Use of Water-Quality Indicators and Environmental Tracers to Determine the Fate and Transport of Recycled Water in Los Angeles County, California

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### CONVERSION FACTORS, VERTICAL DATUM, WATER-QUALITY INFORMATION, AND ABBREVIATIONS

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

\[ °F = (1.8 \times °C) + 32 \]

#### Vertical Datum

**Sea level**: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

**Altitude**, as used in this report, refers to distance above or below sea level.

#### Water-Quality Information

**Specific conductance** is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

**Concentrations of chemical constituents** in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

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#### Conversion Factors

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

\[ °F = (1.8 \times °C) + 32 \]
ABBREVIATIONS (constituents or properties)

- **Ar**: argon
- **ALK**: alkalinity
- **APEC**: alkylphenol polyethoxy carboxylate
- **B**: boron
- **B-11**: boron-11
- **$^{11}$B/$^{10}$B**: boron-11/boron-10 ratio
- **Bact**: total bacteria
- **Br**: bromide
- **C**: carbon
- **Ca**: calcium
- **CaCO$_3$**: calcium carbonate
- **calN**: “back-calculated” nitrogen (assumed to be nitrate)
- **CFCs**: chlorofluorocarbons
- **CFC-11**: trichlorofluoromethane
- **CFC-12**: dichlorodifluoromethane
- **CFC-113**: chlorotrifluoromethane
- **CH$_4$**: methane
- **Cl**: chloride
- **CO$_2$**: carbon dioxide
- **Coli**: total coliform
- **DIST**: horizontal distance to well
- **DO**: dissolved molecular oxygen
- **DOC**: dissolved organic carbon
- **DOM**: dissolved organic matter
- **EDTA**: ethylenediaminetetraacetic acid
- **exB**: calculated “excess” boron
- **exCl**: calculated “excess” chloride
- **$\delta^{11}$B**: delta boron-11/boron-10 ratio
- **$\delta$D**: delta deuterium/protium ratio
- **$\delta^{15}$N**: delta nitrogen-15/nitrogen-14 ratio
- **$\delta^{15}$N-N$_2$**: delta nitrogen-15/nitrogen-14 ratio of dissolved nitrogen gas
- **$\delta^{15}$N-NO$_3$**: delta nitrogen-15/nitrogen-14 ratio of nitrate
- **$\delta^{18}$O**: delta oxygen-18/oxygen-16 ratio
- **F**: fluoride
- **Fe**: iron
- **FLUO**: excitation-emission fluorescence
- **H$_2$O**: water
- **H$_2$S**: hydrogen sulfide
- **H-2**: deuterium
- **$^2$H/$^1$H**: deuterium/protium ratio
- **$^3$H**: tritium
- **He**: helium
- **$^3$He**: helium-3
- **$^4$He**: helium-4
- **HPC**: heterotrophic plate count
- **K**: potassium
- **k**: net denitrification rate constant
- **KjilN**: ammonia plus organic nitrogen (Kjeldahl nitrogen)
- **MBAS**: methylene blue activate substances
- **Mg**: magnesium
- **Mn**: manganese
- **N**: nitrogen
\( \text{N}_2 \quad \text{nitrogen gas} \)
\( \text{N}-15 \quad \text{nitrogen-15} \)
\( ^{15}\text{N}/^{14}\text{N} \quad \text{nitrogen-15/nitrogen-14 ratio} \)
\( \text{Na} \quad \text{sodium} \)
\( \text{Ne} \quad \text{neon} \)
\( \text{NH}_3 \quad \text{ammonia} \)
\( \text{NH}_4 \quad \text{ammonium} \)
\( \text{NO}_2 \quad \text{nitrite} \)
\( \text{NO}_3 \quad \text{nitrate} \)
\( \text{NTA} \quad \text{nitrilotriacetic acid} \)
\( \text{O}_2 \quad \text{oxygen gas} \)
\( \text{O}-18 \quad \text{oxygen-18} \)
\( ^{18}\text{O}/^{16}\text{O} \quad \text{oxygen-18/oxygen-16 ratio} \)
\( \text{P} \quad \text{phosphorus} \)
\( \text{PO}_4 \quad \text{phosphate} \)
\( \text{PATH} \quad \text{three-dimensional distance to well} \)
\( \text{Prot} \quad \text{total protozoa} \)
\( \text{Salm} \quad \text{Salmonella} \text{ bacteria} \)
\( \text{SC} \quad \text{specific conductance} \)
\( \text{SiO}_2 \quad \text{silica} \)
\( \text{Size} \quad \text{average microbial size} \)
\( \text{SO}_4 \quad \text{sulfate} \)
\( \text{SFLU} \quad \text{specific fluorescence} \)
\( \text{SUVA} \quad \text{specific ultraviolet absorbance} \)
\( \text{TDS} \quad \text{total dissolved solids} \)
\( \text{Temp} \quad \text{temperature} \)
\( \text{THM} \quad \text{trihalomethane} \)
\( \text{TIME} \quad \text{stratigraphic-estimated travel time} \)
\( \text{TOC} \quad \text{total organic carbon} \)
\( \text{TOX} \quad \text{total organic halides} \)
\( \text{UV} \quad \text{ultraviolet absorbance} \)
\( \text{Zbot} \quad \text{depth to bottom of perforated interval} \)
\( \text{Zn} \quad \text{zinc} \)
\( \text{Ztop} \quad \text{depth to top of perforated interval} \)

Other abbreviations

\( \alpha \quad \text{level of significance} \)
\( \text{atm} \quad \text{atmospheres} \)
\( \text{AA} \quad \text{atomic adsorption} \)
\( \beta \quad \text{solubility isotope effect} \)
\( \text{cm}^3 \quad \text{cubic centimeters} \)
\( \text{cm}^3 \text{ STP/g} \quad \text{cubic centimeters per gram of water at standard temperature and pressure} \)
\( \text{cm}^3 \text{ STP/L} \quad \text{cubic centimeters per liter at standard temperature and pressure} \)
\( \text{day}^{-1} \quad \text{per day} \)
\( 0^\circ \text{C} \quad \text{degrees Celsius} \)
\( \text{DCP} \quad \text{direct-current plasma} \)
\( \epsilon \quad \text{isotope-separation factor} \)
\( \text{IC} \quad \text{ion chromatography} \)
\( \text{ICP} \quad \text{inductively-coupled plasma} \)
\( \text{GC} \quad \text{gas chromatography} \)
\( \text{GC/MS} \quad \text{gas chromatography/mass spectrometric detector} \)
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**Organizations**

DOHS  (California) Department of Health Services  
EPA  (U.S.) Environmental Protection Agency  
ITL  (USGS) Isotope Tracers Laboratory  
NRP  (USGS) National Research Program Laboratory  
NWIS  (USGS) National Water Information System  
NWQL  (USGS) National Water Quality Laboratory  
SIL  (USGS) Stable Isotope Laboratory  
USGS  U.S. Geological Survey  
WRDSC  Water Replenishment District of Southern California
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 (S) Well numbers consist of 15 characters and follow the format 002S011W018C004. In this report, well numbers are abbreviated and written 2S/11W-18C4. Wells in the same township and range are referred to only by their section designation, 18C4. The following diagram shows how the number for well 2S/11W-18C4 is derived.

Well-numbering diagram (Note: maps in this report use abbreviated well numbers such as “18C4”)
Use of Water-Quality Indicators and Environmental Tracers to Determine the Fate and Transport of Recycled Water in Los Angeles County, California

By Robert Anders and Roy A. Schroeder

ABSTRACT

Tertiary-treated municipal wastewater (recycled water) has been used to replenish the Central Basin in Los Angeles County for over 40 years. Therefore, this area provides an excellent location to investigate (1) the fate and transport of wastewater constituents as they travel from the point of recharge to points of withdrawal, and (2) the long-term effects that artificial recharge using recycled water has on the quality of the groundwater basin. The U.S. Geological Survey has been conducting such investigations in this area for about 10 years, beginning in 1992. For this investigation, a variety of inorganic, organic, and isotopic constituents were analyzed in samples from 23 production wells within 500 feet of the San Gabriel and Rio Hondo Coastal Basin Spreading Grounds, and tritium/helium-3, chlorofluorocarbons, dissolved gases, and nitrogen isotopes were analyzed in five multiple-well monitoring sites along a 10-mile flow path extending from just upgradient of the spreading grounds southward through the Central Basin.

Spearman rank-order correlation coefficients and level of significance calculated for about 40 water-quality indicators and several physical features show significant correlations between numerous inorganic and organic constituents that indicate the presence of recycled water. On the basis of a simple two-member mixing model, chloride, boron, ultraviolet absorbance at 254 nanometers, and excitation-emission fluorescence yielded the most reasonable estimates of wastewater percentages in the production wells. Tritium/helium-3 age determinations indicated that samples of groundwater tested range in age from less than 2 to more than 50 years. Chloride and boron concentrations, along with tritium/helium-3 age determinations, indicate more rapid recharge and (or) displacement of pre-existing ground water at the San Gabriel Coastal Basin Spreading Grounds than at the Rio Hondo Coastal Basin Spreading Grounds. Nitrogen-15 enrichment of the groundwater nitrate and dissolved nitrogen indicates that denitrification, an important process for the removal of nitrate at the shallower depths beneath the spreading grounds, continues to occur at distances of several miles from the spreading grounds and over a period of many years. Analysis of dissolved gases shows that areas that contain recycled water have no detectable methane, whereas methane is present in the native ground water older than 50 years. The absence of methane in the younger ground water suggests that artificial recharge using recycled water has the desirable effect of increasing slightly the redox potential of the groundwater basin. Finally, measured chlorofluorocarbon concentrations and tritium/helium-3 age determinations indicate that chlorofluorocarbon concentrations are markedly elevated above atmosphere-water equilibrium in ground water older than about 20 years but still young enough to contain recycled water.
INTRODUCTION

Artificial Recharge Using Wastewater

Managers of planned ground-water recharge programs facing water shortages intentionally recharge ground water using treated municipal wastewater effluent (recycled water) to supplement the existing water supply. The practice of artificially recharging ground-water basins is accomplished by delivering water, including recycled water, into large holding ponds or spreading grounds, where the water infiltrates through the unsaturated zone to the water table and moves downgradient to drinking-water aquifers. In Los Angeles County, for example, the Los Angeles County Department of Public Works has been augmenting the potable ground-water supply in the Central Ground-Water Basin (Central Basin) using recycled water supplied from the Water Replenishment District of Southern California (WRDSC) for over 40 years.

In the State of California, the California Department of Health Services (DOHS) regulates artificial recharge using recycled water under Title 22 of the California Administrative Code (Barclay's California Code of Regulations, 1978; California Department of Health Services, 1978). In addition to ensuring compliance with the common drinking-water standards for all constituents, these regulations state that the proportion of recycled water in the total recharge to an area is limited to 50 percent annually and to 35 percent within three contiguous years. However, as the demand for drinking water in Los Angeles County continues to increase, water agencies are seeking to increase the percent of recycled water currently permitted for artificial recharge. Recently, the DOHS proposed new regulations for increasing the recycled water contribution for ground-water recharge projects in California. These new regulations limit the amount of nitrogen compounds to 3 mg/L total nitrogen in the recycled water used for ground-water recharge and sets an unregulated- and unknown-contaminant control level at 0.5 mg/L total organic carbon (R. Hultquist, DOHS, oral commun., 2002). Furthermore, these new regulations establish a new compliance point at the mound formed beneath the infiltration basin during recharge, eliminating any removal of nitrogen or organic carbon during subsurface transport as part of the consideration to meet the newly established contaminant levels. These new regulations being proposed are due partially to the lack of information on the fate and transport of wastewater constituents as they travel from the point of recharge to points of withdrawal or the long-term effects that artificial recharge with recycled water has on the quality of the ground water in the basin.

Previous Studies

The earliest studies investigating water-quality changes related to sewage-contaminated ground water were conducted on Cape Cod at the Otis Air Base field site maintained by the U.S. Geological Survey (USGS), where the disposal of secondary-treated sewage onto rapid infiltration beds occurred between 1936 and 1979. According to Garabedian and LeBlanc (1988), the plume of sewage-contaminated ground water was characterized by elevated concentrations of several constituents including dissolved solids, boron, chloride, sodium, phosphorous, ammonium, nitrate, detergents, and, in some locations, volatile organic compounds. Subsequent studies investigated major processes that affect the transport and attenuation of contaminants in the plume (LeBlanc, 1996) and used $^3$H/$^3$He age determinations to delineate the age structure within the plume (Shapiro and others, 1999).

Vengosh and others (1994) utilized the boron isotopic signature of anthropogenic boron in wastewater to show that the source of sewage contamination in the Coastal Plain aquifer of Israel was the Dan Region Sewage Reclamation Project, located south of Tel Aviv, Israel. Furthermore, they monitored the chemical composition of recharge sewage effluent and associated contaminated ground water from the Dan Region Sewage Reclamation Project during 16 years of recharge operation (Vengosh and Keren, 1996). They observed that the recharge of a relatively high salinity effluent into a calcium bicarbonate ground water resulted in cation-exchange and adsorption reactions, although the effect of these reactions was limited to relatively short periods during the first stages of effluent arrival and to the exchangeable sodium percentage of clay minerals in the phreatic aquifer. However, they noted that once the exchangeable and absorbed sites became saturated, Na, K, and B were retained in the effluent and behaved conservatively similar to the chloride ion. Furthermore, they showed that degradation of organic matter takes place mainly in the unsaturated zone and only a small fraction of organic matter is removed during flow of contaminated ground water in the saturated zone.
Fryar and others (2000) investigated the use of playas that focus recharge for wastewater retention. Specifically, they confirmed that microbially mediated reduction limits nitrate loading to the ground water during recharge of industrial wastewater, sewage, and feedlot runoff to the regionally important High Plains (Ogallala) aquifer in the Southern High Plains, Texas. The evidence for microbially mediated reduction of nitrate during ground-water recharge was provided by $\delta^{15}N$ (delta nitrogen-15/nitrogen-14 ratio) values in ground water and soil gases, the presence of denitrifying and nitrate-respiring bacteria, and decreases in $\text{NO}_3/\text{Cl}$ and $\text{SO}_4/\text{Cl}$ ratios with depth in sediment cores.

Anders and Schroeder (1997) and Schroeder and others (2003) conducted three recharge experiments at a constructed research site located adjacent to a large recharge facility in Los Angeles County to better understand the processes that contribute to the changes in the quality of the recycled water during artificial recharge occurring over intervals of several days and distances (vertical and horizontal) of about 25 ft. These recharge experiments showed that the reduction of aqueous nitrogen was slightly greater than one-third and the reduction of dissolved organic carbon (DOC) was about one-third, although actual removal rates of aqueous nitrogen varied under different environmental and operational conditions but DOC did not.

A more comprehensive study of inorganic, isotopic, and organic analyses at 23 production wells within 500 ft of the San Gabriel and Rio Hondo Coastal Basin Spreading Grounds in the Montebello Forebay located in Los Angeles County was conducted to ascertain which constituents of wastewater origin could be identified and used as tracers to determine the presence and estimate the percent of recycled water (Barber and others, 1997; Schroeder and others 1997). No completely quantitative tracer was identified although chloride, boron, ultraviolet absorbance at 254 nanometers, and excitation-emission fluorescence seemed to yield the most reasonable estimates.

Leenheer and others (2001) focused on the nature and chlorine reactivity of organic constituents in recycled water before, during, and after recharge at the Montebello Forebay in Los Angeles County. They found that dissolved organic matter (DOM) in the recycled water was altered, or selected fractions were preferentially degraded, into less polar constituents in the reducing ground-water environment. In fact, the only organic compounds that survive infiltration are sulfonic acid metabolites of anionic surfactants. Furthermore, they found that the bulk of the DOM in infiltrated recycled water is refractory DOM (fulvic acid) derived from wastewater treatment and naturally occurring in the water supply. Finally, they found that the mixing of recycled water with ground water does not appear to degrade the ground-water quality with respect to the production of chlorinated disinfection byproducts in drinking water.

**Purpose and Scope**

The purpose of the investigation was to: (1) identify water-quality indicators of wastewater origin; (2) determine the presence and percent of recycled water in production wells and multiple-well monitoring sites; and (3) evaluate the long-term effects that artificial recharge using recycled water has on the quality of the ground water in the basin. The scope of the investigation included: (1) analysis of a variety of inorganic, organic, and isotopic constituents in 23 production wells located within 500 ft of the San Gabriel and Rio Hondo Coastal Basin Spreading Grounds in the Montebello Forebay in Los Angeles County; and (2) analysis of chlorofluorocarbons (CFCs), tritium/helium-3 ($^3\text{H}/^3\text{He}$), dissolved gases, and nitrogen isotopes in five multiple-well monitoring sites extending along a 10-mi flow path from just upgradient from the spreading grounds southward through the Central Basin.
Description of the Study Area

The study area transects about 25 mi in the eastern part of the Central Basin of Los Angeles County from the Whittier Narrows in the north to the West Coast Basin and lies between the San Gabriel River on the east and the Rio Hondo and Los Angeles River on the west (fig. 1). The water-bearing units contained in the Central Basin consist of unconsolidated to partly consolidated marine and nonmarine alluvial deposits of Holocene, Pleistocene, and Pliocene age (California Department of Water Resources, 1961). These water-bearing deposits compose a complex series of aquifers more than 1,800 ft thick in parts of the study area and are subdivided into four aquifer systems: Recent, Lakewood, Upper San Pedro, and Lower San Pedro, with no active pumping from the underlying Pico stratigraphic unit (Land and others, 2002; Reichard and others, 2003).

Artificial recharge occurs at the Montebello Forebay in the northern part of the Central Basin at two spreading grounds (constructed infiltration basins) that have a total area of recharge of almost 1,000 acres (fig. 1). One of the spreading grounds is adjacent to the San Gabriel River and includes a short unlined part of the downstream river channel. The other is adjacent to the Rio Hondo. The recharged water moves down and laterally from the spreading grounds southward in the direction of regional ground-water flow (Reichard and others, 2003). Aquifer material in the area of the spreading grounds consists of alluvial deposits of nearly all sands and gravels, with some relatively fine-grained materials of possibly limited lateral extent. Bookman-Edmonston Engineering, Inc., (1994) evaluated the potential traveltime of recycled water used for spreading in the Montebello Forebay to wells within 500 ft of the Rio Hondo and San Gabriel Coastal Basin Spreading Grounds using various flow paths. One flow path considered vertical flow at areas of emergence between aquifer units and horizontal flow within these aquifers. An alternative flow path combined a vertical flow path with a distance equal to the depth to the top perforation and a horizontal flow path with a distance equal to the distance of the well to the spreading grounds. This “minimum distance” flow path was considered for two geologic conditions: the clay layers are discontinuous, so vertical flow is through more permeable material; or the clay layers are continuous, so that vertical flow must go through the clay. On the basis of these various assumed flow paths, traveltime estimates in the area were found to range from 24 days to over 16 years.

Historically, most of the recharge in the area originated as precipitation in the mountains to the north and on the basin floor itself, infiltration from the Rio Hondo and San Gabriel River as they entered the basin at the Whittier Narrows from the inland San Gabriel Valley, and a small amount of underflow from the San Gabriel Valley. Artificial recharge using imported water from the Colorado River began in the early 1950s and continued until about 1975. Imported water from northern California was used for artificial recharge after the completion of the State Water Project in the late 1960s. The delivery of recycled water (tertiary-treated wastewater from treatment facilities located north of the Montebello Forebay and outside the Central Basin) began in 1962 (fig. 2). Tertiary treatment includes chlorination-dechlorination and dual-media (charcoal and sand) filtration. In general, the percentage of recycled water has steadily increased with time as the proportion of imported water has decreased, and since about 1991 recycled water has averaged about 30 percent of all the water used to replenish the underlying aquifers annually (fig. 3).

Acknowledgments

The collection of data from the 23 production wells was made possible with the cooperation and support of several local water purveyors. Property access for the five multiple-well monitoring sites was granted by the Downey Unified School District, city of Lakewood, Pico Water District, city of Pico Rivera, and the Los Angeles County Department of Public Works. The Water Replenishment District of Southern California provided cooperative funding for this study.
Figure 1. Location of the study area in Los Angeles County, California, and a photograph of the Rio Hondo Coastal Basin Spreading Grounds in the Montebello Forebay, looking south toward the Pacific Ocean.
Figure 2. Source and amount of water recharged at the Rio Hondo and San Gabriel Coastal Basin Spreading Grounds, Los Angeles County, California.
Figure 3. Percentages of water recharged at the Rio Hondo and San Gabriel Coastal Basin Spreading Grounds, Los Angeles County, California.
FIELD AND ANALYTICAL METHODS

Production Wells Adjacent to Spreading Grounds

USGS personnel sampled 23 production wells within 500 ft of the San Gabriel and Rio Hondo Coastal Basin Spreading Grounds in the Montebello Forebay located in Los Angeles County, apparent background water-quality from a production well about 7 mi northeast of the spreading grounds in the San Gabriel Valley, and recycled water at the research site originating from a wastewater-treatment plant used to augment recharge by delivery to the spreading grounds (fig. 4). The 23 production wells and the background well range in depth from 250 to more than 900 ft, and some of the perforated intervals are as much as several hundred feet (fig. 5). All production wells and the background well were being pumped at the time of sampling at rates ranging from 500 to 3,000 gal/min. Samples were collected from taps located between the wellhead and any holding tanks and before any wellhead treatment, such as coagulation or chlorination.

All water samples were collected using USGS field-sampling procedures (Sylvestre and others, 1990). Field measurements of pH were made using an Orion 250A meter with an Orion model 9106 pH combination electrode calibrated daily using pH 4, 7, and 10 standards. Field specific-conductance measurements were made using a temperature compensated conductivity meter (Orion model 124) calibrated daily against standard reference solutions. Dissolved-oxygen measurements were performed by Winkler titration (Fishman and Friedman, 1989). Water and air temperatures were measured using a hand-held alcohol-filled thermometer.

The water samples were analyzed for major and minor inorganic constituents, nutrients, several isotopes, and selected microbial populations. Water samples for analysis of common inorganic constituents and nutrients were pressure-filtered in the field through inline 0.45-µm polyether sulfone cartridge filters from Gelman Scientific. Aliquots for inorganic chemical analysis were dispensed into clear polyethylene bottles for storage after the bottle was rinsed three times. Bottles used for analysis of cations were acidified to approximately pH 2 by addition of nitric acid. Aliquots for nutrient analysis were distributed into 125-mL, pre-rinsed, opaque, polyethylene bottles and placed on ice to minimize microbial alteration. Inorganic chemical and nutrient analyses were done by the USGS National Water-Quality Laboratory in Arvada, Colorado, using methods described generally by Fishman (1993), Timme (1994), and Struzeski and others (1996).

Samples for analysis of stable hydrogen and oxygen isotopes were collected into 60-mL glass bottles and sealed with a polyseal cap to minimize evaporative loss and exchange with the atmosphere. These samples were analyzed at the USGS Isotope Laboratory in Reston, Virginia, using methods described by Epstein and Mayeda (1953) and Coplen and others (1991). Stable hydrogen and oxygen isotopes concentrations are expressed in terms of per mil relative to Vienna standard mean Ocean Water (Gonfiantini, 1984), and the estimate of precision (two-sigma) is 2 and 0.2 per mil (‰), respectively. Three liters of water for determination of nitrogen isotopes were collected at each production well to ensure availability of sufficient nitrogen for analyses. The samples were collected into three 1-L polyethylene bottles, sealed with a polyseal cap, and frozen until analyzed using methods described by Kendall and Grim (1990), Böhlke and Coplen (1995), and Böhlke and Denver (1995). Tritium (³H) samples were collected in 1-L polyethylene bottles, sealed with polyseal caps, and analyzed at the USGS Tritium Laboratory in Menlo Park, California, by liquid-scintillation counting following electrolytic enrichment (Ostlund and Dorsey, 1977). The tritium content of water is reported in terms of tritium units (TU) with a two-sigma estimate of precision. Each TU is equal to one atom of ³H in 10¹⁸ atoms of hydrogen. Water samples intended for analysis of the stable isotope of boron-11 were collected in 250-mL polyethylene bottles and measured at the USGS Isotope Laboratory in Menlo Park, California, by negative-ion ratio mass spectrometry. The results are reported in per mil relative to the NBS-951 boric acid standard and are precise (two-sigma) to within 0.5 per mil (‰) (T. Bullen, USGS, oral commun., 1996).
Figure 4. Location of 23 production wells near the spreading grounds, background production well upgradient from the Whittier Narrows, and the research site, Los Angeles County, California.
Figure 5. Depth and perforated interval of selected production wells in Los Angeles County, California.
Formalin-preserved and raw water samples were collected in 2.5-L polyethylene bottles and analyzed for selected microbial populations at the USGS Subsurface Microbiology Laboratory in Boulder, Colorado. Formalin-preserved samples were analyzed for total bacterial and protozoan numbers by acridine orange direct counts using epifluorescence microscopy (Harvey and others, 1984), and sizing of both bacteria and protozoa were done by computer-coupled image analyses of the captured epifluorescent images (Harvey and others, 1996). Raw samples were analyzed for heterotrophic (utilize organic compounds as electron donors), total coliform, and Salmonella bacteria populations by standard methods (American Public Health Association, 1985; U.S. Environmental Protection Agency, 1996). It is emphasized that water samples were not analyzed until after the U.S. EPA-suggested maximum holding time for samples of 48 hours. Therefore, these data should be used for comparative purposes only and not for regulatory purposes.

Finally, organic constituents were analyzed by the hierarchical approach described by Barber and others (1997), Leenheer and others (2001), and Schroeder and others (2003). The hierarchical approach is designed to comprehensively characterize organic mater in recycled water.

**Downgradient Monitoring Wells**

Major and minor inorganic constituents, nutrients, chlorofluorocarbons (CFCs), tritium/helium-3 ($^3$H/$^3$He), dissolved gases, and nitrogen isotopes were evaluated from water and gas samples collected from five multiple-well monitoring sites aligned in the direction of ground-water flow from the San Gabriel and the Rio Hondo Coastal Basin Spreading Grounds (fig. 6). The five multiple-well monitoring sites contained 28 monitoring wells screened over short intervals (generally 20 ft) and constructed of small-diameter (generally 2 in.) PVC casing (Land and others, 2002). Other water samples were collected from galvanized-steel well points (2.5-ft screens) and 6-in. stainless steel implants (Geoprobe Systems, Salina, Kans.) installed at a small constructed research site located adjacent to the San Gabriel Coastal Basin Spreading Grounds (fig. 4).

Prior to the collection of water and gas samples, all multiple-well monitoring sites were purged by removing three casing volumes using a variable-speed submersible Redi-Flo2 sampling pump (Grundfos Pumps Corp., Clovis, Calif.). During the purging process, specific conductance, pH, and temperature were monitored using portable pH and conductivity meters and hand-held alcohol-filled thermometers until all measurements had stabilized. In a few cases, dissolved oxygen also was monitored. After the purging process was completed, the Redi-Flo2 pump was removed and replaced with a stainless steel submersible Model 1400 piston pump (Robert Bennett Co., Amarillo, Tex.). The sampling apparatus, which was developed by Busenberg and Plummer (1992) for the collection of CFCs and dissolved gases, was attached to the Bennett pump with ¼-in refrigeration-grade copper tubing. The apparatus prevents contact of the water sample with the atmosphere.
Figure 6. Location of multiple-well monitoring sites and line of hydrogeologic section A–A' along approximate ground-water flow path.
Prior to the collection of water samples for analysis of trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), and chlorotrifluoromethane (CFC-113), water samples were collected and filtered for analysis of common inorganic constituents, nutrients, and selected isotopes through a short length of tubing attached to the sampling apparatus following the same field-sampling procedures used for the production wells. In addition, samples were collected for analysis of several dissolved gases in 150-mL glass bottles and sealed with a rubber septum after making sure no bubbles were adhering to the sides of the bottle. The dissolved gas samples were analyzed at the USGS CFC Laboratory in Reston, Virginia, for nitrogen (N₂), argon (Ar), methane (CH₄), oxygen (O₂) and carbon dioxide (CO₂). After the collection of water and dissolved-gas samples was completed, the flow was switched to allow water to be routed through the sampling apparatus for collection of CFCs using procedures described by Busenberg and Plummer (1992). Water samples were collected in glass ampoules after flushing the ampoule using ultra-pure nitrogen gas; after collection, the ampoules were flame-sealed. Five replicate ampoules were collected from each sampling location and analyzed at the USGS CFC Laboratory in Reston, Virginia, using a purge and trap gas chromatography with an electron-capture detector (Busenberg and Plummer, 1992). CFC concentrations have an analytical uncertainty of approximately 3 percent for concentrations greater than 50 pg/kg and approach 50 percent at the detection limit of 1 pg/kg (Szabo and others, 1996). After the collection of samples for CFCs and dissolved gases was completed, the copper tubing was disconnected from the sampling apparatus. Then approximately 40 mL of water for helium isotope analysis was collected by sealing off a portion of the end of the copper tubing with stainless steel pinch-off clamps while maintaining the water in the copper tube under pressure to avoid degassing of the sample. Helium isotopes were analyzed by Dr. Robert Poreda at the University of Rochester Department of Earth and Environmental Sciences in Rochester, New York. Water and gases were extracted from the copper tube using a vacuum extraction system. After purification and separation of He from Ne by means of a cryogenic cold trap filled with charcoal, the helium-3 (³He) concentration and the helium-3/helium-4 (³He/⁴He) ratio were measured using a dedicated He-isotope mass spectrometer (Poreda and others, 1988). Helium isotope concentrations are reported in TUs. The analytical uncertainty of the ⁴He data is about ±2 percent; that of the ³He/⁴He ratios is about ±1 percent.

Listed in table 1 are the constituents analyzed during this study, reporting limits and precision, laboratory where analyses were done, and the principal reference to methods. Quality-assurance procedures included: (1) laboratory analysis of samples in duplicate; (2) review of water-quality data to determine outliers; (3) the collection of samples from background sites; and (4) the comparison of water-quality data from multiple sampling rounds.
### Table 1. Analyses performed on water samples collected in Los Angeles County, California, 1996–1999

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Where analysis was performed</th>
<th>Analytical method</th>
<th>Reporting limit</th>
<th>Approximate precision</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>Field</td>
<td>Electrometric</td>
<td>1 µS/cm</td>
<td>2%</td>
<td>Wilde and Radtke (1998)</td>
</tr>
<tr>
<td>pH</td>
<td>Field</td>
<td>Electrometric</td>
<td>0–14</td>
<td>0.05</td>
<td>do.</td>
</tr>
<tr>
<td>Temp</td>
<td>Field</td>
<td>Thermometer</td>
<td>°C</td>
<td>0.5</td>
<td>—</td>
</tr>
<tr>
<td>TDS</td>
<td>NWQL</td>
<td>mg/L</td>
<td></td>
<td></td>
<td>Fishman (1993), Timme (1994)</td>
</tr>
<tr>
<td>Ca</td>
<td>NWQL</td>
<td>ICP</td>
<td>.1 mg/L</td>
<td>4%</td>
<td>do.</td>
</tr>
<tr>
<td>Mg</td>
<td>NWQL</td>
<td>ICP</td>
<td>.1 mg/L</td>
<td>4%</td>
<td>do.</td>
</tr>
<tr>
<td>Na</td>
<td>NWQL</td>
<td>ICP</td>
<td>.6 mg/L</td>
<td>10%</td>
<td>do.</td>
</tr>
<tr>
<td>K</td>
<td>NWQL</td>
<td>AA</td>
<td>.2 mg/L</td>
<td>6%</td>
<td>do.</td>
</tr>
<tr>
<td>SiO₂</td>
<td>NWQL</td>
<td>ICP</td>
<td>.1 mg SiO₂/L</td>
<td>7%</td>
<td>do.</td>
</tr>
<tr>
<td>ALK</td>
<td>Field</td>
<td>Titration</td>
<td>1 mg/L</td>
<td>2%</td>
<td>Wilde and Radtke (1998)</td>
</tr>
<tr>
<td>SO₄</td>
<td>NWQL</td>
<td>IC</td>
<td>.3 mg/L</td>
<td>2%</td>
<td>Fishman (1993), Timme (1994)</td>
</tr>
<tr>
<td>Cl</td>
<td>NWQL</td>
<td>IC</td>
<td>.3 mg/L</td>
<td>3%</td>
<td>do.</td>
</tr>
<tr>
<td>Br</td>
<td>NWQL</td>
<td>Colorimetric</td>
<td>.01 mg/L</td>
<td>5%</td>
<td>do.</td>
</tr>
<tr>
<td>NO₃</td>
<td>NWQL</td>
<td>Colorimetric</td>
<td>.05 mg N/L</td>
<td>4%</td>
<td>do.</td>
</tr>
<tr>
<td>NO₂</td>
<td>NWQL</td>
<td>Colorimetric</td>
<td>.01 mg N/L</td>
<td>10%</td>
<td>do.</td>
</tr>
<tr>
<td>NH₃</td>
<td>NWQL</td>
<td>Colorimetric</td>
<td>.01 mg N/L</td>
<td>3%</td>
<td>do.</td>
</tr>
<tr>
<td>KjIN</td>
<td>NWQL</td>
<td>Colorimetric</td>
<td>.2 mg N/L</td>
<td>6%</td>
<td>Patton and Fruit (1992)</td>
</tr>
<tr>
<td>PO₄</td>
<td>NWQL</td>
<td>Colorimetric</td>
<td>.01 mg P/L</td>
<td>10%</td>
<td>do.</td>
</tr>
<tr>
<td>DO</td>
<td>Field</td>
<td>Winkler titration</td>
<td>.2 mg O₂/L</td>
<td>0.2</td>
<td>Fishman and Friedman (1989)</td>
</tr>
<tr>
<td>Fe</td>
<td>NWQL</td>
<td>ICP</td>
<td>3 µg/L</td>
<td>10%</td>
<td>Fishman (1993), Timme (1994)</td>
</tr>
<tr>
<td>Mn</td>
<td>NWQL</td>
<td>ICP</td>
<td>1 µg/L</td>
<td>11%</td>
<td>do.</td>
</tr>
<tr>
<td>Zn</td>
<td>NWQL</td>
<td>ICP</td>
<td>3 µg/L</td>
<td>4%</td>
<td>do.</td>
</tr>
<tr>
<td>δD</td>
<td>SIL</td>
<td>MS</td>
<td>per mil</td>
<td>2</td>
<td>Coplen and others (1991)</td>
</tr>
<tr>
<td>δ¹⁸O</td>
<td>SIL</td>
<td>MS</td>
<td>per mil</td>
<td>0.2</td>
<td>do.</td>
</tr>
<tr>
<td>δ¹¹B</td>
<td>ITL</td>
<td>MS</td>
<td>per mil</td>
<td>0.2</td>
<td>Vengosh and others (1994)</td>
</tr>
<tr>
<td>δ¹⁵N</td>
<td>SIL</td>
<td>MS</td>
<td>per mil</td>
<td>0.2</td>
<td>Kendall and Grim (1990)</td>
</tr>
<tr>
<td>exCl</td>
<td>—</td>
<td>calculated</td>
<td>3 mg/L</td>
<td>3%</td>
<td>Schroeder and others (1997)</td>
</tr>
<tr>
<td>exB</td>
<td>—</td>
<td>calculated</td>
<td>4 mg/L</td>
<td>3%</td>
<td>do.</td>
</tr>
<tr>
<td>B</td>
<td>NWQL</td>
<td>DCP</td>
<td>10 mg/L</td>
<td>3%</td>
<td>Fishman (1993), Timme (1994)</td>
</tr>
<tr>
<td>Parameter</td>
<td>Where analysis was performed</td>
<td>Analytical method</td>
<td>Reporting limit</td>
<td>Approximate precision</td>
<td>Reference</td>
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<tr>
<td>-------------------------</td>
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<td>-------------------</td>
<td>-----------------</td>
<td>-----------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>calN “Back-calculated” nitrogen</td>
<td>—</td>
<td>calculated</td>
<td>.1 mg N/L</td>
<td>0.1</td>
<td>Schroeder and others (1997)</td>
</tr>
<tr>
<td>DOC</td>
<td>NRP</td>
<td>Wet oxidation</td>
<td>.1 mg C/L</td>
<td>0.1</td>
<td>Barber and others (1997)</td>
</tr>
<tr>
<td>TOC</td>
<td>NRP</td>
<td>Wet oxidation</td>
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</tr>
<tr>
<td>UV</td>
<td>NRP</td>
<td>Spectrometry</td>
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<tr>
<td>SUVA UV absorbance/DOC</td>
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<td>calculated</td>
<td>—</td>
<td>—</td>
<td>do.</td>
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<tr>
<td>MBAS Methylene blue active substances</td>
<td>NRP</td>
<td>Colorimetric</td>
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<tr>
<td>FLUO Excitation-emission fluorescence</td>
<td>NRP</td>
<td>Spectrometry</td>
<td>µg/L</td>
<td>1 do.</td>
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<td>—</td>
<td>calculated</td>
<td>—</td>
<td>—</td>
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<td>NTA Nitrilotriacetic acid</td>
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<td>GC</td>
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<tr>
<td>EDTA Ethylenediaminetetraacetic acid</td>
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<td>GC</td>
<td>1 µg/L</td>
<td>1 do.</td>
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<tr>
<td>APEC Alkylphenol polyethoxy carboxylate</td>
<td>NRP</td>
<td>GC</td>
<td>1 µg/L</td>
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<td>THM Total trihalomethanes</td>
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<td>GC/MS</td>
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<td>TOX Total organic halides</td>
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<td>Ztop Depth to top of perforated interval</td>
<td>Field</td>
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<td>ft</td>
<td>1</td>
<td>Bookman-Edmonston Engineering (1994)</td>
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<tr>
<td>Zbot Depth to bottom of perforated interval</td>
<td>Field</td>
<td>published</td>
<td>ft</td>
<td>1 do.</td>
<td>do.</td>
</tr>
<tr>
<td>DIST Horizontal distance to well</td>
<td>Field</td>
<td>published</td>
<td>ft</td>
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<tr>
<td>PATH Length of flow path to well</td>
<td>Field</td>
<td>published</td>
<td>ft</td>
<td>10 do.</td>
<td>do.</td>
</tr>
<tr>
<td>TIME Time of ground-water flow to well</td>
<td>Field</td>
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<tr>
<td>³H Tritium</td>
<td>ITL</td>
<td>Liquid scintillation</td>
<td>.1 TU</td>
<td>10%</td>
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WATER-QUALITY INDICATORS AND ENVIRONMENTAL TRACERS

In Los Angeles County, recycled water has been used to augment the potable ground-water supply in the Central Basin since 1962. Therefore, this area provides an excellent location to investigate the transport and fate of wastewater constituents as they travel from the point of recharge to points of withdrawal and the long-term effects that artificial recharge with recycled water has on the quality of the ground water in the basin. The USGS, in cooperation with the WRDSC, has been conducting such investigations in this area beginning in 1992. The investigation included the analysis of a wide variety of inorganic, organic, and isotopic constituents in 23 production wells located within 500 ft of the San Gabriel and Rio Hondo Coastal Basin Spreading Grounds in the Montebello Forebay in Los Angeles County (fig. 4); and chlorofluorocarbons (CFCs), tritium/helium-3 (\(^3\)H/\(^3\)He), dissolved gases, and nitrogen isotopes in five multiple-well monitoring sites extending along a 10-mi flow path from just upgradient from the spreading grounds southward through the Central Basin (fig. 6).

Production-Well Results

Well information, field measurements, and inorganic, organic, and microbiological data for samples collected in May 1996 from the 23 production wells located within 500 ft of the San Gabriel and Rio Hondo Coastal Basin Spreading Grounds, and an upgradient background well, are given in table 2. The background production well is considered to represent water free of most anthropogenic effects because it is outside the Central Basin and the top of the perforated interval is over 1,000 ft below land surface. These data, previously reported in Schroeder and others (1997) and Barber and others (1997), include chloride, boron, nitrate, ultraviolet absorbance at 254 nanometers, and excitation-emission fluorescence, which are wastewater constituents used to determine presence of recycled water and wastewater percentages in production wells.

Statistical Relations

Nonparametric Test

Spearman rank-order correlation coefficients, \(\rho\), were calculated for 45 constituents in the 23 production wells using data in table 2 to determine which constituents in recycled water are present in the well water and ascertain the statistical strength of the recycled-water signal for each constituent. This statistical test is appropriate for a general evaluation such as this because of the large differences in range of values between constituents and non-normal distribution for most, if not all, of the constituents. A few of the constituents were then chosen for more detailed investigation using parametric tests to estimate percentages of the constituent derived from recycled water.

Spearman rank-order coefficients are linear correlations of the ranks of the variables. The method used for nonparametric or rank correlation is to replace the value of each variable by the value of its rank among all the other variables in the sample, and then the resulting list of numbers will be drawn from a perfectly known distribution function (Press and others, 1992). Furthermore, the significance of a nonzero value of the rank-order correlation coefficient is distributed approximately as a Student's distribution with \(N-2\) degrees of freedom. The key point is that this approximation does not depend on the original distribution of each variable; it is always the same approximation. The Statistical Analysis System (SAS) (Statistical Analysis Software, 1982), a computer system for data analysis, was used to compute the Spearman rank-order coefficients for the 45 constituents.
Table 2. Well information, field measurements, and water-quality data for 23 production wells, a background well (B), and recycled water (E, effluent) in Los Angeles County, California, 1996

[Number below the constituent or property is the data parameter code, which is a 5-digit number used in the U.S. Geological Survey computerized data system, National Water Information System (NWIS), to uniquely identify a specific constituent or property; µS/cm, microsiemens per centimeter at 25°C; °C, degrees Celsius; HPC, heterotrophic plate count; ft, feet below land surface; mg/L, milligrams per liter; µg/L, micrograms per liter; #/mL, number per milliliter; µm, micrometers; nm, nanometers; gal/min, gallon per minute; per mil, parts per thousand; TU, tritium units; NGVD, National Geodetic Vertical Datum of 1929; <, actual value less than value shown; —, no data]

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<th>Altitude of land surface datum, ft above NGVD (72000)</th>
<th>Flow rate, gal/min (00059)</th>
<th>Oxygen, dissolved, mg/L (00300)</th>
<th>pH, water, whole, field, standard units (00400)</th>
<th>Specific conductance, field, µS/cm (00095)</th>
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Table 2. Well information, field measurements, and water-quality data for 23 production wells, a background well (B), and recycled water (E, effluent) in Los Angeles County, California, 1996—Continued

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Table 2. Well information, field measurements, and water-quality data for 23 production wells, a background well (B), and recycled water (E, effluent) in Los Angeles County, California, 1996—Continued

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Table 2. Well information, field measurements, and water-quality data for 23 production wells, a background well (B), and recycled water (E, effluent) in Los Angeles County, California, 1996—Continued

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Results of the nonparametric test are summarized in Table 3. Correlation coefficients (multiplied by 100 to convert decimal values to whole numbers) are listed for each pair of constituents above the diagonal that divides the table. Level of significance ($\alpha$) is designated below the diagonal by three stars ($\alpha < 0.001$; strongly significant), two stars ($\alpha = 0.001$ to 0.05; highly significant), and one star ($\alpha = 0.05$ to 0.10; moderately significant); and referred to as strong, moderate, and weak in subsequent discussions. The three levels of significance are related to the correlation coefficients by the following: $\alpha < 0.001$, $\rho > 0.65$; $\alpha = 0.001$ to 0.05, $\rho = 0.65$ to 0.40; and $\alpha = 0.05$ to 0.10, $\rho = 0.40$ to 0.35. The 45 constituents are listed in order as groups that consist of inorganic species, trace elements, isotopes, “calculated” values, microbes, organic indicators, and physical features.

High numbers of significant correlations are readily apparent within certain groups; for example, several inorganic species and organic indicators. Correlations for more than half of the inorganic pairs and half of the organic pairs are strongly significant ($\alpha < 0.001$). The high number for inorganic species is at least partly an autocorrelation of all major ions with dissolved-solids concentration (TDS) and specific conductance (SC). As expected, correlations are weaker, but still significant, for inorganic species that are less conservative, such as calcium (Ca), magnesium (Mg), alkalinity (ALK), and sulfate (SO$_4$).

The high number of significant correlations for organic pairs is explained by the fact that the organic compounds and broad organic indicators have a common source in the recycled water. In fact, only trihalomethanes (THMs) are uncharacteristic in that they exhibit few significant correlations (2 out of 10 pairs) within the organic group. This could mean that there are THM sources other than chlorinated recycled water, or that THM biodegradation and (or) sorption differs greatly from that of the other constituents tested.

When the two groups are considered together, about half the inorganic-organic pairs exhibit statistically significant correlation; but the number is much higher for sodium and chloride. This reflects the addition of salt to wastewater during the treatment process (Nightingale and McCormick, 1985; Umari and others, 1995). In fact, the correlation coefficients between chloride and organic pairs are increased further when bromide is used to remove natural chloride and yield “excess” chloride (exCl), as discussed in the section “Two-Member Mixing Models for Selected Constituents.” Note that the absence of any significant correlations between bromide (Br) and organic constituents supports the method used to calculate “excess” chloride. Two other inorganic constituents, “excess” boron (exB) and “back-calculated” nitrogen (calN) assumed to be nitrate, also exhibit high numbers of significant correlations with organic pairs and, therefore, are also discussed in detail in the same section.

Three trace elements—iron (Fe), manganese (Mn), and zinc (Zn)—were analyzed in the production wells. Concentrations of these trace elements in recycled water (effluent) are 43, 17, and 160 µg/L, respectively (see Table 2). Although zinc is abundant in wastewater, experiments at the constructed research site indicate that it is reduced by about two-thirds over a distance of less than 25 ft during recharge (Schroeder and others, 2003). Hence, it is not surprising that zinc in the production wells shows no significant correlations with any other constituents that are indicators of recycled water. Elevated iron and manganese concentrations are present in some of the wells, but they are unlikely to have their origin in recycled water. Rather they likely are both mobilized or removed from aquifer soils in response to local environmental conditions. Fe and Mn are moderately correlated (Table 3), reflecting their similar behavior under reducing (soluble) and oxidizing (insoluble) conditions.
Table 3. Spearman rank-order correlation matrix

[Explanation for abbreviations or constituents or properties found in “Conversion Factor” section of report; correlation coefficients (multiplied by 100 to convert decimal values to whole numbers) are listed for each pair of constituents above the diagonal that divides the table; level of significance is designated below the diagonal by three stars (α<0.001; strongly significant), two stars (α=0.001 to 0.05, highly significant), and one star (α=0.05 to 0.10; moderately significant, — (α>0.10))

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Table 3. Spearman rank-order correlation matrix—Continued
Only weak to moderate negative correlations exist in the production wells between several of the organic indicators and physical features such as depth to top (Ztop) and bottom (Zbot) of the perforated interval, stratigraphic-estimated traveltime (TIME), and tritium activity (\( ^3 \)H). The stratigraphic-estimated traveltime is the less of the traveltime for the merged aquifer flow path and the “minimum distance” flow path provided by Bookman-Edmonston Engineering, (1994) (described in the section “Description of Study Area”). Furthermore, very few significant correlations exist between several of the organic indicators and either horizontal (DIST) or three-dimensional (PATH) distance between the spreading grounds and the production wells. Perhaps the most important observation is the lack of a significant correlation between stratigraphic-estimated traveltime and tritium activity (\( \rho = 0.14 \)), presumably owing to the fact that the production wells draw water from various depths and ages owing to large perforated interval.

Six microbial indicators were analyzed and an interpretation was made; however, some uncertainty exists in the data because samples were not analyzed within the 48-hour holding time that is customary for compliance testing. Furthermore, data from microbial analyses are inherently much more variable than are chemical data; therefore, several more samples collected over a longer period would be required for complete confidence. It is noted that the microbial data exhibit few significant correlations, even within the microbial group itself. Furthermore, the microbial data exhibit no significant correlations with factors such as traveltime, distance between the production wells and spreading grounds, or tritium activity, which would be needed to indicate transport from the spreading grounds. This lack of significant correlation suggests that the microbial activity identified in samples from the production wells was from local sources, and not due to transport with water from the spreading grounds. Weak and moderate positive correlations do exist between heterotrophic plate count (HPC) and several organic constituents. This suggests that perhaps the organic matter might serve as substrate stimulating additional activity, either in the production well or in the sample container after collection.

**Graphical Representation**

Although nonparametric statistical tests are useful in indicating sources of wastewater constituents, they cannot be used to estimate percentages of recycled water in wells or to quantify trends. For that reason, percentages of recycled water were calculated using a simple two-member mixing model, which is an arithmetic parametric test. Using the two-member mixing model, a value of zero-percent recycled water is assigned to the lowest concentration (or highest value where appropriate) observed for each constituent in the 23 production wells and 100 percent is assigned to the concentration measured in recycled water (effluent in table 2). The method provides a graphical display that permits visual comparison and contrast between constituents and wells; however, the non-normal distribution among the constituents indicates the analysis cannot provide a precise relation to sources. The relation between percent of recycled water and 22 selected wastewater constituents for each of the 23 production wells is shown in appendix A; the relation between percent of recycled water and 22 wastewater constituents among the 23 production wells is shown in appendix B.

The most important observation from these data is that many of the constituents most closely identified by their significant correlations as indicators of recycled water co-vary fairly closely between wells. Several inorganic and organic indicators show that the percentage of recycled water is higher in the eight production wells (wells 16 through 23) adjacent to the San Gabriel Coastal Basin Spreading Grounds (data in lower rows of table 2 and displayed on right side of figure 5 and appendix B) than in the 15 production wells adjacent to the Rio Hondo Coastal Basin Spreading Grounds. The percentage of recycled water calculated using Cl and B concentrations is about 60 percent in several of the wells near the San Gabriel Coastal Basin Spreading Grounds. The percentage of recycled water calculated using Cl and B concentrations is about 60 percent in several of the wells near the San Gabriel Coastal Basin Spreading Grounds (using data in table 2). These percentages are substantially more than the 35 percent recycled water that is spread annually and suggests that this side of the recharge facilities may represent a greater proportion of recycled water, whereas the Rio Hondo Coastal Basin Spreading Grounds may represent a greater proportion of imported water and (or) stormwater.
The data displayed in the appendixes also show that percentages calculated from organic indicators are generally lower than for B and Cl, suggesting the partial removal of organic constituents. Given the finding that about one-third of organic carbon is removed from recycled water over distances of only several feet and travel times of only a few days on the basis of experiments at the constructed research site (Schroeder and others, 2003), it is very plausible that additional removal or organic constituents occurs as ground-water traveltime and distance increase to these nearby production wells. Furthermore, if there were no additional degradation of organic carbon, conservative tracers such as B and Cl indicate that DOC concentrations in production wells would be about double the observed concentrations, the highest of which is only 1.6 mg/L (from data in table 2).

Data on specific organic compounds (except for THMs) also suggest preferential removal. For example, ethylenediaminetetraacetic acid (EDTA) concentration is low (maximum is 4 µg/L) or nondetectable (<0.2 µg/L) in multiple-well monitoring sites in the Central Basin where ground water ranges in age from about 3 to 30 years (Leenheer and others, 2001) but equals or exceeds 4 µg/L in all but 2 of the 23 production wells. The markedly higher concentrations in production wells in comparison with multiple-well monitoring sites suggests a mixture of very young ground water with substantial EDTA and older (but still younger than 50 years based on tritium values) ground water that contains little or no EDTA because it has been degraded or sorbed onto the aquifer soil.

If calculations based on THM data were presented graphically they would show recycled-water percentages exceeding 200 percent for wells 4, 17, and 18 because the THM concentration in these three wells is more than double the THM concentration in recycled water, which is 17 µg/L. Total organic halide (TOX) concentration is nearly 10 times higher than THM concentration in recycled water (from effluent data in table 2); therefore, degradation of TOX is a potential source of THM after recharge. However, the stratigraphic-estimated traveltimes for wells 4, 17, and 18 are 2.6, 4.7, and 5.6 years (Bookman-Edmonston Engineering, 1994), respectively, and there is nothing distinctive about their water quality or physical features that would suggest post-recharge formation of THMs in these or the other production wells. Regardless of the source, it should be noted that the THM concentration in these three wells is still less than half the regulatory MCL (maximum contaminant level) of 80 mg/L for drinking water.

**Two-Member Mixing Models for Selected Constituents**

An alternative approach to calculate recycled-water percentages in the production wells would be to use concentrations in the recycled water and the upgradient background well (26K3) in a two-member mixing model. In fact, low dissolved solids, high dissolved oxygen, and undetectable tritium are consistent with the absence of anthropogenic effects in the background well. However, ground water from the San Gabriel Valley represents only a minor source (as deep underflow) of either historical or current total recharge to the Montebello Forebay (Schroeder and others, 1997). Therefore, other methods were developed to represent ground water that is free of artificial recharge, although assigning a single background concentration and ignoring the contribution of ground water from the San Gabriel Valley may be an oversimplification.
“Excess” Chloride and Boron

Two constituents added to water during the treatment process, Cl and B, were evaluated as tracers or recycled water in the subsurface. If unfractionated sea salt in atmospheric precipitation is the sole source of chloride (Cl) and bromide (Br), and both halides exhibit completely conservative physical and chemical behavior during subsurface transport, the Cl/Br mass ratio in ground water would be equal to 287, the ratio found in seawater (Schroeder and others, 1993). Cl is indeed enriched relative to Br in the production wells, and in the recycled water itself (Schroeder and others, 1997). Deviation from a seawater-dilution line can be used to estimate recycled-water percentages, designated “excess” chloride, if it is assumed that the process of water reuse adds only Cl but no Br, using the following equation:

\[ [Cl] = (120 - x)287[Br] \]  

where

\[ [Cl] \] = chloride concentration measured in production well [mg/L];  
\[ 120 \] = chloride concentration measured in recycled water [mg/L];  
\[ 287[Br] \] = chloride concentration in production well without recycled water [mg/L]; and  
\[ x \] = calculated percentage of recycled water [%].

Similarly, boron (B) is added to the recycled water in large amounts during water reuse, primarily owing to its presence as a softener in detergents. It is used in a two-member mixing model to calculate recycled water percentages, designated “excess” boron, with the effluent concentration of 399 µg/L being one end member. The two-member mixing model assumes that the lowest concentration measured in any of the 23 production wells (93 µg/L in well 23) represents conditions in which there is no contribution from recycled water. The percentage of recycled water can be estimated using the following equation:

\[ [B] = x(399) + (1 - x)[B_{Native}] \]  

where

\[ [B] \] = boron concentration measured in production well [µg/L];  
\[ 399 \] = boron concentration measured in recycled water [µg/L];  
\[ [B_{Native}] \] = boron concentration in production well without recycled water [µg/L]; and  
\[ x \] = calculated percentage of recycled water [%].

Linear regression analysis was performed on the recycled-water percentages using the software program S-Plus (Mathsoft, Inc., Cambridge, Mass.) and the robust MM regression method. Regression models such as the robust MM regression method are useful for fitting linear relations when the random variation in the data is not Gaussian (normal) or when the data contain significant outliers. Furthermore, the results of the robust MM linear regression method return a model that is almost identical in structure to a standard linear regression model allowing for the production of regression plots. On the basis of the results of the analysis, “excess” Cl and “excess” B are correlated with a coefficient of determination, \( r^2 \), of 0.58 (fig. 7). The fact that “excess” chloride and “excess” boron are correlated supports the hypothesis that both constituents are at least semiquantitative indicators of the percentage of recycled water in the production wells, although the underlying assumptions are only approximately correct since the regression line neither passes through the origin nor has a slope of 1.

Furthermore, the calculated percentages are higher than the average amount of about 30 percent that would be expected on the basis of quantity and sources of water delivered to the spreading grounds for recharge during the last 10 years. It is anticipated that these recycled-water percentages can be improved with more reliable information on background concentrations of ground water prior to recharge, spatial variations within the Montebello Forebay, and the contribution of ground water from the San Gabriel Valley.
Figure 7. Estimates of recycled-water percentages in selected production wells based on “excess” chloride and “excess” boron values, Los Angeles County, California.
**Boron Isotopes**

Isotopic analyses of B may provide another method for quantifying recycled-water percentages (Vengosh and others, 1994). A delta boron-11 ($\delta^{11}\text{B}$) value of +6 per mil ($^{\text{o}}/oo$) for an effluent sample yields a positive correlation between “excess” Cl and $\delta^{11}\text{B}$ (fig. 8) and supports the use of boron as an indicator of recycled water, although the correlation between $\delta^{11}\text{B}$ and “excess” Cl ($r^2 = 0.14$) is considerably weaker than the correlation between “excess” Cl and “excess” B.

**Nitrogen Isotopes**

Nitrogen-isotopes measured during artificial recharge experiments at the San Gabriel Coastal Basin Spreading Grounds provided evidence that denitrification occurs beneath the reservoir site (Anders and Schroeder, 1997). The process of denitrification is accompanied by enrichment in nitrogen-15 in the remaining nitrate. Analyses of the effluent sample (table 2) yielded a delta nitrogen-15 ($\delta^{15}\text{N}$) value of +11.5 $^{\text{o}}/oo$ for nitrate and concentrations of 6.4 and 4.5 mg/L as N for oxidized (NO$_3$ + NO$_2$) and reduced (NH$_4$ + organic) species, respectively. A $\delta^{15}\text{N}$ value of +25.4 $^{\text{o}}/oo$ for ammonia was reported in Schroeder and others (1997). Combining the isotope and concentration data yields an initial nitrogen isotope ratio of +17.2 $^{\text{o}}/oo$ for total N. This value represents a maximum that would occur if all forms of N were completely converted to NO$_3$ and implies that any increment above this value for $\delta^{15}\text{N}$-NO$_3$ in the ground water would indicate denitrification. Because nearly all of the 23 production wells have $\delta^{15}\text{N}$ values that are higher than +17.2 $^{\text{o}}/oo$, and all have values that markedly exceed the $\delta^{15}\text{N}$ value for NO$_3$ in recycled water, most of the NO$_3$ in the production wells is concluded to be the result of partially denitrified recycled water (fig. 9).

On the basis of the assumption of complete oxidation of N in recycled water followed by partial denitrification and negligible dilution with native waters, this enrichment of $\delta^{15}\text{N}$-NO$_3$ can be expressed in terms of an isotope-separation (fractionation) factor, $\varepsilon$, by the Rayleigh fractionation equation:

$$
\delta^{15}N_f = \delta^{15}N_i + \varepsilon \ln \left[\frac{[NO_3]_f}{[NO_3]_i}\right]
$$

where

- $\delta^{15}N_f$ = final nitrogen isotope ratio measured in well at time of sampling ($^{\text{o}}/oo$);
- $\delta^{15}N_i$ = initial (at time of recharge) nitrogen isotope ratio ($^{\text{o}}/oo$);
- [NO$_3$]$_f$ = final nitrate concentration [mg/L]; and
- [NO$_3$]$_i$ = initial (at time of recharge) nitrate concentration [mg/L].

Previous calculations using the Rayleigh fractionation equation and isotope-ratio and nitrate-concentration data from before and after recharge experiments at the research site yielded an isotope-separation factor of about −22 $^{\text{o}}/oo$ (Anders and Schroeder, 1997) (fig. 9). Therefore, the amount of NO$_3$ removal by denitrification during recharge and (or) subsequent ground-water transport to a production well can be estimated from measured isotope ratios by assuming that the isotope-separation factor of −22 $^{\text{o}}/oo$ exists throughout the aquifer. Using the above assumptions yields N removals as high as 50 percent, with the highest N-removal percentage found in well 19M4 (production well number 16) in which $\delta^{15}\text{N} = +31.36^{\text{o}}/oo$. Actual removal rates are likely to be slightly greater than calculated owing to lower $\delta^{15}\text{N}$ values commonly found in stormwater used for recharge, which are composed of N of natural and fertilizer origins that typically have $\delta^{15}\text{N}$ values much lower than those found in wastewater (Heaton, 1986, and Hübner, 1986). Furthermore, attempts were made to relate isotope ratios to plausible individual variables such as ground-water travel times or distance from the spreading grounds, depth of well, redox state as evidenced by oxygen and manganese concentrations, and even NO$_3$ concentration itself. However, these attempts failed to yield any obvious relation owing to the complex interplay of all variables listed, in addition to timing and composition of recharge and mixing of water from different depths (Schroeder and others, 1997).
Figure 8. Boron-isotope ratios and “excess” chloride values in selected production wells, Los Angeles County, California.
Figure 9. Nitrogen-isotope ratios and nitrate concentrations in selected production wells, Los Angeles County, California.
Furthermore, the Rayleigh fractionation equation previously used to calculate NO$_3$ removal percentages by denitrification can be used to calculate NO$_3$ concentrations in the production wells at the time of recharge. For these calculations, the Rayleigh fractionation equation was rearranged to compute [NO$_3$]$_i$ as if there were no denitrification and is referred to as a “back-calculated” nitrogen (assumed to be nitrate) concentration (calN). The result yields a r$^2$ of 0.48 between the “back-calculated” nitrogen concentration and recycled-water percentage from “excess” Cl (fig. 10). Therefore, the “back-calculated” nitrogen concentration in the production-well water represents the concentration from recycled water just as for the conservative species such as Cl and B.

**Organic Constituents**

A number of organic constituents associated with recycled water have been identified in the production wells (Barber and others, 1997). Robust linear regression analysis indicates that ultraviolet absorbance at 254 nanometers (UV) and excitation (300–400 nm filter) — emission (410–500 nm filter) fluorescence are strongly correlated (r$^2 = 0.77$). Furthermore, UV absorbance and fluorescence appear to be quantitative indicators of recycled water in production wells in much the same manner as Cl and B (fig. 11), although calculated percentages are less than those for “excess” Cl and “excess” B (fig. 7). Specific UV absorbance (SUVA) and specific fluorescence (SFLU) values are obtained by dividing by dissolved organic carbon (DOC) concentration. The fact that their “specific values” group together suggests a common origin (recycled water) and preservation (or nonspecific degradation) of the responsive component (perhaps surfactants and whitening agents in detergents) for most of the organic carbon that is present in the well water (fig. 12).

Also, the fact that extrapolation of regression lines for UV absorbance and fluorescence using a standard linear regression method both pass near the data point for recycled water itself indicates little loss of both signals during recharge and subsequent travel to the production wells (fig. 13). This contrasts to the regression line for ethylenediaminetetraacetic acid (EDTA) using a standard linear regression method, whose extrapolated value falls more than 30 percent below its concentration in recycled water, suggesting that EDTA is not conservative.

**Tritium and Well-Water Ages**

Tritium ($^3$H), a radioactive isotope of hydrogen, which has a half-life of 12.4 years, has been widely used to date ground water recharged less than about 50 years before present (Unterweger and others, 1980). This dating technique takes advantage of the natural decay of $^3$H to $^3$He in the environment. The occurrence of $^3$H in the environment is due to atmospheric detonation of thermonuclear devices prior to 1963, and the subsequent gradual decline as a result of continuous removal from the atmosphere and by radioactive decay. The technique of $^3$H age dating of ground water includes the following principles: (1) ground water completely absent of tritium indicates recharge earlier than about 1950; (2) ground water containing the maximum $^3$H concentration indicates recharge water dating to about 1963 and; (3) ground water containing intermediate $^3$H concentrations indicates water recharged more recently than 1963 if recharge took place during the receding limb of the atmospheric source curve, or between 1950 and 1963 if recharge occurred on the rising limb. It should be noted that this simple interpretation of $^3$H concentrations in ground water is complicated when mixing of ground water of differing ages occurs, as could be the case in the Central Basin.
Figure 10. Relation between "back-calculated" nitrogen concentration and "excess" chloride values in selected production wells, Los Angeles County, California.
Figure 11. Estimates of recycled water in selected production wells based on ultraviolet absorbance and fluorescence, Los Angeles County, California.
Figure 12. Specific ultraviolet absorbance and fluorescence (values divided by dissolved organic carbon concentration) in selected production wells, Los Angeles County, California.
Figure 13. Extrapolated standard linear regression lines from selected production-well data (open symbols) and concentration in recycled water (solid symbols) for ultraviolet absorbance (UV), fluorescence, and ethylenediaminetetraacetic acid (EDTA), Los Angeles County, California.
Calculations from a large-scale $^3$H atmospheric-deposition model (Michel, 1989) yield an annual average of about 103 TU (corrected for decay to the time of sampling in 1996) for precipitation in the Los Angeles Basin at the time of the 1963 atmospheric nuclear-bomb maximum. Concentration then declined rapidly until about 1983, after which the decay-corrected annual average remains nearly constant at 3.7 to 4.4 TU. Stratigraphic-estimated traveltimes (described in the section “Description of Study Area”) were calculated using an association between hydraulic properties and known stratigraphy along possible flow paths from the spreading grounds to the 23 production wells in the Montebello Forebay (Bookman-Edmonston Engineering, Inc., 1994). The traveltimes are shown in table 2 and range from 24 days to more than 16 years. If these traveltimes are correct, calculations from a large-scale $^3$H atmospheric-deposition model predicts that the concentrations of $^3$H should be about the same in all 23 production wells. However, the measured $^3$H concentrations differ considerably among the production wells, ranging from about 8 to 19.5 TU (fig. 14; table 2).

The high scatter of most values found in the production wells do not fit the simple decay prediction because a larger proportion of $^3$H-rich and older ground water (older than 15 years but still young enough to contain $^3$H) is drawn through a well screened over intervals intercepting ground-waters that have a wide range of ground-water ages. Furthermore, a single sample of recycled water was found to have a $^3$H concentration of 7.5 TU, indicating that a source of water supplied to the treatment plant itself has a composite age of slightly older ground water (table 2). Multiple-well monitoring-site data discussed in the section “Tritium/Helium-3 Age Determinations” confirms the composite age of well water from production wells.

Multiple-Well Monitoring-Site Results

Water and dissolved-gas samples were collected from five multiple-well monitoring sites, through galvanized-steel well points with stainless steel implants at a small constructed research site located adjacent to the San Gabriel Coastal Basin Spreading Grounds, and from stormwater from the San Gabriel Coastal Basin Spreading Grounds in April, May, and August 1998 and March 1999. The five multiple-well monitoring sites are aligned along the of ground-water flow path from the Montebello Forebay in the north, where the recycled water is applied to the San Gabriel and the Rio Hondo Coastal Basin Spreading Grounds, to the Central Basin in the south (fig. 6). The water-quality data for the five multiple-well monitoring sites are given in table 4, whereas the water-quality data for the research site itself and the recycled water are given in table 5.

The southernmost multiple-well monitoring sites (4S/12W-5H5 through 4S/12W-5H9, excluding 5H10) located along the flow path served as a background insofar as absence of tritium confirmed that the ground water at this site is older than 1950s recharge and, therefore, still ahead of the advancing wastewater front (Land and others, 2002, Reichard and others, 2003). Results for chlorofluorocarbons (CFCs), tritium/helium-3 ($^3$H/$^3$He), chloride, boron, dissolved gases, and nitrogen isotopes were used to determine some of the long-term effects on the aquifer from augmenting recharge of imported water and local water with recycled water.
Figure 14. Relation between tritium concentration in wells and stratigraphic-estimated travel times between spreading grounds and production wells, Los Angeles County, California. [Travel times estimated by Bookman-Edmonston Engineering, Inc. (1994) from stratigraphic information.]
Table 4. Water-quality data for multiple-well monitoring sites in Los Angeles County, California, 1998–1999

[Number below the compound is the data parameter code, which is a 5-digit number used in the U.S.Geological Survey computerized data system, National Water Information System (NWIS), to uniquely identify a specific constituent or property; µS/cm, microsiemens per centimeter at 25°C; °C, degrees Celsius; ft, feet; mg/L, milligrams per liter; µg/L, micrograms per liter; per mil, parts per thousand; TU, tritium units; NGVD, National Geodetic Vertical Datum of 1929; <, actual value less than value shown; —, no data]

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Table 4. Water-quality data for multiple-well monitoring sites in Los Angeles County, California, collected 1998–1999—Continued

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Table 4. Water-quality data for multiple-well monitoring sites in Los Angeles County, California, collected 1998–1999—Continued

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Table 4. Water-quality data for multiple-well monitoring sites in Los Angeles County, California, collected 1998–1999—Continued

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Table 4. Water-quality data for multiple-well monitoring sites in Los Angeles County, California, collected 1998 –1999—Continued

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Table 4. Water-quality data for multiple-well monitoring sites in Los Angeles County, California, collected 1998–1999—Continued

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<th>$^{2}$H/$^{1}$H, H$_{2}$O per mil (82082)</th>
<th>$^{18}$O/$^{16}$O, H$_{2}$O ratio per mil (82085)</th>
<th>Tritium, 2 sigma, TU (75985)</th>
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Table 5. Water-quality data for the research-basin itself and recycled water in Los Angeles County, California, 1998–1999

[Number below the compound is the data parameter code, which is a 5-digit number used in the U.S. Geological Survey computerized data system, National Water Information System (NWIS), to uniquely identify a specific constituent or property; µS/cm, microsiemens per centimeter at 25°C; °C, degrees Celsius; ft, feet; mg/L, milligrams per liter; µg/L, micrograms; per mil, parts per thousand; TU, tritium units; NGVD, National Geodetic Vertical Datum of 1929; <, actual value less than value shown; —, no data]

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<th>Site identification No.</th>
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<th>Time</th>
<th>Depth of well, ft (72008)</th>
<th>Altitude of land surface, ft below NGVD (72000)</th>
<th>Oxygen, dissolved, mg/L (00300)</th>
<th>pH, water, whole, field, standard units (00400)</th>
<th>Specific conductance, field, µS/cm (00095)</th>
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<th>Water temperature, °C (00010)</th>
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<th>Magnesium, dissolved, mg/L as Mg (00925)</th>
<th>Potassium, dissolved, mg/L as K (00935)</th>
<th>Sodium, dissolved, mg/L as Na (00930)</th>
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<th>Alkalinity, fixed endpoint, field, mg/L as CaCO₃ (39036)</th>
<th>Bromide, dissolved, mg/L as Br (71870)</th>
<th>Chloride, dissolved, mg/L as Cl (00940)</th>
<th>Fluoride, dissolved, mg/L as F (00950)</th>
<th>Iodine, dissolved (mg/L) (71865)</th>
<th>Silica, dissolved, mg/L as SiO₂ (00955)</th>
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Table 5. Water-quality data for research-basin and recycled water in Los Angeles County, California, 1998–1999—Continued

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<th>Sulfate, dissolved, mg/L as SO\textsubscript{4} (00945)</th>
<th>Solids, sum of constituents, dissolved, mg/L (70300)</th>
<th>Ammonia plus organic nitrogen, mg/L as N (00623)</th>
<th>Ammonia, dissolved, mg/L as N (00688)</th>
<th>Nitrate plus nitrite, dissolved, mg/L as N (00631)</th>
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<th>Phosphorus, dissolved, mg/L as P (00666)</th>
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<th>\textsuperscript{2}H/\textsuperscript{1}H, H\textsubscript{2}O (per mil (82082))</th>
<th>\textsuperscript{18}O/\textsuperscript{16}O, H\textsubscript{2}O per mil (82085)</th>
<th>Tritium, 2-sigma, TU (75985)</th>
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Tritium/Helium-3 Age Determinations

The interpretation of ages from tritium data alone is complicated because wells, as noted earlier, are screened over intervals that represent a wide range of ground-water ages. Depth-dependent variations in $^3$H concentrations are clearly apparent from data on the multiple-well monitoring sites given in table 4. Furthermore, a simple two-member mixing model cannot accurately represent this phenomenon, as is evident by the failure of the parametric calculations (discussed in section “Two Member Mixing Model, for Selected Constituents”) to yield more reasonable estimates of the wastewater percentages. Questions relating to whether the ground water at depth contains tritium solely from the falling limb (post-bomb peak, or after about 1965) of the tritium curve can further complicate the interpretation. Therefore, tritium/helium-3 ($^3$H/$^3$He) ages were determined to exclude artifacts of mixing of water with various ages and to delineate vertical and lateral extent of recycled water in the Central Basin. $^3$H/$^3$He age determinations depend on measurements of $^3$H and daughter product $^3$He. Furthermore, $^3$H/$^3$He ages represent the time since the water became isolated from the atmosphere and traveled to the sampling point and are independent of the tritium source function. Solomon and Cook (2000) define the $^3$H/$^3$He age of a ground-water sample as:

$$t = \lambda^{-1} \ln \left( \frac{^3He_{tri}}{^3H} + 1 \right)$$

(4)

where

- $t$ = $^3$H/$^3$He age [years];
- $^3He_{tri}$ = tritiogenic $^3$He concentration [TU];
- $^3H$ = measured tritium concentration [TU];
- $\lambda$ = $^3$H decay constant (defined here as Ln2 divided by the half-life of tritium) [year$^{-1}$].

The $^3He_{tri}$ concentration is used to separate the $^3$He in ground water derived from $^3$H decay from other sources including: (1) $^3$He dissolved in the water owing to equilibration with the atmosphere during infiltration; (2) excess air (dissolution of small air bubbles); and (3) subsurface sources (such as degassing of the earth’s mantle and lithium reactions). In most shallow ground-water systems, subsurface sources of $^3$He are minor and the following equation can be used to calculate $^3He_{tri}$ (Jenkins, 1987):

$$^3He_{tri} = 4.021 \times 10^{14} \times \left[ ^4He_{tot} (R_{tot} - R_{atm}) + ^4He_{eq} R_{atm} (1 - \beta) \right] \hfill (5)$$

where

- $^4He_{tot}$ = measured $^4$He concentration of the sample [cm$^3$ STP/g H$_2$O];
- $R_{tot}$ = measured $^3$He/$^4$He ratio of the water sample [dimensionless];
- $R_{atm}$ = $^3$He/$^4$He ratio of atmospheric helium (1.384 x 10$^{-6}$; Clarke and others, 1976) [dimensionless]; and
- $^4He_{eq}$ = $^4$He concentration in air-equilibrated water [cm$^3$ STP/g H$_2$O].

The factor $4.021 \times 10^{14}$ is used to convert cm$^3$ STP/g H$_2$O into TU and $\beta$ is the effect of the difference in solubility of the two isotopes of helium (0.983; Benson and Krause, 1980). Furthermore, the use of this age-dating technique assumes that the system is closed (does not allow $^3$He to escape) and is characterized by piston flow (no hydrodynamic dispersion) (Scanlon and others, 2002). Shown in table 6 are the $^3He_{tri}$ and $^3$He concentrations provided by the University of Rochester Department of Earth and Environmental Sciences and the USGS Tritium Laboratory, respectively, and the $^3$H/$^3$He age determinations from equation 4 for ground-water samples collected from a selected group of multiple-well monitoring sites located along the northeast-southwest flow path (fig. 15). On the basis of the analytical uncertainties for the $^3$H and $^3$He measurements, the minimum age error is assumed to be about ±1 year. Previously collected tritium data were used to avoid analyzing water samples that have tritium concentrations less than 0.1 TU (samples older than 50 years). One tritium-dead sample was analyzed from a monitoring well located in Lakewood (4S/12W-5H7) to confirm the (expected) absence of tritiogenic $^3$He.
Table 6. Tritium/helium-3 data, recharge ages, “excess” chloride, “back-calculated” nitrogen, and net denitrification-rate constants for selected monitoring wells in Los Angeles County, California, 1998–1999

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<th>Site identification No.</th>
<th>Date</th>
<th>Time</th>
<th>3He (in TU)</th>
<th>3H (in TU)</th>
<th>3H/3He (age in years)</th>
<th>exCl (percent)</th>
<th>15N/14N (per mil)</th>
<th>calN (mg/L)</th>
<th>k (day⁻¹)</th>
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<td>1800</td>
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<tr>
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Figure 15. Tritium concentration in 5 multiple-well monitoring sites and tritium/helium-3 ages in 16 monitoring wells along groundwater flow path (see fig. 6 for locations), Los Angeles County, California.
The youngest $^3$H/$^3$He age of 0.6 year was found in the water sample collected from a depth of 120 ft below land surface adjacent to the San Gabriel Coastal Basin Spreading Grounds (2S/12W-25G8). Other water samples collected from monitoring wells adjacent to the San Gabriel Coastal Basin Spreading Grounds at depths between 255 and 1,200 ft below land surface had $^3$H/$^3$He ages ranging from 3.2 to 22.0 years. $^3$H/$^3$He ages for water samples collected from monitoring wells located adjacent to the Rio Hondo Coastal Basin Spreading Grounds at depths between 160 and 930 ft below land surface ranged from 2.7 to 30.8 years. The $^3$H/$^3$He age for water samples collected from the monitoring wells located in the city of Downey at depths between 270 and 960 ft below land surface ranged from 25.9 to 34.1 years. These $^3$H/$^3$He ages indicate that recycled water is present to a depth of more than 900 ft below land surface adjacent to both spreading grounds and to a distance of more than 4 mi downgradient from both spreading grounds.

Linear regression analysis with the robust MM regression method (Mathsoft, Inc., Cambridge, Mass.) was performed using the $^3$H/$^3$He ages and the depth of the monitoring wells located adjacent to the San Gabriel Coastal Basin (2S/12W-25G4 through 25G8) and Rio Hondo Coastal Basin Spreading Grounds (2S/12W-26D10 through 26D14). The resulting correlation was higher adjacent to the Rio Hondo Coastal Basin Spreading Grounds ($r^2 = 0.89$) than adjacent to the San Gabriel Coastal Basin Spreading Grounds ($r^2 = 0.56$) (fig. 16).

Although these correlations were calculated using a small number of data points and do not take into consideration asymmetric vertical flow that probably exists beneath the spreading grounds, they do provide some information about the recharge characteristics of the recycled water applied at the spreading grounds. The lower correlation for the monitoring wells adjacent to the San Gabriel Coastal Basin Spreading Grounds, along with similar $^3$H/$^3$He ages of 22.1 and 20.9 years for water samples collected from 580 (2S/12W-25G5) and 850 (2S/12W-25G4) ft below land surface, respectively (fig. 15), probably is due to mixing and (or) complete displacement of recharged water with pre-existing ground water at these depths. The higher correlation for the monitoring wells at the Rio Hondo Coastal Basin Spreading Grounds owing to the linear increase in age with depth suggests less displacement of pre-existing ground water than at the San Gabriel Coastal Basin Spreading Grounds.

Tracers of Recycled Water

Chloride and Boron

Chemical results from the production wells suggested that Cl and B would be most useful in locating the extent of the recycled water along the flow path, and this expectation is confirmed by data from the multiple-well monitoring sites (fig. 17). Values of “excess” Cl and “excess” B were determined for the monitoring wells following the same procedure used for estimating recycled-water percentages in the production wells (table 6). One end-member used to calculate the “excess” boron value was the average boron concentration from the monitoring well in Lakewood previously identified as containing no contribution from recycled water (62.5 mg/L in well 4S/12W-5H7). The “excess” Cl and “excess” B values of the monitoring wells show an $r^2$ of 0.42 (fig. 18). Similarly, the “excess” Cl and “excess” B values of the production wells show an $r^2$ of 0.58 (fig. 7).

The percentage of recycled water in three of the five monitoring wells (2S/12W-25G6–8) adjacent to the San Gabriel River Coastal Basin Spreading Grounds is similar to the highest values found in the production wells along the east side of the San Gabriel Coastal Basin Spreading Grounds (figs. 7 and 18). The high percentage of recycled water at the San Gabriel Coastal Basin Spreading Grounds exceeds the 35-percent limit DOHS sets on the allowable amount of recycled water that can be applied during any 3-year period, suggesting either greater use of this side for replenishment purposes during the dry months or higher natural levels of B and Cl on this side.

Furthermore, those “excess” Cl and “excess” B values not showing a strong correlation either have a high concentration of bromide (4S/12W-5H10) or boron (3S/12W-9J6, 2S/11W-18C4, and 2S/11W-18C7) probably owing to surface anthropogenic effects such as oil-field brines and (or) local aquifer properties such as clay content or soil type.
Figure 16. Relation between tritium/helium-3 ages and depth of the monitoring wells adjacent to the San Gabriel and Rio Hondo Coastal Basin Spreading Grounds, Los Angeles County, California.
Figure 17. Chloride and boron concentrations in multiple-well monitoring sites along ground-water flow path (see fig. 6 for locations), Los Angeles County, California.
Figure 18. Estimates of recycled water in multiple-well monitoring sites based on “excess” chloride and “excess” boron values, Los Angeles County, California.
On the basis of $^3$H/$^3$He age determinations, the highest recycled-water percentages calculated from “excess” Cl values are found in the three shallowest monitoring wells at the San Gabriel Coastal Basin Spreading Grounds (2S/12W-25G6 through 25G8) (fig. 19). The high recycled-water percentages in the youngest ground water in monitoring wells adjacent to the San Gabriel Coastal Basin Spreading Grounds further suggest more rapid recharge and (or) greater displacement of pre-existing ground water during recharge than at the Rio Hondo Coastal Basin Spreading Grounds.

Several monitoring wells, especially those not expected to contain recycled water on the basis of $^3$H/$^3$He age determinations, have negative “excess” Cl values owing to background chloride concentrations estimated from bromide concentrations that are greater than the actual measured concentrations (see eq. 1). These higher estimated background concentrations indicate a Cl/Br ratio less than 287, the ratio that is expected if the only source of Cl and Br is atmospheric precipitation. Therefore, more precise values for the background Cl and Br concentrations in ground water prior to the introduction of artificial recharge, as well as the identification of other sources of Cl and Br in the Central Basin, might make “excess” Cl a more quantitative indicator for the presence of recycled water.

Nitrogen

Initial nitrogen concentrations in the monitoring wells during recharge were calculated using the Rayleigh fractionation equation, measured isotope ratios, and an isotope separation factor of $-22\%_{oo}$, as described in the section “Two Member Mixing Model for Selected Constituents” (table 6). However, the “back-calculated” nitrogen concentrations for the multiple-well monitoring sites (fig. 20) show a weaker correlation with “excess” Cl ($r^2 = 0.15$), as do the values of the production wells (fig. 10). In fact, the rapid decrease in nitrate concentrations suggests denitrification is a possible removal process for nitrate in the shallower depths beneath the spreading grounds instead of dilution with native ground water.

Therefore, the “back-calculated” nitrogen concentrations derived from the Rayleigh fractionation equation, along with $^3$H/$^3$He age determinations for the monitoring wells, were used to estimate the net denitrification rates during recharge (table 6). The net denitrification rate constant, defined by a first-order rate expression (Laidler, 1987), relates the consumption of nitrate to the overall ground water age by the following equation:

$$k = \frac{1}{t} \ln \left( \frac{[NO_3]_i}{[NO_3]_f} \right)$$

where

- $[NO_3]_f$ = the measured nitrate concentration in the monitoring well [M/L];
- $[NO_3]_i$ = the “back-calculated” nitrogen (assumed to be nitrate) concentration [M/L];
- $t$ = the $^3$H/$^3$He age determined for each monitoring well [days];
- $k$ = the net denitrification rate constant [days$^{-1}$].

The highest net denitrification rate constant of $5.3 \times 10^{-3}$ day$^{-1}$ is obtained from the shallowest monitoring well adjacent to the San Gabriel Coastal Basin Spreading Grounds (2S/12W-25G8). The remaining net denitrification rate constants are distributed into two groups (fig. 21). The first group, which contains the monitoring wells between about 150 and 350 ft below land surface adjacent to the San Gabriel (2S/12W-25G6 and -25G7) and the Rio Hondo (2S/12W-26D13 and -26G14) Coastal Basin Spreading Grounds, has denitrification rate constants that range between about $9.4 \times 10^{-4}$ and $1.7 \times 10^{-4}$ day$^{-1}$. The other group contains the deeper monitoring wells along the spreading grounds that have net denitrification rate constants ranging from $4.4 \times 10^{-5}$ to $1.7 \times 10^{-5}$ day$^{-1}$. 

\[\text{58 Use of Water-Quality Indicators and Environmental Tracers to Determine the Fate and Transport of Recycled Water in Los Angeles County, California}\]
Figure 19. Tritium/helium-3 age determinations and recycled-water percentages in multiple-well monitoring sites based on “excess” chloride values, Los Angeles County, California.
Figure 20. Relation between “back-calculated” nitrogen concentrations and estimates of recycled-water percentages in multiple-well monitoring sites based on “excess” chloride values, Los Angeles County, California.
Figure 21. Relation between net denitrification rate constants estimated from “back-calculated” nitrogen concentrations and depth of the monitoring wells adjacent to the San Gabriel and Rio Hondo Coastal Basin Spreading Grounds, Los Angeles County, California.
It should be noted that these rate constants take into consideration all the same assumptions used previously when the inverse of the Rayleigh fractionation equation was used to calculate NO$_3$ concentrations in the production wells at the time of recharge and, therefore, are only estimates of denitrification rate constants. However, they do indicate that denitrification is an important process for the removal of nitrate at the shallower depths beneath the spreading grounds. Finally, the net denitrification rate constants approach a value of about 3 x 10$^{-5}$ day$^{-1}$, suggesting also that the process of denitrification continues to occur at distances of several miles from the spreading grounds and over a period of many miles (fig. 22), albeit at a very slow rate.

**Dissolved Gases**

Further evidence for the long-term sustainability of denitrification is shown in the dissolved gases collected along the flow path. The dissolved-gases data, concentrations of excess air, and calculated recharge temperatures for the five multiple-well monitoring sites are given in table 7. Recharge temperatures were derived from N$_2$/Ar data and assumes that the sample contains N$_2$ and Ar from air-water equilibrium and dissolution of excess air, as well as N$_2$ from denitrification. In this approach, a back-solving routine iterates on the recharge temperature until the amount of excess air calculated from N$_2$ and Ar are the same. Although most calculated recharge temperatures ranged from 15°C to 18°C, some were much higher. These unrealistically high recharge temperatures, along with their corresponding high excess air concentrations, were reduced by increasing the amount of N$_2$ produced by denitrification. The amount of excess N$_2$ required to lower the high calculated recharge temperatures to 17°C ranged from 0.5 to more than 5 mg/L in several of the monitoring wells (fig. 23). Delta nitrogen-15 enrichment of the ground-water dissolved nitrogen gas (shown in table 8) was used to confirm the presence of denitrification, since denitrification produces N$_2$ with a higher $\delta^{15}$N value than that of the residual nitrogen (Kendall and Aravena, 2000).

The dissolved-oxygen concentrations from the multiple-well monitoring site samples indicate that the drinking-water aquifers are mostly suboxic (O$_2$ < 1 mg/L) (table 7). The excess air concentrations owing to air trapped by rapid infiltration during recharge (in excess of equilibrium) and dissolved nitrogen gas produced from denitrification ranged from 3.2 cm$^3$ STP/L to 13.2 cm$^3$ STP/L, with higher values associated with parts of the ground-water basin where recycled water is present (fig. 24). Furthermore, the highest excess-air concentrations found adjacent to the San Gabriel Coastal Basin Spreading Grounds are consistent with the highest recharge rates and denitrification rates found at the same location. These areas also have no detectable methane, whereas older water deeper or farther from the spreading basins contains methane between 0.3 µg/L and 19.3 µg/L. It is no longer possible to definitely determine what oxygen concentrations were prior to artificial recharge, but data from Lakewood, which predate recharge using imported Colorado River water, indicate either very little O$_2$, or even slight H$_2$S (Land and others, 2002) at some depths. Therefore, the absence of methane in parts of the aquifer where recycled water is present suggests that artificial recharge using recycled water has increased slightly the redox potential of the ground-water basin. One monitoring well, 2S/11W-18C4, located upgradient from the spreading grounds has a methane concentration of 2.2 mg/L, indicating ground water that has not received any recycled water (fig. 24).

This observation is counterintuitive insofar as wastewater is generally thought to increase oxygen demand. For example, at the Cape Cod site discussed in section “Previous Studies,” reducing conditions exist within the wastewater plume (Garabedian and LeBlanc, 1988). Possible reasons for the increase in the redox potential (more oxidizing conditions) observed in the Central Basin owing to the addition of recycled water include: (1) addition of massive amounts of excess air during recharge; (2) lower levels of biodegradable organic carbon in the wastewater organic matter than in the natural organic matter; and (3) inhibition of methanogenesis by higher sulfate in imported Colorado River water and recycled water than in natural recharge (note very low sulfate concentrations in older water at wells 4S/12W-5H5–10).
Figure 22. Relation between net denitrification rate constants and tritium/helium-3 age determinations.
Table 7. Dissolved-gases data, excess air concentrations, and calculated recharge temperatures for multiple-well monitoring sites in Los Angeles County, California, 1998–1999

[cm$^3$ STP/L, cubic centimeters per liter at standard temperature and pressure; °C, degrees Celsius; mg/L, milligrams per liter; *, indicates sample leaked]

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<th>State well No.</th>
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<th>Methane (mg/L)</th>
<th>Carbon dioxide (mg/L)</th>
<th>Nitrogen (mg/L)</th>
<th>Oxygen (mg/L)</th>
<th>Argon (mg/L)</th>
<th>Recharge temperature (°C)</th>
<th>Excess air (cm$^3$ STP/L)</th>
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<td>0.6761</td>
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<td>04/29/98</td>
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<td>1.967</td>
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<td>.6477</td>
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</tr>
<tr>
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<td>0.0031</td>
<td>1.695</td>
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<td>0.042</td>
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<td>0.0127</td>
<td>2.461</td>
<td>19.821*</td>
<td>.067*</td>
<td>.6484*</td>
<td>18.3*</td>
<td>4.4*</td>
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<td>8.380</td>
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<td>.7754</td>
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<td>9.803</td>
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</tr>
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<td>1200</td>
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<td>9.835</td>
<td>24.368*</td>
<td>0.089*</td>
<td>1.7201*</td>
<td>18.9*</td>
<td>9.2*</td>
</tr>
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<tr>
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<td>.5254</td>
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</table>
Figure 23. Amount of excess nitrogen required to lower high-calculated recharge temperatures to 17 degrees Celsius in four monitoring wells, Los Angeles County, California.
Table 8. Delta nitrogen-15 ($\delta^{15}N$) values of the ground-water dissolved nitrogen gas in multiple-well monitoring sites in Los Angeles County, California, 1998–1999

[Per mil, parts per thousand; $N_2$, nitrogen gas]

<table>
<thead>
<tr>
<th>State well No.</th>
<th>Date</th>
<th>Time</th>
<th>$\delta^{15}N$–$N_2$ (per mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4S12W-5H7</td>
<td>04/29/98</td>
<td>1800</td>
<td>0.8</td>
</tr>
<tr>
<td>3S/12W-9J4</td>
<td>05/03/98</td>
<td>1130</td>
<td>leaked</td>
</tr>
<tr>
<td>3S/12W-9J5</td>
<td>05/04/98</td>
<td>1100</td>
<td>1.7</td>
</tr>
<tr>
<td>2S/12W-25G3</td>
<td>03/31/99</td>
<td>1600</td>
<td>.8</td>
</tr>
<tr>
<td>2S/12W-25G4</td>
<td>03/30/99</td>
<td>1400</td>
<td>.7</td>
</tr>
<tr>
<td>2S/12W-25G5</td>
<td>04/01/99</td>
<td>1700</td>
<td>.6/0.8</td>
</tr>
<tr>
<td>2S/12W-25G6</td>
<td>03/30/99</td>
<td>1900</td>
<td>1.1/1.2</td>
</tr>
<tr>
<td>2S/12W-25G7</td>
<td>04/01/99</td>
<td>1200</td>
<td>2.7/3.1</td>
</tr>
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<td>03/31/99</td>
<td>1100</td>
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<td>1230</td>
<td>.7</td>
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<td>1130</td>
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</tr>
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<td>1800</td>
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</table>
Figure 24. Methane and excess-air concentration in multiple-well monitoring sites along ground-water flow path (see fig. 6 for locations), Los Angeles County, California.
Chlorofluorocarbons

Other environmental tracers commonly used to date young ground water are chlorofluorocarbons (Busenberg and Plummer, 1992). Concentrations of chlorofluorocarbons (CFCs) in ground water indicate recharge after 1945, or mixing of older water with post-1950 water. The distribution of CFCs in water samples collected from the five multiple-well monitoring sites is shown in figure 25. Given in table 9 are the CFC aqueous concentrations (average value of 3 ampoules) along with the calculated atmospheric partial pressure in equilibrium with the aqueous concentration and modeled CFC recharge dates based on a comparison to known atmospheric levels. Recycled water (effluent) and standing water from the San Gabriel River Coastal Basin Spreading Grounds indicate only slight enrichment of CFC aqueous concentrations. Very low concentrations at Lakewood (none are zero) indicate the possibility of some contamination during sampling. The deviation from a 1:1 ratio of CFC-11 and CFC-12-modeled recharge ages indicates that there are processes altering the CFC-11 and CFC-12 concentrations to different extents (fig. 26). According to previous studies, anaerobic microbial degradation of CFC-11 is more rapid than that of CFC-12 (Lovley and Woodward, 1992) and sorption of CFC-11 by soils is stronger than that for CFC-12 (Russell and Thompson, 1983). Since modeled CFC-11 recharge ages are greater than modeled CFC-12 recharge ages for post-1970 water, sorption and degradation appears to occur during the initial stage of recharge. The greater modeled CFC-12 recharge ages for pre-1970 water suggests greater amounts of CFC-11 were reaching the ground water in the past than in the present, an observation noted by Dawson and others (2003). Furthermore, all three CFCs are known to degrade in environments where methane is present (Dunkle and others, 1993), a condition possibly present in the Central Basin prior to the use of recycled water. Therefore, CFCs do not provide reliable ground-water ages in most water samples collected from the multiple-well monitoring sites along the flow path. However, they do provide a sensitive tracer for recycled water and a comparison of the present recharge operation with the early period of recharge using recycled water.

The expected equilibrium chlorofluorocarbon concentrations were derived using the \(^{3}H/^{3}He\) age determinations and CFC atmospheric concentrations provided by production records and release data of the Chemical Manufacturing Association (McCarthy and others, 1977). According to Plummer and Busenberg (2000), Henry’s law gives the CFC solubility in water as:

\[
C_i = K_{H,i} \times p_i
\]  

(7)

where

\[
C_i = \text{CFC concentration of the } i\text{th CFC compound in water [pM/kg]}; \\
K_{H,i} = \text{Henry’s law constant for the } i\text{th CFC compound [M atm}^{-1}]; \text{ and} \\
p_i = \text{partial pressure of the } i\text{th compound in the atmosphere in equilibrium with the water [atm].}
\]

The partial pressure is defined as:

\[
p_i = x_i(P - p_w)
\]  

(8)

where

\[
x_i = \text{dry air mole fraction of the } i\text{th CFC}; \\
P = \text{total atmospheric pressure [atm]; and} \\
p_w = \text{water vapor pressure [atm].}
\]

A recharge altitude of 150 ft above sea level was used to estimate the total atmospheric pressure and the vapor pressure of water at the selected recharge temperature. The expected equilibrium CFC concentrations were calculated using Henry’s law constants from tabulated CFC solubility data provided by the USGS CFC Laboratory and recharge temperatures of 10\(^{\circ}\)C, 15\(^{\circ}\)C, and 20\(^{\circ}\)C (fig. 27).

Plots showing the ratio of the measured CFC concentration to the expected equilibrium concentration in ground water, using the \(^{3}H/^{3}He\) age determinations, reveal markedly elevated CFC concentrations in older ground water, with the greatest CFC enrichment (>100) occurring in ground water older than about 20 years but still young enough to contain recycled water (fig. 28). One possible explanation is that recycled water prior to about 1980 was much more contaminated with CFCs, and treatment was less efficient in the past.
Figure 25. Chlorofluorocarbons (CFCs) concentrations in multiple-well monitoring sites along ground-water flow path (see fig. 6 for locations), Los Angeles County, California.
Table 9. Chlorofluorocarbon (CFC) data and calculated recharge dates for multiple-well monitoring sites along section A–A’ in Los Angeles County, California, 1998–1999 (see fig. 6 for locations)

<table>
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<th>Time</th>
<th>Concentration in solution</th>
<th>Calculated atmospheric partial pressure</th>
<th>Modeled CFC recharge dates</th>
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<td>CFC-12 (pg/kg)</td>
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[Pg/kg, picograms per kilogram; pptv, parts per trillion by volume; Contam., contaminated; <, less than]
Figure 26. Comparison of modeled CFC-11 and CFC-12 recharge ages in multiple-well monitoring sites (see fig. 6 for locations), Los Angeles County, California.
Figure 27. Historical record of aqueous chlorofluorocarbon (CFC) concentrations at 10 degrees Celsius, 15 degrees Celsius, and 20 degrees Celsius in equilibrium with atmospheric levels.
Figure 28. Enrichment (depletion) in aqueous chlorofluorocarbon (CFC) concentrations in selected multiple-well monitoring sites relative to theoretical atmosphere-water equilibrium, Los Angeles County, California.
SUMMARY AND CONCLUSIONS

A variety of inorganic, organic, and isotopic constituents were analyzed in 23 production wells located within 500 ft of the San Gabriel and Rio Hondo Coastal Basin Spreading Grounds in the Montebello Forebay in Los Angeles County. The production wells range in depth from 250 to 900 ft, are screened over intervals ranging from 100 to 900 ft below land surface, and yielded 500 to 3,000 gal/min at the time of sampling.

Spearman rank-order correlation coefficients and level of significance were calculated for about 40 water-quality indicators and several physical features such as well depth and distance from spreading grounds to the production wells. The statistical testing indicated that significant correlations ($\alpha < 0.001$) existed between “excess” chloride and “excess” boron (defined as the amount above the natural background level), and “back-calculated” nitrogen concentrations (using nitrogen-isotope data to determine nitrogen concentrations at the time of recharge). However, these methods appeared to overstate recycled-water percentages. The estimates based on these naturally occurring constituents should improve if background concentrations can be obtained that better represent ground water that is free of artificial recharge. Furthermore, the failure of parametric calculations to yield precise estimates of the wastewater percentage show that the production wells draw water from various depths and ages (with variable extent of degradation) that are not accurately represented by a simple two-member mixing model.

The organic indicators of UV absorbance and fluorescence yielded lower percentages than those derived from the conservative inorganic constituents, suggesting that some degradation of organic matter occurs in the aquifer. Furthermore, it appears that the presence of specific organic compounds, such as EDTA, in the production wells is actually due to dilution of fairly young water with water more than several years old, in which the compound is absent, rather than a simple indication of removal during subsurface transport. Finally, tritium data confirms that ground water of differing ages enters production wells that are often perforated over long intervals and open to multiple zones.

Measurements of chlorofluorocarbons (CFCs), tritium/helium-3 ($^3$H/$^3$He), chloride, boron, dissolved-gas concentrations, and nitrogen isotopes were collected from five multiple-well monitoring sites extending along a 10-mi flow path from just upgradient from the San Gabriel and Rio Hondo Coastal Basin Spreading Grounds southward through the Central Basin. On the basis of tritium/helium-3 age determinations, ground-water samples ranged in age from less than 2 to more than 50 years. The age determinations based on tritium/helium-3 data eliminate the complications associated with tritium data alone.

Chloride and boron concentrations generally are highest in the youngest ground water $^3$H/$^3$He age determinations) and indicate the locations where the percentage of recycled water exceeds 60 percent. These high recycled-water percentages in the youngest ground water in monitoring wells adjacent to the San Gabriel Coastal Basin Spreading Grounds suggest more rapid recharge and (or) greater displacement of pre-existing ground water during recharge than at the Rio Hondo Coastal Basin Spreading Grounds. The $^3$H/$^3$He ages with depth also suggest a more rapid infiltration or displacement of pre-existing ground water at the San Gabriel Coastal Basin Spreading Grounds than at the Rio Hondo Coastal Basin Spreading Grounds.

Denitrification, an important process for the removal of nitrate at the shallow depths beneath the spreading grounds, continues to occur even at times and distances from the spreading grounds of many years and over several miles. The presence of denitrification is confirmed by nitrogen-15 enrichment of the ground-water dissolved nitrogen. Analysis of dissolved gases shows that areas that contain recycled water have no detectable methane, whereas methane is present in the native ground water older than 50 years. These results suggest that artificial recharge using recycled water has the desirable effect of slightly increasing the redox potential of the ground water in the basin. Also, dissolved gases have higher concentrations of excess air in parts of the ground-water basin where recycled water is present. Some of the excess air probably originates as air trapped by rapid infiltration at the spreading grounds, but part has been identified as dissolved nitrogen resulting from denitrification. Finally, using tritium/helium-3 age determinations, in conjunction with measured CFC concentrations, it was found that CFC concentrations are markedly elevated above atmosphere-water equilibrium in ground water older than about 20 years but still young enough to contain recycled water.
REFERENCES CITED


California Department of Health Services, 1978, Wastewater reclamation criteria, an excerpt from the California Administrative Code, Title 22, Division 4, Environmental Health: Engineering Section, Berkeley Calif., (loose leaf).


References Cited 77


APPENDIX A: RELATION BETWEEN PERCENT RECYCLED WATER AND 22 SELECTED WASTEWATER CONSTITUENTS FOR EACH OF THE 23 PRODUCTION WELLS LOCATED IN LOS ANGELES COUNTY, CALIFORNIA

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<thead>
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<th>Description</th>
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<td>Specific conductance</td>
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<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>Na</td>
<td>Sodium</td>
</tr>
<tr>
<td>K</td>
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<tr>
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<td>Oxygen-18/16</td>
</tr>
<tr>
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<td>Boron-11/10</td>
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<tr>
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<td>“Excess” chloride</td>
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<tr>
<td>exB</td>
<td>“Excess” boron</td>
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<tr>
<td>calN</td>
<td>“Back-calculated” nitrogen</td>
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<tr>
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<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
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<tr>
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<td>Methylene blue activated substance</td>
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<td>Fluorescence</td>
</tr>
<tr>
<td>SFLU</td>
<td>Specific fluorescence</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraactic acid</td>
</tr>
<tr>
<td>APEC</td>
<td>Alkylphenol polyethoxy carboxylate</td>
</tr>
<tr>
<td>TOX</td>
<td>Total organic halides</td>
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Figure A.1. Relations between percent recycled water and specific conductance (SC) and magnesium (Mg) for each of the 23 production wells located in Los Angeles County, California.
Figure A.2. Relations between percent recycled water and sodium (Na) and potassium (K) for each of the 23 production wells located in Los Angeles County, California.
Figure A.3  Relations between percent recycled water and chloride (Cl) and deuterium (H-2) for each of the 23 production wells located in Los Angeles County, California
Figure A.4. Relations between percent recycled water and oxygen-18 (O-18) and boron-11 (B-11) for each of the 23 production wells located in Los Angeles County, California.
Figure A.5. Relations between percent recycled water and nitrogen-15 (N-15) and “excess” chloride (exCl) for each of the 23 production wells located in Los Angeles County, California
Figure A.6. Relations between percent recycled water and “excess” boron (exB) and “back-calculated” nitrogen (calN) (assumed to be nitrate) for each of the 23 production wells located in Los Angeles County, California
Figure A.7. Relations between percent recycled water and dissolved organic carbon (DOC) and total dissolved carbon (TOC) for each of the 23 production wells located in Los Angeles County, California.
Figure A.8. Relations between percent recycled water and ultraviolet absorbance (UV) and specific ultraviolet adsorbance (SUVA) for each of the 23 production wells located in Los Angeles County, California.
Figure A.9. Relations between percent recycled water and methylene blue activated substance (MBAS) and fluorescence (FLUO) for each of the 23 production wells located in Los Angeles County, California.
Figure A.10. Relations between percent recycled water and specific fluorescence (SFLU) and ethylenediaminetetraacetic acid (EDTA) for each of the 23 production wells located in Los Angeles County, California.
Figure A.11. Relations between percent recycled water and alkylphenol polyethoxy carboxylate (APEC) and total organic halides (TOX) for each of the 23 production wells located in Los Angeles County, California
APPENDIX B: RELATION BETWEEN PERCENT RECYCLED WATER IN EACH OF THE 23 PRODUCTION WELLS LOCATED IN LOS ANGELES COUNTY, CALIFORNIA, FOR 22 SELECTED CONSTITUENTS

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</tr>
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Figure B.1. Relations between percent recycled water in wells 1 and 2 located in Los Angeles County, California, for 22 selected constituents.
Figure B.2. Relations between percent recycled water in wells 3 and 4 located in Los Angeles County, California, for 22 selected constituents.
Figure B.3. Relations between percent recycled water in wells 5 and 6 located in Los Angeles County, California, for 22 selected constituents.
Figure B.4. Relations between percent recycled water in wells 7 and 8 located in Los Angeles County, California, for 22 selected constituents.
Figure B.5. Relations between percent recycled water in wells 9 and 10 located in Los Angeles County, California, for 22 selected constituents.
Figure B.6. Relations between percent recycled water in wells 11 and 12 located in Los Angeles County, California, for 22 selected constituents.
Figure B.7. Relations between percent recycled water in wells 13 and 14 located in Los Angeles County, California, for 22 selected constituents.
Figure B.8. Relations between percent recycled water in wells 15 and 16 located in Los Angeles County, California, for 22 selected constituents.
Figure B.9. Relations between percent recycled water in wells 17 and 18 located in Los Angeles County, California, for 22 selected constituents.
Figure B.10. Relations between percent recycled water in wells 19 and 20 located in Los Angeles County, California, for 22 selected constituents.
Figure B. 11. Relations between percent recycled water in wells 21 and 22 located in Los Angeles County, California, for 22 selected constituents.
Figure B.12. Relations between percent recycled water in well 23 located in Los Angeles County, California, for 22 selected constituents.