (C_{init}). C_{init} is represented by the injection water samples from the storage experiments and C_{wat} by the water extracted at the beginning of the extraction period. Samples of injection water with the least admixed ground water are most likely to be extracted at the beginning of the extraction period. For an organic carbon content of 0.05 percent, equations 1–4 predict that the $(Br/Cl)_{THM}$ values for the extraction water at the beginning of the extraction period (that is, injection water equilibrated with aquifer materials) would be 30 percent lower than the $(Br/Cl)_{THM}$ values for the water from the storage experiment (that is, injection water that has not interacted with aquifer materials). However, the $(Br/Cl)_{THM}$ values for the injection water from the storage experiment and for the extracted water at the beginning of the extraction period are approximately equal (fig. 5*I*). This analysis suggests that sorption of THMs to aquifer materials did not occur to a significant, measurable extent during the third injection, storage, and recovery cycle.

Mixing

Once significant biodegradation and sorption effects have been ruled out, $(Br/Cl)_{THM}$ can be used as an indicator of the relative concentrations of bromide and DOC in the water in which the THMs formed. For a constant DOC concentration, $(Br/Cl)_{THM}$ increases as the initial dissolved bromide concentration increases (for example, Amy and others, 1985; Symons and others, 1993), and for a constant bromide concentration, $(Br/Cl)_{THM}$ should increase as the DOC concentration decreases. Therefore, $(Br/Cl)_{THM}$ should increase as the ratio of bromide to DOC concentrations increases. Using the amount of bromine incorporated into the THMs in the THMFP experiment (0.013 mg/L) as a minimum estimate of the initial concentration of bromide in the water, the estimated bromide to DOC concentration ratio in the ground water (greater than or equal to 0.065 milligram of bromide per milligram of DOC) is approximately 10 times greater than the ratio for the injection water (greater than or equal to 0.006 milligram of bromide per milligram of DOC). Thus, THMs formed in mixtures of ground water and injected water would have higher $(Br/Cl)_{THM}$ values than THMs formed in pure injection water. Mixing between ground water and injection water after THM formation would produce a pattern of decreasing THM concentrations and constant $(Br/Cl)_{THM}$ values in the

extracted water as extraction proceeded. Mixing between ground water and injection water before THM formation is complete would produce a pattern of decreasing THM concentrations and increasing $(Br/Cl)_{THM}$ values in the extracted water as extraction proceeded.

The observed decrease in THM concentrations in the extracted water during the extraction period (fig. 5*A*) is consistent with mixing between injection water containing THMs and THM-free ground water. The increase in $(Br/Cl)_{THM}$ values in the extracted water during the first phase of extraction (fig. 5*I*) further implies that some of the mixing happened before THM formation was complete. The relatively constant $(Br/Cl)_{THM}$ values in the extracted water during the second phase of extraction (fig. 5*I*) suggests that the mixing that produced these water samples occurred primarily after THM formation was complete.

Mass Balance of Chloride, Dissolved Organic Carbon, and Trihalomethanes

The preceeding discussion identified dilution from mixing as the dominant process controlling the progressive decrease in THM concentrations in the water extracted from well 4-32 during the third injection, storage, and recovery cycle. In this section, mass balance calculations are used to estimate the proportions of injected water and ground water in the extracted water and the percentage of THMs injected into the aquifer that was retrieved.

The amount of injected water that was extracted was determined using three constituents present in the injection water: chloride, DOC, and THM. The mass balances for chloride and DOC were determined for only one point in the extraction cycle—at the end of the first phase of extraction from well 4-32 (October 24, 1998). At this point, the total volume of water extracted from well 4-32 was 132 percent of the total volume of water injected (fig. 3*B*).

Mass Balance Calculations

Mass balances were calculated using estimates for the concentrations of the constituents in the average injected water and average ground water (the injection water and ground water end-members, respectively) and for the measured concentrations of the constituents in the extracted water. The concentrations of chloride, DOC, and THMs in the injection water and ground water end-members are listed in table 4.

Table 4. Average concentrations of constituents in injected water and ground water used in mass-balance, tracer mixing model, and descriptive mixing model calculations

[DOC, dissolved organic carbon; THM, trihalomethane; SF_6, sulfur hexafluoride. mg/L, milligram per liter; µg/L, microgram per liter; µmol/L, micromole per liter; pmol/L, picomole per liter]

Constituent	Injected water concentration (C_{inj})	Ground water concentration (C_{gw})
Chloride	7.5 mg/L[1]	21 mg/L[3]
DOC	1.76 mg/L[1]	.2 mg/L[4]
THMs	58 µg/L[2]	0 µg/L[5]
THMs	.48 µmol/L[2]	0 µmol/L[5]
SF_6	63.6 pmol/L[1]	0 pmol/L[4]

[1]Based on average concentration in injection water samples
[2]Based on average concentration in selected samples extracted from well 7N/12W-27P2 (4-32) and piezometers 7N/12W-27P6 and 27P7
[3]Selected from range of concentrations measured in ground water
[4]Measured in ground water prior to the third cycle
[5]Concentration assumed to be zero

The mass-balance calculations entailed a comparison of the mass of the constituent injected with the mass of the constituent extracted. M_{inj} is the difference between the mass of the constituent in the injection water and the mass of the constituent in the ground water (fig. 9; equation 5). M_{inj} may be positive or negative depending on whether the concentration of the constituent in the injection water is greater than or less than the concentration in the ground water.

$$M_{inj} = V_{inj}C_{inj} - V_{inj}C_{gw} \quad (5)$$

where

V_{inj} is the total volume of water injected,

C_{inj} is the average concentration of the constituent in the injected water, and

C_{gw} is the average concentration of the constituent in the ground water.

The volumes of water injected and extracted are expressed as *V*, the equivalent volume. The value of *V* is given by equation 6 for the injection period and by equation 7 for the extraction period. *V* increases from –1 to 0 during the injection period and then increases from 0 to a positive number during the extraction period. When *V* equals 1, the volume of water extracted equals the volume of water injected.

$$V = \frac{V_{inj*}}{V_{inj}} - 1 \quad (6)$$

$$V = \frac{V_{ext}}{V_{inj}} \quad (7)$$

where, at the time for which *V* is being calculated,

V_{ext} is the cumulative volume of water extracted, and

V_{inj*} is the cumulative volume of water injected.

M_{ext} is the difference between the mass of the constituent in the extracted and mass of the constituent in the ground water (fig. 9; equation 8). M_{ext} may be positive or negative depending on whether the concentrations of the constituent in the extracted water are greater than or less than the concentration in the ground water.

$$M_{ext} = \int_0^{V_{ext}} C_{ext}(V)dV - V_{ext}C_{gw} \quad (8)$$

where

$C_{ext}(V)$ is the function fit to the extraction data.

The percentage recovery of the injected constituent is the ratio of M_{ext} to M_{inj} (equation 9). The percentage recovery may be less than or greater than 100 percent. Values greater than 100 percent indicate that there was a source of the constituent in the aquifer. Values less than 100 percent indicate that the constituent was not completely recovered. Incomplete recovery may be caused by either destruction of the constituent in the aquifer or dilution of the injected water by mixing with ground water.

$$\text{recovery} = \frac{M_{ext}}{M_{inj}} \times 100 \quad (9)$$

If there are no sources or losses of the constituent in the aquifer and there is no mixing between the injected water and ground water, then the variation in concentration of the constituent in the extracted water can be described by figure 9*A* or *B*. The injected water is completely recovered during the extraction period between $V = 0$ and $V = 1$. If there is no mixing of the injected water with ground water, the concentration of the constituent in the extracted water, $C_{ext}(V)$, is represented by two line segments: $C_{ext}(V)$ equals the concentration in the injected water from $V = 0$ to $V = 1$ during the extraction period and then equals the concentration in the ground water for extraction beyond $V = 1$.

If there is mixing between the injected water and ground water, the variation in concentration of the constituent in the extracted water can be described by figure 9*C* or *D*. The concentration of the constituent in the extracted water varies as a function of *V*. For the mass-balance calculations presented in this report, $C_{ext}(V)$ was determined by using least squares regression to fit a polynomial expression to the data. The polynomial expression can be integrated and evaluated for any point *V* in the extraction period to calculate M_{ext} at that point in the extraction period.

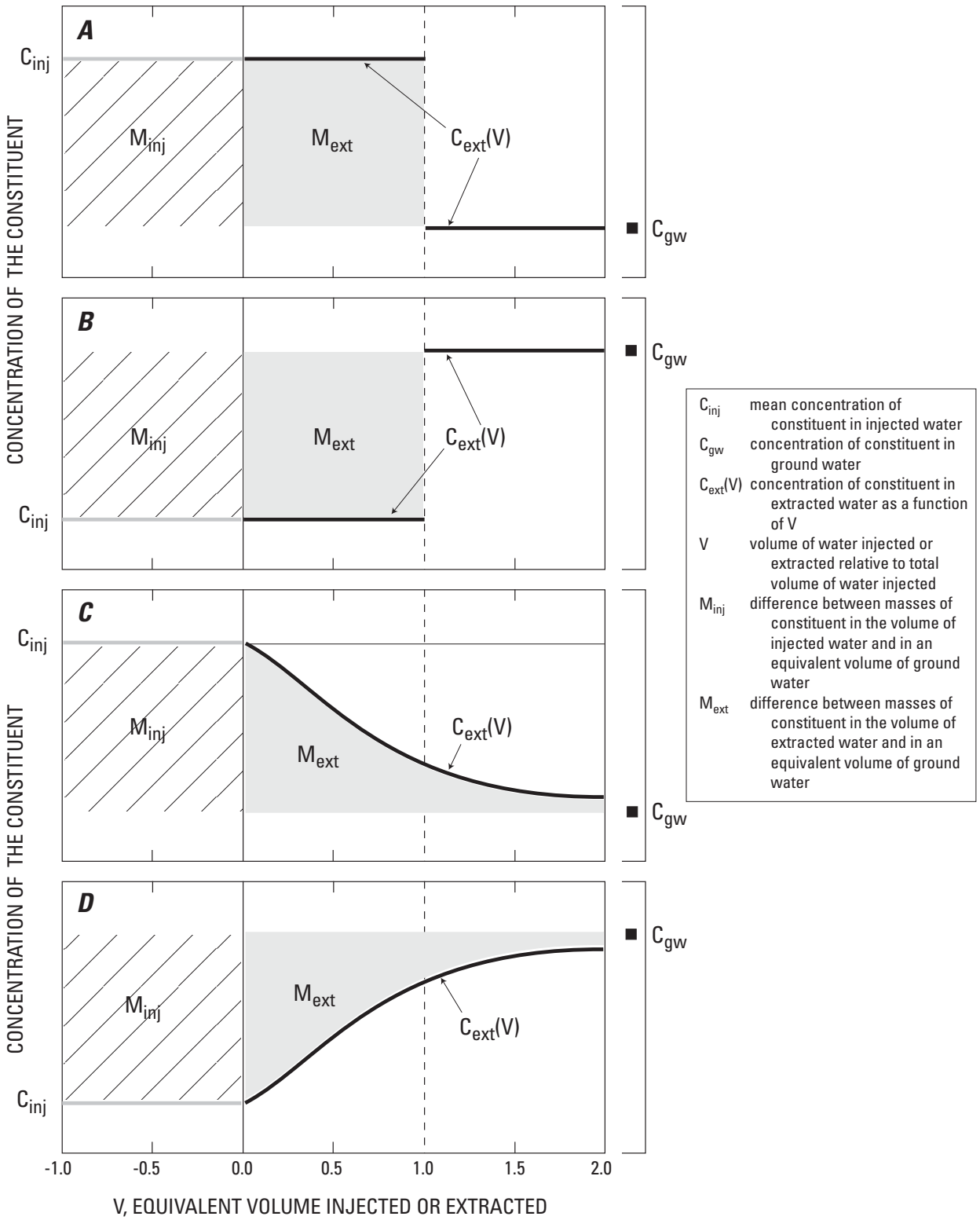

Figure 9. Method for calculating mass balance of a conservative constituent without ***(A,B)*** and with ***(C,D)*** mixing between injected water and ground water.

Mass Balance Results

Chloride

We constructed a chloride mass-balance calculation for the first phase of extraction, $V = 0$ to $V = 1.32$ (June 30, 1998, to October 24, 1998), when the chloride concentrations in water extracted from well 4-32 rose smoothly from 7 to about 20 mg/L (fig. 10*A*). M_{inj} was calculated using equation 5, the estimates of C_{inj} and C_{gw} given in table 4, and $V_{inj} = 1$. $C_{ext}(V)$ was determined by fitting the chloride concentrations in the extraction water for the period $V = 0$ to $V = 1.32$ with a cubic function using the curve-fitting function in SigmaPlot2001(fig. 10*A*). M_{ext} was calculated using equation 8, the estimate of C_{gw} given in table 4, and $V_{ext} = 1.32$. The calculation yielded a 68 percent recovery of injected chloride. Because chloride is a conservative constituent, chloride recovery is a proxy for recovery of the injected water. Therefore, on the basis of chloride concentrations, only 68 percent of the injected water was recovered by the time the volume of water extracted reached 132 percent of the volume of water injected.

The error associated with the mass balance calculation is estimated by considering the uncertainties in the estimates of C_{inj} and C_{gw}. $C_{ext}(V)$ is assumed to have no error. Variation of C_{inj} between 7 and 9 mg/L results in variation in the percentage recovery of chloride between 65 and 76 percent, respectively. Variation of C_{gw} between 20 and 23 mg/L results in variation in the percentage recovery of chloride between 63 and 76 percent, respectively. C_{gw} cannot be less than 20 mg/L because the maximum concentration of chloride in the extraction water during the first phase of extraction was 20 mg/L (figs. 5*F* and 10*A*).

It is noteworthy that after pumping from well 4-32 resumed on February 22, 1999, the chloride concentrations in the extracted water followed a trend substantially different from that of the first part of the recovery phase of the cycle. Chloride concentrations decreased from 15 to 11 mg/L between $V = 1.32$ and $V = 2.50$ (fig. 10*A*), suggesting that the injection water was mixing with different ground water end-members during phases 1 and 2. The ground water end-member during the second phase of extraction apparently contained approximately 11 mg/L of chloride. This apparent shift in the composition of the ground-water end-member may be explained by the heterogeneity of the ground water near well 4-32 before the third cycle, the movement of water in the aquifer caused by pumping at well 4-34 when well 4-32 was idle, and the increased drawdown at well 4-32 during the period when both wells were being pumped.

Dissolved Organic Carbon

DOC concentrations in the water extracted from well 4-32 during the first phase of extraction declined smoothly from 1.70 mg/L at $V = 0$ to 0.27 mg/L at $V = 1.32$. The data were fit with a cubic function (fig. 10*B*) using the curve-fitting algorithm in SigmaPlot2001 to give $C_{ext}(V)$. M_{inj} and M_{ext} were calculated using equations 5 and 8, respectively, the estimates of C_{inj} and C_{gw} given in table 4, $V_{inj} = 1$, and $V_{ext} = 1.32$. These calculations yielded only a 39 percent recovery of injected DOC at $V = 1.32$. Recovery of DOC was lower than that for chloride, indicating that DOC did not behave conservatively in the aquifer. Even if C_{inj} was as high as 2 mg/L (the maximum DOC concentration in the injection water samples), the calculated percentage recovery of DOC would only be 51 percent, which is still significantly less than the recovery of chloride.

The low percentage recovery of DOC suggests that injected DOC degraded in the aquifer. Field and laboratory studies involving introduction of DOC from surface waters into aquifers composed of clastic sediments report substantial degradation of the DOC (Quanrud and others, 1996; Barber and others, 1997). DOC concentrations in samples from the piezometers support the conclusion that injected DOC degraded in the aquifer. The water samples collected from piezometers 27P6 and 27P7 on June 15, 1998, had concentrations of THMs (fig. 5*A*), chloride (fig. 5*F*), and other major ions (Fram and others, 2002) similar to concentrations in samples from well 4-32, but had significantly lower concentrations of DOC (fig. 5*B*). This suggests that DOC in the injected water degraded as the water travelled from well 4-32 to the piezometers. If this degradation occurred rapidly, before all the residual free chlorine in the injected water was exhausted, it may also partially explain why the estimated amount of THMs formed from the injected water after injection into the aquifer (58 μg/L) was less than the amount of THMs formed in the storage experiment (86 μg/L).

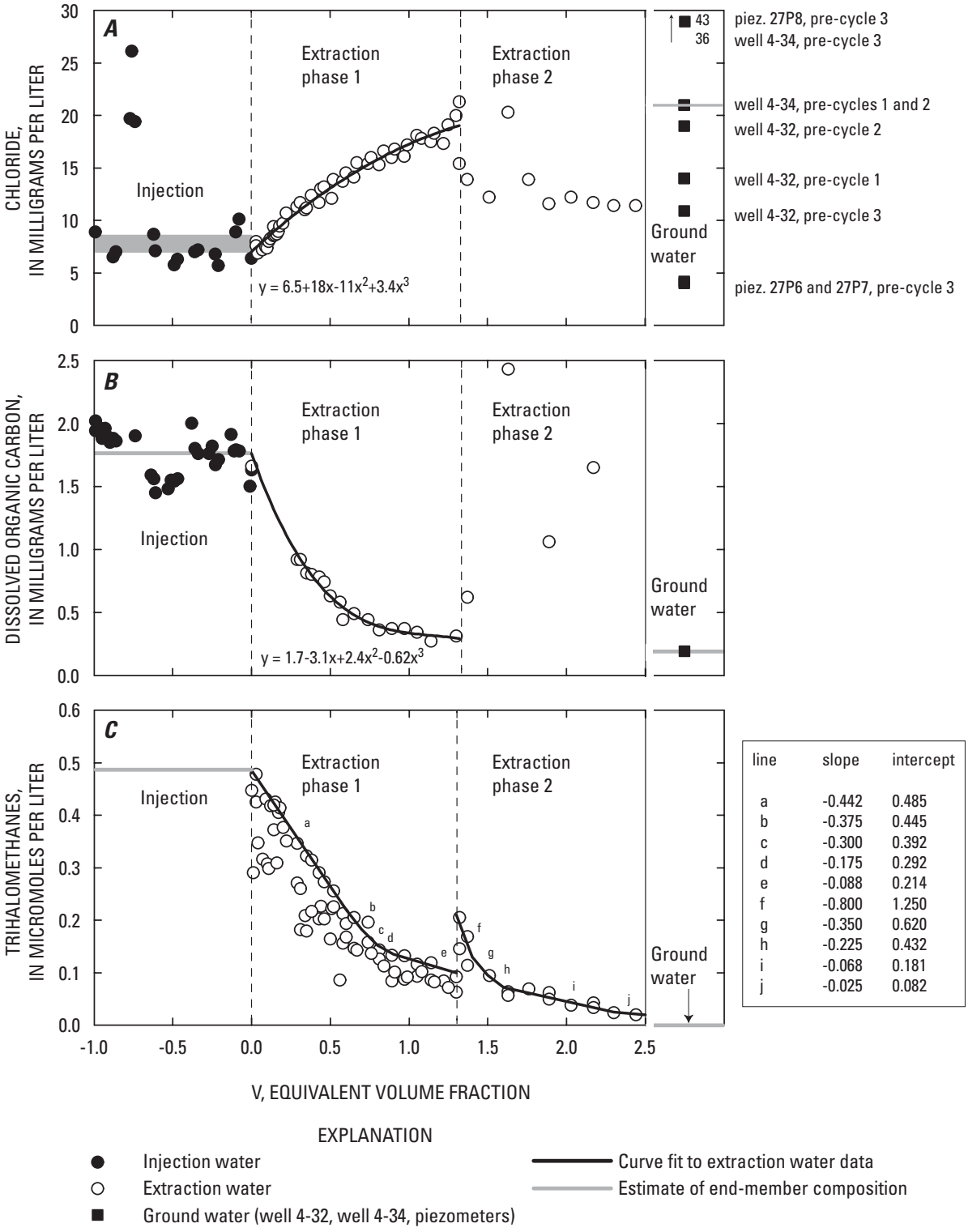

Figure 10. chloride (A), dissolved organic carbon (B) and trihalomethane (C) concentrations in ground-water collected before the first, second, and third cycles (April 1996 through April 1999), and in injection and extraction water collected from well 7N/12W-27P2 (well 4-32) during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

V is the cumulative volume of water extracted (positive numbers) or injected (negative numbers) relative to the total volume of water injected at well 4-32. Equations of the best-fit curves to the concentration data in the first phase of extraction are shown on panels A and B and adjacent to panel C. Data are from Fram and others (2002), Metzger and others (2002) and table 3.

Trihalomethanes

The percentage of the THMs injected into the aquifer that were extracted from well 4-32 was calculated using a method similar to that used for the chloride and DOC mass-balance calculations. The THM concentrations in the extracted water could not be fit adequately using a single mathematical function (as were the data for chloride and DOC for V equaling 0 through 1.32); thus, $C_{ext}(V)$ was determined by fitting the data to a series of 10 linear segments (fig. 10*C*). The 10 segments were fit to the high concentration side of the data to maximize the estimated mass of THMs extracted. THM concentrations are plotted in molar units rather than mass units to eliminate variation owing to the differences in mass of THMs having different $(Br/Cl)_{THM}$ values. M_{inj} was calculated using equation 5, the estimates of C_{inj} and C_{gw} given in table 4, and $V_{inj} = 1$. Values of M_{ext} were calculated at values of V_{ext} ranging from 0 to 2.50 using equation 8, the estimate of C_{gw} given in table 4, and the appropriate set of lines (a through j, fig. 10) for $C_{ext}(V)$. The total number of moles of THM extracted (M_{ext}) and the percentage recovery of THMs (eq 9) are plotted as the solid curve in figure 11. By $V = 1.32$, 70 moles of THMs had been extracted and by $V = 2.50$, 84 moles of THMs had been extracted.

The THM mass-balance calculation indicates that 66 percent of the injected THMs were recovered by $V = 1.32$. The recovery of THMs is similar to that of chloride, a conservative constituent, and higher than that of DOC, a nonconservative one. This suggests that THMs behaved conservatively in the aquifer (after accounting for the THMs formed in the aquifer after injection due to reaction of the residual chlorine in the injected water).

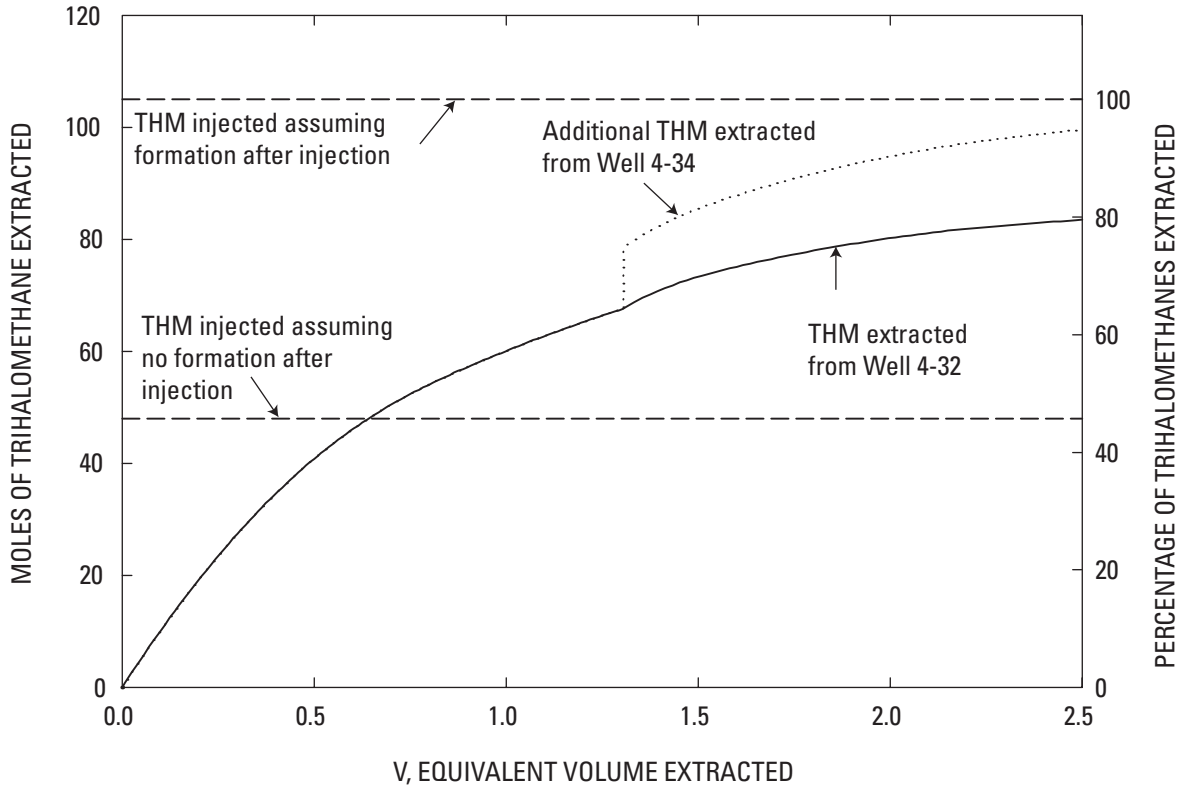

Figure 11. Cumulative moles of trihalomethanes (THM) recovered during the extraction period of the third injection, storage, and recovery cycle (March 1998 through April 1999) Lancaster, Antelope Valley, California.

Note different scales for moles of THMs extracted (left) and percentage of THMs extracted (right).

THM recovery from well 4-32 increased only to 84 moles, or 80 percent of the amount injected, as *V* increased to 2.50 (fig. 11). Extrapolating the trend of THM extraction as a function of the volume of water extracted suggests that extracting 100 percent of the THMs injected would require extraction of a nearly infinite volume of water.

Implications for Water Flow in the Aquifer

The results of the mass-balance calculations and the water-quality and water-level monitoring at well 4-32 and the nested piezometers can be combined to form a conceptual model of the injection, storage, and recovery cycle. The conventional model of injection, storage, and recovery envisions the injected water forming a discrete dome or "balloon" around the injection well (for example, Singer and others, 1993; Pyne, 1995) (model A in fig. 12). Extraction from the well then deflates the balloon, and all of the injected water is recovered. In this model, ground water is only extracted from the well if the volume of water extracted exceeds the volume of water injected or the balloon of injected water is advected away from the well by the regional ground-water flow prior to extraction. Applying the balloon model (model A) to data from injection, storage, and recovery projects can profoundly affect interpretation of the data. For example, in the injection, storage, and recovery projects examined by Singer and others (1993), the known hydraulic gradients in the aquifers were too small to move the balloon of injected water away from the wells prior to extraction. Therefore, Singer and others (1993) concluded that the extracted water must have been injected water with no admixed ground water, and any observed decrease in THM concentrations in the extracted water must have been due to biodegradation.

The conventional conceptual model, the balloon model, does not explain the data collected during the aquifer injection, storage, and recovery tests for this study. Mass-balance results from the third cycle indicated that only 80 percent of the injected water had been recovered by the time the volume of water extracted reached 250 percent of the volume of water injected, implying that a large amount of mixing had occurred between injected water and ground water. Furthermore, the variations in $(Br/Cl)_{THM}$ values suggest that some of the mixing occurred during or shortly after injection while DOC and residual free chlorine in the injected water were still reacting to form THMs. The data collected for this study suggest a new conceptual model for injection, storage, and recovery that is illustrated by model B in figure 12.

Mixing between the injected water and ground water occurs primarily by advective transport and hydrodynamic dispersion. Hydrodynamic dispersion describes the spreading of a solute by mechanical dispersion and molecular diffusion (Bear, 1979). Mechanical dispersion is caused by velocity variations at the microscopic scale, and molecular diffusion is caused by the solute concentration gradient (Bear, 1979). Molecular diffusion is on a much smaller scale than mechanical dispersion and its effect on mixing can be neglected. Dispersion occurs as individual parcels of fluid take different torturous paths through a porous medium. The greater the dispersion, the more the injected water will mix with the native ground water. Streetly (1998) used a numerical model of fluid flow to investigate the effect of dispersion on mixing between injected water and ground water. The numerical model consisted of an aquifer with no hydraulic gradients and no density contrasts between the ground water and injected water, and an equal volume of water was injected and extracted. Recovery of the injected water increased from 45 to 75 percent as the coefficient of dispersion was decreased from 40 to 2.5 meters (Streetly, 1998).

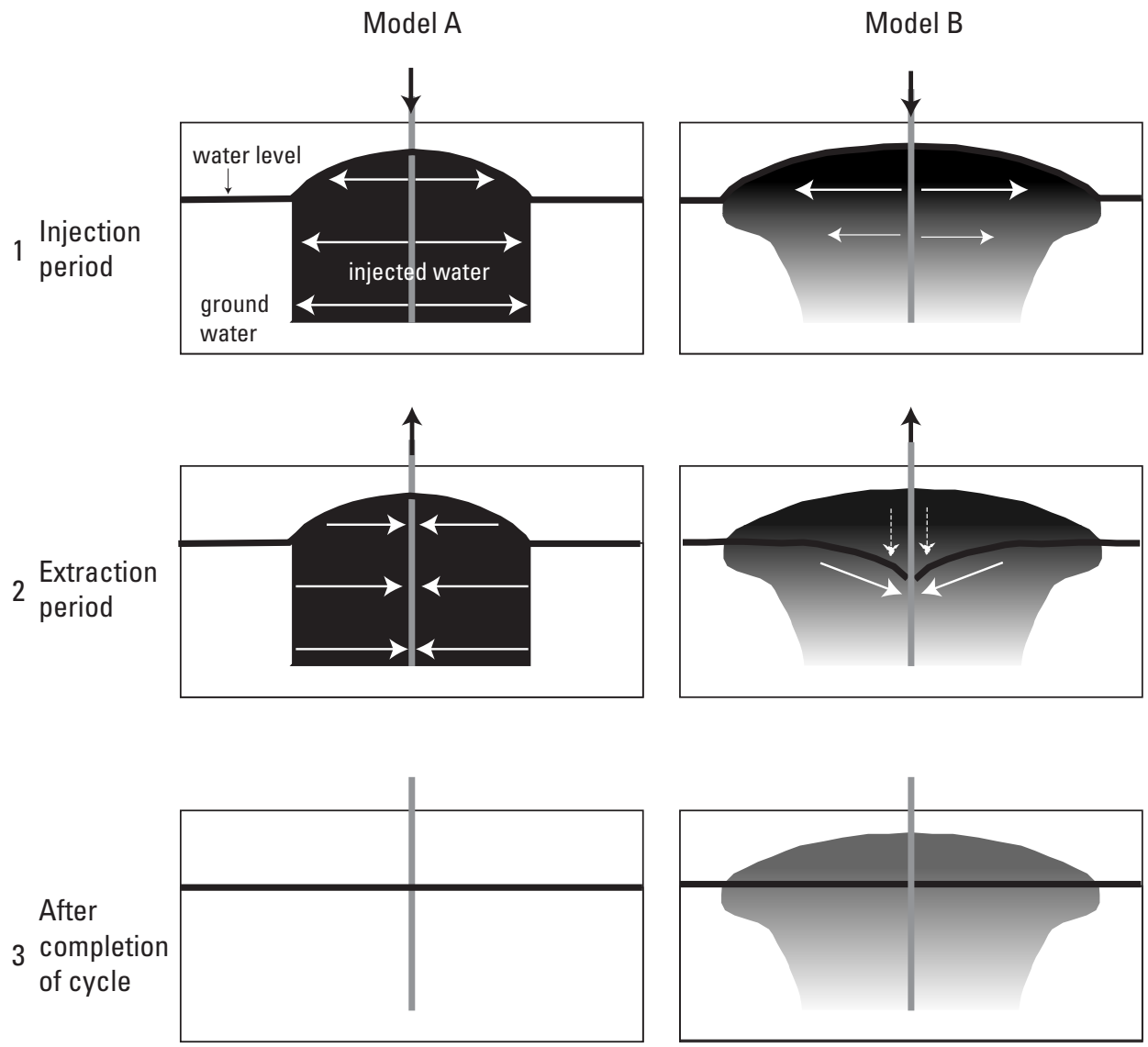

Figure 12. A simple balloon conceptual model ***(A)*** and a more realistic conceptual model ***(B)*** for water flow in the aquifer during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Advective transport also causes mixing of the injected water and ground water at the Lancaster site because the injection and extraction flow paths are not mirror images in a heterogeneous unconfined aquifer. The screened interval in the injection/extraction well used for this study (well 4-32) almost fully penetrated the upper and middle aquifers, extending continuously from 282 to 717 ft below land surface (fig. 2). Cores collected during the installation of the nested piezometers indicate that both of these aquifers consist of sand layers interbedded with layers of small gravel and layers of fine sand and silt (Fram and others, 2002). The simulation/optimization model, developed to evaluate the injection, storage, and recovery tests at Lancaster, required hydraulic conductivity values of 17 and 1.7 ft per day for the upper and middle aquifers, respectively, to simulate the water levels observed during the tests (Phillips and others, in press). Therefore, a higher percentage of the injected water is expected to have entered the upper aquifer because of its significantly higher hydraulic conductivity. This is shown schematically in panel 1 of model B, figure 12.

During the extraction period, aquifer loss and well loss caused by turbulent flow through the well screen and inside the well to the pump intake caused a water-level drawdown in well 4-32 of greater than 70 ft (Phillips and others, in press). This drawdown reduced the effective aquifer thickness of the upper aquifer and thereby likely reduced the percentage of flow from the upper aquifer and likely increased the percentage of flow from the middle aquifer. In addition, the drawdown in the extraction well would effectively strand injected water in the upper part of the upper aquifer because it could no longer flow laterally into the extraction well, and the fine sand and silt layers present in the aquifer would retard its downward movement. The slow downward movement of this stranded injected water into the underlying producing aquifer zone could explain the continued presence of low concentrations of THMs in the extraction water, even after the volume of water extracted reached 250 percent of the volume of water injected.

The change in the composition of water extracted from well 4-32 after the 4-month hiatus in extraction also provides insights into the nature of fluid flow in the aquifer. THM concentrations in the water extracted from well 4-32 were significantly higher at the start of the second phase of extraction than they had been at the end of the first phase (figs. 5*A* and 10*C*) and the chloride concentrations in the extraction water at the end of the second phase of extraction were lower than concentrations in the extracted water sampled at the end of the first phase of extraction (figs. 5*F* and 10*A*). After the pump failed at well 4-32, there was no extraction from the site for about 2 months. This cessation of pumping allowed water-levels to rise (fig. 3*C*), and ground water from the upper aquifer that had relatively high THM and chloride concentrations (sampled by piezometer 27P8 [fig. 5*A*,*F*]) mixed with water in the underlying aquifer zones. When pumping resumed, this water—with its higher THM and chloride concentrations—was extracted quickly, resulting in a pulse of higher THM and chloride concentrations in the extracted water (fig. 5). The continued pumping from both wells 4-32 and 4-34 resulted in the largest water-level declines for piezometer 27P6 observed in the third cycle (fig. 3*C*). Pumping from both wells produced a large drawdown at well 4-32, which effectively eliminated the contribution of water high in THM and chloride concentrations from the upper part of the upper aquifer (this part of the upper aquifer is sampled by piezometer 27P8). Therefore, the chloride concentration in the extraction water at the end of the second phase of extraction reflects mixing between the remaining injected water and the native ground water that has a higher proportion of water from deeper zones that contain relatively low concentrations of chloride (about 4 mg/L in samples from piezometers 27P7 and 27P6 collected prior to the third injection cycle; (fig. 5*F*).

The results of this study indicate that the injection, storage, and recovery cycle at Lancaster cannot be described by a simple balloon model. We propose an alternative conceptual model that includes extensive mixing between injected water and ground water, and heterogeneities in the aquifer system. These heterogeneities, combined with significant drawdown in the extraction well, effectively strand injected water in the upper part of the aquifer system. This stranded injected water will be difficult to remove without modifying the extraction process. One possible modification would be reducing the pumping rate during the extraction period to reduce the drawdown in the extraction well. This would allow more of the injected water in the upper part of the aquifer system to directly enter the extraction well. Another would be installing additional extraction wells screened only in the upper aquifer. Without a modified extraction program, the results of this study indicate that the water quality of the aquifer system will be affected by the water quality of the injected water, even if 250 percent more water is recovered from the aquifer system than is injected into the aquifer system. Even if the extraction program is modified, the extensive mixing between injected water and ground water may make recovery of all injected water difficult.

Conclusions

The results presented in this section of the report support the following conclusions:

1. The amount of continued THM formation in the injection water after injection into the aquifer was limited by the amount of residual chlorine present in the injection water at the time of injection. Reaction between DOC and residual chlorine to produce THMs continued for approximately four weeks after injection. Re-chlorinating injection water after extraction would result in additional THMs. The mean concentration of THMs formed in the injection water, including THMs formed before and after injection into the aquifer, was estimated to be 58 μg/L. Dechlorination of the injection water immediately before injection would reduce the total amount of THMs formed.

2. The changes in the concentrations of dissolved constituents in the extraction water during the extraction period were consistent with changes that would be caused by mixing the injection water with the ground water. The observed increasing $(Br/Cl)_{THM}$ values concomitant with decreasing THM concentrations during the first phase of extraction (June 30, 1998, through October 24, 1998) was inconsistent with predicted changes caused by biodegradation or sorption of THMs in the aquifer, but is consistent with predicted changes caused by mixing between THM-free ground water with a high bromide to DOC concentration ratio and injection water containing THMs and having a low bromide to DOC concentration ratio. At least some of the mixing must have occurred before all the residual chlorine in the injection water was consumed.

3. Mass-balance calculations showed that 67 percent of the chloride and THMs injected into the aquifer were recovered by the time that 132 percent of the volume of water injected had been extracted. Continued extraction of water to 250 percent of the volume injected only increased the percentage recovery of injected THMs to 80 percent.

4. Dilution due to mixing of injection water and ground water was sufficient to explain the decrease of THM concentrations in the extracted water during the extraction period. Once we accounted for THM formation from reaction of the residual chlorine in the injected water, THMs behaved as conservative constituents in the aquifer.

5. The response of the ground-water flow system in the aquifer to injection, storage, and recovery cycles is extremely complex and does not follow a simple balloon model. Extensive mixing of injection water and ground water occurs and the water flow paths during injection and recovery are different; therefore, the injection water will be difficult to remove without modifying the extraction process. Without a modified extraction program, the results of this study indicate that the water quality of the aquifer system will be affected by the water quality of the injected water, even if 250 percent more water is recovered from the aquifer system than is injected into the aquifer system. Even if the extraction program is modified, the extensive mixing between injected water and ground water may make recovery of all injected water difficult

III. MODELING DISSOLVED CONSTITUENTS, TRIHALOMETHANES, AND SULFUR HEXAFLUORIDE TRACER CONCENTRATIONS IN EXTRACTED WATER

By Brian A. Bergamaschi *and* Jordan F. Clark

The goal of the research presented in this section is to understand the decrease in trihalomethane (THM) concentrations in the extracted water: that is, were THM concentrations lower because of THM loss in the aquifer resulting from biodegradation or sorption, or were THM concentrations lower because of dilution by mixing with ground water? Results presented by Thomas and others (2000) suggest a potential for THMs to biodegrade in an oxic aquifer. Other studies report significant adsorption of THMs to soils (Walton and others, 1992) and humic coals and shales (Grathwohl, 1990). Miller and others (1993) and Thomas and others (2000) found that the observed decrease in THM concentrations in extracted water from injection, storage, and recovery cycles at the Las Vegas, Nevada site was primarily due to mixing between the injected water and ground water.

In this section, we further explore whether dilution of the injected water by ground water can explain the observed decrease in THM concentrations in the extraction water. Two independent models were used to estimate THM concentrations in extracted water; both assumed that mixing was the only process that reduced THM concentrations. The first modeling approach used a conservative tracer to predict THM concentrations in extracted water. The second modeling approach was to derive a simple descriptive mixing model to estimate physical processes in the aquifer. If the model-derived THM concentrations accurately represent the observed concentrations, then the assumptions inherent in the models are presumed to be correct, and mixing is presumed to cause the observed decline. If, on the other hand, model-derived concentrations diverge significantly from the observed values, then mixing cannot explain the observed decline, and the assumptions inherent in the models must be inaccurate. This approach relies on the fact that significant loss of THMs in the aquifer owing to adsorption to aquifer sediments or bacterial degradation would cause divergence from model-calculated values.

Sulfur Hexafluoride as a Tracer

A tracer was necessary to model the THM concentrations because without a tracer there was no way to directly measure the relative amount of ground water and injected water in a given sample of extracted water. A tracer can be defined as a measurable substance, naturally present in a system or artificially introduced, that can be used to evaluate biogeochemical and hydrologic processes within that system. In this case, it is important that the tracer is conservative; tracer concentration should not be altered by sorption onto aquifer materials or by bacterial degradation.

Because tracer concentration is not dependent on total mass balance, it is insensitive to changes in pumping rate, a hiatus in pumping, or simultaneous extraction from nearby wells. Thus, it provides an accurate assessment of the contribution of ground water to each individual sample. For a tracer that is not present in the ground water, the fractional contribution of ground water to a sample of extracted water is simply one minus the ratio of the measured concentration of the tracer in a sample to the measured concentration in the injection water.

Some natural tracers have been used to characterize flow and mixing within aquifers; for example, chloride and bromide concentrations in water and the oxygen isotopic composition ($\delta^{18}O$) of the water commonly are used. However, most of these tracers were not deemed reliable for this experiment. Chloride concentrations varied substantially within the aquifer. Bromide reacted with the residual chlorine in the injection water and became incorporated into THMs and other disinfection by-products. $\delta^{18}O$ values for injection water were not sufficiently different from those for the native ground water or the ground water influenced by previous cycles to permit its use to accurately assess mixing.

Sulfur hexafluoride (SF_6) was introduced as a tracer into the injection flow stream (Fram and others, 2002) because no reliable natural tracers existed for this system. Results of the experiment indicated that chloride could be used as a tracer. We chose SF_6 as a tracer because it was important that the introduced tracer not alter the water-quality with respect to its use as drinking water. SF_6 has extremely low toxicity, even at extraordinarily high levels and, therefore, is suitable for use in potable water systems. As an example of its low toxicity, animals breathing 80 percent SF_6 and 20 percent oxygen exhibited no symptoms of distress (Hathaway and others, 1991). The Federal standard allows 6 grams of SF_6 per cubic meter of breathing air. The target concentration in this experiment was 100 picomole per liter (pmol/L), or 15 parts per trillion, in the injection water. The actual concentration in the injection water was estimated to be approximately 63 pmol/L.

From the standpoint of chemistry, SF_6 is an excellent tracer. It is a gas at room temperature, boiling at 20°C. It is slightly soluble in water, but it is readily purged and may be measured at extremely low levels using a gas chromatograph fitted with an electron capture detector. The hexavalent, symmetric character of the molecule causes it to be chemically stable, resistant to biodegradation, and relatively unreactive with mineral surfaces. SF_6 usually does not occur at measurable concentrations in nature. In the environmental sciences, it has been used extensively to characterize flow and gas exchange in surface-water systems (for example, Wannikhof and others, 1987; Clark and others, 1994). In engineering applications, it commonly is used as a leak indicator. More recently, it has been used to investigate infiltration of surface water into a ground-water basin (Gamlin and others, 2001).

The use of a tracer alone, however, does not provide a clear picture of the physical processes in the aquifer. To help understand these processes and to estimate the cumulative effect of repetitive cycles of injection, storage, and recovery, we applied a simple descriptive mixing model, using measured or estimated boundary conditions. In doing so, we were able to analytically estimate the physical dynamics of mixing within the aquifer. Comparing the concentrations predicted by the mixing model with chloride and SF_6 tracer data indicated that reasonable estimates were obtained from the model. By using the model to simulate 10 successive cycles, we were able to asses potential long-term effects of annual subsurface injection, storage, and recovery cycles.

Experimental Methods

The procedures for collecting water samples from well 4-32 and the analytical methods used to measure THM, residual chlorine, and chloride concentrations and pH, temperature, and THM formation potential (THMFP) are described in detail by Fram and others (2002).

The procedures for adding SF_6 to the injection water and collecting water samples for SF_6 analysis, and the analytical method used to measure SF_6 concentrations also are described in detail by Fram and others (2002) and are summarized briefly here. SF_6 was added to the injection water flow stream by bubbling a calibrated gas mixture of 100 parts per million SF_6 in nitrogen through a gas diffuser in the center of the flow stream. The gas flow rate was controlled at 70 milliliters per minute to achieve a target concentration in the injection water of 100 pmol/L. Due to fluctuations in operational conditions, the actual concentration was less than the target concentration. Water samples were collected from a sampling port on well 4-32 and put directly into 100-milliliter (mL) gas tight syringes that had secure luer port valves. Each water sample was equilibrated with 20 mL of ultrapure nitrogen gas that was added to the syringe, and then the headspace gas was drawn into a 20-mL evacuated container. The gas was analyzed by a gas chromatograph fitted with an electron capture detector (Wannikhof and others, 1987; Clark and others, 1994); the detection limit of the method was 0.04 pmol/L.

Tracer Results

The goal of the tracer portion of this experiment was to provide an independent method of estimating the amount of injected water in a sample at any given time during extraction. We used two independent modeling approaches to derive the amount of extracted water and thus the THM concentration expected if mixing was the dominant reason for changes during extraction. For both models, we used the injected tracer, SF_6, as well as a natural tracer, chloride. Chloride concentrations varied smoothly during the modeled extraction period, suggesting that chloride may be useful as a secondary tracer. Chloride is conservative in ground water systems and is not subject to sampling and analytical artifacts that are common to volatile constituents such as SF_6 and THMs. To derive the concentration values expected during extraction, both modeling approaches used a mean injection water concentration for THMs, chloride, and SF_6.

Estimations of the mean concentrations of THMs and chloride in injection water have been presented previously (table 4), but a concentration was needed for SF_6.

The target concentration for SF_6 in the injection water was 100 pmol/L. However, measurements of SF_6 concentrations during the injection period showed a large amount of variability, and the concentrations were almost universally below this value (fig. 13). Measured values for SF_6 concentrations ranged from 23 to 105 pmol/L (RSD = 43 percent); the median was 40 pmol/L (fig. 13). In addition to the high variability between samples, replicate samples also had a much greater variability than expected. The average RSD for the 22 replicate samples analyzed was 19 percent. Analytical replicates typically are reproducible to within less than 2 percent of the measured value (Clark and others, 1994).

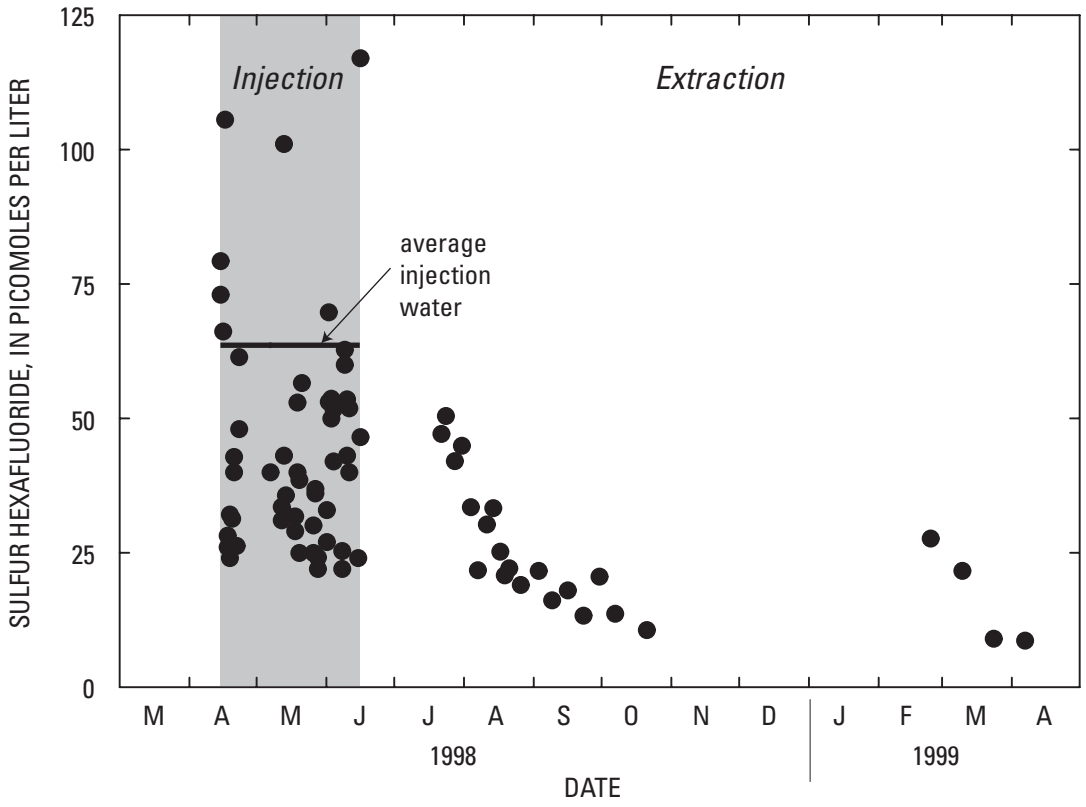

Figure 13. Sulfur hexafluoride (SF_6) concentrations in injection and extraction water collected from well 7N/12W-27P2 (well 4-32) during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Data are from Fram and others (2002).

The high replicate variability provided clues to the reasons for erratic values during injection and led us to discard many values in determining the mean concentration. Variations in SF_6 concentration may be the result of (1) a large variability in pumping rate, (2) poor equilibration of SF_6 during the transit between the diffuser and the sampling point, (3) bubble formation in the injection line, or (4) losses during sampling. Because the pumping rate was monitored continuously (fig. 3), it could be eliminated as a possible confounding factor. All remaining scenarios would result in measured SF_6 concentrations lower than actual injected concentrations. Anecdotal observations suggest that all scenarios contributed to the observed high variability (Fram and others, 2002). We chose the mean of the upper 50 percent of the measurements to represent the injected SF_6 concentrations because it provided a statistically robust estimate of the mean injection water concentration, but without skewing the mean by incorporating anomalously low values. The mean SF_6 concentration in the injection water thus obtained was 63.6 pmol/L (RSD = 29 percent) (fig. 13).

The variations in injected SF_6 and THM concentrations during the extraction period provide a good indicator of important processes occurring in the aquifer. Following completion of the injection period, well 4-32 remained idle for 2 weeks before the extraction period began (fig. 3*A*). Once extraction began, the THM and SF_6 concentrations in extraction water samples (figs. 5*A* and 13) declined roughly exponentially during the first stage of extraction (June 30 to October 24, 1998), as may be expected from a process controlled by mixing (Berner, 1980). Samples collected 24 days after the onset of extraction, when 31 percent of the injection water volume had been extracted, contained SF_6 concentrations of 50 pmol/L (fig. 13), corresponding to 78 percent of the concentration in the injection water. Near the time that the extracted water volume equaled the injected water volume, samples collected contained SF_6 concentrations of 14 pmol/L, corresponding to 22 percent of the concentration in the injection water. SF_6 concentrations declined until pump failure on well 4-32 on October 24, 1998, caused a hiatus in extraction. A few days prior to pump failure, on October 21, 1998, extraction water samples contained 11 pmol/L of SF_6 (fig. 13), corresponding to 17 percent of the concentration in the injection water.

SF_6 concentrations increased during the pumping hiatus at well 4-32, suggesting a higher fraction of injection water migrated into the high-velocity zone of the aquifer during this time (see the second section of this report for further discussion). The SF_6 concentration again declined following resumption of extraction. Even 10 months after extraction began and after extracting 250 percent of the volume of water that was injected (as well as a similar volume from nearby well 4-34) (fig. 3), SF_6 concentrations declined to only 9 pmol/L (fig. 13), corresponding to 14 percent of the concentration in the injection water.

Modeling

The initial hypothesis was that systematic decrease in the THM concentrations in the extraction water during the extraction period was not significantly different from the decrease expected from mixing between injection water and ground water in the aquifer. To test this hypothesis, the tracer model and the descriptive mixing model explicitly assume that mixing is the only process that reduced THM concentrations in the extraction water. The modeling was simplified by assuming that variability in many of the parameters did not strongly affect the results. In particular, we assumed that the concentrations of constituents in the injection water and the ground water were adequately represented by mean concentrations.

Tracer Mixing Model

If THMs behave conservatively and the only process affecting their concentration is mixing, the THM concentration in any sample of extracted water can be predicted using the tracer mixing model. A significant difference between the predicted THM concentrations in the extracted water and the measured concentrations would indicate that processes other than mixing must have affected the THM concentrations. The tracer mixing model only requires data for the concentrations of the tracer and of the constituents of interest in the ground water, the injected water, and the extracted water. No data for water volumes and no assumptions concerning the physical scenario in which mixing occurs are needed. The tracer is assumed to be perfectly conservative, and samples of extracted water are assumed to be simple mixtures of injected water

and ground water. The predicted concentration of a conservative constituent in any sample of extracted water, C_t, is calculated from the known concentrations of the tracer and the constituent in the ground water and injected water and the measured concentration of the tracer in the sample of extracted water (equations 10 and 11):

$$C_t = f_t C_0 + (1 - f_t) C_{gw} \quad (10)$$

where

$$f_t = \frac{C_t^{tracer} - C_{gw}^{tracer}}{C_0^{tracer} - C_{gw}^{tracer}} \quad (11)$$

and where

C_t is the concentration of the constituent in the extraction water at any time t.

f_t is the fraction of injected water in the water extracted at any time t,

C_0 is the concentration of the constituent in the injection water,

C_{gw} is the concentration of the constituent in the ground water, and

C_t^{tracer} is the concentration of the tracer in the extraction water at any time t,

C_0^{tracer} is the concentration of the tracer in the injection water,

C_{gw}^{tracer} is the concentration of the tracer in the ground water,

The tracers SF_6 and chloride were used in the tracer mixing model to predict concentrations of THMs in the extraction water samples. There was good correspondence between the THM concentrations predicted using SF_6 or chloride as the tracer (fig. 14) and the concentrations measured in the extracted water during the first phase of extraction before the pump failed on October 24, 1998. These results indicate that THMs behaved as a conservative constituent; no systematic deviation was observed between the model-predicted and the measured THM concentrations as would have been expected if significant biodegradation or sorption of THMs had occurred. Thus, the results of the tracer mixing model suggest that mixing between injected water and ground water was the primary mechanism controlling the concentration of THMs in the extracted water.

The THM concentrations predicted using SF_6 as the tracer also correspond well to the THM concentrations measured in the extracted water during the second phase of extraction, after resumption of pumping at well 4-32 on February 22, 1999 (fig. 14*A*). However, the THM concentrations predicted using chloride as the tracer do not match the measured THM concentrations during this period (fig. 14*B*). The failure of the chloride tracer during the second phase of the extraction period likely reflects a change in the composition of the ground water near well 4-32 caused by pumping from nearby well 4-34 (see the second section of this report for more discussion).

Another way of looking at the tracer data is to examine the relation between the SF_6 tracer concentrations and the THM concentrations in the extraction water samples (fig. 15). Linear regression of these two constituents yielded a slope of 0.72 µg THM per pmol SF_6 and an r^2 value of 0.55, indicating that they are correlated —as would be expected if they had been diluted simultaneously by mixing with ground water containing no SF_6 or THMs. The slope approximates the average expected concentration ratio of 0.91 THM:SF_6 (fig. 15), the initial THM concentration in the injected water in the aquifer (58 mg/L) divided by the SF_6 concentration in the injected water (63.6 pmol/L), supporting the conclusion that THM concentrations and SF_6 tracer concentrations in extraction water samples were controlled by the same process. The same calculation was not done for chloride because chloride does not trace mixing over the entire extraction period.

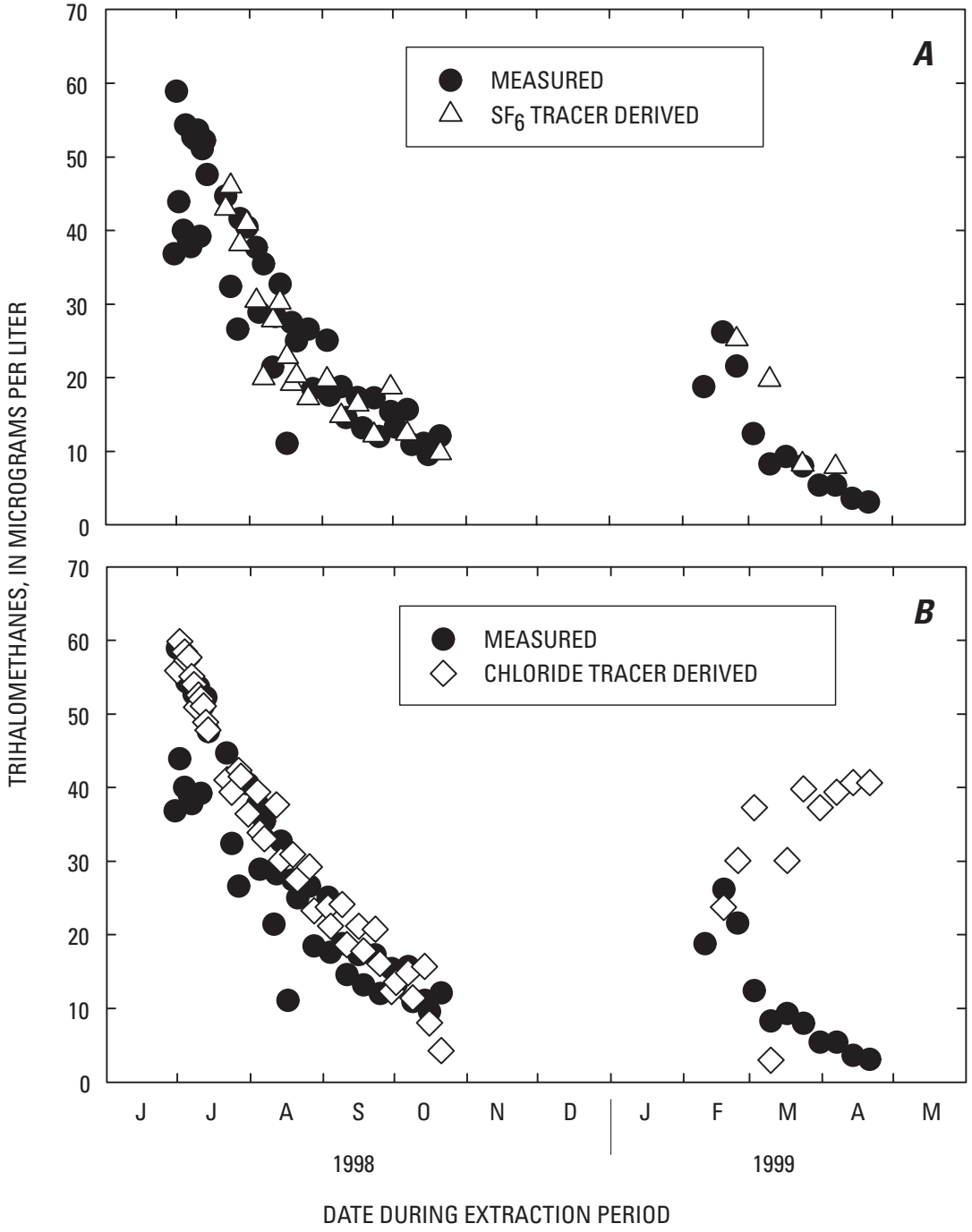

Figure 14. Measured and sulfur hexafluoride (SF_6) tracer-derived ***(A)*** and chloride tracer-derived ***(B)*** trihalomethane concentrations in extraction water collected from well 7N/12W-27P2 (well 4-32) during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Descriptive Mixing Model

A simple model was used to evaluate if mixing of native ground water with the injection water could explain the observed THM concentrations in the extraction water. The model selected is a single-zone mixing model commonly used to assess the exponential decrease in concentration of conservative constituents associated with dilution and mixing (for example, Berner, 1980). The correspondence between the model and the physical environment may be conceptualized by assuming that water injected into the aquifer displaces the ground water surrounding the injection well and that upon extraction, the injected water mixes homogeneously with the displaced water within the mixing zone (fig. 16). Thus, the volume of the mixing zone (V) is defined in the model to equal the volume of injected water, and constituents dissolved in the water within this mixing zone are assumed to be homogeneously distributed by mixing. Thus, the concentration of dissolved constituents in extracted water at any time (t) during the extraction period is assumed to equal the concentration of the constituents in the mixing zone at that time (C_t). The concentrations of constituents in the ground water entering the mixing zone from the surrounding aquifer (C_{gw}) are assumed to equal the concentrations measured in samples from the well collected prior to the injection period and invariant with time. To maintain mass-balance, the volume of ground water entering the mixing zone from the surrounding aquifer per unit time is set equal to the volume of water extracted from the well (Q).

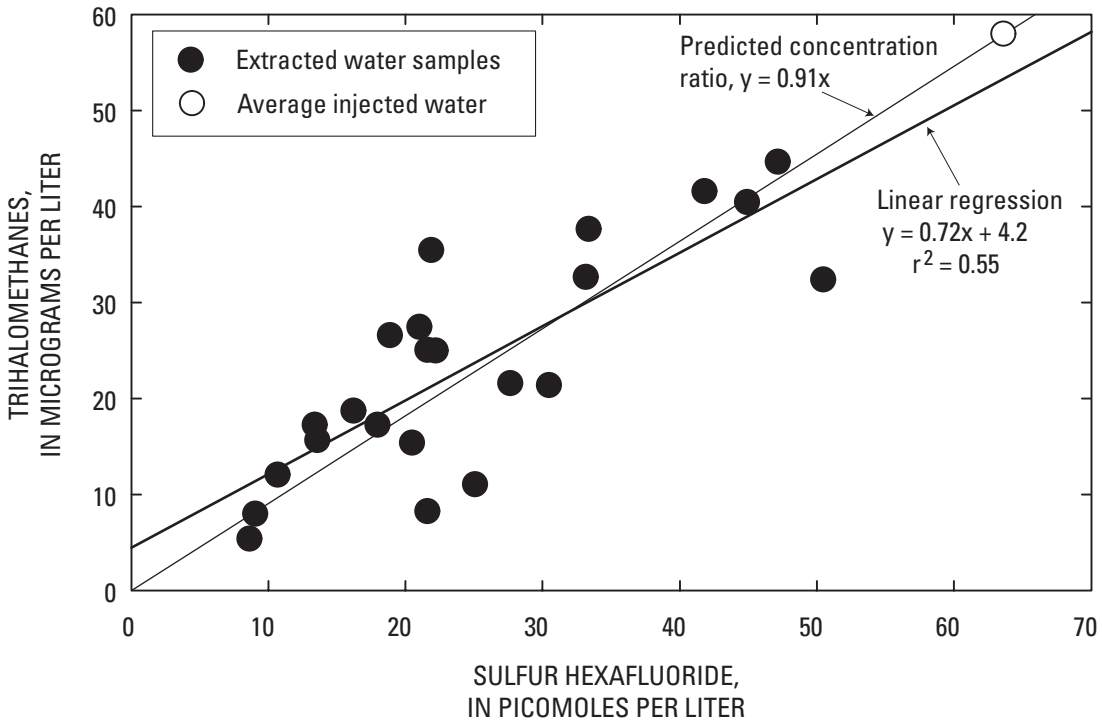

Figure 15. Trihalomethane and sulfur hexafluoride concentrations in extraction water collected from well 7N/12W-27P2 (well 4-32) during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

The concentration ratio predicted from the average injected water composition and the linear regression of the concentration data are shown as solid lines.

Note that this model is not intended to represent the actual physical mixing processes within the aquifer. Undoubtedly physical mixing occurs both during injection and extraction, and the mixing process is not simply the mixing of water from two sources. Evidence of inhomogeneous distribution of ground water and injection water surrounding the injection well is obtained from microgravity surveys, velocity log data, and water-quality data (Fram and others, 2002; Metzger and others, 2002; Phillips and others, in press). Nevertheless, this model is a useful heuristic tool to assess the effects of mixing during this injection, storage, and recovery cycle as well as other operational scenarios.

The change in mass (M) of any conservative constituent in the mixing zone over time (t) is given by the following equation:

$$\frac{dM}{dt} = Q_{gw}C_{\mathrm{gw}} - Q_{ext}C_t \qquad (12)$$

where

M is the mass of a conservative constituent in the mixing zone,

t is any time.

Q_{gw} is the volume of water that enters the mixing zone per unit time from ground water,

C_{gw} is the concentration of the constituent in the ground water and the concentration of the constituent in the mixing zone,

Q_{ext} is the volume of water extracted from the mixing zone per unit time by pumping, and

C_t is the time dependent concentration of the constituent in the mixing zone (C_t is the same as the concentration in the water extracted by pumping).

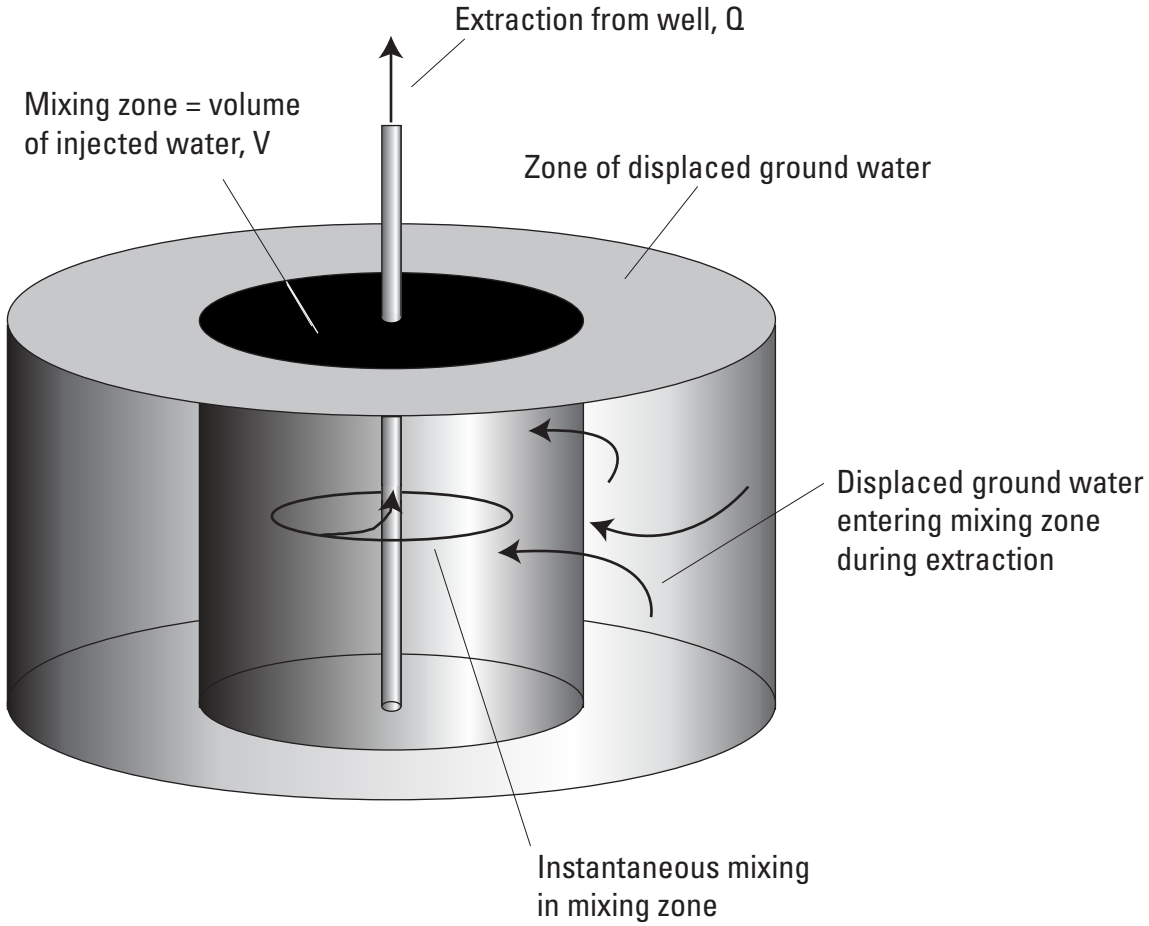

Figure 16. Diagram of the descriptive mixing model for mixing between injection water and ground water during extraction.

To obtain information about concentration, the mass (M) of a constituent in the mixing zone can be separated into the volume of the mixing zone (V), which does not vary over time, and the concentration of the constituent in the mixing zone (C_t), which does:

$$V\frac{dC_t}{dt} = Q(C_{gw} - C_t) \quad (13)$$

where

Q is equal to Q_{ext}, which equals Q_{gw} because the model is constrained to maintain mass balance of water in the mixing zone

Solving the equation for C_t, then integrating over the extraction time gives a continuous function of concentration during the extraction period:

$$C_t = C_{gw} + \beta e^{-(Q/V)t} \quad (14)$$

where

β is the integration constant.

The value of β may be obtained by solving the expression at the initial condition of the model:

$$\beta = C_{t=0} - C_{gw} \quad (15)$$

where

$C_{t=0}$ is the concentration of the constituent in the extracted water at the beginning of the extraction period.

For conservative constituents, $C_{t=0}$ equals the concentration of the constituent in the injection water (C_{inj}). The single-zone mixing model was used to estimate the changes in concentration of SF_6, chloride, and THMs due to mixing during the extraction period for the third injection, storage, and recovery cycle. Calculating C_t using equations 14 and 15 requires values for C_{inj} and C_{gw}. Values of C_{inj} and C_{gw} for SF_6, THMs, and chloride are given in table 4.

The form of the solution (equation 14) shows that the model-derived change in concentration of a conservative constituent is an exponential function in time, but has a linear dependence on the concentration of the constituent in both injection and ground water. According to the initial assumptions, the exponential argument is a function of Q, the extraction rate, and V, the total volume of water injected. Model-derived concentrations of SF_6, chloride and THMs for Q/V values of 0.010 and 0.024 per day bracket the majority of the concentrations measured in extraction water samples (fig. 17*A–C*). The average pumping rate over the modeled period (June 30 to October 24, 1998) was 670,000 gallons per day (fig. 3*A*), and the total volume of water injected was 58 million gallons (fig. 3*B*), which corresponds to a Q/V of 0.012 per day. Using a value of 0.012 per day for Q/V in the model yields computed concentrations that are greater than the measured SF_6 and THM concentrations and are less than the measured chloride concentrations (fig. 17*A–C*). Since the initial concentrations of SF_6, chloride, and THMs, and the pumping rate are known, the divergence between the model-derived concentrations and the observed concentrations may indicate that one of the initial assumptions was inaccurate, namely, the assumption that the mixing zone was equal to the total volume of water injected. A Q/V of 0.014 per day yielded the smallest difference between the measured SF_6 and chloride concentrations and the model-derived concentrations. The difference was quantified using the sum of the squares of the differences between the measured and calculated values. A Q/V of 0.014 per day corresponds to a mixing zone volume of 48 million gallons, about 10 million gallons less than the volume actually injected. Recall that results from this study suggest that drawdown in the extraction well effectively isolated injected water in the shallow part of the aquifer system (see section "Implications for Water Flow in the Aquifer" in the second section of this report), preventing it from mixing. The modeled THM concentrations using a Q/V of 0.014 per day reasonably matched the measured THM concentrations.

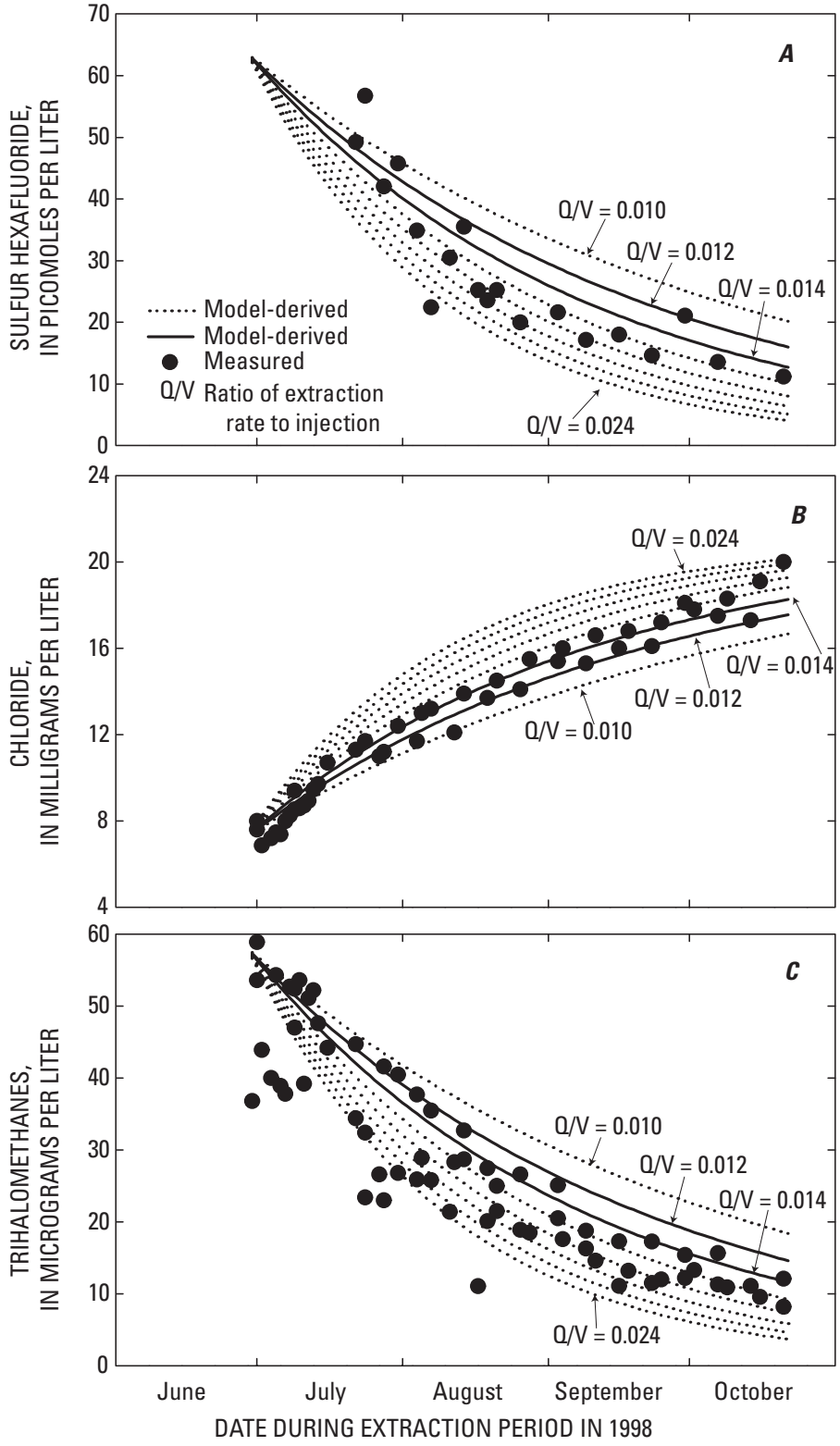

Figure 17. Measured and model-derived sulfur hexafluoride concentrations ***(A)***, chloride concentrations ***(B)***, and trihalomethane concentrations ***(C)*** in extraction water collected from well 7N/12W-27P2 (well 4-32) during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Based on the good correspondence between the rate of change in the concentrations of THMs, SF_6, and chloride and the rate predicted by the model using realistic estimates of the concentrations in the injected water and ground water, we concluded that the simple mixing of the injected water with ground water can explain the observed time-dependent variations in SF_6, chloride, and THM concentrations in the extraction water during the third injection, storage, and recovery cycle. In addition, comparing model results with concentrations measured in extraction water samples suggests that not all of the water injected during a cycle is easily extracted during that cycle. Finally, the good correspondence between the measured concentrations and the model-derived values indicates that using a Q/V of 0.014 in the model reasonably reproduced concentration variations over this cycle and could be used to predict the effects of repetitive injection, storage, and recovery cycles. This value was used for all subsequent model calculations.

Potential Implications of Mixing for Repetitive Cycles of Injection, Storage, and Recovery

The concordant results from the two independent tracers as well as the THMs indicated that the simplified mixing model was sufficiently accurate as a descriptive tool to use it for estimating mixing processes within the aquifer during successive cycles of injection and extraction and during different scenarios of volumes of water injected and extracted. Using the model to test scenarios and forecast the results of successive cycles assumes that the simple descriptive modeling approach will continue to provide a reasonable estimate of the complex physical processes occurring in the aquifer and that advection does not affect the concentration of conservative constituents in the ground water by moving "new" ground water into the mixing zone.

The first scenario tested was ten annual repetitions of a cycle like the one at well 4-32 described in this report—2 months of injection followed by 6 months of extraction. The ratio of the rate of extraction to the total volume of water injected *(Q/V)* was held at 0.014 per day during all ten cycles. At the onset of each cycle, the concentration of THMs (or of any conservative constituent) in the mixing zone was set to equal 100 percent of the concentration in the injection water, and the concentration in the zone of displaced ground water was set to equal the concentration in the water in the mixing zone at the end of the previous cycle (the residual concentration in the aquifer). The model was run for 10 annual cycles of injection and extraction to assess whether constituents from the injection water accumulate in the aquifer.

Constituents from the injection water accumulated in the mixing zone (fig. 18*A*) during the ten cycles. The rate of decline of the concentration in the mixing zone decreased in each subsequent cycle, resulting in an increase in the concentration in the mixing zone at the end of each subsequent cycle (the residual concentration). This residual concentration was 57 percent of the injected water concentration after 10 years (fig. 18*A*). Note that this model scenario was based on pumping 2.5 times more water from the aquifer than was injected every year for ten years. So in essence, this scenario represents a best-case scenario for preventing build-up of injected conservative constituents in the aquifer. As can be demonstrated by modeling more realistic injection, storage, and recovery operations, if the volume of water extracted is closer to the volume injected, then the residual concentration after each cycle will be higher.

Subsequent tests used a more realistic operational scenario wherein the injection and extraction periods were each six months, and the volume of water injected was equal to the volume of water extracted. This cycle was repeated to assess the cumulative effect of ten annual cycles (fig. 18*B*). The residual concentrations in the water in the aquifer at the end of each cycle were much higher in this scenario than those in the original scenario, and the rate of increase of the residual concentrations during the first five annual cycles was also much greater (fig. 18*A*,*B*). The residual concentration in the water in the aquifer was indistinguishable from the concentration in the injection water after 10 annual cycles.

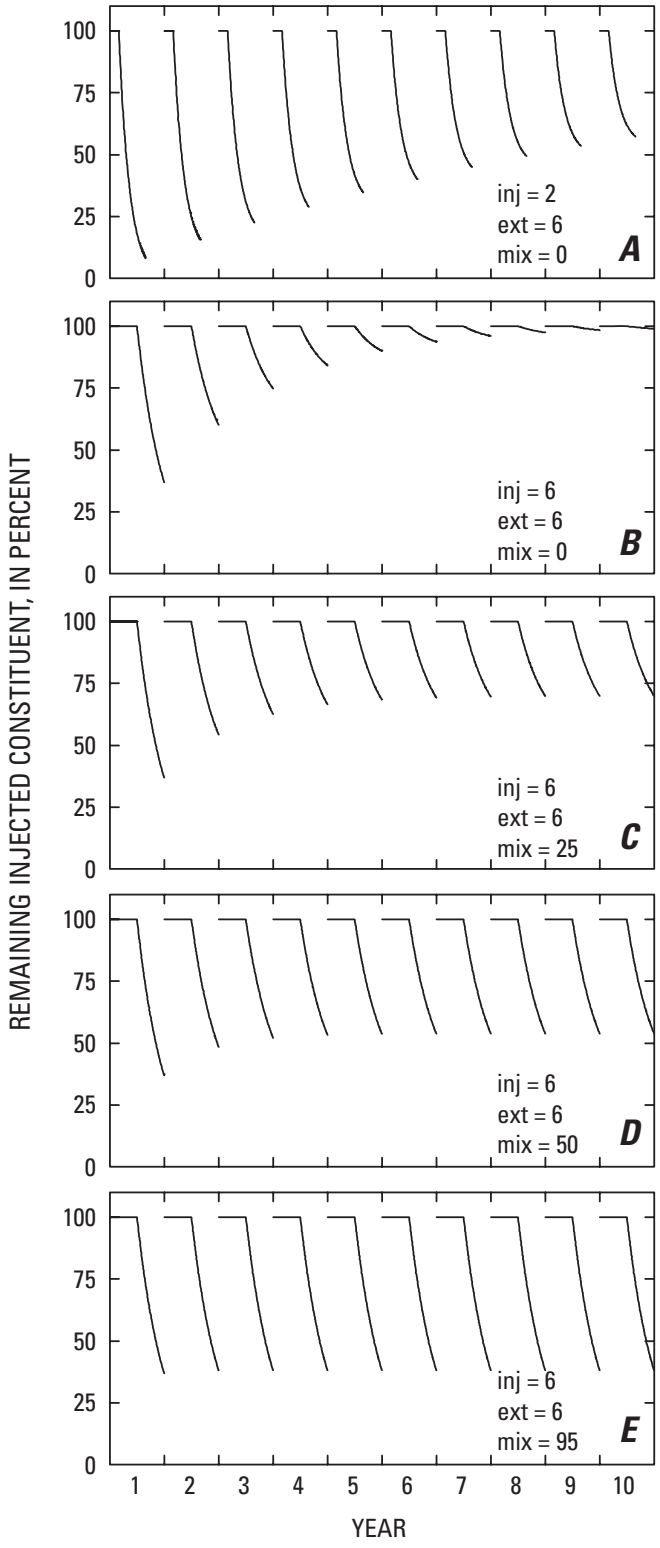

Figure 18. Predicted concentrations of a conservative injected constituents in an aquifer during 10 annual cycles of injection, storage, and recovery for two different injection period durations ***(A,B)*** and four different amounts of mixing between cycles ***(B,C,D,E)***.

Inj (injection) and ext (extraction) are the durations of the injection and extraction periods in months, and mix is the percentage of mixing between cycles.

However, the model assumes no mixing between the model boundary and surrounding, constituent-free ground water, such as may occur in the aquifer. Mixing across the model boundary between the zone of displaced ground water and surrounding, constituent-free ground water would result in greater dispersion, but slower increase in residual concentration. To simulate possible outcomes of such mixing, the descriptive mixing model was revised to instantaneously lower the residual concentration at the end of each cycle by 25 percent, 50 percent, and 95 percent and to use the modified value as the model input for the ground water concentration in the next cycle (fig. 18*C*,*D*,*E*).

Note that increasing the mixing of the residual ground water lowers the ultimate extent of accumulation but not the rate (fig. 18*C*,*D*,*E*). Also, when 95 percent of the residual THM is lost by dispersion between cycles, the eventual accumulation of THM in the mixed zone is nearly 40 percent of that in the original injected water. Regardless of the mixing of the displaced ground water, these results suggest that THM and other conservative constituents present in injection water will accumulate in the aquifer, and they will accumulate more rapidly as injection times are longer and extraction times are shorter, regardless of the extracted volume. Longer extraction times will result in greater removal.

Removal of this residual concentration at a later time may be difficult because the ratio of injected water to ground water in the extracted water declines asymptotically owing to mixing. Thus, removing the residual concentration would require pumping several times the injected-water volume. Reducing the concentration of a constituent in the water in the mixing zone in the aquifer to 10 percent of its concentration in the injected water would require removal of 2.3 times the volume of water injected, reducing it to 1 percent would require removing 4.6 volumes, and reducing it to 0.1 percent would require removal of 9 volumes. Thus, based on the model results for two scenarios of 10 annual cycles of injection, storage, and recovery, we conclude that there are substantial potential long-term consequences to the injection of conservative constituents into the aquifer.

Conclusions

The results of these modeling efforts support the following conclusions:

1. The measured variation in THM concentrations during the extraction period of the third injection, storage, and recovery cycle may be explained fully by mixing of injected water with ground water, as shown by the tracer mixing and the descriptive mixing models. Extensive mixing with ground water appears to be the cause of the observed decline in THM concentrations during the extraction period.

2. THMs behaved conservatively in the aquifer. THM formation continues in the aquifer due to reaction between residual chlorine and DOC in the injection water at the time of injection. However, there was no evidence that biodegradation or sorption within the aquifer caused a decrease in THM concentrations, nor was there evidence for enhanced formation of THMs in the aquifer.

3. By using a simple descriptive mixing model calibrated to measured data, it was possible to forecast the effects of repeated injection, storage, and recovery cycles. Repeated cycles may increase the residual concentration of THMs (or any conservative constituent with a concentration greater in the injected water than in the ground water) in the aquifer. The extent of this increase was directly related to the ratio of the rate of extraction to the total volume injected *(Q/V)* and to amount of mixing across model boundaries. For realistic ratios of the volume of extracted to injected water, repeated cycles should yield residual concentrations in the aquifer approaching 100 percent of injection-water concentrations by the end of 10 annual cycles if residual concentrations are not lowered by further mixing.

IV. THE POTENTIAL FOR BIODEGRADATION OF TRIHALOMETHANES BY AQUIFER BACTERIA

By Kelly D. Goodwin

The purpose of this part of the study was to determine whether bacterial degradation of THMs can attenuate THM concentrations in the ground water after injecting surface water into the aquifer system. Three types of studies were performed: sediment microcosm experiments, water enrichment microcosm experiments, and measurements of bacterial densities in water samples. The sediment microcosms consisted of aquifer sediment and ground water, and the water enrichment microcosms consisted of ground water or extraction water amended with bacteria and particles concentrated from a larger volume of water. Live and sterilized vials of sediment microcosms and water enrichment microcosms were prepared, and many were amended with nutrients and vitamins. $CHCl_3$ and $CHBr_3$ were added to the vials and the amounts were monitored during an incubation period. Biodegradation of the $CHCl_3$ or $CHBr_3$ by bacteria in the aquifer sediment or in the water samples would be indicated in these experiments by a decrease in the amount of $CHCl_3$ or $CHBr_3$ detected in the live vial relative to the amount in the corresponding sterile vial. Bacterial densities were measured in water samples collected from the wells and the nested piezometers to determine if the population of bacteria in the aquifer was affected by the injection, storage, and recovery cycle. Detailed descriptions of the experimental and analytical methods used are given by Fram and others (2002).

Biodegradation of halogenated organic compounds has been observed in a variety of environments, including anaerobic ground water (McCarty and others, 1984), freshwater, estuarine water, seawater, and water from a hyper saline lake (Goodwin and others, 1998). Phylogenetically diverse bacteria having the ability to degrade halogenated organic compounds have been isolated. Biodegradation typically is carried out by one of three mechanisms: co-metabolic dehalogenation, aerobic metabolism, or reductive dehalogenation.

When dehalogenation occurs co-metabolically, halogenated organic compounds degrade without bacterial growth. The bacteria seem to receive no benefit; instead, compounds are dehalogenated by an enzyme that has broad substrate specificity (Wackett and others, 1992). Methane-, ammonia-, toluene-, and butane-oxidizing bacteria have been shown to degrade halogenated organic compounds co-metabolically (Henson and others, 1988; McClay and others, 1996; Hamamura and others, 1997; Moran and Hickey, 1997). Degradation of $CHCl_3$ and $CHBr_3$ can be mediated by certain methane- (Bartnicki and Castro, 1994) and toluene-oxidizing bacteria (McClay and others, 1996). Furthermore, acclimating soils to an air and natural gas mixture stimulated the biological oxidation of $CHCl_3$ to carbon dioxide (Strand and Shippert, 1986).

Metabolism (degradation with growth) occurs when dehalogenation creates a compound that is used in the metabolic pathway of the organism, allowing the organism to use the halogenated organic compound as a source of carbon and energy (Leisinger and Bader, 1993). Bacteria that can grow on methyl chloride (Vannelli and others, 1998), methyl bromide (Connell Hancock and others, 1998), dichloromethane (Doronina and Trotsenko, 1994), and dibromomethane (Doronina and Trotsenko, 1994; Goodwin and others, 1998) have been isolated. Some of these bacteria are facultatively methylotrophic, meaning that they can grow by consuming organic compounds other than halogenated methanes. For example, a bacterium isolated from agricultural soil, strain ImB-1, can grow on methylamines and glucose as well as on halogenated methanes (Connell Hancock and others, 1998). A bacterium isolated from a seawater enrichment culture (Goodwin and others, 1998), *Leisingeria methylohalidivorans* strain MB2, can grow on halogenated methanes, yeast extract, and casein (Schaefer and others, 2002). The ability to grow on a variety of substrates probably is an important survival strategy for bacteria that can metabolize halogenated organic compounds and live in nonpolluted environments because concentrations of halogenated organic compounds are very low in nonpolluted environments—typically at the picomole per liter (pmol/L) level (Manley and others, 1992; Moore and Tokarczyk, 1993). Bacteria do consume halogenated

organic compounds present at nanomole per liter (nmol/L) (Goodwin and others, 1998) and pmol/L concentrations (King and Saltzman, 1997; Hines and others, 1998). For example, *L. methylohalidivorans* and strain ImB-1 can consume 2.4 pmol/L (equivalent to approximately 12 parts per trillion) of methyl bromide, though both routinely are grown on 100 μmol/L (micromole per liter) of methyl bromide (Goodwin and others, 2001).

Methanes with three or more halogen atoms seem to be more difficult to metabolize in aerobic environments than methanes with one or two halogen atoms. Aerobic metabolism of trihalomethanes has not been observed definitively, and bromoform ($CHBr_3$) has been found to be resistant to biodegradation in several aerobic, aquatic environments (Goodwin and others, 1998). However, carbon tetrachloride was biodegraded in aerobic ground water and soils (Happell and Wallace, 1998). Studies of the fate of THMs in the aerobic aquifer system used for injection, storage, and recovery in Las Vegas, Nevada, have yielded conflicting results. Some investigators concluded that the decline in THM concentrations during water extraction was due to biodegradation (Singer and others, 1993; Pyne and others, 1996), whereas others concluded that the declines in THMs were due solely to dilution of the injected water by mixing with the ground water (Miller and others, 1993; Bernholtz and others, 1995). Most recently, Thomas and others (2000) concluded that both cases are true. In the early years of the Las Vegas project, declines were due solely to dilution, but in later years, biodegradation of brominated THM species seems to have contributed to the observed decline in THM concentrations during extraction. The decline in concentrations of brominated THM species was greater than expected for dilution alone, and the inorganic chemistry of the system did not change significantly with time, making changes in abiotic processes an unlikely explanation. However, the population of bacteria in the aquifer increased greatly with time as indicated by heterotrophic plate counts and bacterial growth on well screens. An acclimation period—the time period when no biological destruction of a chemical is detected—was observed in many environments for a variety of chemicals (Alexander, 1994). In fact, absence of an acclimation period usually indicates chemical, not biological, mechanisms of destruction (McCarty and others, 1984).

THMs are susceptible to reductive dehalogenation. This process typically is mediated by anaerobic bacteria (Bagley and Gossett, 1995; Kohler-Staub and others, 1995), although aerobic reductive dehalogenation has been observed in the laboratory (Castro, 1993). Numerous field studies have shown evidence for degradation of halogenated organic compounds in anaerobic aquifers (Bouwer and others, 1981, 1984; McCarty and others, 1984; Roberts, 1985) including aquifers used for injection, storage, and recovery projects (Singer and others, 1993). It is possible that aerobic aquifers contain microzones that have little or no oxygen. Happell and Wallace (1998) maintained that the carbon tetrachloride degradation observed in aerobic ground water and soils could have been due to such microzones. It also is possible that microzones of low oxygen could explain the results in the report by Thomas and others (2000). Although oxygen concentrations generally were in the range of 4 to 6 mg/L in the Las Vegas aquifer, sulfate- and iron-reducing bacteria sometimes were noted during plate counts, which indicated that anaerobic conditions existed near some of the wells used for injection and recovery.

Sediment Microcosm Experiments

Sediment microcosms were constructed using water collected from well 4-32 on March 4, 1998 (before the injection period) and sediment from the core taken from the depth corresponding to that of the screened interval of piezometer 27P7 (Fram and others, 2002). Enriched sediment microcosms were made by amending some of the sediment microcosms with nutrients and vitamins. The microcosms were placed in sealed vials and were spiked with known masses of $CHCl_3$ or $CHBr_3$ prior to incubation for 145 days under aerobic or anaerobic conditions. Anaerobic conditions were established by flushing the headspace of the vial with nitrogen to remove oxygen. Sterile controls were prepared by filtering the water through sterile 0.2-micron pore-size filters prior to filling some of the vials, or by autoclaving the microcosms. The mass of $CHCl_3$ or $CHBr_3$ in the headspace of each vial was measured several times during the incubation period using head-space gas chromatography and a gas chromatograph fitted with an electron-capture detector.

Aerobic sediment microcosms spiked with $CHCl_3$ or $CHBr_3$ showed no significant bacterial degradation of $CHCl_3$ or $CHBr_3$ after 145 days of incubation, as indicated by the overlap of the data for the live and sterile vials for each measurement time (fig. 19*A*,*B*). In addition, the slopes of the mass of $CHCl_3$ or $CHBr_3$ versus time were calculated for the live and the sterile control samples; the standard errors of the two slopes overlapped (not shown). The standard error of the slope is the error in the slope of the linear regression equation fit to the data (for example, Helsel and Hirsch, 1995). Overlap of the standard error of the slopes for the live and sterile control samples indicates that regression of the two data sets yields lines with statistically indistinguishable slopes—in other words, the change in the mass of $CHCl_3$ or $CHBr_3$ during the incubation period is the same for the live and sterile control samples.

Aerobic enriched sediment microcosms were made by amending sediment microcosms with potassium dihydrogen phosphate (KH_2PO_4) (0.02 gram per liter), ammonium chloride (NH_4Cl) (0.5 gram per liter), and vitamins including B_{12} (1 milliliter per liter) (Pfennig, 1978). Adding minerals and vitamins should have increased the likelihood of biodegradation compared with unamended sediment microcosms. Aerobic enriched sediment microcosms showed no significant bacterial degradation of $CHCl_3$ or $CHBr_3$ after 145 days of incubation, as indicated by the overlap of the data for the live and sterile control samples at most measurement times (fig. 20*A*,*B*), and the overlap of the standard errors for the slopes of the mass versus time data for the live and sterile control samples (not shown).

Biodegradation of halogenated organic compounds has been reported in anaerobic aquifers (Bouwer and others, 1981, 1984), including those used for injection, storage and recovery (Singer and others, 1993). Therefore, a second set of enriched sediment microcosm samples was incubated under anaerobic conditions. Anaerobic conditions were established by flushing the headspace of the vial with nitrogen gas to remove oxygen.

The live and sterile control anaerobic, enriched sediment microcosms behaved differently than the aerobic microcosms during the incubation period. An equal amount of $CHCl_3$ was present in live and sterile control anaerobic enriched sediment microcosms after 11 days of incubation (fig. 21). However, the amount of $CHCl_3$ in live and sterile control samples differed significantly at 53 days of incubation (the Student *t* test, $\alpha = 0.05$). However, between 53 and 145 days of incubation, the mass of $CHCl_3$ in the live samples did not decline relative to the mass in the sterile control samples, as indicated by overlap in the standard error of the slopes for live and control samples for days 53–145. The live samples contained 26 percent less $CHCl_3$ than did the autoclaved sterile control samples at 53 days and 28 percent less at 145 days of incubation (fig. 21).

Bacterial degradation of $CHBr_3$ was observed in one of the two live anaerobic enriched sediment microcosms. In the microcosm that showed biodegradation, live B, the mass of $CHBr_3$ was undetectable after 14 days of incubation (fig. 22). Additions of $CHBr_3$ (respikes) at 14.4, 43.5, and 56.5 days of incubation were also consumed by the bacteria in the sample. However, the mass of $CHBr_3$ in the replicate live sample, live A, was not significantly different from the mass of $CHBr_3$ in the sterile control sample during the entire incubation period. Inconsistent behavior in replicate vials has been observed in other experiments, and probably occurs because not all vials contain an adequate number of the bacteria that degrade the halogenated organic compounds to establish a viable culture (Goodwin 1996).

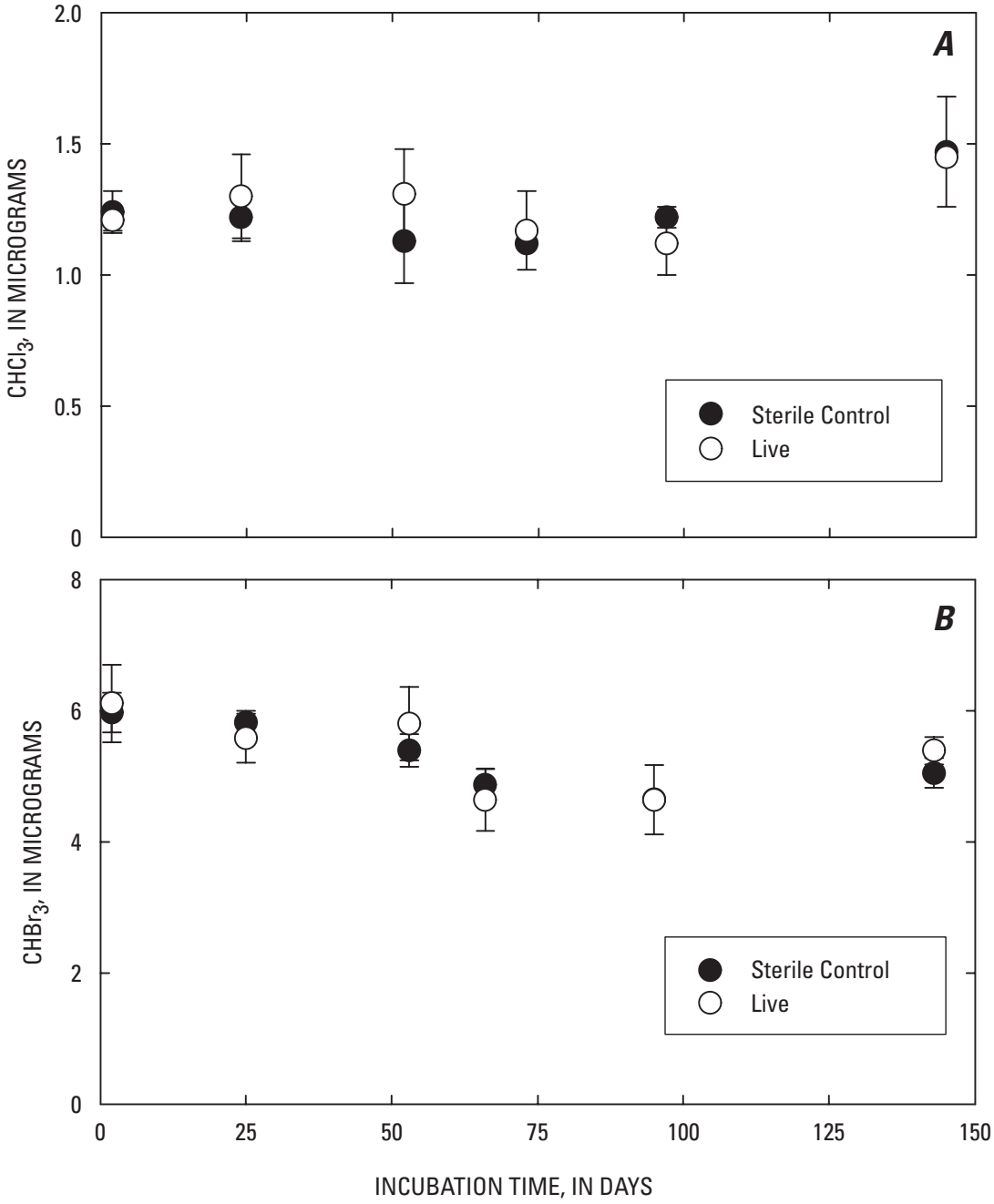

Figure 19. Mass of chloroform ($CHCl_3$) ***(A)*** and bromoform ($CHBr_3$) ***(B)*** in sediment microcosms containing sediment and ground water from Lancaster, Antelope Valley, California.

Data points represent the mean of two to four replicate analyses and the error bars represent plus or minus one standard deviation about the mean. Data are from Fram and others (2002).

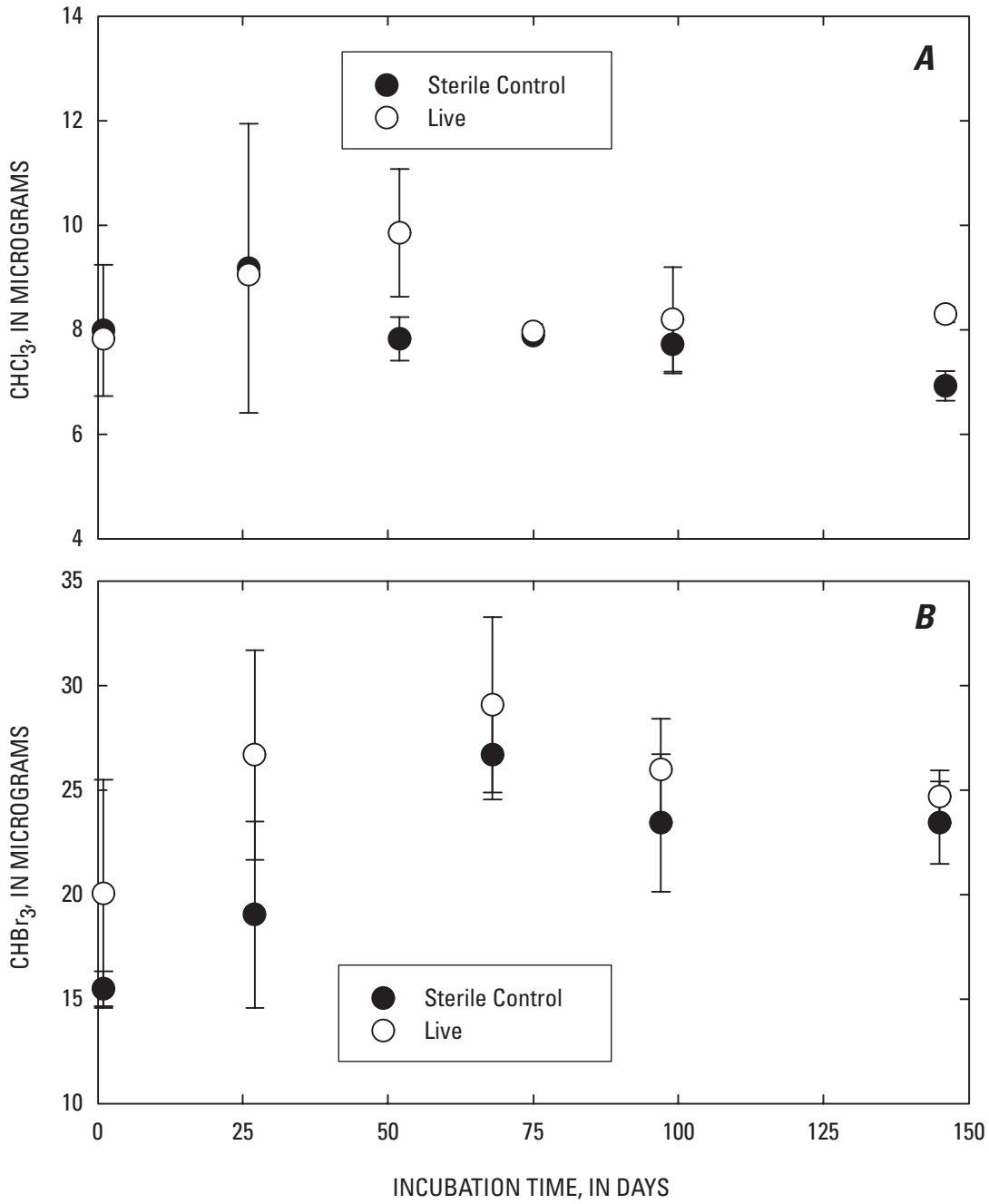

Figure 20. Mass of chloroform ($CHCl_3$) ***(A)*** and bromoform ($CHBr_3$) ***(B)*** in aerobic, enriched sediment microcosms containing sediment and ground water from Lancaster, Antelope Valley, California.

Data points represent the mean of two to four replicate analyses and the error bars represent plus or minus one standard deviation about the mean. Data are from Fram and others (2002).

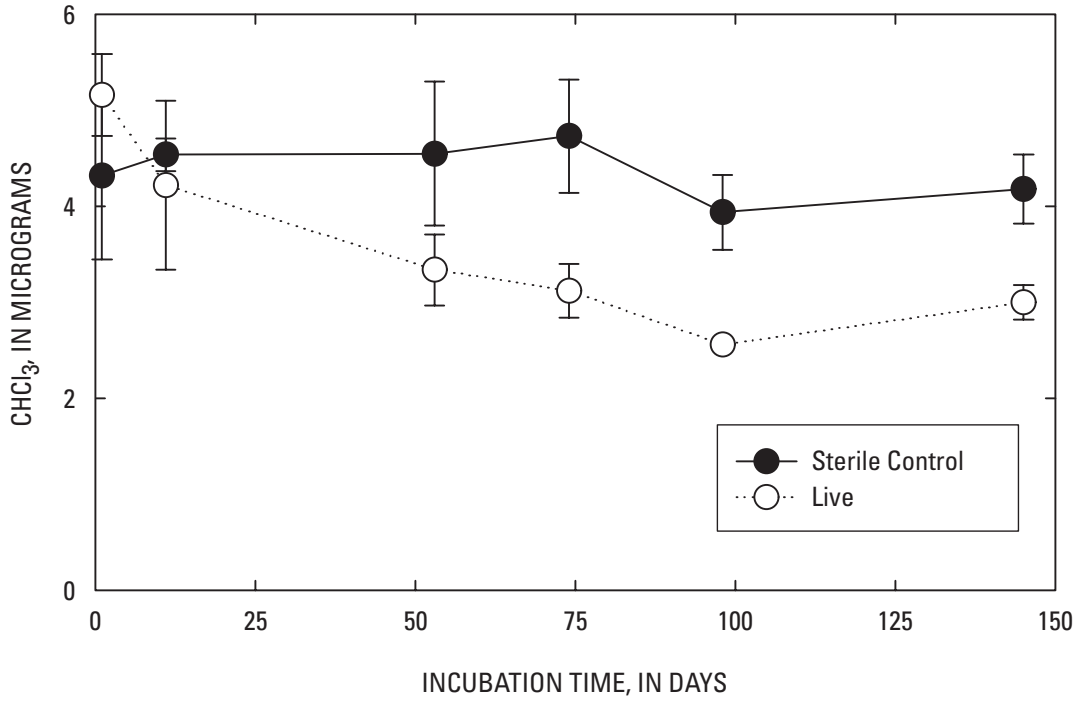

Figure 21. mass of chloroform ($CHCl_3$) in anaerobic, enriched sediment microcosms containing sediment and ground water from Lancaster, Antelope Valley, California.

Data points represent the mean of two to four replicate analyses and the error bars represent plus or minus one standard deviation about the mean. Data are from Fram and others (2002).

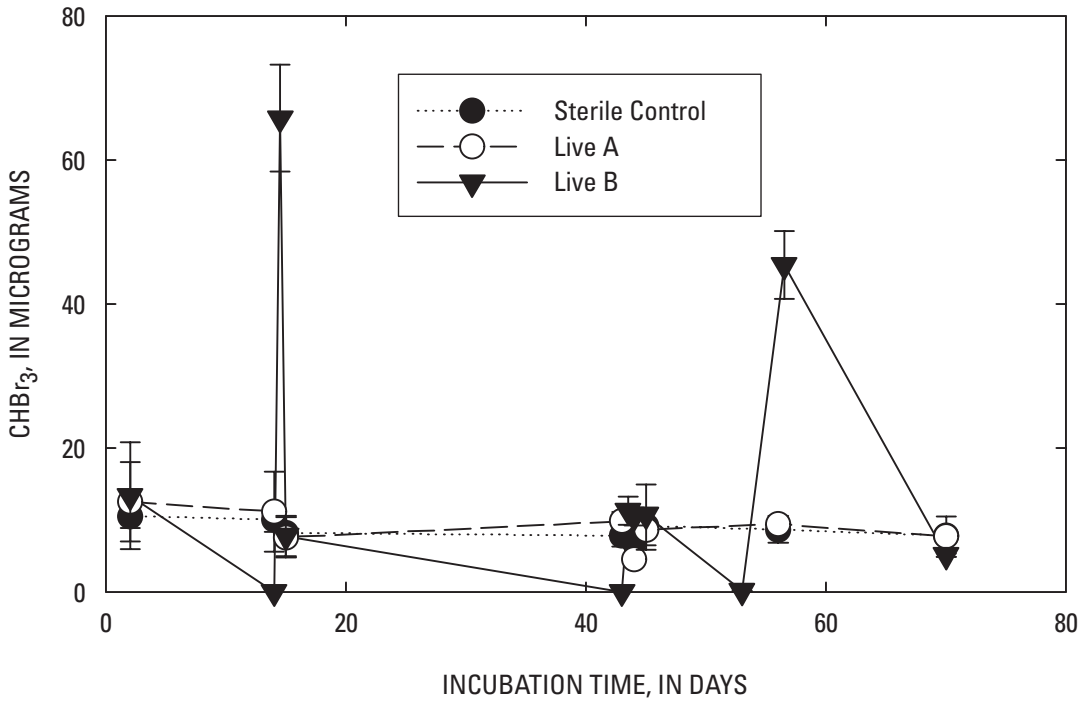

Figure 22. Mass of bromoform ($CHBr_3$) in anaerobic, enriched sediment microcosms containing sediment and ground water from Lancaster, Antelope Valley, California.

Data points represent the mean of two to four replicate analyses and the error bars represent plus or minus one standard deviation about the mean. Data are from Fram and others (2002).

Water Enrichment Microcosm Experiments

The water enrichment microcosm experiments consisted of ground water or extraction water amended with KH_2PO_4, NH_4Cl, and vitamins, plus the bacteria and particles concentrated from a larger volume of the same type of water. No sediment was added to these microcosms. Centrifugation or filtration was used to concentrate bacteria and particles for use in these microcosms. Extraction water was centrifuged at 14,000 rotations per minute and then the lower third of the water was used for the microcosms. Bacteria and particles were also concentrated from ground water or extraction water by filtering 2 liters of water through a 0.2-micrometer pore-size filter. The filters were then placed in serum vials containing 30 mL of ground water or extraction water. The vials were spiked with known masses of $CHCl_3$ and $CHBr_3$ (equivalent to approximately 195 μg/L and 380 μg/L, respectively, in the water), and incubated for up to 83 days. One set of sterile control microcosms consisted of autoclaved, enriched ground water or extraction water, and the second set consisted of extraction water sterilized by filtration through a sterile, 0.2-μm pore-size filter, plus or minus a sterile filter. All of the water enrichment microcosms were incubated under aerobic conditions.

No significant bacterial degradation of $CHCl_3$ was observed in any of the water enrichment microcosms after 83 days of incubation, as indicated by the similar behavior of the autoclaved sterile control and the live samples (fig. 23*A*). Bacterial degradation of $CHBr_3$ also was not observed in microcosms containing bacteria concentrated by centrifugation (fig. 23*B*). However, the mass of $CHBr_3$ did decrease in microcosms containing bacteria concentrated by filtration. The slopes of the mass versus time data for both live samples were significantly different from the slope for the autoclaved sterile control sample (the Student *t* test, $\alpha = 0.05$). The amount of $CHBr_3$ loss in the two microcosms was remarkably consistent, even though they contained two different kinds of water. The average percentage loss in bottles concentrated by filtration relative to controls was 37 percent at 13 days, 54 percent at 34 days, and 60 percent at 83 days. Although $CHCl_3$ was also present in these vials, there was no analogous $CHCl_3$ loss (fig. 23*A*).

The second set of sterile control microcosms was used to determine if the loss of $CHBr_3$ was an artifact caused by adsorption of $CHBr_3$ onto the filter paper. Microcosms with and without filters behaved similarly, showing no significant difference in loss of either $CHCl_3$ or $CHBr_3$ after 30 days of incubation (fig. 24). This result suggests that the pattern of $CHBr_3$ loss shown in figure 24*B* was not an artifact caused by $CHBr_3$ adsorption, and thus, the loss may have been due to biodegradation. Landmeyer and others (2000) and Thomas and others (2000) observed biodegradation of $CHBr_3$ in the Las Vegas, Nevada aquifer and suggested that it may have occurred in anaerobic microzones within the otherwise aerobic aquifer. The vials were not expected to contain such microzones, although the existence of such microzones in the pores of the filters could not be ruled out. Cometabolism of $CHBr_3$ could not have occurred in the microcosms because no cometabolic substrates were added. However, aerobic biodegradation of $CHBr_3$ has not been reported previously; therefore, these results need to be reproduced before confidence can be placed in this interesting outcome.

Bacterial Density

Bacterial density was monitored in water samples collected from the injection and extraction well (well 4-32) and from three of the nested piezometers (27P6–8) (fig. 2). Water samples were collected in sterile, 2-mL cryotubes, preserved with gluteraldehyde, and stored at –70°C until analysis. Cell numbers were determined by acridine orange direct count (AODC) (Hobbie and others, 1977), and sterile sodium citrate was added during filtration to remove background fluorescence (Harvey, 1987).

Ground water collected from well 4-32 on March 6, 1998, (before the beginning of the third cycle injection period) contained a lower concentration of bacteria than did extraction water collected in August, September, and October 1998, although the cell counts were within 1 standard deviation of each other (fig. 25). Injection water sampled at well 4-32 in June contained almost no bacteria; in fact, the concentration was not significantly different from zero (fig. 25). This result was expected because the injection water was chlorinated.

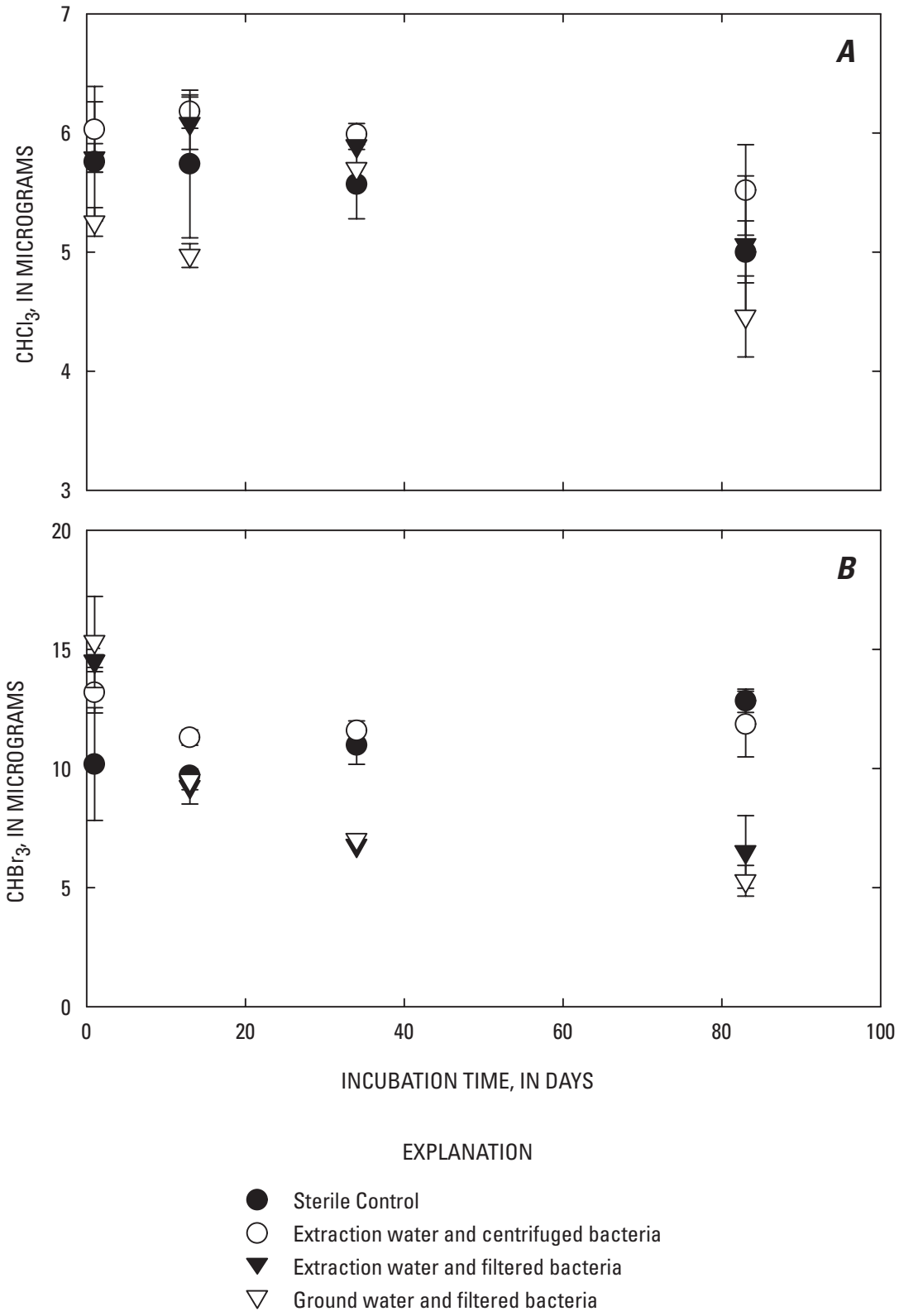

Figure 23. Mass of chloroform ($CHCl_3$) ***(A)*** and bromoform ($CHBr_3$) ***(B)*** in water enrichment microcosms stored for an incubation period and containing extraction water or ground water from Lancaster, Antelope Valley, California.

Data points represent the mean of two to four replicate analyses and the error bars represent plus or minus one standard deviation about the mean. Data are from Fram and others (2002).

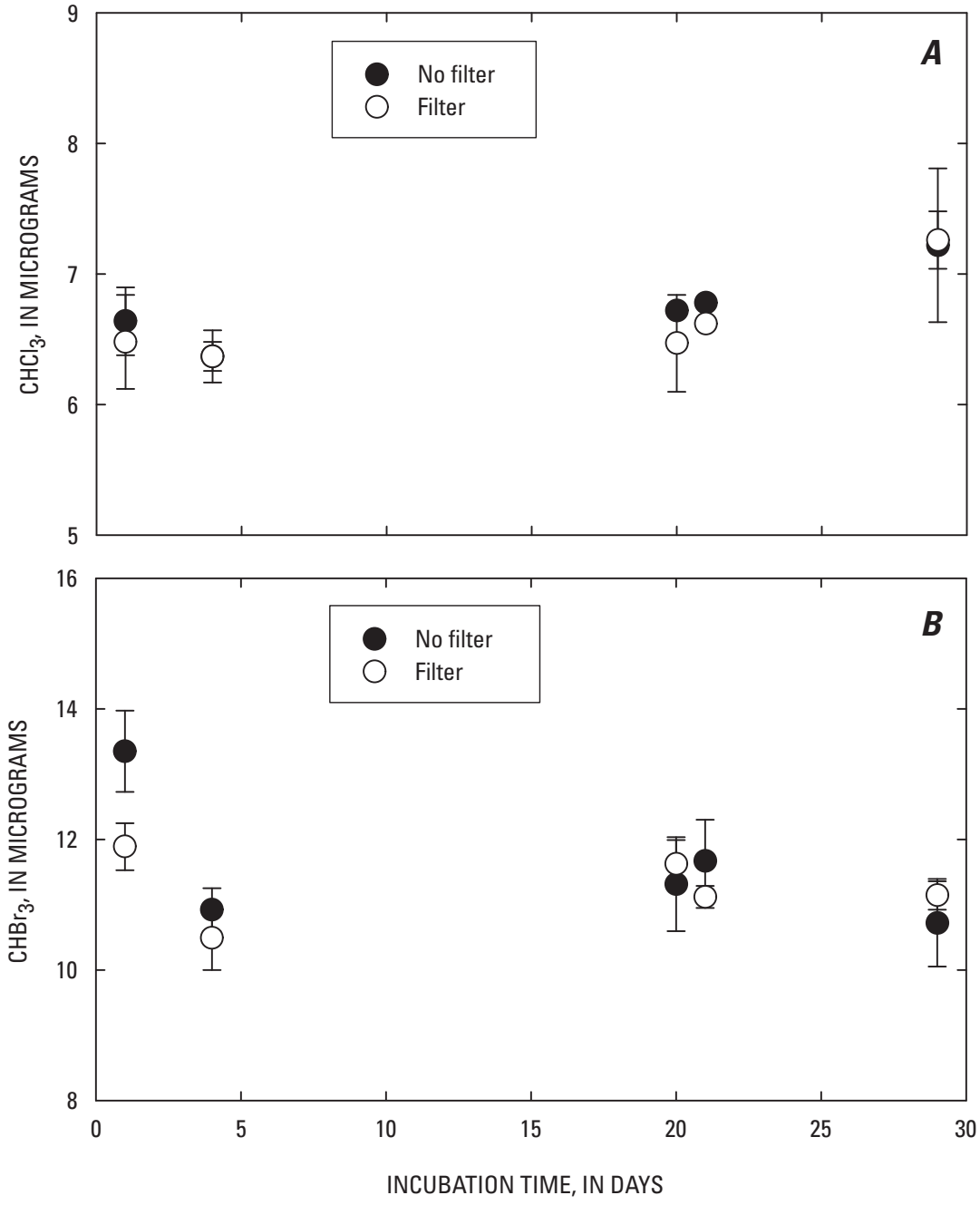

Figure 24. Mass of chloroform ($CHCl_3$) ***(A)*** and bromoform ($CHBr_3$) ***(B)*** in sterile control samples for water enrichment microcosms stored for an incubation period and containing sterile filters and extraction water from Lancaster, Antelope Valley, California.

Data points represent the mean of two to four replicate analyses and the error bars represent plus or minus one standard deviation about the mean. Data are from Fram and others (2002).

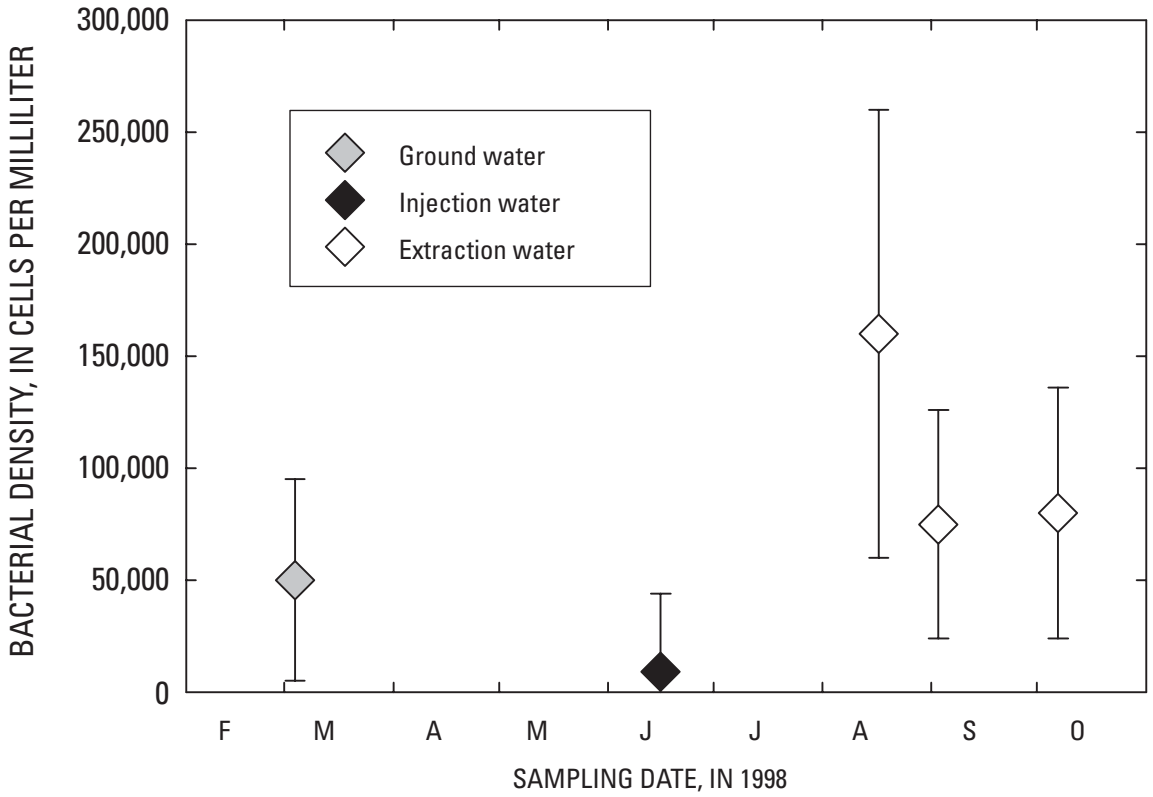

Figure 25. Bacterial densities in water samples collected from well 7N/12W-27P2 (well 4-32) during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Data points represent the mean of three replicate samples and the error bars represent plus or minus one standard deviation about the mean. Data are from Fram and others (2002).

Bacterial density in samples collected from piezometers at different depths (fig. 2) did not differ significantly except in October 1998 (fig. 26) when bacterial density was significantly higher in samples from the shallower piezometers, 27P7 and 27P8, than in samples from the deepest piezometer, 27P6. Bacterial densities were higher in October than in other months, and the bacteria were noticeably larger, as determined by visual inspection. In October, samples also were collected from wells 4-13, 4-33, and 4-42, which were outside the plume of injection water (see Metzger and others, 2002). Bacterial density in samples from the nested piezometers and well 4-32 were significantly higher than in samples from wells 4-13, 4-33, and 4-42 (fig. 27), indicating that concentration of bacteria in the aquifer increased in response to the injection, storage, and recovery process at well 4-32. An increase in the concentration of bacteria in the aquifer near injection wells has been observed by other researchers; indeed, such an increase with time was cited as evidence for the development of $CHBr_3$ biodegradation in the Las Vegas, Nevada injection, storage, and recovery project (Thomas and others, 2000).

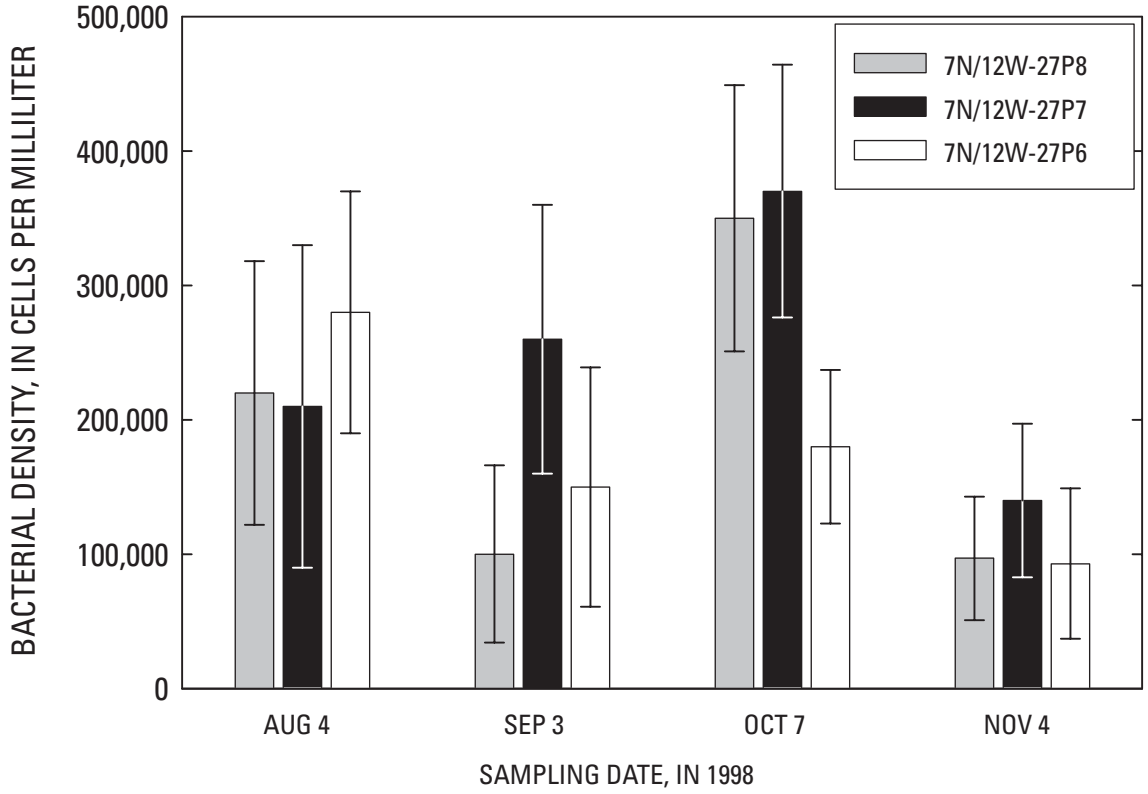

Figure 26. Bacterial densities in water samples collected from nested piezometers 7N/12W-27P6, 27P7, and 27P8 during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Data points represent the mean of three replicate samples and the error bars represent plus or minus one standard deviation about the mean. Data are from Fram and others (2002).

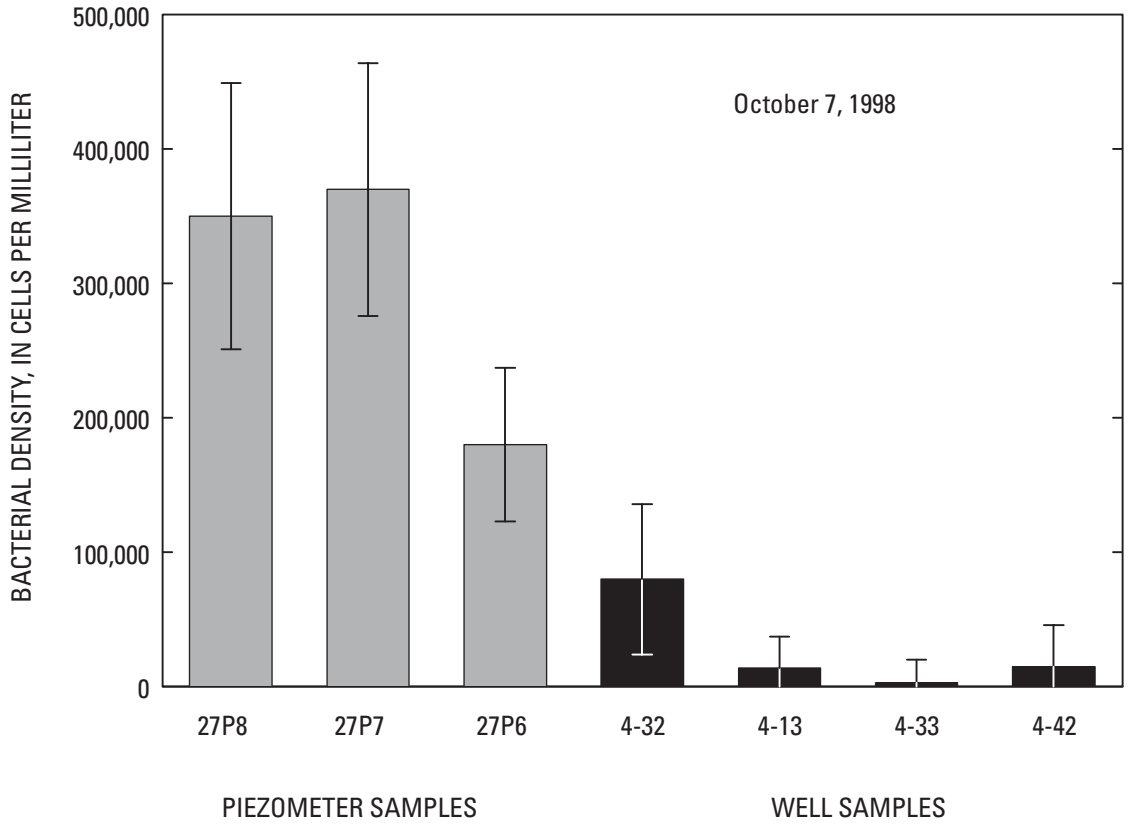

Figure 27. Bacterial densities in water samples collected from wells 7N/12W-27P2 (well 4-32), 7N/12W-27J4 (well 4-13), 7N/12W-27H3 (well 4-33), and 7N/12W-27J6 (well 4-42), and the nested piezometers 7N/12W-27P6, 27P7, and 27P8, during the third injection, storage, and recovery cycle (March 1998 through April 1999), Lancaster, Antelope Valley, California.

Data points represent the mean of three replicate samples and the error bars represent plus or minus one standard deviation about the mean. Data are from Fram and others (2002).

Conclusions

The experimental results support the following conclusions:

1. No significant bacterial degradation of chloroform ($CHCl_3$) or bromoform ($CHBr_3$) was observed in aerobic sediment microcosms or in aerobic water enrichment microcosms. In anaerobic experiments, there was some initial loss of $CHCl_3$ in live samples compared to sterile control samples, but that degradation was not sustained between days 53 and 145. However, biodegradation of $CHBr_3$ was observed in an anaerobic sediment microcosm. This result suggests that although the Lancaster aquifer is aerobic, bacteria capable of degrading $CHBr_3$ under anaerobic conditions are present. If anaerobic microzones developed in the aquifer, $CHBr_3$ could biodegrade. The development of such microzones and acclimation of the bacterial community probably accounts for the $CHBr_3$ biodegradation seen in the Las Vegas, Nevada injection, storage, and recovery project; a similar situation could develop in the Lancaster aquifer. However, the water in fully anaerobic aquifers can acquire unpleasant odors and tastes and would represent a shift from the aquifer's natural redox state; therefore, the level of oxygenation of the aquifer should be closely monitored in the extraction water with time. Because the dominant THM in the extraction water during the third cycle was $CHCl_3$, biodegradation of $CHBr_3$ would not have reduced THM concentrations significantly. It is possible that acclimation of the bacterial community could result in $CHBr_3$ biodegradation in subsequent injection, storage, and recovery cycles, as has been

observed in the Las Vegas project (Thomas and others, 2002). However, it should be noted that $CHCl_3$ biodegradation was not observed in the field nor in microcosms constructed using the Las Vegas aquifer (Landmeyer and others, 2000) or the Lancaster aquifer (this study) sediments. Therefore, even if $CHBr_3$ biodegradation were to occur, $CHCl_3$ is expected to persist.

2. No biodegradation of $CHCl_3$ was observed in the water enrichment microcosms containing bacteria concentrated by centrifugation or filtration, but a significant decline in $CHBr_3$ was observed in microcosms containing bacteria concentrated by filtration, although the loss was not complete. However, the pattern of $CHBr_3$ loss was remarkably similar for both waters, which raised suspicion that the result was due to some type of experimental artifact. Loss from leaks was ruled out because both $CHCl_3$ and $CHBr_3$ were present in the vials, and leaks would have affected both compounds. No specific adsorption of $CHBr_3$ to the filters was observed in sterile control experiments. These results indicate that the loss of $CHBr_3$ might have been due to some aerobic, biological mechanism, but this conclusion must viewed with caution until it can be reproduced.

3. Water samples from well 4-32 and nested piezometers 27P6–8 contained significantly higher concentrations of bacteria than samples from wells outside the influence of the injection well, indicating that the injection, storage, and recovery process increased bacterial numbers near the injection site.

V. SUMMARY AND CONCLUSIONS

By Miranda S. Fram, Roger Fujii, Brian A. Bergamaschi, and Kelly D. Goodwin

This study addresses the formation and fate of trihalomethanes (THMs) in the aquifer system used for the injection, storage, and recovery demonstration project in Lancaster, Antelope Valley, California. Injection, storage, and recovery is a water-management method that involves injection of surface water into an aquifer system for storage during periods when surface water is plentiful and recovery of the stored water by extraction during periods when surface water is scarce. Surface water from the State Water Project's California Aqueduct was treated before injection into the Lancaster aquifer. Disinfection (chlorination in this case) is necessary to prevent biofouling and introducing microbial contaminants into the aquifer. Natural organic matter, mostly dissolved organic carbon, present in surface water reacts with chlorine during treatment to form carcinogenic disinfection by-products such as THMs. The concentration of THMs in drinking water is regulated by the U.S. Environmental Protection Agency. Therefore, when treated surface water is injected into an aquifer system, the possible persistence of THMs in the aquifer poses a potential problem for the long-term feasibility of injection, storage, and recovery because of the need to assure that ground-water quality is not significantly degraded. Thus, this study was designed to address the following questions:

1. What controls the continued formation of THMs in the aquifer after injection?

2. What causes the continued presence of low concentrations of THMs in the extracted water after all the injection water presumably has been retrieved?

3. What causes the decrease in THM concentrations as extraction proceeds?

4. Are there natural attenuation mechanisms that can decrease the THM concentrations in the aquifer?

Our monitoring and experimental results lead us to conclude that the major factor controlling the continued formation of THMs in the aquifer after injection (question 1) was the concentration of residual chlorine in injected waters. The injection water contained averages of 27.5 μg/L THM and 0.79 mg/L residual free chlorine at the time of injection. An experiment consisting of storing samples of injection water for up to 16 weeks prior to analysis showed that THM formation caused by reaction between the dissolved organic carbon and residual chlorine in the injection water stopped after 4 weeks, when the residual chlorine was essentially consumed. The mean total concentration of THMs formed from the injection water after injection and storage in the aquifer was estimated as 58 μg/L, based on samples of extraction water and samples from the nested piezometers that were judged to represent pure injected water with no admixed ground water. Adding dechlorination treatment of the injected water immediately before injection would reduce the total amount of THMs formed from the injected water. The concentration of THMs formed in the injected water after injection and storage in the aquifer was an average of 89 μg/L less than the THM concentrations determined by THM

formation potential experiments, indicating that re-chlorinating the water after extraction would result in formation of additional THMs.

Evidence clearly shows that dilution due to mixing of injected water with ground water was the major process affecting the concentration of THMs in water extracted during the third cycle. Mixing of injected water with ground water can explain the continued low levels of THMs in the extracted water after all of the injection water had presumably been extracted (question 2) and the decrease in THM concentrations as extraction proceeded (question 3).

Mass balance calculations, results of the sulfur hexafluoride (SF_6) tracer study, and inferences from a mathematical mixing model for the third cycle indicated that mixing of the injected water with the ground water occurred in the aquifer. Mass balance calculations showed that only about 67 percent of the chloride and THMs injected into the aquifer system were recovered by the time that 132 percent of the injected water volume had been extracted. Continued extraction to 250 percent of the injected water volume only increased the recovery to 80 percent of the injected THMs. The similar recoveries for chloride and THMs indicate that THMs behaved conservatively in the aquifer (after accounting for the THMs formed from the residual free chlorine in the injected water).

A conservative tracer, SF_6, was added to the injection water throughout the injection period and then its concentration in the extraction water was monitored. SF_6 concentrations were used to calculate the relative proportions of injected water and ground water in extraction water samples, and then these proportions were used to predict THM concentrations in the extraction water. Close agreement between predicted and measured THM concentrations in the extraction water indicated that THMs behaved conservatively (after accounting for the THMs formed from the residual free chlorine in the injected water) and that attenuation of THMs and SF_6 was due to dilution of injected water with ground water that contained no THMs or SF_6. Calculations using chloride as a tracer yielded similar results.

A descriptive mixing model representing a simple scenario of mixing between injected water and ground water during the extraction process was derived and used to predict concentrations of conservative constituents in the extracted water. The concentrations of THMs, SF_6, and chloride in the extracted water predicted by the model closely matched the measured concentrations. The low concentrations of THMs in water extracted at the end of the third cycle represent mixtures consisting of a small proportion of injected water and a large proportion of ground water. Thus, the results suggest that mixing of injected water and ground water can adequately explain extraction water composition without further consideration of other mechanisms, such as microbial degradation or sorption.

The descriptive mixing model was used to forecast the accumulation of conservative constituents present in the injection water after 10 annual cycles of injection, storage, and recovery. For realistic ratios of the volumes of injected to extracted water, the model predicts that the concentrations of injected constituents in the water remaining in the aquifer at the injection site after the 10th cycle would approach 100 percent of injection water concentrations. Removal of this residual concentration at a later time, using existing extraction methods, may be difficult because the ratio of injected water to ground water in the extracted water declines asymptotically owing to mixing. Thus, removing the residual concentration would require pumping several times the injected water volume. Reducing the concentration of a constituent in the water near the injection/extraction well to 10 percent of its concentration in the injected water would require removal of 2.3 times the volume of water injected, reducing it to 1 percent would require removing 4.6 volumes, and reducing it to 0.1 percent would require removing 9 volumes. The results of this study indicate that the concentrations of THMs (or any conservative constituent present in the injection water at a concentration exceeding that in the native ground water) will increase in the aquifer surrounding the injection site.

Our results indicate that the natural attenuation mechanisms, biodegradation and sorption, did not significantly decrease the concentration of THMs in the aquifer (question 4). The potential for biodegradation of THMs by aquifer bacteria was assessed using two types of experiments: sediment microcosms prepared from aquifer sediment and ground water incubated with and without amendation with nutrients, incubated under aerobic and anaerobic conditions, and water enrichment microcosms prepared from ground water or extraction water amended with nutrients and with bacteria and particles concentrated from a larger volume of water and incubated under aerobic conditions. Results from these experiments showed no

bacterial degradation of chloroform ($CHCl_3$) or bromoform ($CHBr_3$) under aerobic conditions, such as those in the aquifer in this study. Bacterial degradation of $CHBr_3$ under anaerobic conditions was observed. However, because the Lancaster aquifer is aerobic and because $CHBr_3$ comprises only a small proportion of the THMs, biodegradation is not considered an important attenuation mechanism for THMs in this aquifer.

Measurements of bacterial densities in water samples collected during the cycle showed that water samples collected from the injection well and the nearby nested piezometers during the extraction period contained significantly more bacteria than water samples collected from wells farther away. This result suggests that the injection process may increase bacterial population in the aquifer near the injection site.

Comparison of the $(Br/Cl)_{THM}$ values in the injection water from the storage experiments with the values in the extraction water sampled at the beginning of the extraction period suggests that sorption was not an important process for controlling THM concentrations in this aquifer. No evidence was observed for the preferential removal of brominated THM species as would have been expected had sorption occurred. In addition, the close correspondence of the change in THM concentrations during the extraction period to the changes in the concentrations of SF_6 and chloride (species known not to be sorbed to the aquifer material) also suggests that sorption of THMs to aquifer materials was not an important process.

Finally, our results provided some insights into the ground-water flow system during the injection, storage, and recovery cycle. The data and modeling results lead us to conclude that the aquifer-system response to injection, storage, and recovery cycles was very complex. Extensive mixing between injected water and ground water occurred, and the water flow paths during injection and extraction seemed to be different. We proposed a conceptual model for water flow in the aquifer during the third injection, storage, and recovery cycle at the Lancaster site. Although the injection/extraction well was continuously screened through the upper and middle aquifers, injected water preferentially flowed into high hydraulic conductivity zones in the upper aquifer. Mechanical dispersion resulted in some mixing between injected water and native ground water during injection. During extraction, water-level drawdown around the injection/extraction well resulted in inefficient transport of water from the upper portions of the aquifer to the well, thus increasing the proportion of water extracted from deeper portions of the aquifer. As a result, injected water was stranded in upper portions of the aquifer. The water extracted from the injection/extraction well consisted of mixtures of injected water and native ground water. This hydraulic regime resulted in incomplete recovery of the injected water.

REFERENCES CITED

Alexander, M., 1994, Biodegradation and bioremediation: San Diego, Calif., Academic Press, 302 p.

Amy, G.L., Chadik, P.A., Chowdhury, Z.K., King, P.H., and Cooper, W.J., 1985, Factors affecting incorporation of bromide into brominated trihalomethanes during chlorination, *in* Jolley, R.L., Bull, R.J., Davis, W.P., Katz, S., Roberts, M.H. Jr., Jacobs, V.A., eds., Water chlorination: chemistry, environmental impact and health effects, v. 5: Boca Raton, Lewis Publishers, Inc., p. 907–922.

Babcock, D.B., and Singer, P.C., 1979, Chlorination and coagulation of humic and fulvic acids: Journal of the American Water Works Association, v. 71, no. 3, p. 149–152.

Bagley, D.M., and Gossett, J.M., 1995, Chloroform degradation in methanogenic methanol enrichment cultures and by *Methanosarcina barkeri* 227: Applied and Environmental Microbiology, v. 61, no. 9, p. 3195–3201.

Barber, L.B., II, Brown, G.K., Kennedy, K.R., Leenheer, J.A., Noyes, T.I., Rostad, C.E., and Thorn, K.A., 1997, Organic constituents that persist during aquifer storage and recovery of reclaimed water in Los Angeles County, California, *in* Kendall, D.R., ed., Proceedings of AWRA Symposium, Conjunctive Use of Water Resources, Aquifer Storage and Recovery: Herndon, Virginia, American Water Resources Association, TPS-97-2, p. 261–272.

Bartnicki, E.W., and Castro, C.E., 1994, Biodehalogenation: rapid oxidative metabolism of mono- and polyhalomethanes by *Methylosinus trichosporium* OB-3b: Environmental Toxicological Chemistry, v. 13, no. 2, p. 241–245.

Bear, Jacob, 1979, Hydraulics of groundwater: New York, McGraw-Hill, 569 p.

Berner, R.A., 1980, Early diagenesis, a theoretical approach: Princeton, N.J., Princeton University Press, 237 p.

Bernholtz, A., Brothers, K., and Katzer, T., 1995, Artificial ground-water recharge in Las Vegas Valley, Clark County, Nevada: Storing today, treating tomorrow?, *in* Johnson, A.I., and Pyne, R.D.G., eds., Artificial recharge of ground water, II, Proceedings of the Second International Symposium on Artificial Recharge of Ground Water: New York, American Society of Civil Engineers, p. 548–557.

Bloyd, R.M., Jr., 1967, Water resources of the Antelope Valley–East Kern Water Agency area, California: U.S. Geological Survey Open-File Report [67-20], 73 p.

Bouwer, E.J., McCarty, P.L., Bouwer, H., and Rice, R.C., 1984, Organic contaminant behavior during rapid infiltration of secondary wastewater at the Phoenix 23rd Avenue Project: Water Research, v. 18, no. 4, p. 463–472.

Bouwer, E.J., Rittmann, B.E., and McCarty, P.L., 1981, Anaerobic degradation of halogenated 1- and 2-carbon organic compounds: Environmental Science and Technology, v. 15, no. 5, p. 596–599.

Brothers, K., and Katzer, T., 1990, Water banking through artificial recharge, Las Vegas Valley, Clark County, Nevada: Journal of Hydrology, v. 114, p. 77–103.

Campbell, B.G., Conlon, K.J., Mirecki, J.E., and Petkewich, M.D., 1997, Evaluation of aquifer storage recovery in the Santee Limestone/Black Mingo Aquifer near Charleston, South Carolina, 1993–95: U.S. Geological Survey Water-Resources Investigations Report 96-4283, 89 p.

Carlson, C.S., Leighton, D.A., Phillips, S.P., and Metzger, L.F., 1998, Regional water table (1996) and water-table changes in the Antelope Valley ground-water basin, California: U.S. Geological Survey Water-Resources Investigations Report 98-4022, 2 sheets.

Castro, C.E., 1993, Biodehalogenation: The kinetics and rates of the microbial cleavage of carbon-halogen bonds: Environmental Toxicology and Chemistry, v. 12, no. 9, p. 1609–1618.

Chin, Y-P., Aiken, G., and O'Loughlin, E., 1994, Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances: Environmental Science and Technology, v. 28, no. 11, p. 1853–1858.

Chiou, C.T., Peters, L.J., and Freed, V.H., 1979, A physical concept for soil-water equilibria for nonionic organic compounds: Science, v. 206, no. 4420, p. 831–832.

Chiou, C.T., Porter, P.E., and Schmedding, D.W., 1983, Partition equilibria of nonionic organic compounds between soil organic matter and water: Environmental Science and Technology, v. 17, no. 4, p. 227–231.

Clark, J.F., Wannikhof, R., Schlosser, P., and Simpson, H.J., 1994, Gas exchange in the tidal Hudson River using a dual tracer technique: Tellus, v. B46, p. 274–285.

Connell Hancock, T.L., Costello, A.M., Lidstrom, M.E., and Oremland, R.S., 1998, Strain ImB-1, a novel bacterium for the dissipation of methyl bromide in fumigated agricultural soils: Applied and Environmental Microbiology, v. 64, no. 8, p. 2899–2905.

Curtis, G.P., Roberts, P.V., and Reinhard, M., 1986, A natural gradient experiment of solute transport in a sand aquifer 4. Sorption of organic solutes and its influence on mobility: Water Resources Research, v. 22, no. 13, p. 2059–2067.

Dibblee, T.W., Jr., 1967, Areal geology of the western Mojave Desert, California: U.S. Geological Survey Professional Paper 522, 153 p., 4 pls. in pocket.

Doronina, N.V., and Trotsenko, Y.A., 1994, *Methylophilus leisingerii* sp. nov., a new species of restricted facultatively methylotrophic bacteria: Microbiology, v. 63, p. 298–302.

Dutcher, L.C., and Worts, G.F., 1963, Geology, hydrology, and water supply of Edwards Air Force Base, Kern County, California: U.S. Geological Survey Open-File Report [63-05], 225 p.

Fram, M.S., Berghouse, J.K., Bergamaschi, B.A., Fujii, R., and Clark, J.F., 2002, Water quality monitoring and studies of the formation and fate of trihalomethanes during the third injection, storage, and recovery test at Lancaster, Antelope Valley, California, March 1998 through April 1999: U.S. Geological Survey Open-File Report 02-102, 48 p.

Fujii, R., Ranalli, A.J., Aiken, G.R., and Bergamaschi, B.A., 1998, Dissolved organic carbon concentrations and compositions, and trihalomethane formation potentials in waters from agricultural peat soils, Sacramento–San Joaquin Delta, California: Implications for drinking-water quality: U.S. Geological Survey Water Resources Investigations Report 98-4147, 75 p.

Gamlin, J.D., Clark, J.F., Woodside, G., and Herndon, R., 2001, Large-scale tracing of ground water with sulfur hexafluoride: Journal of Environmental Engineering, v. 127, no. 2, p. 171–174.

Goodwin, K.D., 1996, Natural cycles of brominated methanes: Macroalgal production and marine microbial degradation of bromoform and dibromomethane: Ph.D. thesis, California Institute of Technology.

Goodwin, K.D., Schaefer, J.K., and Oremland, R.S., 1998, Bacterial oxidation of dibromomethane and methyl bromide in natural waters and enrichment cultures: Applied and Environmental Microbiology, v. 64, no. 12, p. 4629–4636.

Goodwin, K.D., Varner, R.K., Crill, P.M., and Oremland, R.S., 2001, Consumption of tropospheric levels of methyl bromide by C_1 bacteria and comparison to saturation kinetics: Applied and Environmental Microbiology, v. 67, no. 12, p. 5437–5443.

Grathwohl, P., 1990, Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications of KOC correlations: Environmental Science and Technology, v. 24, no. 11, p. 1687–1693.

Gschwend, P.M., and Wu, S., 1985, On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants: Environmental Science and Technology, v. 19, no. 1, p. 90–96.

Hamamura, N., Page, C., Long, T., Semprini, L., and Arp, D.J., 1997, Chloroform cometabolism by butane-grown CF8, *Pseudomonas butanovora*, and *mycobacterium vaccae* JOB5 and methane-grown *methylosinus trichosporium* OB3b: Applied and Environmental Microbiology, v. 63, no. 9, p. 3607–3613.

Happell, J.D., and Wallace, D.W.R., 1998, Removal of atmospheric CCl_4 under bulk aerobic conditions in groundwater and soils: Environmental Science and Technology, v. 32, no. 9, p. 1244–1252, 1998.

Harvey, R.W., 1987, A fluorochrome-staining technique for counting bacteria in saline, organically enriched, alkaline lakes: Limnology and Oceanography, v. 32, p. 993–995.

Hathaway, G.J., Proctor, N.H., Hughes, J.P., and Fischman, M.L., eds., 1991, Proctor and Hughes' chemical hazards of the workplace: New York, Van Nostrand Reinhold, 666 p.

Helsel, D.R., and Hirsch, R.M., 1995, Statistical methods in water resources: Amsterdam, The Netherlands, Elsevier Science Publishers, Studies in Environmental Science Series, v. 49, 529 p., software in pocket (3 1/2 inch diskette).

Henson, J.M., Yates, M.V., Cochran, J.W., and Shackleford, D.L., 1988, Microbial removal of halogenated methanes, ethanes, and ethylenes in an aerobic soil exposed to methane: FEMS Microbial Ecology, v. 53, p. 193–201.

Hines, M.E., Crill, P.M., Varner, R.K., Talbot, R.W., Shorter, J.H., Kolb, C.E., and Harris, R.C., 1998, Rapid consumption of low concentrations of methyl bromide by soil bacteria: Applied and Environmental Microbiology, v. 64, no. 5, p. 1864–1870.

Hobbie, J.E., Daley, R.J., and Jasper, S., 1977, Use of nucleopore filters for counting bacteria by fluorescence microscopy: Applied and Environmental Microbiology, v. 33, p. 1225–1228.

Howle, J.F., Phillips, S.P., Denlinger, R.P., and Metzger, L.F., in press, Determination of specific yield and changes in water-table surface using temporal microgravity surveys during freshwater injection tests, Lancaster, Antelope Valley, California, 1996–97: U.S. Geological Survey Water-Resources Investigations Report 03-4019.

Ikehara, M.E., and Phillips, S.P., 1994, Determination of land subsidence related to ground-water-level declines using global positioning system and leveling surveys in Antelope Valley, Los Angeles and Kern Counties, California, 1992: U.S. Geological Survey Water-Resources Investigations Report 94-4184, 101 p.

Karickhoff, S.W., Brown, D.S., and Scott, T.A., 1979, Sorption of hydrophobic pollutants on natural sediments: Water Research, v. 13, no. 3, p. 241–248.

King, D.B., and Saltzman, E.S., 1997, Removal of methyl bromide in coastal seawater: Chemical and biological rates: Journal of Geophysical Research, v. 102, no. C8, p. 18715–18721.

Kohler-Staub, D., Frank, S., and Leisinger, T., 1995, Dichloromethane as the sole carbon source for *Hyphomicrobium* sp. Strain DM2 under denitrification conditions: Biodegradation, v. 6, p. 229–235.

Landmeyer, J.E., Bradley, P.M., and Thomas, J.M., 2000, Biodegradation of disinfection by-products as a removal process during aquifer storage extraction: Journal of the American Water Resources Association, v. 36, no. 4, p. 861–868.

Larson, R.A., and Weber, E.J., 1994, Reaction mechanisms in environmental organic chemistry: Boca Raton, Lewis Publishers, 433 p.

Leighton, D.A., and Phillips, S.P., 2003, Simulation of ground-water flow and land subsidence in the Antelope Valley ground-water basin, California: U.S. Geological Survey Water-Resources Investigations Report 03-4016., available only on the Internet at URL http://water.usgs.gov/pubs/wri/wrir034016/text.htm.

Leisinger, T., and Bader, R., 1993, Microbial dehalogenation of synthetic organohalogen compounds, hydrolytic dehalogenases: Chimia, v. 47, p. 116–121.

Londquist, C.J., Rewis, D.L., Galloway, D.L., and McCaffrey, W.F., 1993, Hydrogeology and land subsidence, Edwards Air Force Base, Antelope Valley, California, January 1989–December 1991: U.S. Geological Survey Water-Resources Investigations Report 93-4114, 74 p.

Los Angeles County Department of Public Works, 2000, Lancaster subbasin aquifer storage and recovery (ASR) demonstration project final report: Los Angeles County Department of Public Works, Waterworks and Sewer Maintenance Division, Waterworks District 40, Antelope Valley, Water Quality and Engineering Section, Water Resources Unit, 40 p. plus appendices.

Mabey, D.R., 1960, Gravity survey of the western Mojave Desert, California: U.S. Geological Survey Professional Paper 316-D, p. 51–73.

MacIntyre, W.G., and Stauffer, T.B., 1988, Liquid chromatography applications to determination of sorption on aquifer materials: Chemosphere, v. 17, no. 11, p. 2161–2173.

Mackay, D., Shiu, W.Y., and Ma, K.C., 1993, Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals: v. III, Volatile organic chemicals: Boca Raton, Lewis Publishers, 916 p.

Manley, S.L., Goodwin, K., and North, W.J., 1992, Laboratory production of bromoform, methylene bromide and methyl iodide by macroalgae and distribution in nearshore southern California waters: Limnology and Oceanography, v. 37, no. 8, p. 1652-1659.

McCarty, P.L., Rittmann, B.E., and Bouwer, E.J., 1984, Microbiological processes affecting chemical transformations in groundwater, *in* Bitton, G., and Gerba, C.P., eds., Groundwater Pollution Microbiology, New York, John Wiley & Sons, p. 90–115.

McClay, K., Fox, B.G., and Steffan, R.J., 1996, Chloroform mineralization by toluene-oxidizing bacteria: Applied and Environmental Microbiology, v. 62, no. 8, p. 2716–2722.

Metzger, L.F., Ikehara, M.E., and Howle, J.F., 2002, Vertical-deformation, water-level, microgravity, geodetic, water-chemistry, and flow-rate data collected during injection, storage, and recovery tests at Lancaster, Antelope Valley, California, September 1995 through September 1998: U.S. Geological Survey Open-File Report 01-414, 149 p.

Miller, C.J., Wilson, L.G., Amy, G.L., and Brothers, K., 1993, Fate of organochlorine compounds during aquifer storage and recovery: The Las Vegas experience: Groundwater, v. 31, no. 3, p. 410–416.

Mirecki, J.E., Campbell, B.D., Conlon, K.J., and Petkewich, M.D., 1998, Solute changes during aquifer storage recovery testing in a limestone/clastic aquifer: Ground Water, v. 36, no. 3, p. 394–403.

Moore, R.M., and Tokarczyk, R., 1993, Volatile biogenic halocarbons in the northwest Atlantic: Global Biogeochemical Cycles, v. 7, p. 195–210.

Moran, B.N. and Hickey, W.J., 1997, Trichloroethylene biodegradation by mesophilic and psychrophilic ammonia oxidizers and methanotrophs in groundwater microcosms: Applied and Environmental Microbiology, v. 63, no. 10, p. 3866–3871.

Morris, J.C., 1978, The chemistry of aqueous chlorine in relation to water chlorination, *in* Jolley, R.L., ed., Water Chlorination: Environmental Impact and Health Effects, v. 1: Ann Arbor, Mich., Ann Arbor Science Publishers, Inc., p. 21–33.

Oliver, B.G., 1980, Effect of temperature, pH, and bromide concentration on the trihalomethane reaction of chlorine with aquatic humic material, *in* Jolley, R.L., Brungs, W.A., and Cumming, R.B., eds., Water Chlorination: Environmental Impact and Health Effects, v. 3, Ann Arbor, Mich., Ann Arbor Science Publishers, Inc., p. 141–149

Peng, D., and Dural, N.H., 1998, Multicomponent adsorption of chloroform, carbon tetrachloride, and 1,1,1-trichloroethane on soils: Journal of Chemical Engineering Data, v. 43, p. 283–288.

Pfennig, N., 1978, *Rhodocyclus purpureus* gen. nov. and sp. nov., a ring-shaped, vitamin B_{12}-requiring member of the family *rhodospirillaceae*: International Journal of Systematic Bacteriology, v. 28, p. 283–288.

Phillips, S.P., Carlson, C.S., Metzger, L.F., Howle, J.F., Sneed, Michelle, Galloway, D.L., Ikehara, M.E., Hudnut, K.W., Behr, J.A.,King, N.E., and Lewis, A.S., in press, Analysis of pilot tests of subsurface injection, storage, and recovery of freshwater in Lancaster, Antelope Valley, California: U.S. Geological Survey Water-Resources Investigations Report 03-4061.

Pyne, R.D.G., 1995, Groundwater recharge and wells; a guide to aquifer storage and recovery: Boca Raton, Lewis Publishers, CRC Press, Inc., 376 p.

Pyne, R.D., Singer, P.C., and Miller, C.T., 1996, Aquifer storage and extraction of treated drinking water: Denver, American Water Works Association Research Foundation and American Water Works Association, 176 p.

Quanrud, D.M., Arnold, R.G., Wilson, L.G., Gordon, H.J., Graham, D.W., and Amy, G.L., 1996, Fate of organics during column studies of soil aquifer treatment: Journal of Environmental Engineering, v. 122, p. 314–321.

Reckhow, D.A., Singer, P.C., and Malcolm, R.L., 1990, Chlorination of humic materials: By-product formation and chemical interpretations: Environmental Science and Technology, v. 24, no. 11, p. 1655–1664.

Roberts, P.V., 1985, Field observations of organic contaminant behavior in the Palo Alto Baylands, *in* Asano, T., ed., Artificial Recharge of Groundwater: Boston, Butterworth Publishers, p. 647–679.

Roberts, P.V., Goltz, M.N., and Mackay, D.M., 1986, A natural gradient experiment on solute transport in a sand aquifer 3. Retardation estimates and mass balances for organic solutes: Water resources Research, v. 22, no. 13, p. 2047–2058.

Roberts, P.V., Schreiner, J., and Hopkins, G.D., 1982, Field study of organic water quality changes during groundwater recharge in the Palo Alto baylands: Water Research, v. 16, p. 1025–1035.

Rook, J.J., 1977, Chlorination reactions of fulvic acids in natural waters: Environmental Science and Technology, v. 11, no. 5, p. 478–483.

Rook, J.J., Grass, A.A., and Van der Heijden, J., 1978, Bromide oxidation and organic substitution in water treatment: Journal of Environmental Science and Health, v. 13, p. 91–116.

Schaefer, J.K., Goodwin, K.D., McDonald, I.R., Murrell, J.C., and Ormland, R.S., 2002, *Leisingeria methylohalidivorans* gen. nov., sp. nov., a marine methyltroph that grows on methyl bromide: International Journal of Systematic and Evolutionary Microbiology, v. 52, no. 3, p. 851–859.

Schwarzenbach, R.P., and Westall, J., 1981, Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies: Environmental Science and Technology, v. 15, no. 11, p. 1360–1367.

Singer, P.C., Pyne, R.D.G., Mallikarjun AVS, Miller, C.T., and Mojonnier, C., 1993, Examining the impact of aquifer storage and recovery on DBPs: Journal of the American Water Works Association, v. 85, no. 11, p. 85–94.

Strand, S.E., and Shippert, L., 1986, Oxidation of chloroform in an aerobic soil exposed to natural gas: Applied and Environmental Microbiology, v. 52, p. 203–205.

Streetly, M.J., 1998, The use of modeling to predict the behavior of ASR systems: *in* Peters, J.H., ed., Artificial recharge of groundwater: Proceedings of the Third International Symposium on Artificial Recharge of Groundwater, TISAR 98, Amsterdam, The Netherlands, 21–25 September, 1998: A.A. Balkema, Rotterdam, p. 263–267.

Stumm, W., and Morgan, J.J., 1996, Aquatic Chemistry (3d ed.): New York, John Wiley & Sons, Inc., 1022 p.

Symons, J.M., Krasner, S.W., Simms, L.A., and Sclimenti, M., 1993, Measurement of THM and precursor concentrations revisited; The effect of Bromide ion: Journal of the American Water Works Association, v. 85, no. 1, p. 51–62.

Thomas, J.M., McKay, W.A., Cole, E., Landmeyer, J.E., and Bradley, P.M., 2000, The fate of haloacetic acids and trihalomethanes in an aquifer storage and recovery program, Las Vegas, Nevada: Groundwater, v. 38, no. 4, p. 605–614.

Traina, S.J., Novak, J., and Smeck, N.E., 1990, An ultraviolet absorbance method of estimating the percent aromatic carbon content of humic acids: Journal of Environmental Quality, v., 19, no. 1, p. 151–153.

Vannelli, T., Studer, A., Ketesz, M., and Leisinger, T., 1998, Chloromethane metabolism by *Methlobacterium* sp. Strain CM_4: Applied and Environmental Microbiology, v. 64, no. 5, p. 1933–1936.

U.S. Environmental Protection Agency, 1998, Environmental Protection Agency: 40 CFR parts 9, 141, and 142: National Primary Drinking Water Regulations: Disinfectants and disinfection by-products, final rule: Federal Register, v. 63, no. 241, p. 69390–69476.

Wackett, L.P., Logan, M., Block, F.A., and Bao-li, C., 1992, A mechanistic perspective on bacterial metabolism of chlorinated methanes: Biodegradation, v. 3, p. 19–36.

Walton, B.T., Hendricks, M.S., Anderson, T.A., Griest, W.H., Merriweather, R., Beauchamp, J.J., and Francis, C.W., 1992, Soil sorption of volatile and semivolatile organic compounds in a mixture: Journal of Environmental Quality, v. 21, no. 4, p. 552–558.

Wannikhof, R., Mulholland, P.J., Broecker, W.S., and Hamilton, M., 1987, Gas exchange rates on Mono Lake and Crowley Lake, California: Journal of Geophysical Research, v. 92, p. 14567–14580.