

Human Pharmaceuticals, Antioxidants, and Plasticizers in Wastewater Treatment Plant and Water Reclamation Plant Effluents

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ABSTRACT: The primary objective of this study was to determine the presence of unregulated organic chemicals in reclaimed water using complementary targeted and broad spectrum approaches. Eleven of 12 targeted human pharmaceuticals, antioxidants, and plasticizers, and 27 tentatively identified non-target organic chemicals, were present in secondary effluent entering tertiary treatment trains at a wastewater treatment plant and two water reclamation facilities. The removal of these compounds by three different tertiary treatment trains was investigated: coagulant-assisted granular media filtration (California Title-22 water, 22 CCR §§60301-60357; Barclay [2006]), lime clarification/reverse osmosis (lime/RO), and microfiltration-reverse osmosis (MF/RO). Carbamazepine, clofibric acid, gemfibrozil, ibuprofen, *p*-toluenesulfonamide, caffeine, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and *N*-butyl benzenesulfonamide (*N*-BBSA) were present at low to high nanogram-per-liter levels in Title 22 water. The lime/RO product waters contained lower concentrations of clofibric acid, ibuprofen, caffeine, BHA, and *N*-BBSA (<10 to 71 ng/L) than their Title 22 counterparts. The MF/RO treatment reduced concentrations to levels below their detection limits, although BHT was present in MF/RO product water from one facility. The presence of the target analytes in two surface waters used as raw drinking water sources and a recharged groundwater was also examined. Surface waters used as raw drinking water sources contained caffeine, BHA, BHT, and *N*-BBSA, while recharged groundwater contained BHT, BHA, and *N*-BBSA. Nontarget compounds in recharged groundwater appeared to be attenuated with increased residence time in the aquifer. *Water Environ. Res.*, **79**, 156 (2007).

KEYWORDS: pharmaceutical, antioxidant, personal care product ingredient, reclaimed water, wastewater, plasticizer.

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Introduction

Nonpotable and indirect potable reuse of reclaimed wastewater is increasing in arid areas of the world, as growing populations place

additional demands on water resources. Such water recycling may represent a viable strategy to extend limited water resources (Sedlak et al., 2000). The presence of unregulated organic microcontaminants (e.g., pharmaceuticals, hormones, personal care product ingredients) in reclaimed wastewater is perceived by the public as a potential health hazard; however, exposure to low levels of these compounds in drinking water has not been demonstrated to result in adverse health effects in humans. In the United States, wastewater intended for reuse must undergo tertiary treatment to protect individuals consuming or coming in contact with recycled water.

In the state of California, the most common type of reuse conforms to Title 22 (T-22) regulations, and wastewater that has undergone such treatment is referred to as T-22 water. The T-22 water is used for irrigation of highway landscaping, golf courses, parks, and agricultural crops, and in cooling towers. The degree of treatment required depends on the intended use of the reclaimed water. Title 22 requires biological secondary treatment followed by filtration and disinfection (Crook et al., 2001); additional treatment, including clarification and filter aids, is used when required to meet T-22 product water standards (e.g., turbidity <2 NTU and 7-day median total coliform bacteria <2.2 most probable number/100 mL).

In the state of California, reclaimed wastewater is used to recharge groundwater to prevent saltwater intrusion to coastal aquifers that may serve as drinking water sources. Because this water may eventually enter drinking water wells, such reclaimed water must undergo treatment beyond that required by T-22 to ensure that its quality is sufficient for potable use. Two processes currently used to treat secondary wastewater effluent before groundwater recharge are a combination of either lime coagulation and reverse osmosis (lime/RO) or microfiltration and reverse osmosis (MF/RO). An additional requirement for this indirect potable reuse of reclaimed water is that the retention time in the aquifer exceed a specified minimum (e.g., 1 year) before the water enters drinking water wells. Growing demand on aquifers in the future will likely result in increased indirect reuse of recycled water from these systems to augment potable water supplies.

California T-22 mandates that reclaimed water be routinely analyzed for a limited suite of "target" chemicals using a gas chromatography-mass spectrometry (GC-MS) method (e.g., U.S. Environmental Protection Agency [U.S. EPA] [Washington, D.C.] method 625) having detection limits in the microgram-per-liter range. No requirement currently exists to conduct analyses for the large number of unregulated organic contaminants potentially

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present in wastewater at microgram-per-liter levels. The authors consider it prudent to require additional monitoring and reliability controls for indirect potable reclamation projects to address potential public health and environmental health concerns.

Secondary effluent may contain a variety of unregulated organic microcontaminants, including natural and synthetic hormones, personal care product ingredients (PCPIs), antioxidants, plasticizers, diagnostic contrast media, “nutraceuticals”, alkylphenols, phthalates, pesticides, and pharmaceutically active compounds (PhACs) and their metabolites (Adams et al., 2002; Allen et al., 1999; Daughton and Ternes, 1999; Huang and Sedlak, 2001; Jobling and Sumpter, 1993; Jones et al., 2002; Kolpin et al., 2002; Metcalfe et al., 2003; Öllers et al., 2001; Snyder et al., 2003; Soto et al., 1991; Ternes, 1998). Runoff from agricultural fields irrigated with T-22 water has been shown to contain blood-lipid-regulating drugs, antiepileptic drugs, steroidal hormones, PCPIs, antioxidants, plasticizers, and flame-retardant chemicals (Pedersen et al., 2003, 2005). In addition, these compounds have been found in aquatic environments and soils at nanogram-per-liter and nanogram-per-kilogram levels (Payne et al., 2000; Pedersen et al., 2003).

The primary objective of this study was to determine the presence of unregulated organic chemicals in reclaimed water using complementary targeted and broad spectrum approaches. These compounds can be considered “target” analytes if specifically targeted by an analytical method or “nontarget” if mass spectrometry is used to identify chemicals not on a target analyte list. A secondary objective of this study was to determine whether a series of targeted PhACs, PCPIs, antioxidants, and plasticizers, and also nontarget organic chemicals, were present in effluents from wastewater treatment plants (WWTPs) and water reclamation plants (WRPs). One WWTP and two WRPs were investigated in this study. All included a treatment train producing water conforming to T-22 requirements. The two water reclamation facilities each used two additional, parallel treatment trains—lime/RO and MF/RO. The present study was not designed to quantitatively evaluate the efficiency of the treatment trains in removing these compounds, but rather to provide a snapshot of the concentrations of these compounds in secondary effluent and reclaimed water and to make comparisons with levels in raw drinking water sources in southern California.

Materials and Methods

Chemicals. All reference standards were of analytical grade and obtained from Sigma-Aldrich (Saint Louis, Missouri). The GC-pesticide-grade dichloromethane (DCM), hexane, and high-performance-liquid-chromatography-grade methanol were purchased from Burdick and Jackson (Muskegon, Michigan). Helium carrier gas of 99.99% purity was used.

Site Descriptions. One WWTP and two WRPs in southern California were investigated. Figure 1 displays the treatment trains used in each. Pertinent details of these facilities are provided below.

Wastewater Treatment Plant 1. The T-22 treatment train of this facility received treated secondary effluent from the main wastewater plant and had the basic T-22 configuration shown in Figure 1.

Water Reclamation Plant 2. Water reclamation plant 2 received treated secondary effluent from a wastewater plant and operated the following three treatment trains in parallel (Figure 1): T-22, lime/RO, and MF/RO. Each of these parallel treatment trains were sampled in this study. A 50:50 mixture of lime/RO and MF/RO effluents (sometimes combined with Colorado River water or State

Project water, see below) was used for groundwater recharge to prevent saltwater intrusion to a coastal aquifer. The lime/RO treatment train (19 000 m³/d [5 mgd]) consisted of lime clarification (raising pH to 11) followed by recarbonation to lower the pH to 7 (to remove suspended solids, heavy metals, and dissolved minerals), mixed media filtration (to remove suspended solids), reverse osmosis (for demineralization and removal of other constituents), and finally chlorine disinfection. The RO system consisted of three stages operating in a 72/36/18 vessel pattern and achieved 85% recovery. A total of 756 spiral-wound cellulose acetate membranes were in operation.

In the MF/RO treatment train, the MF and RO units had production rates of 11 000 and 95 000 m³/d (3 and 2.5 mgd), respectively. The MF system consisted of five parallel microfilters with 450 membrane units and achieved 88% recovery operating at 210 kPa (30 psi). This filtration process removes particles larger than approximately 0.2 μ m. The RO operation used 756 polyamide membrane units in a 60/36/12 vessel pattern, operated at 1170 kPa (170 psi), and had a recovery of 85%.

Water Reclamation Plant 3. Water reclamation plant 3 received treated secondary effluent from a nearby wastewater plant and operated the same three treatment trains as WRP 2 (Figure 1). In the 19 000-m³/d (5-mgd) lime/RO treatment train, the lime system was operated as in WRP 2. The RO system was composed of a six-bank vessel pattern and achieved 80% recovery. Approximately 1500 spiral-wound cellulose-acetate-membrane elements with 0.1-nm pore size were in operation.

The 2700 m³/d (0.7-mgd) MF/RO train in WRP 3 was operated at pilot-scale conditions. The MF pretreatment unit consisted of four hollow-fiber micro-porous membrane elements composed of polypropylene with 0.2- μ m pore size, operated at 34 to 83 kPa (5 to 12 psi), and achieved a recovery of 90%. The pilot system used 18 spiral-wound elements of thin film composite polyamide RO membranes, was operated at 1100 kPa (160 psi), had 75% recovery, and had a total dissolved solids rejection of 96%.

Wastewater Treatment Plant and Water Reclamation Plant Sampling. In this paper, we refer to water entering the tertiary treatment processes as secondary effluent and that exiting these processes as product water. We collected samples over a 24-hour period from secondary effluents (10 L total) and final treated product water (40 L total) at the WWTP and WRPs described above. Sampling locations are indicated in Figure 1. At plants 1 and 3, samples were collected every 6 hours, for 24 hours, and composited. At WRP 2, samples were collected hourly, for 24 hours, and composited. Samples were refrigerated during collection, transported on ice, and maintained at 4°C until processed. Effluent samples were taken before disinfection to observe the efficiency of the T-22, lime-RO, and MF-RO treatment processes in removing target and nontarget compounds. Table 1 presents background water quality information for the secondary effluents and product waters.

Surface Water Sampling. The Colorado River and the Sacramento-San Joaquin River Delta serve as raw drinking water sources for much of southern California. Colorado River water (CRW) is conveyed to 13 southern California municipalities via the Colorado River aqueduct. Water from the Sacramento-San Joaquin River Delta, referred to as State Project Water (SPW), is transported to southern California through a system of reservoirs and aqueducts extending two-thirds of the length of California. On October 13, 1999, one 40-L raw surface water sample was collected before

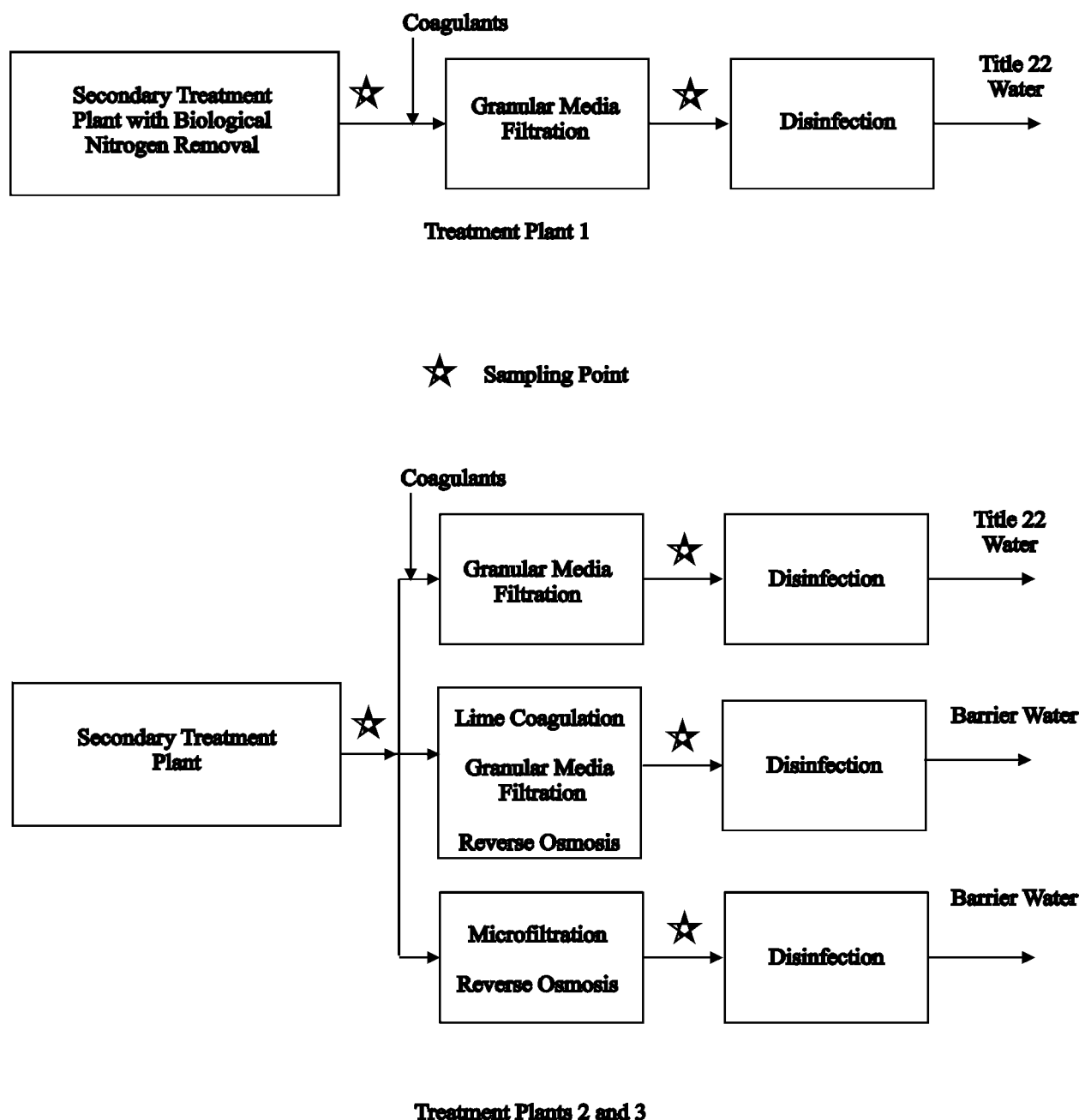


Figure 1—Wastewater treatment and water reclamation plants: T-22, lime/RO, and MF/RO treatment trains.

treatment at the outlet of two drinking water reservoirs—Lake Matthews (CRW) and Castaic Lake (SPW).

Recharged Groundwater Sampling. A 50:50 mixture of lime/RO and MF/RO treated water from WRP 2 used to recharge groundwater to minimize seawater intrusion was sampled. Groundwater samples (40 L) were collected from three monitoring wells (designated A, B, and C) down gradient from the injection zone of the saltwater barrier near WRP 2 to obtain a snapshot of the quality of reclaimed water after injection, as this water may eventually affect drinking water wells. Groundwater was collected from monitoring wells using a submersible pump after purging three well-case volumes. The distances from the groundwater recharge salt water barrier wells to the monitoring wells were approximately

1500, 1800, and 2200 m for wells A, B, and C, respectively. Depths to groundwater were 22.3, 37.5, and 33.8 m for wells A, B, and C, respectively.

Sample Extraction. Unfiltered water samples were extracted with DCM using an on-line Teflon coil continuous liquid-liquid extractor (CLLE) at 10 L/h, as described previously (Baker et al., 1987; Soliman et al., 2004). This method represented a scaled-up version of the 2-L CLLE method that is comparable with the U.S. EPA 625 compliance method (Baker et al., 1987). Sample pH was adjusted to 3 by addition of phosphoric acid. Ascorbic acid (10 mg/L) and sodium sulfate (75 mg/L) were added before extraction to minimize oxidation and emulsion formation and to increase extraction efficiency. A water-to-DCM ratio of 10:1 was maintained

Table 1—Characteristics of secondary effluent and product water from wastewater treatment and water reclamation plants.

WWTP	Secondary effluents			T-22			Lime/RO		MF/RO	
	1	2	3	1	2	3	2	3	2	3
pH	7.7	7.3	7.6	7.6	7.3	7.9	5.9	7.3	6.0	6.4
TSS (mg/L)	5	13	3	3	1	2	Not detected	Not detected	Not detected	Not detected
Total dissolved solids (mg/L)	1020	720	870	1100	820	870	86	46	26	26
Conductivity ($\mu\text{mho} \cdot \text{cm}^{-1}$)*	1460	1400	1500	1330	1430	1500	180	100	43	60

* Note: $\mu\text{mho} \cdot \text{cm}^{-1} \times 100 = \text{S} \cdot \text{m}^{-1}$.

during extraction. To achieve enrichment factors 10 to 40 times higher than U.S. EPA method 625 and detect target analytes in the nanogram-per-liter range, 10-L secondary effluent, and 40-L product water, raw water, and groundwater samples were extracted. Solvent was recycled, and the resulting approximately 40-mL extract was concentrated by Kuderna-Danish evaporation to a final volume of 1 mL. Thus, 10- and 40-L samples were concentrated by factors of 10 000 and 40 000, respectively. Some samples were solvent exchanged into hexane for other analyses.

During recovery studies using Milli-Q water (18 M Ω ·cm resistivity; Millipore Corporation, Bedford, Massachusetts), CLLE extracts were found to contain di-*n*-butyl phthalate, bis(2-ethyl-hexyl) phthalate, and *p*-chlorophenol. Therefore, we do not report the presence of these compounds in the samples analyzed, although they may have been present.

Gas Chromatography-Mass Spectrometry Analysis. Extracts were analyzed by a rapid GC-MS screening method (Soliman et al., 2004) using a 6890 Hewlett-Packard GC (Hewlett-Packard, Palo Alto, California) coupled with a Hewlett-Packard 5973 mass selective detector. Target analytes, their biochemical functions, and their method detection limits (MDLs), based on a 40-L sample, are given in Table 2. Many secondary effluent sample extracts required 10- to 50-fold dilution to enable GC-MS identification and quantification. Analyte separation was achieved on a 12 m $\times$ 0.20 mm internal diameter capillary HP-1 (dimethyl polysiloxane) column with a 0.33- μm film thickness (J&W, Agilent Technologies, Wilmington, Delaware). Injector temperature was maintained at 280°C, and the oven was programmed as follows: initial 1-minute 50°C hold, then an 18°C·min⁻¹ temperature ramp to 285°C, followed by an 8-minute hold at 285°C. Samples (2 μL) were injected in splitless mode; after 75 seconds, the split valve was opened. The GC-MS interface was held at 285°C. The mass selective detector was operated in the electron impact ionization mode at 70 eV and 230°C. The analyzer mass range was 50 to 500 *m/z*, with 1 *u* mass resolution and a scan rate of 3 scans·s⁻¹. Mass spectral data were acquired in the total ion chromatogram (TIC) and selected ion monitoring (SIM) modes. The SIM mode provided higher sensitivity; the TIC mode was useful for detecting additional nontarget analytes (i.e., chemicals not included in the list of targeted compounds). A Hewlett Packard Chemstation G-1701DA was used for data acquisition and handling. The NIST98 and PMW-TOX3 spectral libraries were used for mass spectral matching (Agilent Technologies, Wilmington, Delaware).

As originally described (Soliman et al., 2004), the GC-MS method used in this study included steroidal hormones (17 β -estradiol, estrone, 17 α -ethinyl estradiol, estriol, progesterone, stanolone, and testosterone) as target analytes. Specific and, as of yet, unidentified compounds present in complex wastewater

matrices can interfere with GC-MS analysis of steroidal hormones in SIM mode and result in enhanced apparent concentrations. For example, the apparent levels of 17 α -ethinyl estradiol in secondary effluents from the facilities examined in this study were 40 to 50 ng/L, significantly higher than those reported by investigators using analytical methods not prone to this artifact (i.e., Ericson et al., 2002). This issue has been noted by other researchers (e.g., Huang and Sedlak, 2001; Ternes et al., 1999); therefore, we do not report levels of steroidal hormones in this paper.

Results and Discussion

Analytical Method. The performance of the analytical method has been detailed elsewhere (Soliman et al., 2004). Briefly, target analyte recoveries from acidified (pH 3) Milli-Q water ranged from 57 to 120% (Soliman et al., 2004). The overall method recovery was 82.5%, with a relative standard deviation of 21.4%, comparing favorably with the recoveries reported for the analytical methods used by Kolpin et al. (2002). These investigators used liquid chromatography-mass spectrometry to analyze 21 drugs in solid phase extracts (85.1 $\pm$ 11.6%). The results reported here have not been corrected for recovery.

Identification of Nontarget Compounds. In addition to identifying and quantifying the 12 target analytes, we examined mass spectra in the TIC mode to tentatively identify a number of

Table 2—Target analytes screened by the rapid GC-MS method.

Analytes	MDL-SIM* (ng/L)	Function
BHA	10	Antioxidant
Acenaphthene-d10	25	Surrogate standard
BHT	8	Antioxidant
Clofibrilic acid	25	Blood lipid regulator metabolite
Ibuprofen	20	Analgesic/anti-inflammatory
<i>p</i> -toluenesulfonamide	20	Hypoglycemic metabolite, chloramine-T metabolite
<i>N</i> -butyl benzenesulfonamide	10	Plasticizer
Caffeine	15	Stimulant
Carisoprodol	10	Skeletal muscle relaxant
Gemfibrozil	10	Blood lipid regulator
Carbamazepine	10	Antiepileptic; analgesic
Diazepam	25	Psychiatric drug
Fenofibrate	20	Blood lipid regulator

* MDL-SIM is the MDL in selected ion monitoring mode based on a 40-L sample (Soliman et al., 2004).

Table 3—Nontarget analytes: relative retention time, SI value, and function.

Analyte	Relative retention time ^a	SI value ^b	Function
Benzaldehyde	0.230	0.97	Solvent, dye manufacture, flavors
Benzonitrile	0.248	0.86	Solvent
Triethyl phosphate	0.347	0.94	Ethylating agent; insecticide synthesis
Benzoic acid	0.387	0.86	Antifungal; food and juice preservative
Naphthalene	0.396	0.91	Used in motor fuel and lubricants
2,4-Dichlorophenol	0.405	0.96	Possible disinfection byproduct
Benzothiazole	0.415	0.90	Organic syntheses
Phthalic anhydride	0.456	0.87	Plastic manufacturing
Biphenyl	0.515	0.94	Heat transfer agent; fungistat for oranges
Chloroxylenol	0.517	0.90	Antiseptic
Dimethyl phthalate	0.548	0.97	Plasticizer
Mandelamide	0.578	0.90	Antibacterial
Phenol,2,4,-bis(dimethyl, ethyl)	0.590	0.93	Manufacture of amino phenol disulfonic acids
Diethyltoluamide	0.620	0.90	Insect repellent
Diethyl phthalate	0.626	0.98	Plasticizer
Benzothiazole, 2-(methylthio)	0.632	0.97	Rubber vulcanization accelerator, fungicide
Benzophenone	0.646	0.94	Fragrance fixative, manufacture of insecticides and hypnotics
Nonylphenol	0.698	0.87	Surfactant metabolite
Tris(2-chloroethyl) phosphate	0.700	0.83	Fire-retardant
Phenanthrene	0.727	0.96	Polycyclic aromatic hydrocarbon
Dibutyl phosphate	0.761	0.72	Plasticizer
Galaxolide	0.762	0.96	Synthetic musk
Methyl parathion	0.770	0.95	Insecticide
Chlorophene	0.776	0.92	Household, hospital and veterinary disinfectant
Dodecyl acrylate	0.779	0.90	Monomer in polymer manufacture
Metolachlor	0.814	0.87	Herbicide
Triclosan	0.864	0.89	Antibacterial disinfectant
Naproxen	0.865	0.93	Anti-inflammatory, antipyretic
Benzyl butyl phthalate	0.954	0.91	Plasticizer
Triphenyl phosphate	0.968	0.95	Plasticizer
Erucylamide	1.109	0.91	Additive to adhesives used in food packaging
Squalene	1.143	0.83	Bactericide, intermediate in pharmaceuticals manufacture
Cholestanol	1.288	0.93	In human feces, gallstones and eggs
Cholesterol	1.333	0.58	Plant/animal steroid
Cholest-4-en-3-one	1.366	0.90	Cholesterol metabolite under aerobic conditions using activated sludge
Stigmasterol	1.433	0.90	Plant steroid

^a Relative to the chrysene-d12 internal standard; retention time = 13.4 minutes.

^b SI value = library search purity value.

nontarget compounds. Thirty-six nontarget compounds were tentatively identified in secondary effluents and product waters, surface waters, and groundwater (Table 3). Tentatively identified compounds included benzophenone (fixative for heavy perfumes, used in the manufacture of antihistamines, hypnotics, and insecticides); *N,N*-diethyltoluamide (DEET, insect repellent); and triclosan (antibacterial agent commonly used in household products and antibacterial soaps). Nontarget analytes were not quantified.

Secondary Effluents. Background information on secondary effluents is shown in Table 1. The WRP 2 exhibited the highest total suspended solid (TSS) concentration (13 mg/L). The variation in secondary effluent quality among the three plants probably reflected differences in both raw wastewater quality and the efficiency of biological treatment.

Concentrations of target analytes and nontarget compounds detected in secondary effluents of the treatment plants are presented in Figure 2 and Table 4. We detected 10 target and 16 nontarget analytes and measured the highest concentrations of ibuprofen

and *p*-toluenesulfonamide (*p*-TSA) in WWTP 1 secondary effluent (Figure 2a, Table 4). The WRP 2 secondary effluent contained 10 target and 18 nontarget analytes and exhibited the highest concentrations of the following four target compounds: butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), caffeine, and gemfibrozil (Figure 2b, Table 4). Ten target and 20 nontarget analytes were detected in WRP 3 secondary effluent (Figure 2c, Table 4). Secondary effluent concentrations of clofibric acid, *N*-BSSA, carisoprodol, carbamazepine, and fenofibrate were considerably higher at WRP 3 than at the other two plants, while ibuprofen and gemfibrozil concentrations were substantially lower. The target compound diazepam was not detected in any secondary effluent samples. With the exception of *N*-butyl benzenesulfonamide (*N*-BBSA) at all plants and BHA at one plant, secondary effluent concentrations of all target analytes were in the nanogram-per-liter range. Secondary effluent concentrations of most target analytes in WWTP 1 secondary effluent were in the range 10 to 20 ng/L; ibuprofen and *p*-TSA represented notable exceptions with second-

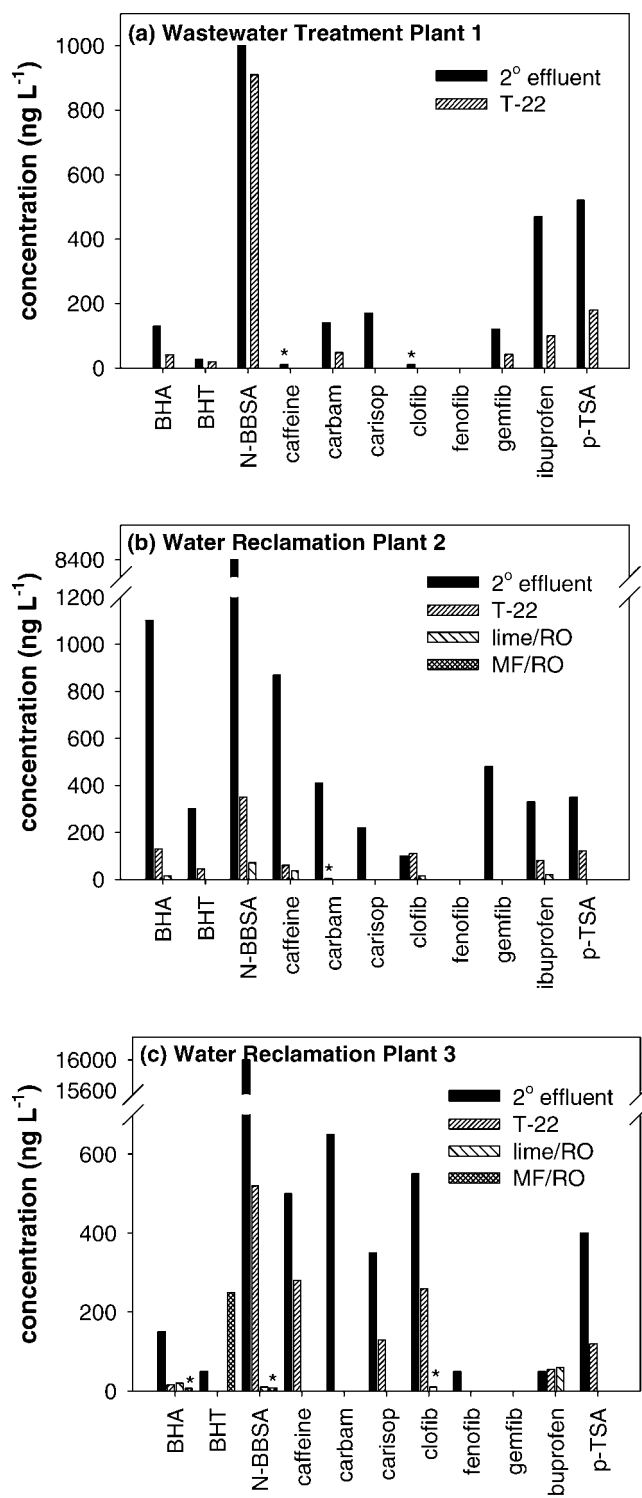


Figure 2—Target analyte concentrations in secondary effluent and product waters for (a) WWTP 1, (b) WRP 2, and (c) WRP 3. Diazepam was not detected at any plant. An asterisk (*) indicates that the compound was detected, but was below the MDL. The concentrations in T-22 water were previously reported by Soliman et al. (2004). The DCM extract of the MF/RO sample for WRP 2 was exchanged into hexane. Abbreviations: carbam = carbamazepine; carisop = carisoprodol; clofib = clofibric

ary effluent concentrations of approximately $0.5 \mu\text{g} \cdot \text{L}^{-1}$. For 8 of 12 target analytes, secondary effluent concentrations were somewhat higher at WRP 2 than WWTP 1 (Figure 2). The WRP 2 secondary effluent concentrations of most target analytes were between 100 and 400 ng/L; N-BBSA and BHA concentrations were $8.4 \mu\text{g} \cdot \text{L}^{-1}$ and $1.0 \mu\text{g} \cdot \text{L}^{-1}$. For WRP 3, target analytes generally exhibited secondary effluent concentrations between <100 and 650 ng/L; N-BBSA was an exception, with a secondary effluent concentration of $16.3 \mu\text{g} \cdot \text{L}^{-1}$. Of the 27 nontarget compounds tentatively identified in secondary effluents, approximately 30% were detected at all facilities. These data indicate that, in general, secondary wastewater treatment does not effect complete removal of these chemicals, a finding in agreement with data reported by others (i.e., Daughton and Ternes, 1999).

Examination of Figure 2 and Table 4 reveals that secondary effluent from WWTP 1 had lower contaminant levels than the other two plants. The two exceptions were ibuprofen and *p*-TSA. The WWTP 1 practiced enhanced biological nitrogen removal, which requires longer hydraulic retention time and mean cell retention time (MCRT). The WRP 2 had a very low MCRT and was optimized to provide secondary treatment at minimum cost. The WRP 3 was a medium hydraulic retention time plant, but did not practice enhanced nitrogen removal. A quantitative comparison of the removal efficiencies was not possible, because primary effluents were not analyzed; however, our data suggest that enhanced secondary treatment may provide additional removal of the compounds, consistent with the findings of others demonstrating more efficient removal of biodegradable organic carbon (Babcock et al., 2001).

Qualitative Broad Spectrum Analysis of Reclaimed Water Before and After Groundwater Recharge. Figure 3 presents example reconstructed chromatograms obtained for broad spectrum analysis of two parallel treatment trains (lime/RO and MF/RO) at WRP 2 producing water for groundwater recharge. Because each peak represents one or more compounds and because peak height is a direct response to the amount present, semiquantitative evaluation of these graphs is possible. The MF/RO effluent contained 21 detectable compounds, with one having an apparent concentration of over 100 ng/L, while the lime/RO product water contained at least 61 compounds, with more than 50% having an apparent concentration > 100. These preliminary observations confirm the trends reported by Levine et al. (1999), who found that MF/RO produced higher quality effluent than lime/RO in terms of trace organic compounds detectable by GC-MS. These data are also consistent with the findings of Dawes et al. (2000) and Levine et al. (2001).

Figure 4 displays reconstructed chromatograms from three monitoring wells down gradient of the injection wells used to prevent saltwater intrusion. These samples were collected to provide a snapshot of how reclaimed water injected to an aquifer might influence drinking water wells. The water entering the aquifer was a 50:50 mixture of MF/RO and lime/RO. The number of detected compounds decreased as distance from the injection zone increased. Apparent concentrations (y-axis in Figure 4) were estimated relative to response of the internal standards that were added to each sample.

acid; fenofib = finofibrate; gemfib = gemfibrozil; N-BBSA = *N*-butyl benzenesulfonamide; and *p*-TSA = *p*-toluenesulfonamide.

Table 4—Nontarget analytes in secondary (2°) effluent and T-22, lime/RO, and MF/RO product waters.

Compound	WWTP 1		WRP 2				WRP 3			
	2° effluent	T-22	2° effluent	T-22	Lime/RO	MF/RO	2° effluent	T-22	Lime/RO	MF/RO
Benzoic acid	x	x	x		x		x	x		
Benzophenone	x	x	x	x			x	x		
Benzothiazole							x	x		
Benzothiazole, 2-(methylthio)	x	x	x	x			x	x		
Benzyl butyl phthalate										x
Biphenyl							x	x		
Chloroxylenol	x	x				x				
Cholestanol	x	x	x	x			x			
Cholest-4-en-3-one			x	x						
Cholesterol	x	x	x	x			x			
Diethyl phthalate	x	x	x	x		x				x
Diethyltoluamide	x		x	x			x	x	x	
Dodecyl acrylate							x			
Erucylamide	x	x	x				x	x		
Galaxolide	x	x	x	x			x			
Mandelamide							x			
Naproxen	x	x					x	x		
Nonylphenol	x	x								
Phenol, 2,4-bis(dimethyl-ethyl)							x			
Phenol, 2,4-dichloro		x								
Phthalic anhydride		x	x	x			x	x		
Squalene							x			
Stigmasterol							x			
Tributyl phosphate	x	x	x	x						
Triclosan			x							
Triphenyl phosphate	x	x	x							
Tris(2-chloroethyl) phosphate	x						x	x		

This approach allowed comparison of apparent concentrations among samples analyzed by the same method. The identified peaks by GC/MS are shown by number on Figure 4; other unidentified compounds present in the samples appear as unlabeled spikes.

Water from the monitoring well closest to the injection barrier (well A) contained more detectable organic compounds than that from more distant wells. The compounds present in water from well A also appeared to be higher in concentration. Figure 4 suggests that aquifer treatment might be an adequate final polishing step to the treatment process; nontarget compounds in recharged groundwater appeared to be attenuated with increased residence time in the aquifer. We note that 9 of the 10 compounds identified in groundwater by mass spectroscopy (Figure 4) were not detected in reclaimed water from WRP 2. These chemicals could have been present in past reclaimed water, may have resulted from biological breakdown products of natural organic matter or other compounds in reclaimed water, or may indicate infiltration from surface sources. Only BHT appeared to have potential as a tracer for reclaimed water (Table 4).

For both lime/RO and well A samples, peaks eluted beyond a Kovats index of 2400. On the other hand, no peaks were detected beyond a Kovats index of 2000 for the MF/RO sample. This observation confirms the trend noted by Levine et al. (1999), that larger molecular mass and less volatile compounds were removed from the effluent, resulting in an unbalanced total ion chromatogram, for which most of the peaks corresponded to earlier eluting compounds. This initial analysis proved useful in identifying trends. However, quantitative evaluation was not possible with these data.

Wastewater Treatment Plant and Water Reclamation Plant Product Waters. Concentrations of target analytes and identities of nontarget analytes detected in product waters from the tertiary treatment trains used at the WWTP and WRPs are presented in Figure 2 and Table 4.

Wastewater Treatment Plant 1. The WWTP 1 used a T-22 treatment train after secondary treatment (Figure 1). The tertiary treatment processes used were expected to remove only those organic contaminants associated with colloidal and settleable particles. In conjunction with the data from T-22 treatment trains at plants 2 and 3, this information can be used to establish general trends in target analyte removal. Secondary effluent samples contained 10 target analytes, while 7 were detected in product water samples. Secondary effluent and product water concentrations were highest for *N*-BBSA (approximately 1.0 µg/L). Concentration reductions were observed for all target compounds in T-22 product water (Table 5). Three compounds (clofibric acid, caffeine, and carisoprodol) were removed to levels below their MDLs. Two of the 14 non-target compounds were apparently removed by T-22; however, two additional new nontarget compounds (2,4-dichlorophenol and phthalic anhydride) were detected in T-22 product water (Table 4). The 2,4-dichlorophenol was probably not a disinfection byproduct, as the sample was taken before disinfection, and no other chlorinated products were identified in the analyses.

Table 5 presents target analyte removals for the T-22 treatment train. The composite sample analyzed was collected by combining four 6-hour samples over a 24-hour period and was not timed to

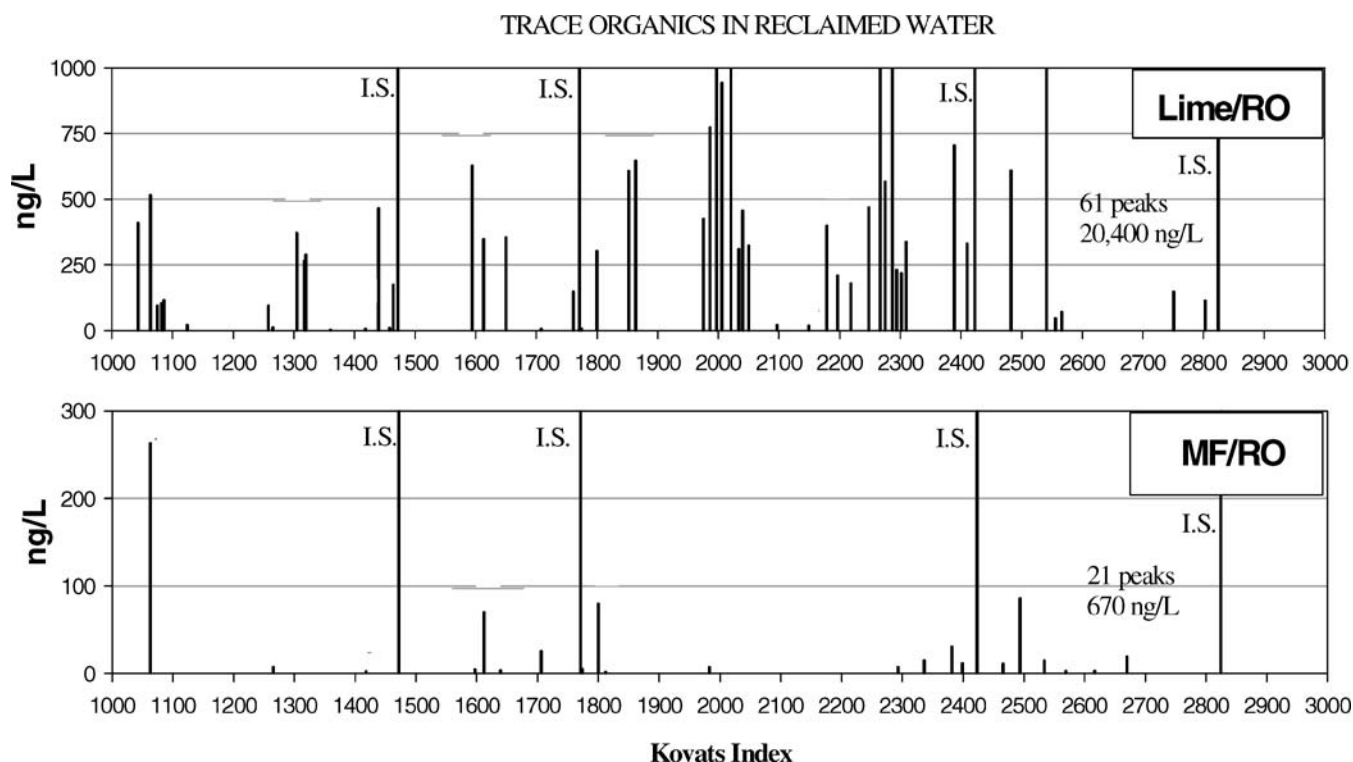


Figure 3—Example of reconstructed chromatograms for broad spectrum analysis of parallel treatment trains at WRP 2. Apparent concentrations were estimated relative to response of the I.S. The Kovats Index compares the adjusted retention time of the analyte to those for a series of *n*-alkanes (for details, see Barry, 1995). Each chromatogram indicates the number of peaks detected and the estimated total concentration of detected compounds.

follow a specific water parcel through the treatment plant. The authors therefore express some reservation in reporting analyte removals. The hydraulic retention times of the various processes used in Figure 1 were much less than 24 hours, and a 24-hour composite sample should include the time of travel of a water packet through the plant. However, even if Lagrangian sampling had been used, the repeatability of the calculated removals for identical secondary effluents would not be guaranteed because of the dynamic nature of water treatment processes. Additional studies are needed to confirm removal values shown in Table 5.

Water Reclamation Plant 2. The WRP 2 used the following three separate postsecondary treatment trains: T-22, lime/RO, and MF/RO (Figure 1). As mentioned above, T-22 treatment should remove only contaminants associated with colloidal and settleable particles. Lime treatment may result in the base-catalyzed hydrolysis of some analytes. Significant removal of organic contaminants by MF/RO was expected.

Target analyte concentrations in WRP 2 T-22 product water were broadly similar to those in WWTP 1 product water, although BHA and clofibric acid concentrations were substantially higher and *p*-TSA and *N*-BBSA concentrations considerably lower (Figure 2). Both plants achieved similar target analyte removals for the majority of compounds (Table 5). A notable exception was clofibric acid, for which T-22 treatment effected no change in concentration at WRP 2, but complete removal at WWTP 1. Compared with WWTP 1, T-22 treatment at WRP 2 removed BHA, BHT, *N*-BBSA, and carbamazepine more efficiently. Two target compounds (carisoprodol and gemfibrozil) and five nontarget compounds were removed to levels below detection (Tables 4 and 5). Although Lagrangian

sampling was not used at WRP 2, composites were composed of 24 1-hour samples. Calculated removals would therefore be expected to better represent actual removals than for WWTP 1.

The lime/RO removal efficiencies substantially exceeded those of T-22 treatment, with $\geq 99\%$ removal for the majority of target analytes and all but one of the 14 nontarget analytes being reduced to below limits of detection (Table 6). Removal of three target compounds was greater than 99%—clofibric acid (90%), ibuprofen (94%), and caffeine (96%). The RO system appeared to efficiently remove most of the analytes under study.

The MF/RO removal efficiencies were superior to those of T-22 treatment and equaled or surpassed those of lime/RO treatment (Table 5). No target analytes and only two phthalates were detected in MF/RO product water. Microfiltration would effect removal of colloidal-associated analytes. Dissolved target analytes were removed to levels below their MDLs (8 to 85 ng/L) by reverse osmosis. We note that the MF/RO product water sample was extracted with dichloromethane, then solvent-exchanged into hexane because of prior GC analysis with electron capture detection. The authors are confident in the results obtained from this sample, because hexane-exchanged groundwater extracts gave comparable results to the original DCM extracts (data not shown). Analyte degradation was not observed during solvent exchange.

Water Reclamation Plant 3. The WRP 3 used the following three postsecondary treatment trains: T-22 treatment, lime/RO, and MF/RO (Figure 1). For WRP 3, samples for 24-hour composites were collected every 6 hours, and results are therefore most directly comparable with those from WWTP 1. However, general

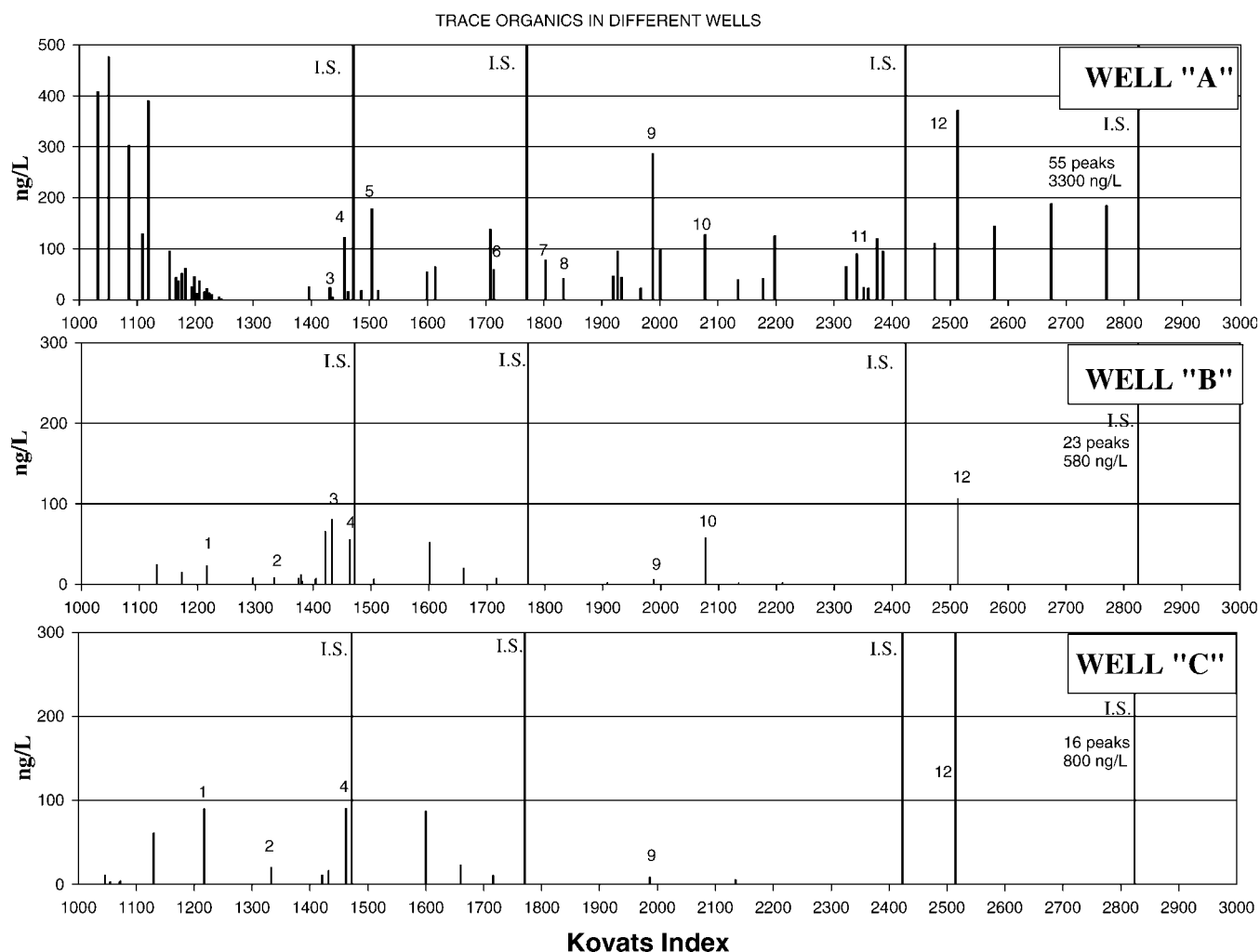


Figure 4—Tentative peak identification by GC-MS from broad spectrum analysis of recharged groundwater. Apparent concentrations were estimated relative to response of the I.S. The Kovats Index compares the adjusted retention time of the analyte to those for a series of *n*-alkanes (for details, see Barry, 1995). Each chromatogram indicates the number of peaks detected and the estimated total concentration of detected compounds. Tentative identities of peaks 1–12 are given in Table 7.

comparisons with WRP 2 can also be made. With the exceptions of higher clofibric acid and lower caffeine and carisoprodol concentration reductions at WRP 3, target analyte removal by T-22 treatment was comparable at plants 2 and 3 (Table 5). Concentrations of 6 of 12 target and 9 of 18 nontarget analytes were reduced to levels below detection by WRP 3 T-22 treatment (Tables 4 and 5).

Target analyte removal by WRP 3 lime/RO treatment was generally approximately 100%, far exceeding that of T-22 treatment (Table 5). Seven of the 10 target compounds present in the secondary effluent were removed to levels below their MDLs. Exceptions were BHA (90% removal) and clofibric acid (98% removal). At WRP 3, T-22 and lime/RO treatment effected comparable BHA removals (90%).

The WRP 3 MF/RO removal efficiencies far exceeded those for T-22 treatment and were comparable with or superior to those for lime/RO treatment (Table 5). With the exception of BHT and traces of BHA, no target analytes were present at detectable levels in MF/RO product waters (Figure 2c). Two phthalates were also

detected in WRP 3 MF/RO product water (Table 4). The BHT concentrations were five times higher in MF/RO product water than in secondary effluent (250 versus 50 ng/L). This observation suggests contamination during MF/RO treatment, perhaps as a result of leaching of BHT from pipe materials. Brocca et al. (2002) reported BHT to be among the dominant organic compounds leaching from polyethylene pipes used in drinking water treatment. We note that BHT was removed to levels below its MDL by both T-22 and lime/RO treatment at WRP 3.

Removal of Organic Wastewater Contaminants. Several physicochemical and biochemical mechanisms are responsible for the removal of organic contaminants during wastewater treatment. Aerobic and anaerobic biodegradation and abiotic hydrolysis, oxidation, and photolysis cause the transformation or mineralization of reactive organic wastewater contaminants, such as alkylphenol polyethoxylates and caffeine (Halling-Sørensen et al., 1998). These processes also break down high-molecular-weight polymeric organic matter to form low-molecular-weight organic compounds that can be analyzed by gas chromatography. Compared with MF/

Table 5—Target analyte removal.

Compound	WWTP 1	WRP 2			WRP 3		
	T-22	T-22	Lime/RO	MF/RO ^a	T-22	Lime/RO	MF/RO
BHA	70	90	99	100	90	90	95
BHT	30	90	100	100	100	100	Contaminated
<i>N</i> -BBSA	10	96	99	100	97	100	100
Caffeine	100	90	96	100	40	100	100
Carisoprodol	100	100	100	100	60	100	100
Carbamazepine	70	99	100	100	100	100	100
Clofibric acid	100	0	90	100	50	98	100
Diazepam	NA ^b	NA ^b	NA ^b	NA ^b	NA ^b	NA ^b	NA ^b
Fenofibrate	NA ^b	NA ^b	NA ^b	NA ^b	100	100	100
Gemfibrozil	60	100	100	100	NA ^b	NA ^b	NA ^b
Ibuprofen	80	80	94	100	0	0	100
<i>p</i> -TSA	70	70	100	100	70	100	100

^a DCM solvent exchanged to hexane.

^b Not applicable (not detected in secondary effluent).

RO, the abundance of peaks in lime/RO product water for WRP 2 (Figure 3) may be partially attributable to abiotic hydrolysis of such organic matter.

The following two target analytes were present in all secondary effluents and T-22 product waters: clofibric acid (0 to 50% removal) and ibuprofen (60 to 80% removal). Two out of three secondary effluents contained gemfibrozil; the T-22 treatment train effected a 60 to 100% removal of this compound. Caffeine was present at measurable concentrations in secondary effluents at plants 2 and 3 (870 and 500 ng/L, respectively); traces were detectable in WWTP 1 secondary effluent. Removal of caffeine by the T-22 treatment train was 40 to 93% at plants 2 and 3. The T-22 product waters contained a number of nontarget compounds, including benzoic acid; benzothiazole; phthalic anhydride; biphenyl; benzyl butyl phthalate; diethyl phthalate; *N,N*-diethyltoluamide; and galaxolide. Combining the data from the three plants, T-22 processes appeared relatively inefficient in eliminating these compounds. Removals achieved by lime/RO and MF/RO were generally much higher.

Although MF/RO treatment entails high operational costs, the combination of these processes resulted in complete removal of all target analytes in this study (with the exception of BHT contamination at WRP 3). Only two nontarget compounds (diethyl phthalate and benzyl butyl phthalate) were detected in MF/RO product waters. We note that dibutyl phthalate and bis (2-ethylhexyl) phthalate were artifacts of the analysis (Soliman et al., 2004). Although much more efficient than T-22 treatment, lime/RO was less effective at removing some target compounds (BHA, clofibric acid, ibuprofen, *N*-BBSA, and caffeine) than MF/RO.

The T-22 product waters contained a variety of nontarget organic wastewater microcontaminants, including insect repellants, flame retardants, pesticides, solvents, and antimicrobial agents. The T-22 water also contained a synthetic polycyclic musk; *N,N*-diethyltoluamide; nonylphenol; and benzophenone (Table 4). Nonylphenols are persistent degradation products of nonylphenol ethoxylate surfactants (Smith et al., 2000; Van Ry et al., 2000) and exhibit estrogenic activity in mammals and fish (Lye et al., 1999; Reiter et al., 1998). Phthalates were present in T-22 product waters from WWTP 1 and WRP 2 and in MF/RO product waters from WRPs 2 and 3. Phthalates are commonly used plasticizers, finding use in numerous consumer products (e.g., plastic children toys, baby

pacifiers, food packaging, and intravenous blood bags). Dimethyl phthalate, tentatively identified in MF/RO product water, is used as a solvent and plasticizer in cellulose acetate and cellulose acetate-butyrate manufacture (O'Neill et al., 2001). Thus, dimethyl phthalate may have derived from cellulose acetate membranes used in WRP 2. The WRP 3 does not use cellulose acetate membranes. Some phthalates disrupt normal endocrine function (Blair et al., 2000; Harris et al., 1997; Jobling et al., 1995).

Surface Waters and Recharged Groundwater. Pharmaceuticals and their metabolites have been detected in surface and groundwaters in the United States (e.g., Eckel et al., 1993; Glassmeyer et al., 2005; Heberer et al., 2001; Kolpin et al., 2002; Sedlak and Pinkston, 2001; Seiler et al., 1999) and Europe (e.g., Buser et al., 1998; Halling-Sørensen et al., 1998; Heberer and Stan, 1997; Holm et al., 1995; Stan et al., 1994; Ternes, 1998). Table 6 lists the target and nontarget compounds identified in this study in DCM extracts of 40-L samples from two surface waters and one recharged groundwater (RGW; Well A). These samples represent actual (CRW and SPW) and potential (RGW) raw water sources for drinking water treatment plants. Of the target analytes, CRW contained measurable levels of BHA and BHT, traces of *N*-BBSA, and seven nontarget compounds. The SPW contained carbamazepine at its MDL (10 ng/L), traces of BHT (MDL = 8 ng/L) and caffeine (MDL = 15 ng/L), and two nontarget compounds. The SPW appeared to be less contaminated by PhACs than the CRW.

The groundwater sampled had been recharged with a 50:50 mixture of lime/RO and MF/RO product water from WRP 2. The RGW contained appreciable levels of BHT (190 ng/L) and four nontarget compounds (Table 7). As mentioned above, the BHT may have leached from polyethylene pipe materials (Brocca et al., 2002). *N*-butyl benzenesulfonamide was present below its MDL of 10 ng/L.

Conclusions

This study demonstrates the presence of a number of pharmaceutically active compounds, personal care product ingredients, antioxidants, and plasticizers in reclaimed wastewater, artificially recharged groundwater, and raw drinking water sources. Our data suggest that enhanced secondary treatment may provide higher

Table 6—Target and nontarget analytes in recharged groundwater and surface waters.

Target and nontarget analytes	Groundwater	Surface water	
	WRP 2 (ng/L)	CRW (ng/L)	SPW (ng/L)
BHA	7*	24	Not detected
BHT	190	26	3*
N-BBSA	9*	8*	Not detected
Caffeine	Not detected	Not detected	12*
Carbamazepine	Not detected	Not detected	10
Carisoprodol	Not detected	Not detected	Not detected
Clofibric acid	Not detected	Not detected	Not detected
Diazepam	Not detected	Not detected	Not detected
Fenofibrate	Not detected	Not detected	Not detected
Gemfibrozil	Not detected	Not detected	Not detected
Ibuprofen	Not detected	Not detected	Not detected
p-TSA	Not detected	Not detected	Not detected
Subtotal target compounds	3	3	3
Benzyl butyl phthalate		Present, not quantified	
Benzophenone		Present	
Benzothiazole	Present, not quantified	Present	Present, not quantified
Cholesterol		Present	
Diethyl phthalate	Present	Present	Present, not quantified
Dimethyl phthalate	Present		
Erucylamide		Present	
Methyl parathion		Present	
Naphthalene	Present, not quantified		
Subtotal nontarget compounds	4	7	2
Total number of compounds	7	10	5

* Below MDL.

removals of the targeted analytes than secondary treatment trains lacking enhanced biological nitrogen removal. Treatment trains using reverse osmosis removed target analytes to a much larger extent than T-22 tertiary treatment consisting of flocculation, coagulation, sedimentation, and filtration. Tertiary treatment of reclaimed wastewater by membrane filtration followed by reverse osmosis proved more efficient in removing these compounds than lime clarification followed by reverse osmosis. The organic microcontaminant present at the highest concentration was *N*-BBSA ($16.3 \mu\text{g} \cdot \text{L}^{-1}$); the remaining compounds studied were present at concentrations below $0.6 \mu\text{g} \cdot \text{L}^{-1}$.

Credits

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Table 7—Nontarget compounds tentatively identified in recharged groundwater (Well A).

No.	Compound
1	1-Hexanol, 2-ethyl
2	1H-Indene, 1-methylene
3	Propanoic acid, 2-methyl-,3-hydroxy-2,4,4-trimethylpentyl ester
4	Dimethyl phthalate
5	Butylated hydroxytoluene (BHT)
6	1,1'-Biphenyl, 2,2'-diethyl
7	Octadecane
8	Isopropyl myristate
9	Dibutyl phthalate
10	Cyclic octaatomic sulfur
11	Phenol, 2,4-bis(1-phenylethyl)
12	Bis(2-ethylhexyl) phthalate*

* Present in blank.

The deadline to submit Discussions of this paper is May 15, 2007.

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