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

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The nature and chlorine 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 ^{3}H and ^{3}He isotopes, and determinations of organic and inorganic C 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" in *Environmental Science and Technology* (*1*) 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-

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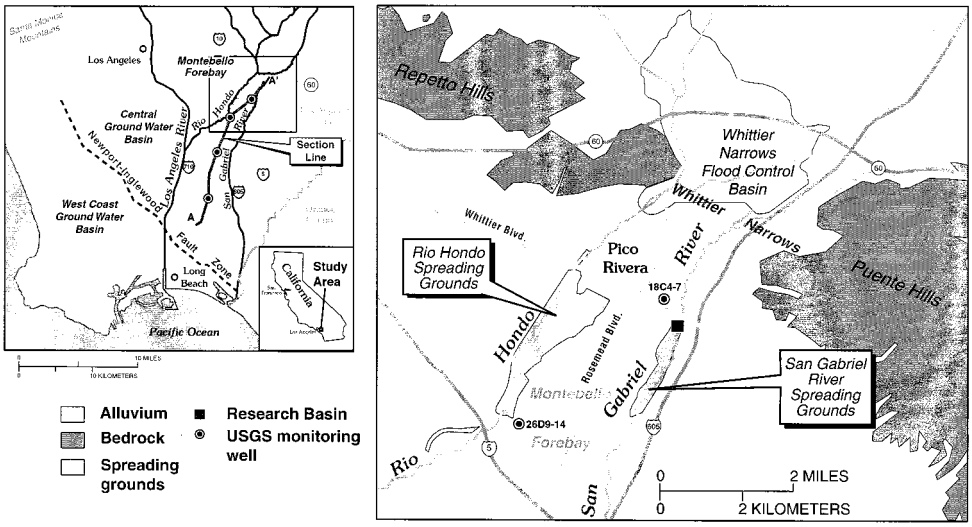

FIGURE 1. Map showing physiographic features and location of USGS multilevel monitoring wells in Central Groundwater Basin (left) and in Montebello Forebay recharge area (right).

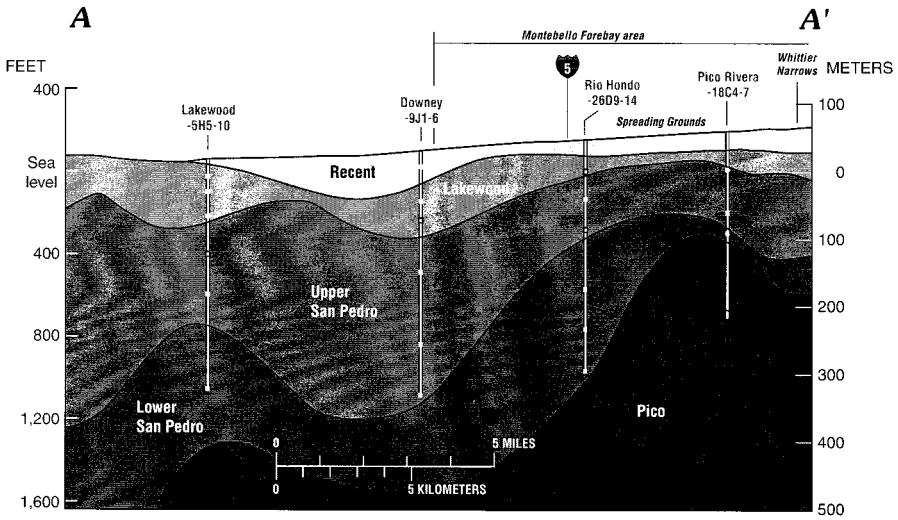

FIGURE 2. Location and depth of aquifer systems and USGS multilevel monitoring wells on geohydrologic section A−A′ (see Figure 1) aligned in the direction of groundwater flow.

structed 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 (UV_{254}), 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 Tritium 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. UV_{254} 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 formalin-preserved sample was spiked with 1 μg of d_{12}-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 extracts were 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/minute to 140 °C followed by 7 °C/minute to 300 °C for 5 min. SIM data were collected for the protonated molecular ion [M^+] of the propyl ester derivatives of NTA, EDTA, and NP2EC [m/z 317 for NTA, 460 for EDTA, 472 for d_{12}-EDTA, and 362 for nonylphenol-2-ethoxycarboxylate (NP2EC)] and for the base peaks (m/z 230 for NTA and EDTA, 236 for d_{12}-EDTA, and 103 for NP2EC). Quantitation was based on the [M^+] peak area of the d_{12}-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 μg/L for NPEC.

DOM Fractionation and Isolation. The 100-L filtered water samples were passed through l-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 (HPO-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 transphilic 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 alkylphenolethoxylates 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 (CP-MAS) ^{13}C-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 ^{13}C 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 Alemany et al. (*16*) indicate that these are optimum parameters for quantitatively determining the contributions of different carbon structural groups to the DOC ^{13}**C-**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 CO_2 by sealed-tube CuO oxidation and was purified. A CO_2 split was converted to graphite and measured for ^{14}C by accelerator mass spectrometry (*17*). The remaining CO_2 was analyzed for δ^{13}C 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.

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

sample	well depth (ftBLS)	DOC (mg/L)	SUVA (L/mg-m)	SF (L/mg-cm)	EDTA (μg/L)	NP2EC (μg/L)	SC (μS)	DO (mg/L)	NO_3 (mg/L as N)	B (μg/L)	Cl (mg/L)	$^3H/^3He$ age(yr)
reclaimed water		8.4	1.5	7.8	311	45	1006	4.2	2.21	424	115	0
ponded water on San Gabriel Spreading Grounds		5.5	1.9	3.9	64	18	673	9.4	1.27	153	53	ND
Pico Rivera												
well 18C7	190	0.8	1.2	3.3	5.2	<1.0	930	0.15	1.54	217	70	ND
well 18C6	400	0.7	1.1	3.1	5.7	1.5	1041	0.05	0.05	170	82	ND
well 18C5	480	0.3	1.4	5.4	<0.2	<1.0	506	0.15	0.05	69	18	ND
well 18C4[b]	900	3.4	4.6	27.6	<0.2	<1.0	574	0.05	0.05	609	4	ND
Rio Hondo												
well 26D14[b]	160	1.3	1.7	5.8	ND	ND	566	0.10	0.18	152	47	2.7
well 26D13	300	1.0	1.4	4.0	<0.2	<1.0	586	0.10	1.19	149	45	3.0
well 26D12[b]	450	0.9	1.5	4.0	4.5	<1.0	750	0.15	3.00	203	64	14
well 26D11	730	0.6	1.0	2.2	<0.2	<1.0	722	0.75	2.58	148	57	20
well 26D10	930	0.3	1.0	3.8	ND	ND	703	0.15	0.05	54	47	31
well 26D9	1130	0.5	2.0	10.1	<0.2	<1.0	453	0.20	0.05	74	19	ND
Downey												
well 9J6	110	0.7	1.2	4.2	<0.2	2.3	1266	0.15	0.05	220	93	ND
well 9J5	270	0.6	0.7	2.5	<0.2	2.4	857	0.20	0.05	103	59	26
well 9J4[b]	390	0.7	1.2	2.8	<0.2	1.9	871	0.20	2.60	195	73	26
well 9J3	600	0.5	1.2	0.9	<0.2	<1.0	793	3.20	2.81	79	63	30
well 9J2	960	0.4	1.3	0.6	<0.2	<1.0	570	3.03	1.82	69	25	34
well 9J1	1190	0.4	1.1	0.1	<0.2	<1.0	347	0.15	0.05	64	6	ND
Lakewood												
well 5H10	90	1.4	2.4	4.9	<0.2	1.0	1133	0.40	0.05	91	210	ND
well 5H9	160	0.4	2.3	8.8	<0.2	1.2	398	0.30	0.05	84	10	ND
well 5H8	300	0.6	2.2	9.9	<0.2	<1.0	435	0.85	0.05	76	19	ND
well 5H7[b]	470	0.5	2.1	10.3	<0.2	<1.0	349	0.50	0.05	62	9	>50
well 5H6	660	0.5	2.7	7.8	<0.2	3.0	322	0.30	0.05	53	7	ND
well 5H5	1009	1.7	3.1	15.0	1.9	ND	271	0.50	0.05	63	19	ND

[a] Well depth in feet below land surface; ND, not determined. [b] 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 UV_{254} 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, UV_{254} 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 5H5 excepted), low specific UV_{254} 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 NP2EC 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

TABLE 2. Selected Constituents Measured in Reclaimed Water, Ponded Water, and Groundwater during Infiltration in Research Basin, June 1999[a]

sample	specific conductance (μS)	dissolved oxygen (mg/L)	DOC (mg/L)	SUVA (L/mg-m)	SF (L/mg-m)	NTA (μg/L)	EDTA (μg/L)	NP2EC (μg/L)	TOX yield (μg/mg DOC)	THM yield (μg/mg DOC)
reclaimed water	962	3.4	7.6	1.6	1.5	4.6	386	65	ND	ND
ponded water in Research Basin	1008	8.2	7.8	1.5	1.2	5.6	328	64	159	46
geoprobes										
1-foot	989	0.3	6.1	1.9	1.5	2.5	203	67	138	47
2-foot	986	0.3	6.0	2.0	2.1	2.7	223	54	154	53
3-foot	982	0.1	5.6	1.9	1.7	2.4	224	64	136	46
wells										
WP-1, 5-foot	980	0.2	4.9	2.0	1.8	2.1	198	54	ND	ND
WP-2, 10-foot depth	971	0.1	4.7	2.0	1.8	2.0	175	67	ND	ND

[a] ND, not determined.

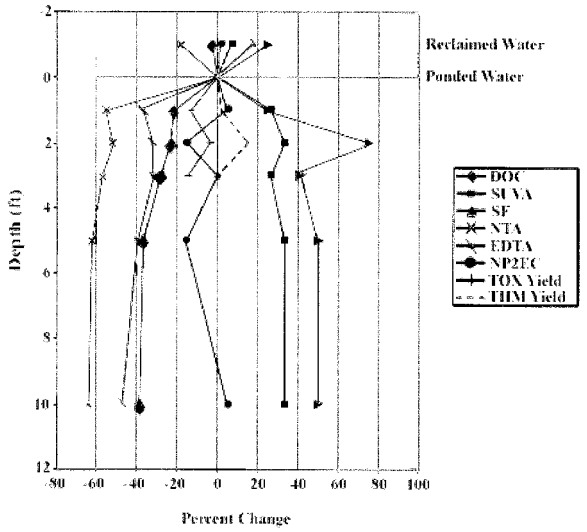

FIGURE 3. Percentage change with depth of various constituents in reclaimed water during infiltration at the research basin.

contribution 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 UV_{254} 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, UV_{254}, 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 degradations 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).

DOM Fractionations and Spectral Characterizations. The DOM fractionation coupled with IR and ^{13}C NMR was designed to meet the primary objective of comprehensively characterizing DOM at the compound class level of characterization and to provide fraction isolates for chlorine reactivity studies (*15*). DOM fractionations were performed on samples from five observation wells collected in August 1998 and on the reclaimed water sampled in June 1999. The latter sampling of reclaimed water was performed to take advantage of recent advances in DOM fractionation and isolation (*15*). Selection of the groundwater samples was based on the results from May 1998 presented in Table 1. The Pico Rivera well 18C4 was selected as a background "end member" for groundwater that underlies the water bearing San Pedro aquifer. The Rio Hondo well 26D14 was selected because its shallow depth and comparatively low specific conductance suggested a large component of recent stormwater that infiltrated the Rio Hondo basin during the previous period of high rainfall. Specific conductance of well 26D14 decreased by 146 μS in the August 1998 sample compared to the May 1998 sample indicating dilution by infiltrated stormwater. The deeper Rio Hondo well 26D12 was selected because constituents such as boron indicated that this groundwater contained a significant percentage of reclaimed water that, although older, had migrated a relatively short distance from the spreading grounds. The Downey well 9J4 was sampled because it contained reclaimed-water indicators and because it would represent groundwater with a substantial travel time and distance from the spreading grounds. The Lakewood well 5H7 displays no indicators of reclaimed water and the groundwater age predates recharge at the spreading grounds; hence, groundwater from this well is considered representative of background conditions.

A bar diagram of DOM fractionations for the reclaimed-water and groundwater samples is shown in Figure 4. The

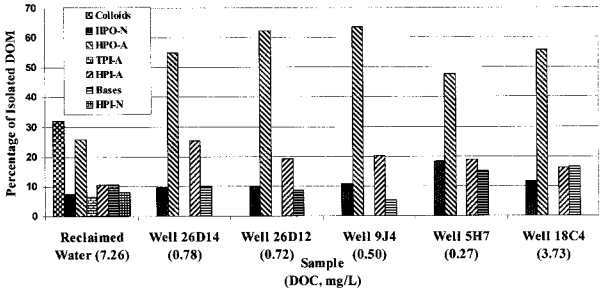

FIGURE 4. Bar diagram of DOM fractionations of reclaimed water and groundwater samples as a percentage of dissolved organic matter (DOM).

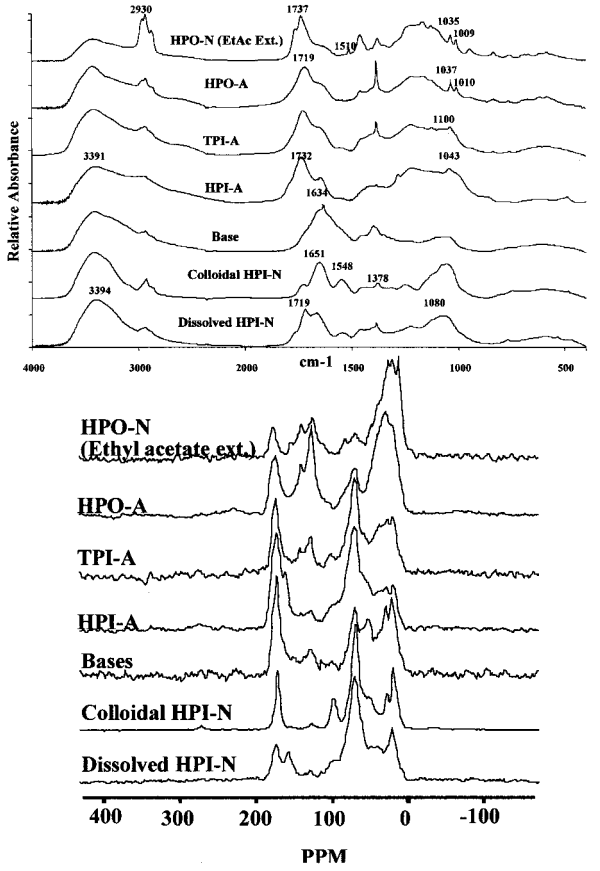

FIGURE 5. Infrared and ^{13}C NMR spectra of DOM fractions isolated from reclaimed water.

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 18C4 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 alkylphenolpolyethyoxylates 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 noncarbohydrate 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

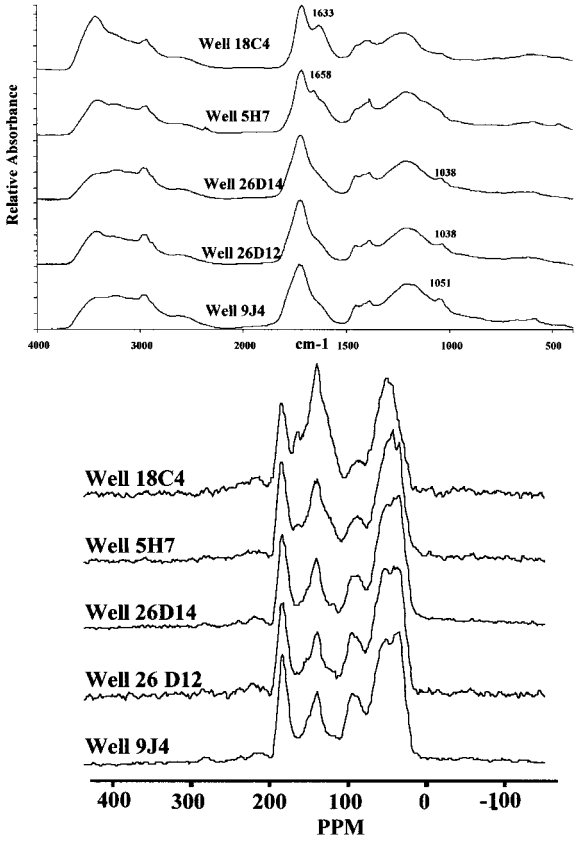

FIGURE 6. Infrared and ^{13}C NMR spectra of HPO-A fractions isolated from groundwater samples.

TABLE 3. Carbon Isotope Determinations for Groundwater DOM Isolates

	$\delta^{13}C$ (per million, ‰)		^{14}C (percent modern carbon)	
sample	organic	inorganic	organic	inorganic
well 18C4	−25.8	−3.9	8	1.6
well 5H7	−25.5	−12.9[b]	39	16[b]
well 9J4	−25.9	−11.2[b]	80	111[b]
well 26D12	−24.8	−11.7	71	96
well 26D14	−25.5	ND[a]	59	ND[a]

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

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 and a phenol subpeak near 150 ppm that are typical for aquatic humic substances. These aromatic humic components also are evidenced by the broad IR peaks near 1633 and 1658 cm^{-1}.

Groundwater DOM Isolate Characteristics and Chlorine Reactivity. DOM fractions isolated from the five groundwater samples were recombined in the same proportions (Figure 4) in which they were isolated to determine carbon isotopes and chlorine reactivity on the whole reconstituted DOM. The results for the carbon isotope determinations are given in Table 3.

The organic δ ^{13}C results in Table 3 show little variation and are typical for DOM derived from a mixture of carbohydrate, lipid, lignin, and petroleum hydrocarbon precursors

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

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

(*27*). However, the organic ^{14}C 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 ^{14}C value than wells 26D12 and 26D14 because this water was recharged 26 years ago (Table 1) when atmospheric ^{14}C levels were greater than present levels because of the atomic testing program (Michael T. Land, USGS, oral communication). The pattern of high ^{14}C 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 ^{14}C in wells 9J4 and 26D14 indicate the persistence in groundwater of DOM associated with recharge that occurred some two decades before the present. ^{14}C and $\delta^{13}C$ 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 ($\delta^{13}C = -22.8$), and the hydrophobic acids were 50% modern carbon ($\delta^{13}C = -26.5$). The unusually low ^{14}C for the hydrophobic acids is consistent with sulfonic acid coproducts and metabolites originating from petroleum synthesis. The ^{14}C and $\delta^{13}C$ of the colloidal fraction indicated mostly biologically derived amino sugars.

Chlorine 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 reconstituted 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 ($r^2 = 0.95$ for THM yield and $r^2 = 0.98$ 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 30−50% of the molar absorptivity at 254 nm of analogous aromatic carboxylate and phenol standards (*29*).

The organic ^{14}C isotope results (Table 3) were negatively correlated with both TOX yield ($r^2 = 0.94$) and THM yield ($r^2 = 0.87$). 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 UV_{254} absorbance and fluorescence characteristics (*30*). The ^{13}C NMR spectra of Figure 6 indicate phenolic aromatic carbon (a small peak near 150 ppm) in the background groundwaters

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

(1) Pinholster, G. *Environ. Sci. Technol.* **1995**, *29*, 174**A**−179**A**.
(2) Barber, L. B.; Thurman, E. M.; Schroeder, M. P.; LeBlanc, D. R. *Environ. Sci. Technol.* **1988**, *22*, 205−211.
(3) Reichard, E. G.; Land, M. T.; Crawford, S. M.; Shipke-Paybins, K.; Nishikawa, T.; Everett, R.; Johnson, T. A. *Geohydrology, geochemistry, and groundwater simulation of the Central and West Coast Basins, Los Angeles County, California*; U.S. Geological Survey Water-Resources Investigations Report 00-XXXX; Sacramento, CA, 2000; in press.
(4) Anders, R. Masters Thesis, San Diego State University, 1997; 247 p.
(5) Schroeder, R. A.; Anders, R.; Bohlke, J. K.; Michel, R. L.; Metge, D. W. In Proceedings of AWRA Symposium, *Conjunctive Use of Water Resources: Aquifer Storage and Recovery*; Kendall, D. R., Ed.; American Water Resources Association: Herndon, VA, 1997; pp 273−284.
(6) Anders, R.; Schroeder, R. A. American Geophysical Union Meeting, Boston, MA, May 26−29, 1998; EOS Transactions Supplement, April 28, 1998; Abstract H61B-23, p S141.
(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.
(8) Anders, R.; Schroeder, R.A. In Proceedings of AWRA Symposium, *Conjunctive Use of Water Resources: Aquifer Storage and Recovery*; Kendall, D. R., Ed.; American Water Resources Association: Herndon, VA, 1997; pp 285−296.
(9) Leenheer, J. A.; Noyes, T. I. *A Filtration and Column-Adsorption System for Onsite Concentration and Fractionation of Organic Substances from Large Volumes of Water;* U.S. Geological Survey Water-Supply Paper 2230, Reston, VA, 1984; 16 p.
(10) Fishman, M. J.; Friedman, L. C. *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments;* U.S. Geological Survey Techniques of Water −Resources Investigations, Book 5, Reston, VA, 1989; 545 p.
(11) Timme, P. J. *National Water Quality Laboratory 1994 Services Catalog;* U.S. Geological Survey Open-File Report 94-304; Reston, VA, 1994; 103 p.
(12) Thurman, E. M. *Organic Geochemistry of Natural Waters*; Martinus Nijhoff/Dr. Junk Pub.: Boston, MA, 1985; pp 312−316.
(13) Schaffner, C.; Giger, W. *J. Chromatogr.* **1984**, *312*, 413−421.
(14) Barber, L. B.; Brown, G. K.; Zaugg, S. A. In *Analysis of Environmental Endocrine Disruptors, American Chemical Society Symposium Series 747;* Keith, L., Jones-Lepp, T., Needham, L., Eds.; Washington, DC, Chapter 7, in press.
(15) Leenheer, J. A.; Croue, J.-P.; Benjamin, M.; Korshin, G. V.; Hwang, C. J.; Bruchet, A.; Aiken, G. R. In *Natural Organic Matter and Disinfection By-Products;* Barrett, S. E., Krasner, S. W., Amy, G. L., Eds.; ACS Symposium Series 761; Washington, DC, 2000; pp 68−83.
(16) Alemany, L. B.; Grant, D. M.; Pugmire, R. J.; Alger, T. D.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 2142−2147.
(17) Vogel, J. S.; Southon, J. R.; Nelson, D. E *Nucl. Instrum. Methods Phys. Res.* **1987**, *B29*, 50−56.
(18) AWWA. *Standard Methods for the Examination of Water and Wastewater*, 18th ed.; Washington, DC, 1992.
(19) U.S. Environmental Protection Agency, Method 551. In *Methods for the Determination of Organic Compounds in Drinking Water, Supplement 1, July 1990*; PB91-146027, EPA-600/4-90/020; 1990; pp 169−200.
(20) Barber, L. B.; Brown, G. K.; Kennedy, K. R.; Leenheer, J. A.; Noyes, T. I.; Rostad, C. E.; Thorn, K. A. In *Proceedings of AWRA Symposium, Conjunctive Use of Water Resources: Aquifer Storage and Recovery;* Kendall, D. R., Ed.; American Water Resources Association: Herndon, VA, 1997; pp 261−272.
(21) Kari, F. G.; Giger, W. *Environ. Sci. Technol.* **1995**, *29*, 2814−2827.
(22) Ding. W.-H.; Wu, J.; Semadeni, M.; Reinhard, M. *Chemosphere* **1999**, *39*, 1781−1794
(23) Ball, H. A.; Reinhard, M.; McCarty, P. L. *Environ. Sci. Technol.* **1989**, *23*, 951−961.
(24) Leenheer, J. A.; Wershaw, R. L.; Brown, P. A.; Noyes, T. I. *Environ. Sci. Technol.* **1991**, *25*, 161−168.
(25) Field, J. A.; Leenheer, J. A.; Thron, K. A.; Barber, L. B.; Rostad, C.; Macalady, D. L.; Daniel, S. R. *J. Contaminant Hydrol.* **1992**, *9*, 55−78.
(26) Field, J. A.; Barber, L. B.; Thurman, E. M.; Moore, B. L.; Lawrence, D. L.; Peake, D. A. *Environ. Sci. Technol.* **1992**, *26*, 1140−1148.
(27) Galimov, E. M. *The Biological Fractionation of Isotopes*; Academic Press: New York, 1985.
(28) Poiger, T.; Field, J. A.; Field, T. M.; Giger, W. *Environ. Sci. Technol* **1996**, *30*, 2220−2226.
(29) *The Sadtler Handbook of Ultraviolet Spectra*; Sadtler Research Laboratories; Simons, W. W., Ed.; Philidelphia, PA, 1979.
(30) Larson, R. A.; Weber, E. J. *Reaction Mechanisms in Environmental Organic Chemistry*; Lewis Publishers: Ann Arbor, MI, 1994; 433 p.

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