Nature and Chlorine Reactivity of Organic Constituents from Reclaimed Water in Groundwater, Los Angeles County, California

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The nature and chloric reactivity of organic constituents in reclaimed water (tertiary-treated municipal wastewater) before, during, and after recharge into groundwater at the Montebello Forebay in Los Angeles County, CA, was the focus of this study. Dissolved organic matter (DOM) in reclaimed water from this site is primarily a mixture of aromatic sulfonates from anionic surfactant degradation, N-acetyl amino sugars and proteins from bacterial activity, and natural fulvic acid, whereas DOM from native groundwaters in the aquifer to which reclaimed water was recharged consists of natural fulvic acids. The hydrophilic neutral N-acetyl amino sugars that constitute 40% of the DOM in reclaimed water are removed during the first 3 m of vertical infiltration in the recharge basin. Groundwater age dating with 3H and 3He isotopes enabled clear differentiation of recent recharged water from older native groundwater. Phenol structures in natural fulvic acids in DOM isolated from groundwater produced significant trihalomethanes (THM) and total organic halogen (TOX) yields upon chlorination, and these structures also were responsible for the enhanced SUVA and specific fluorescence characteristics relative to DOM in reclaimed water. Aromatic sulfonates and fulvic acids in reclaimed water DOM produced minimal THM and TOX yields.

Introduction

A feature article entitled “Drinking Recycled Wastewater” Environmental Science and Technology examined the issue of whether groundwater recharge of treated wastewater (recycled or reclaimed water) could safely address the drinking-water needs of the Los Angeles metropolitan area. Two particular concerns are lack of characterization of organic constituents in reclaimed water and receiving groundwater and potential disinfection hazards. Previous studies on rapid infiltration disposal of treated wastewater (2) show that once wastewater organic constituents reach the water table, they can be transported considerable distances (>>10 km) and persist for long periods of time (> 50 yr). The primary objective of this study is to comprehensively assess the nature of dissolved organic matter (DOM) in reclaimed water and receiving groundwaters by isolating and fractionating DOM into characteristic compound classes followed by spectral characterization of the fractions. Secondary objectives are to relate DOM characterization data to chlorine disinfection byproducts and formation potentials in reclaimed water and native groundwaters and to determine the extent of migration of reclaimed water recharged into groundwater.

Hydrologic Setting

Reclaimed municipal wastewater from treatment plants, stormwater runoff, and imported water recharge the aquifer through infiltration basins in areas known as spreading grounds. The spreading grounds recharge the aquifer system from the Montebello Forebay in the Central Groundwater Basin that extends from Whittier Narrows in the north toward the Pacific Ocean (Figure 1). The aquifer system is comprised of several units of unconsolidated fluvial and shallow marine sand and gravel deposits overlying the consolidated Pico formation of Pliocene age. The water-bearing units above the Pico merge or are in direct hydraulic contact with one another, at the spreading grounds where hydraulic conductivities as high as 250 m/day have been reported (3), and only thin discontinuous lenses of silt and clay are present (3, 4).

Reclaimed wastewater has become a greater proportion of total recharged water since it was first introduced in 1961 and now comprises about one-third of the approximately 150 000 acre-ft recharged annually (5). Its level of purification at the treatment plants also has increased over time and now includes conventional secondary treatment followed by dual-media (sand and charcoal) filtration and chlorination–dechlorination.

Depth to water in the Montebello Forebay ranges from land surface during periods of active spreading to about 10 m following several weeks of desiccation at the spreading grounds. Depth to groundwater further down gradient in the Central Basin ranges to about 30 m. The direction of groundwater flow, today and historically, is southward, so the geohydrologic section line A to A’ (Figure 2) is believed to be generally aligned in the direction of groundwater flow. Long-term groundwater velocities inferred from particle-tracking simulations (3), the distinctive chemical characteristics of recharged water imported from the Colorado River (5–8), and measured tritium activities (3, 5) all indicate that reclaimed water should have traveled nearly 10 km from the spreading grounds and would now extend to somewhere between the multilevel monitoring wells in Downey and Lakewood on section line A–A’.

Methods

Field Sampling. Groundwater samples for this study were collected from a transect of multilevel monitoring wells, section A–A’, aligned in the direction of groundwater flow from the San Gabriel River and Rio Hondo Spreading Grounds. Additional groundwater samples were collected from probes and from well points installed in a small research infiltration basin (Figure 1). The research basin was con-
structured at the north end of the San Gabriel River Spreading Grounds by emplacing a berm to isolate it from the spreading grounds (additional details are given in refs 4 and 8). Samples also were collected of reclaimed water and of water ponded in an infiltration basin.

Samples were collected in May 1998 from the 22 multilevel monitoring wells at four locations on section A–A′ (Figure 2) and from ponded water in the San Gabriel River Spreading Grounds using a Bennett stainless steel submersible pump attached to 1/4-in. id refrigeration-grade copper tubing. Large-volume water samples collected in August 1998 were obtained after replacing the copper tubing with Teflon tubing. Samples collected in June 1999 were obtained from 6-in. stainless steel probes installed at 1, 2, and 3 ft beneath the floor of the research basin (geoprobes 1–3, respectively) from 2-ft stainless steel well points installed at depths of 5 and 10 ft beneath the floor of the research basin (WP1 and WP2, respectively), and from ponded water in the research basin. These samples were obtained with a peristaltic pump and 1/4-in. PFE Teflon tubing. All samples were collected only after at least three casing volumes had been removed and field constituent measurements had stabilized. Reclaimed water itself was sampled directly from a spigot located atop the culvert where tertiary-treated wastewater from the San Jose Creek Reclamation Plant is diverted into the San Gabriel Spreading Grounds.

Water samples for analysis of common inorganic constituents and most isotopes were pressure-filtered in the field through inline 0.45-μm cartridge filters (polyether sulfone from Gelman Scientific) and distributed into glass or polyethylene bottles for any additional preservation and storage. Specific conductance, pH, temperature, alkalinity (titration to pH 4.5), and dissolved oxygen (Winkler titration) were measured directly in the field.

Samples for dissolved organic carbon (DOC), ultraviolet absorbance at 254 nanometers (UV254), and fluorescence were pressure-filtered through 0.45-μm silver membranes and collected in precleaned amber glass bottles (as were all samples for organic analysis). Samples for nitrolotriacetic acid (NTA), ethylenediamine tetraacetic acid (EDTA), and nonylphenolethoxycarboxylate (NPEC) analyses were pressure-filtered through 1-μm glass-fiber filters and preserved with 2% (v/v) formalin. All samples were stored at 4 °C until analysis.

In May 1998, samples from the four multilevel observation wells shown in Figure 2 (a total of 22 sampling points) were analyzed for about 40 constituents. On the basis of results of the May sampling, samples from five of the 22 points were
collected in August 1998 and analyzed for DOM fractionation and characterization studies. For each sample, 100 L was filtered in the field through Balston 25-μm and 1.0-μm glass cartridge filters in series (9), collected in 20-L polyethylene cubitainers, and shipped in coolers with ice to the laboratory. To focus on the nature and changes in reclaimed-water organic constituents at the point of infiltration, reclaimed water was sampled in June 1999 at the research basin and at 1, 2, 3, 5, and 10-ft depths below the research basin after about a month of steady infiltration.

**Reclaimed Water Indicator Measurements.** Inorganic chemical analyses were done by the USGS National Water-Quality Laboratory in Arvada, CO using methods described by Fishman and Friedman (10) and Timme (11). For age determinations, tritium analyses were performed (Robert L. Michel at the USGS Tridium Laboratory in Menlo Park, CA) by liquid-scintillation counting following electrolytic enrichment, and helium-3 analyses were done by Robert Poreda at the University of Rochester in Rochester, NY, by mass spectrometry. DOC was measured by UV-enhanced persulfate oxidation using a Sievers Model 800 Carbon Analyzer. UV254 was determined using a Bausch and Lomb Spectronics Model 710 spectrophotometer and a 1-cm quartz cell; this measurement provides an indication of the humic and fulvic acid contribution to the total DOC (12). Fluorescence was measured on a Turner Designs Model 10-AU fluorometer using an excitation filter (300–400 nm) and an emission filter (410–500 nm) to identify materials consistent with fluorescent whitening agents found in domestic laundry detergents, although other types of compounds may fluoresce at similar wavelengths.

EDTA, NTA, and NPEC were measured using the method of Schaffner and Giger (13) with some modifications (14). A 100-mL form-in-washed sample was spiked with 1 μg of d12-EDTA (Cambridge Isotope Laboratories, Andover, MA) as a surrogate standard and the sample was evaporated to dryness in an oven at 85 °C (~48 h). The sample residue was acidified with 2 mL of 50:50 (v/v) formic acid: distilled water and vacuum-evaporated to dryness. The residue was derivatized to form the propyl esters of NTA, EDTA, and NPEC by adding 1.5 mL of 10% (v/v) acetyl chloride/propanol, heating at 85 °C for 1 h, and extracting the esters into chloroform. The chloroform extract was evaporated to dryness and redissolved in 100 μL of toluene. The derivatized extracts were analyzed in full scan and selected ion monitoring (SIM) by GC/MS using the following splitless conditions: injection port temperature, 280 °C; initial oven temperature, 100 °C for 1 min; ramp rate, 20 °C/min to 140 °C followed by 7 °C/min to 300 °C for 5 min. SIM data were collected for the protonated molecular ion [M+H]+ of the propyl ester derivatives of NTA, EDTA, and NPEC as the base peaks (m/z 230 for NTA, m/z 247 for EDTA, m/z 252 for d12-EDTA, and m/z 262 for nonylphenol-2-ethoxycarboxylate (NP2EC)) and for the base peaks (m/z 230 for NTA and EDTA, m/z 247 for d12-EDTA, and m/z 252 for NP2EC). Quantitation was based on the [M+H]+ peak area of the d12-EDTA surrogate standard and response factors determined from a six-point calibration curve. The detection limits were about 0.2 μg/L for NTA and EDTA and about 1.0 μg/L for NPEC.

**DOM Fractionation and Isolation.** The 100-L filtered water samples were passed through 1-L bed-volume columns of Amberlite XAD-8 resin, MSC-1H cation-exchange resin, and Duolite A-7 anion-exchange resin in series. DOM was fractionated into the hydrophobic neutral fraction (HPI-N) by sorption to the XAD-8 resin, base fraction by sorption to the MSC-1H resin, and acid fraction by sorption to the Duolite A-7 resin. The hydrophilic neutral fraction (HPI-N) is not retained by the resin sorbents (9). The preparation and elution of the resin columns are discussed in previous reports of preparative DOM fractionation methodology (9, 15). The acid fraction was further subdivided into hydrophobic acids (HPO-

A) by sorption to a 100-mL bed-volume column of XAD-8 at pH 2 and transphosphoric acids (TPI-A) by sorption to a 100-mL bed-volume column Amberlite XAD-4 resin at pH 2; the hydrophilic acid fraction (HPI-A) was not retained by either resin. Elution and desalting procedures for these acid fractions are published elsewhere (15). For the reclaimed-water sample, the column eluent containing the HPI-N fraction was vacuum-evaporated to 100 mL, and this fraction was subdivided into colloidal HPI-N and dissolved HPI-N by dialysis through a 2000 dalton cellulose membrane. Therefore, colloids are submicron organic particulates ranging in size between 1.0 μm of the glass fiber filter and the 2000 dalton dialysis membrane. Silica that coisolated with the colloidal HPI-N fraction was removed by dialysis against dilute HF. Dialysis of the evaporated residue of 20 L of an unfractionated reclaimed-water sample increased the recovery of the colloidal HPI-N fraction from 10.8% to 31.1% of the DOM. The HPO-N fraction was partitioned between ethyl acetate and water at pH 1 to enrich this fraction with alkylphenol ethoxylates and their carboxylated metabolites. Ethyl acetate extracted 69% of the mass of the HPO-N fraction.

For the groundwater samples, the HPI-N was not isolated because of the large volume of water to be evaporated, and the TPI-A fraction was operationally combined and isolated with the HPI-A fraction.

**DOM Spectral Characterizations.** Infrared spectra were obtained using 2–5 mg of DOM fraction isolates in potassium bromide pellets. The Perkin-Elmer System 2000 Fourier Transform Infrared (FT-IR) spectrometer was set to scan from 4000 to 400 cm−1, averaging 10 scans at 1.0 cm−1 intervals with a resolution of 4.0 cm−1. All spectra were normalized after acquisition to a maximum absorbance of 1.0 for comparative purposes.

Solid-state cross-polarization magic angle spinning (CPMAS) 13C-nuclear magnetic resonance (NMR) spectra were obtained on 20–200 mg of DOM samples. The acid and neutral DOM fractions were in hydrogen form, and the base fractions were in ammonium-salt form. CPMAS 13C NMR spectra were obtained on a 200-megahertz (MHz) Chemagnetics CMX spectrometer with a 7.5-mm-diameter probe. The spinning rate of the sapphire rotor was 5000 Hz. The acquisition parameters included a contact time of 5 ms, pulse delay of 1 s, and a pulse width of 4.5 μs for the 90° pulse. Variable contact time studies by Alemay et al. (16) indicate that these are optimum parameters for quantitatively determining the contributions of different carbon structural groups to the DOC 13C-NMR spectra.

**DOM Isolate Measurements.** After IR and NMR spectral characterizations, the groundwater DOM fractions were redissolved in distilled water in the same proportions in which they had been isolated. They were freeze-dried and distributed for DOM isotope measurements. The DOM was combusted to CO2 by sealed-tube CuO oxidation and was purified. A CO2 split was converted to graphite and measured for 13C by accelerator mass spectrometry (17). The remaining CO2 was analyzed for δ13C by isotope ratio mass spectrometry and was normalized to the NBS PDP standard.

Total organic halide (TOX) and trihalomethane (THM) were determined on the redissolved DOM isolates using American Water Works Association (AWWA) Standard Method 5320 for TOX measurement (18) and U.S. Environmental Protection Agency Method 551 for THM measurement (19). Seven-day nonpurgeable total organic halide formation potential (TOX-FP) and trihalomethane formation potential (THM-FP) analyses were performed on selected samples using AWWA Standard Method 5710 (18). All THM and TOX samples were analyzed in duplicate to compensate for the inherent variability of the analytical procedures. Samples with relative-percent differences of the duplicates that exceeded 30% were reanalyzed.

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TABLE 1. Selected Constituents Measured in Reclaimed Water, Ponded Water, and Groundwaters during May 1998 Sampling

<table>
<thead>
<tr>
<th>sample</th>
<th>DOC (mg/L)</th>
<th>SUVA (L/mg-m)</th>
<th>SF (L/mg-cm)</th>
<th>EDTA (µg/L)</th>
<th>NP2EC (µg/L)</th>
<th>SC (µS)</th>
<th>DO (mg/L)</th>
<th>NO₃⁻ (mg/L as N)</th>
<th>B (µg/L)</th>
<th>Cl (mg/L)</th>
<th>δ¹³C/δ³⁷Ar (‰)</th>
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<tr>
<td>reclaimed water</td>
<td>8.4</td>
<td>1.5</td>
<td>7.8</td>
<td>311</td>
<td>45</td>
<td>1006</td>
<td>4.2</td>
<td>2.21</td>
<td>424</td>
<td>115</td>
<td>ND</td>
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<tr>
<td>ponded water on San Gabriel Spreading Grounds</td>
<td>5.5</td>
<td>1.9</td>
<td>3.9</td>
<td>64</td>
<td>18</td>
<td>673</td>
<td>9.4</td>
<td>1.27</td>
<td>153</td>
<td>53</td>
<td>ND</td>
</tr>
</tbody>
</table>

Pico Rivera
well 18C7                | 190        | 0.8           | 1.2          | 3.3         | 5.2          | <1.0    | 930       | 0.15             | 1.54     | 217       | 70               |
well 18C6                | 400        | 0.7           | 1.1          | 3.1         | 5.7          | 1.5     | 1041      | 0.05             | 0.05     | 170       | 82               |
well 18C5                | 490        | 0.3           | 1.4          | 5.4         | <0.2         | <1.0    | 506       | 0.15             | 0.05     | 69        | 18               |
well 18C4ᵇ                | 900        | 3.4           | 4.6          | 27.6        | <0.2         | <1.0    | 574       | 0.05             | 0.05     | 609       | 4                |

Rio Hondo
well 26D14ᵇ               | 160        | 1.3           | 1.7          | 5.8         | ND           | ND      | 566       | 0.10             | 0.18     | 152       | 47               |
well 26D13               | 300        | 1.0           | 1.4          | 4.0         | <0.2         | <1.0    | 586       | 0.10             | 1.19     | 149       | 45               |
well 26D12ᵇ               | 450        | 0.9           | 1.5          | 4.0         | 4.5          | <1.0    | 750       | 0.15             | 3.00     | 203       | 64               |
well 26D11               | 730        | 0.6           | 1.0          | 2.2         | <0.2         | <1.0    | 722       | 0.75             | 2.58     | 148       | 57               |
well 26D10               | 930        | 0.3           | 1.0          | 3.8         | ND           | ND      | 703       | 0.15             | 0.05     | 54        | 47               |
well 26D9                | 1130       | 0.5           | 2.0          | 10.1        | <0.2         | <1.0    | 453       | 0.20             | 0.05     | 74        | 19               |

Downey
well 9J 6                | 110        | 0.7           | 1.2          | 4.2         | <0.2         | 2.3     | 1266      | 0.15             | 0.05     | 220       | 93               |
well 9J 5                | 270        | 0.6           | 0.7          | 2.5         | <0.2         | 2.4     | 857       | 0.20             | 0.05     | 103       | 59               |
well 9J 4ᵇ                | 390        | 0.7           | 1.2          | 2.8         | <0.2         | 1.9     | 871       | 0.20             | 2.60     | 195       | 73               |
well 9J 3                | 600        | 0.5           | 1.2          | 0.9         | <0.2         | <1.0    | 793       | 3.20             | 2.81     | 79        | 63               |
well 9J 2                | 960        | 0.4           | 1.3          | 0.6         | <0.2         | <1.0    | 570       | 3.03             | 1.82     | 69        | 25               |
well 9J 1                | 1190       | 0.4           | 1.1          | 0.1         | <0.2         | <1.0    | 347       | 0.15             | 0.05     | 64        | 6                |

Lakewood
well 9H10               | 90         | 1.4           | 2.4          | 4.9         | <0.2         | 1.0     | 1133      | 0.40             | 0.05     | 91        | 210              |
well 9H9                | 160        | 0.4           | 2.3          | 8.8         | <0.2         | 1.2     | 398       | 0.30             | 0.05     | 84        | 10               |
well 9H8                | 300        | 0.6           | 2.2          | 9.9         | <0.2         | <1.0    | 435       | 0.85             | 0.05     | 76        | 19               |
well 9H7ᵇ               | 470        | 0.5           | 2.1          | 10.3        | <0.2         | <1.0    | 349       | 0.50             | 0.05     | 62        | 9                |
well 9H6                | 660        | 0.5           | 2.7          | 7.8         | <0.2         | 3.0     | 322       | 0.30             | 0.05     | 53        | 7                |
well 9H5                | 1009       | 1.7           | 3.1          | 15.0        | 1.9          | 1.9     | 271       | 0.50             | 0.05     | 63        | 19               |

* Well depth in feet below land surface; ND, not determined. † Resampled in August 1998 for DOM characterization.

Results and Discussion

Reclaimed Water Indicator Studies. The areal distribution of reclaimed water in receiving groundwater needed to be established before samples for DOM fractionation, spectral characterizations, and chlorine reactivity studies were taken to observe changes in reclaimed water DOM resulting from soil aquifer treatment. Selected results from the survey (Table 1) of about 40 constituents measured in groundwater from distant downgradient (Downey) and background (Lakewood) wells indicate that trace amounts of reclaimed-water contaminants were present in some of the wells but at concentrations that were significantly less than had been observed near the infiltration beds in previous studies (4–6, 20) of groundwater from 23 production wells in the immediate vicinity of the Montebello Forebay spreading grounds. Boron, chloride, nitrate, DOC, EDTA, fluorescence, and UV₂₅₄ absorbance were evaluated as reclaimed-water indicators. Many of these indicators are of limited use in the distant wells because of dilution, degradation, and natural variations in aquifer hydrogeology and water quality. A previous study (6) found that excess (above background) boron, excess chloride, UV₂₅₄ absorbance, and fluorescence gave the highest correlations with reclaimed water percentages. Dissolved-boron concentration is the best single indicator of reclaimed water for this study, with concentrations in excess of the 50–80 µg/L background being an indicator of reclaimed-water content. Well 18C4 is an exception because of the high natural boron concentration in the marine Pico Formation that underlies the main water-bearing San Pedro units. There appears to be little if any mixing between the two formations. The best organic indicators for reclaimed water are DOC (concentrations in excess of 0.5 mg/L, wells 18C4 and 9H5 excepted), low specific UV₂₅₄ absorbance (SUVA) in the range of 1.0–1.5 L/mg-m, and specific fluorescence (SF) in the range of 2–4 L/mg-cm. Groundwater samples whose tritium age is less than about 30 years all contain reclaimed-water indicators, whereas these indicators are absent in older groundwater. The infiltration basins have been recharging stormwater and imported Colorado River water since the early 1950s, but recharge of reclaimed water has occurred only since 1962 (5). Although the proportion of recharge represented by reclaimed water was initially quite small, it gradually increased to about 30% in the 1990s.

For both the previous study of reclaimed water in the production wells (20) and this study of reclaimed water in observation wells (Table 1), concentrations of the organic indicators of reclaimed water, such as EDTA, decreased more rapidly with travel distance than did the concentrations of inorganic indicators, such as boron and chloride. To obtain a better understanding of the processes that transform the organic indicators during infiltration, additional data were collected at the research infiltration basin (location shown in Figure 1) during June 1999. These data are presented in Table 2 and Figure 3. In June 1999, all water supplied to the research basin was reclaimed water, as indicated by the nearly identical specific conductance values at all depths in Table 2. Concentrations of DOC, NTA, EDTA, and NPZEC also are similar to average values measured in a variety of wastewaters from the Upper Midwest (14). However, note that there was a significant decrease in EDTA concentrations in the ponded water, suggesting possible removal by photolytic processes (21). In contrast, differences in concentrations between the reclaimed water and ponded water from the San Gabriel Spreading Grounds in samples collected during May 1998 were much greater (Table 1), with concentrations of some constituents in the ponded water in the spreading grounds being only 20% the concentrations in the reclaimed water. This larger difference is attributed to the much greater
consumption from stormwater runoff in the infiltration pond during May 1998, an El Niño year characterized by unusually heavy rainfall. These differences illustrate the dynamic nature of the recharge-water composition. As a result, composition of the groundwater at any given point is a function of its original blend of ambient groundwater, reclaimed water, and stormwater as well as transformation processes that occur during subsurface transport. Concentrations of DOC, EDTA, and NTA were attenuated during infiltration at the research basin (Table 2, Figure 3), with the greatest reduction occurring within the first 1 foot, and only minor additional decreases over an additional 9 feet of infiltration. Although the levels of DOC and EDTA decreased during the 10 ft of infiltration, they still remained significantly higher (1–2 orders of magnitude) than in any of the downgradient wells (Table 1), indicating additional attenuation during subsequent subsurface transport or lower percentages of reclaimed-water inputs in the past. Similar results for loss of these organic tracers has been reported during recharge of Santa Ana River into the underlying aquifers in Orange County, CA (22).

TOX yield, THM yield, and NP2EC values did not change significantly during infiltration. Therefore, DOM precursors of disinfection byproducts in reclaimed water are not rapidly removed by soil aquifer treatment. APECs such as NP2EC are transient intermediates and can be formed and removed at the same time (23). SUVA and specific fluorescence values increased inversely to DOC loss. This inverse relationship (DOC is the denominator in SUVA and specific fluorescence) indicates that the DOC loss is specific to organic matter that has low UV254 absorbance and fluorescence.

The fact that dissolved oxygen disappears almost completely within the first foot of infiltration indicates a high level of microbiologic oxidation of organic carbon and reduced nitrogen at the infiltration interface. This rapid loss of oxygen partially explains why almost all the observation-well samples in Table 1 have very little oxygen, although some native groundwaters also have dissolved oxygen. The peaks and valleys in the fluorescence, UV254, EDTA, and NTA removals as opposed to monotonic trends shown in Figure 3 may be related to diurnal variations in wastewater composition or to photolytic and microbiological degradation of these indicators. Dilution by resident groundwater is not likely a factor in these indicator-losses because there are no significant variations in specific conductance with depth (Table 2).

**TABLE 2. Selected Constituents Measured in Reclaimed Water, Pondered Water, and Groundwater during Infiltration in Research Basin, June 1999**

<table>
<thead>
<tr>
<th>sample</th>
<th>specific conductance (µS)</th>
<th>dissolved oxygen (mg/L)</th>
<th>DOC (mg/L)</th>
<th>SUVA (L/mg-m)</th>
<th>SF (L/mg-m)</th>
<th>NTA (µg/L)</th>
<th>EDTA (µg/L)</th>
<th>NP2EC (µg/L)</th>
<th>TOX yield (µg/mg DOC)</th>
<th>THM yield (µg/mg DOC)</th>
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<tr>
<td>reclaimed water</td>
<td>962</td>
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<td>4.6</td>
<td>386</td>
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<td>ponded water in Research Basin</td>
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<td>1-foot</td>
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<td>2.5</td>
<td>203</td>
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<td>1.8</td>
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<td>2.0</td>
<td>175</td>
<td>67</td>
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* ND, not determined.

**FIGURE 3. Percentage change with depth of various constituents in reclaimed water during infiltration at the research basin.**
greater hydrophobic acid percentage in the groundwater samples compared to reclaimed water is the most pronounced difference in DOM fraction composition. Wells 26D12 and 9J4, which contain significant amounts of reclaimed water as indicated by the indicator concentrations, had higher hydrophobic acid and lower base percentages than did the background wells 1BC4 and 5H7. Well 26D14, in which reclaimed water is thought to be diluted by storm runoff water, had the greatest hydrophilic acid percentage, and its hydrophobic acid and base percentages were intermediate between those of the background wells and reclaimed-water end members. The infrared and $^{13}$C NMR spectra of the reclaimed-water DOM fractions are shown in Figure 5.

Spectral peak references labeled with reciprocal centimeters (cm$^{-1}$) refer to IR spectra, and peaks labeled with parts per million (ppm) refer to $^{13}$C NMR spectra of Figure 5 in the following discussion. Minor quantities of alkylphenolpolyethoxylates were found in the HPO-N fraction as shown by the peak at 1510 cm$^{-1}$ and peaks near 150, 115, and 70–80 ppm. The ethoxy chains must be short as evidenced by the small peaks at 70–80 ppm (24). The peak at 80 ppm is likely the methylene carbon between the ether linkage and the carboxyl group for the alkylphenol-1-ethoxycarboxy metabolite. The HPO-N fraction appears to consist of alkyl aromatic sulfonates, as evidenced by the aromatic sulfonic acid group (1035 and 1009 cm$^{-1}$ and 130 and 140 ppm) and the alkyl group (2930 cm$^{-1}$ and 0–50 ppm) (25). Alkyl carboxylic acids (1737 cm$^{-1}$ and 175 ppm) also are present.

The HPO-A fraction contains aromatic sulfonic acids, as indicated by the peaks designated previously. These aromatic sulfonic acids are likely carboxylated (peaks at 1719 cm$^{-1}$ and 175 ppm) metabolites of anionic surfactants. A portion of the DOM in this fraction also is natural organic matter (NOM) derived from the drinking-water input to reclaimed water (15). The TPI-A fraction contains smaller amounts of aromatic sulfonic acids and greater amounts of carbohydrates (IR plateau at 1100 cm$^{-1}$ and NMR peaks at 75 and 105 ppm) and carboxylic acids. The HPI-A contains only trace amounts of aromatic sulfonic acids, and it appears to be predominantly hydroxy acids (3391 and 1043 cm$^{-1}$ and 75 ppm) and carboxylic acids (1732 cm$^{-1}$ and 175 ppm).

The base fraction appears to be primarily proteinaceous in composition, with its combination amide/carboxylic acid peaks (1634 cm$^{-1}$ and 173 ppm) and C–N linkage at 55 ppm. The colloidal HPI-N spectra are typical for bacterial peptidoglycan cell-wall components in which N-acetyl units are shown by methyl peaks at 1378 cm$^{-1}$ and 22 ppm, secondary amide peaks at 1651 cm$^{-1}$ and 1548 cm$^{-1}$, and the C–N linkage at 55 ppm (15). The anomeric carbon unit of the amino sugar component is exceptionally well defined by the peak at 100 ppm. The dissolved HPI-N fraction is rich in alcohols (peaks at 3394 cm$^{-1}$, 1080 cm$^{-1}$, and 75 ppm), but the anomeric carbon peak near 100 ppm is of low intensity, which indicates that most of the alcohols are of non-carbohydrate nature. Peaks for N-acetylamino sugars also were found for the colloidal fraction, but the peak near 160 ppm is different. This peak, in combination with the IR peak at 1719 cm$^{-1}$, might indicate urea precursors, such as allantoin, that are an end product of purine metabolism. The presence of urea itself is excluded by the IR spectrum of this fraction.

The rapid 40% DOC loss during infiltration of reclaimed water (Figure 3) can now be explained by the combined removal of colloidal and dissolved hydrophilic neutral fractions that do not have aromatic carbon (Figure 5) and hence have comparatively low UV$_{254}$ absorbance and fluorescence. These hydrophilic neutral fractions also account for about 40% of the DOM in Figure 4.

To detect DOM derived from reclaimed water on the basis of spectral characterization in groundwater after infiltration, dilution, mixing, degradation, and migration, the spectral signature requirements must be for an organic component that is abundant, is different from NOM, is biologically and geochemically conservative, and has strong and recognizable spectral peaks. Only the aromatic sulfonic acid metabolites, especially the more biologically refractory metabolites such as dialkyltetralin sulfonates (26), meet all of these requirements. Aromatic sulfonate metabolites occur primarily in the HPO-A fraction; therefore, this fraction was selected to detect the presence of reclaimed-water DOM in groundwater. The infrared and the $^{13}$C NMR spectra of the groundwater DOM fractions are shown in Figure 6.

The aromatic sulfonate peak derived from reclaimed water in Wells 26D14, 26D12, and 9J4 was detected as an IR peak in the 1038–1051 cm$^{-1}$ range and as a weak shoulder at 140 ppm for the $^{13}$C NMR spectra. IR spectrometry appears to be a better detector than $^{13}$C NMR spectrometry for aromatic
sulfonates in these groundwater samples. The HPO-N fraction showed even weaker peaks for aromatic sulfonates (spectra not shown), and the other fractions did not show any spectral peaks other than those typically observed for natural DOM. The two background groundwater samples (wells 18C4 and 5H7) had aromatic carbon spectral profiles between 110 and 160 ppm that are broader than samples from wells containing reclaimed water. Well 9J4 has a higher 13C value than wells 26D12 and 26D14 because this water was recharged 26 years ago (Table 1) when atmospheric 14C levels were greater than present levels because of the atomic testing program (Michael T. Land, USGS, oral communication). The pattern of high 14C associated with the bomb peak is also preserved in the inorganic carbon, and both are similar to the pattern for tritium itself (5). The higher levels of 14C in wells 9J4 and 26D14 indicate the persistence in groundwater of DOM associated with recharge that occurred some two decades before the present. 14C and 13C were also measured on colloidal hydrophilic neutrals and the hydrophobic acid fractions isolated from reclaimed water used for recharge. The colloidal fraction was 96% modern carbon (13C = -22.8), and the hydrophobic acids were 50% modern carbon (13C = -26.5). The unusually low 14C for the hydrophobic acids is consistent with sulfonic acid coproducts and metabolites originating from petroleum synthesis. The 13C and 14C of the colloidal fraction indicated mostly biologically derived amino sugars.

Chlorination reactivity with DOM isolates from the groundwater samples is presented in Table 4. The low TOX-FP and THM-FP yields found in the reclaimed water recharge basin, and nearby sites have been reported previously (20). Yields for both TOX-FP and THM-FP in the reconstructed DOM isolates from wells 9J4, 26D12, and 26D14 are also very low and are similar to the whole water yields reported previously (20). These low yields are more indicative of yields for reclaimed water, in contrast to the yields for the background wells, 18C4 and 5H7.

Chlorination yields in Table 4 are positively correlated with SUVA (r = 0.95 for THM yield and r = 0.98 for TOX yield). Yields and SUVA were lower in wells that contained reclaimed water than in uncontaminated wells because fluorescent whitening agents that give high SUVA and specific fluorescence values may not persist long after recharge owing to their tendency to sorb onto sediment surfaces (28). Well 26D14, which contained mostly infiltrated stormwater, gave higher yields than did wells with greater amounts of reclaimed water. A significant amount of the aromatic carbon in reclaimed water (Figures 5 and 6) has sulfonic acid substituents with minor amounts of synthetic alkylphenol polyethoxylate carboxylates. Apparently, these compound classes have low chlorination yields, and they also have low SUVA and specific fluorescence values. Single-ring aromatic sulfonate standards have about 30% of the molar absorbance and fluorescence characteristics (29). The organic 13C isotope results (Table 3) were negatively correlated with both TOX yield (r2 = 0.94) and THM yield (r2 = 0.87). Aromatic carbon with phenol substituents derived from tannins and lignins is known to be responsible for much of the THM and TOX production, along with enhanced UV254 absorbance and fluorescence characteristics (30). The 13C NMR spectra of Figure 6 indicate phenolic aromatic carbon (a small peak near 150 ppm) in the background groundwater.

**TABLE 3. Carbon Isotope Determinations for Groundwater DOM Isolates**

<table>
<thead>
<tr>
<th>sample</th>
<th>313C (per million, %) organic</th>
<th>313C (percent modern carbon) inorganic</th>
<th>14C (percent modern carbon) organic</th>
<th>14C (percent modern carbon) inorganic</th>
</tr>
</thead>
<tbody>
<tr>
<td>well 18C4</td>
<td>-25.8</td>
<td>-3.9</td>
<td>8</td>
<td>1.6</td>
</tr>
<tr>
<td>well 5H7</td>
<td>-25.5</td>
<td>-12.9b</td>
<td>39</td>
<td>16b</td>
</tr>
<tr>
<td>well 9J4</td>
<td>-25.9</td>
<td>-11.2b</td>
<td>80</td>
<td>111b</td>
</tr>
<tr>
<td>well 26D12</td>
<td>-24.8</td>
<td>-11.7</td>
<td>71</td>
<td>96</td>
</tr>
<tr>
<td>well 26D14</td>
<td>-25.5</td>
<td>NDa</td>
<td>59</td>
<td>NDa</td>
</tr>
</tbody>
</table>

* ND, not determined. b Inorganic data from next deeper wells 5H6 and 9J3.

**TABLE 4. Trihalomethane (THM) and Total Organic Halide (TOX) Yields for Groundwater DOM Isolates**

<table>
<thead>
<tr>
<th>sample</th>
<th>µg THM/mg DOC</th>
<th>µg TOX/mg DOC</th>
<th>SUVA (L/mg-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>well 18C4</td>
<td>90</td>
<td>189</td>
<td>4.9</td>
</tr>
<tr>
<td>well 5H7</td>
<td>68</td>
<td>137</td>
<td>3.3</td>
</tr>
<tr>
<td>well 9J4</td>
<td>51</td>
<td>80</td>
<td>2.1</td>
</tr>
<tr>
<td>well 26D12</td>
<td>37</td>
<td>63</td>
<td>1.9</td>
</tr>
<tr>
<td>well 26D14</td>
<td>50</td>
<td>93</td>
<td>2.3</td>
</tr>
</tbody>
</table>

(27). However, the organic 14C results show considerable variation, with values for the two background wells (18C4 and 5H7) being lower than those for the wells that contain reclaimed water. Well 9J4 has a higher 14C value than wells 26D12 and 26D14 because this water was recharged 26 years ago (Table 1) when atmospheric 14C levels were greater than present levels because of the atomic testing program (Michael T. Land, USGS, oral communication). The pattern of high 14C associated with the bomb peak is also preserved in the inorganic carbon, and both are similar to the pattern for tritium itself (5). The higher levels of 14C in wells 9J4 and 26D14 indicate the persistence in groundwater of DOM associated with recharge that occurred some two decades before the present. 14C and 13C were also measured on colloidal hydrophilic neutrals and the hydrophobic acid fractions isolated from reclaimed water used for recharge. The colloidal fraction was 96% modern carbon (13C = -22.8), and the hydrophobic acids were 50% modern carbon (13C = -26.5). The unusually low 14C for the hydrophobic acids is consistent with sulfonic acid coproducts and metabolites originating from petroleum synthesis. The 13C and 14C of the colloidal fraction indicated mostly biologically derived amino sugars.

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that is not present in the wells containing infiltrated reclaimed water. Therefore, natural DOM in groundwater produces more chlorinated disinfection byproducts than does reclaimed-water DOM. This finding was reported previously for the production well study (20), but the present study has identified the DOM structural characteristics that are responsible for the chlorination reactivity differences.

Conclusions
Infiltration of reclaimed water into groundwater at this study site does not appear to degrade the groundwater quality with respect to production of chlorinated disinfection byproducts in drinking water. Most of the anthropogenic organic tracers detected in reclaimed water were removed by soil aquifer treatment (or diluted beyond detection limits of this study) with only trace amounts of aromatic sulfonates and 2P2EC metabolites derived from anionic and nonionic surfactants remaining 26 years after infiltration. The bulk of the DOM in infiltrated reclaimed water is refractory DOM (fulvic acid) derived from wastewater treatment and natural fulvic acid in the water supply.

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Literature Cited
(7) Bookman-Edmonston Engineering, Inc. Engineering background studies for Rand Corporation’s health effects study; Water Replenishment District of Southern California, 12621 E. 166th St., Cerritos, CA, May 1993; 7 sections.

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