

# Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds

Paul E. Stackelberg<sup>a,\*</sup>, Jacob Gibs<sup>b</sup>, Edward T. Furlong<sup>c</sup>, Michael T. Meyer<sup>d</sup>,  
Steven D. Zaugg<sup>c</sup>, R. Lee Lippincott<sup>e</sup>

<sup>a</sup> U.S. Geological Survey, 425 Jordan Road, Troy, NY 12180, USA

<sup>b</sup> U.S. Geological Survey, 810 Bear Tavern Road, West Trenton, NJ 08628, USA

<sup>c</sup> U.S. Geological Survey, Denver Federal Center, Building 95, MS 407, Lakewood, CO 80225, USA

<sup>d</sup> U.S. Geological Survey, 4821 Quail Crest Place, Lawrence, KS 66049, USA

<sup>e</sup> New Jersey Department of Environmental Protection, P.O. Box 409, Trenton, NJ 08628, USA

Received 11 July 2006; received in revised form 23 January 2007; accepted 28 January 2007

Available online 23 March 2007

## Abstract

Samples of water and sediment from a conventional drinking-water-treatment (DWT) plant were analyzed for 113 organic compounds (OCs) that included pharmaceuticals, detergent degradates, flame retardants and plasticizers, polycyclic aromatic hydrocarbons (PAHs), fragrances and flavorants, pesticides and an insect repellent, and plant and animal steroids. 45 of these compounds were detected in samples of source water and 34 were detected in samples of settled sludge and (or) filter-backwash sediments. The average percent removal of these compounds was calculated from their average concentration in time-composited water samples collected after clarification, disinfection (chlorination), and granular-activated-carbon (GAC) filtration. In general, GAC filtration accounted for 53% of the removal of these compounds from the aqueous phase; disinfection accounted for 32%, and clarification accounted for 15%. The effectiveness of these treatments varied widely within and among classes of compounds; some hydrophobic compounds were strongly oxidized by free chlorine, and some hydrophilic compounds were partly removed through adsorption processes. The detection of 21 of the compounds in 1 or more samples of finished water, and of 3 to 13 compounds in every finished-water sample, indicates substantial but incomplete degradation or removal of OCs through the conventional DWT process used at this plant.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Organic chemicals; Drinking water; Pharmaceuticals

## 1. Introduction

More than 100,000 synthetic chemicals are used in a variety of domestic, industrial, and agricultural applications (Jørgensen, 2004). Numerous studies have documented that many of these compounds, including

pharmaceuticals, fragrances and flavorants, flame retardants and plasticizers, detergent metabolites, components of personal care products, and products of petroleum use and combustion are incompletely degraded or removed during wastewater treatment and are persistent in the aquatic environment. Reviews of the occurrence and fate of organic compounds (OCs) in wastewaters and the aquatic environment are available (Metcalf et al., 2004; Focazio et al., 2004; Daughton,

\* Corresponding author. Tel.: +1 518 285 5652.

E-mail address: [pestack@usgs.gov](mailto:pestack@usgs.gov) (P.E. Stackelberg).

2001; Halling-Sørensen et al., 1998; Daughton and Ternes, 1999). Fewer studies have documented the occurrence of these OCs in drinking-water supplies. Exceptions include documentation of low-level concentrations of OCs in plant-scale studies of drinking-water supplies (Loraine and Pettigrove, 2006; Petrovic et al., 2003; Adams et al., 2002; Ternes et al., 2002; Reddersen et al., 2002; Heberer and Stan, 1997) and evaluation of their fate in laboratory-scale simulations of drinking-water-treatment (DWT) processes (Westerhoff et al., 2005; Huber et al., 2005; Pinkston and Sedlak, 2004; Zwiener and Frimmel, 2000).

In 2001, the potential for 106 OCs to survive a conventional DWT process and persist in finished, potable water was investigated (Stackelberg et al., 2004). The results provided the first documentation that a wide variety of OCs, most of which are currently unregulated in drinking-water supplies, can survive conventional DWT, but limitations in the study design precluded quantitative comparison of the degradation or removal of OCs by individual water treatments. Subsequent sampling at the same DWT plant in 2003 by the U.S. Geological Survey in cooperation with the New Jersey Department of Environmental Protection addressed these limitations by including (1) collection of multiple time-composited water samples at each treatment step to account for retention time through the DWT plant and diurnal variations in source-water quality, and (2) collection of solids samples for evaluation of the effectiveness of adsorptive processes in removing OCs. This paper uses data from the 2003 sampling to evaluate the average percent removal (concentration decreases) and fate of OCs that were detected in the DWT plant's source waters.

## 2. Description of DWT plant and sample collection

The DWT plant is in a heavily populated, highly urbanized drainage basin in which more than 50 STPs discharge effluent to the two streams (or their tributaries) that provide source water for the DWT plant. The DWT plant treats and provides an average of 235 million L/day to about 850,000 people. Supernatant water that is decanted from settled sludge and filter backwash sediments is recycled to the head of the plant (Fig. 1). This recycled water represents about 9% of water entering the treatment process. Three modifications to the treatment process were made after the 2001 study but before the 2003 sampling: (1) discontinuation of powder-activated carbon, (2) addition of microsand to enhance the clarification process, and (3) reversal of the order of clarification and primary disinfection. An

additional difference was that the GAC in the filters in 2001 was 3 years old and nearly exhausted, whereas the GAC in the filters in 2003 was only 2 months old. Except for these modifications and the condition of the GAC filters, the treatment process at the time of the present study was as described in Stackelberg et al. (2004).

Sample collection entailed collection of 12 water samples at each of six sampling points (72 samples) over a 3-week period during July and August, 2003 (Fig. 1). The six sampling points represent source water (site 1), source and recycled water (site 2), settled water (site 3), disinfected water (site 4), filtered water (site 5), and finished water (site 6) (Fig. 1). To account for retention times in the DWT plant and diurnal variability in source-water quality, water samples were collected as constant flow, 24-h composites of 4-L by use of a metering pump. The composite samples were split into prebaked, 1-L amber-glass bottles that were chilled on ice and sent overnight to participating laboratories. The samples of disinfected, filtered, and finished effluents were preserved with 0.1 g ascorbic acid in the field to prevent further reaction with free chlorine (Westerhoff et al., 2005; Winslow et al., 2001). All water samples were filtered at participating laboratories with 0.7- $\mu\text{m}$ -nominal-pore-size glass-fiber filters prior to extraction and analysis, unlike the samples collected in the earlier

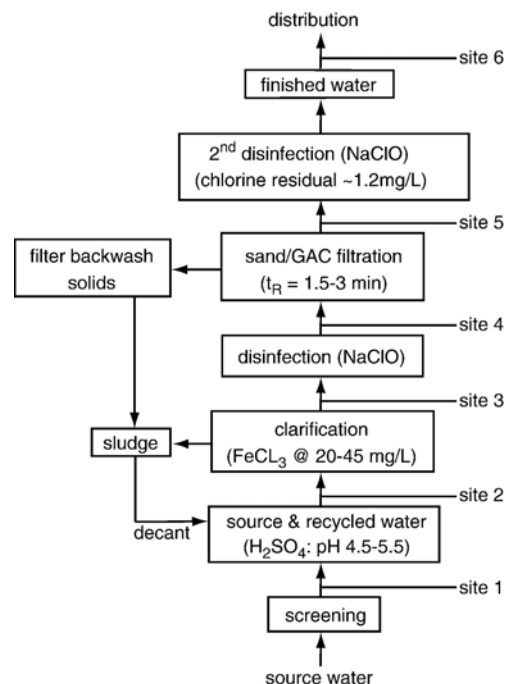


Fig. 1. Schematic diagram of primary-treatment processes and sample-site locations.

Table 1A  
Compounds detected in source water or solids samples

Compound and method	CAS number	Use/category	RL water ( $\mu\text{g}/$ L)	RL solids ( $\mu\text{g}/$ kg)	DF in source water (%) ( $N=12$ )	Max in source water ( $\mu\text{g}/\text{L}$ )	DF in finished water (%) ( $N=12$ )	Max in finished water ( $\mu\text{g}/\text{L}$ )	Detected in solids samples? (Y/N)
<i>Pharmaceuticals</i>									
Acetaminophen <sup>a</sup>	103-90-2	Antipyretic	0.036	0.76	75	0.12	17	0	N
Caffeine <sup>a</sup>	58-08-2	Stimulant	0.016	1.33	42	0.1	0	ND	N
Caffeine <sup>b</sup>	58-08-2		0.5	1.33	100	0.19	25	0.06	N
Carbamazepine <sup>a</sup>	298-46-4	Anticonvulsant	0.011	1.65	92	0.6	100	0.14	Y
Codeine <sup>a</sup>	76-57-3	Analgesic	0.015	1.32	8	0.01	8	0.03	N
Cotinine <sup>a</sup>	486-56-6	Nicotine degrade	0.014	1.3	92	0.01	75	0.02	N
Cotinine <sup>b</sup>	486-56-6		1.0	1.3	0	ND	0	ND	N
Dehydronifedipine <sup>a</sup>	067035-22-7	Nifedipine degrade	0.015	1.69	25	0	17	0	N
Diphenhydramine <sup>a</sup>	58-73-1	Antihistamine	0.015	1.35	0	ND	8	0	Y
Erythromycin <sup>c</sup>	114-07-8	Antibiotic	0.01	1.66	17	0.04	0	ND	N
Erythromycin <sup>d</sup>	114-07-8		0.10	1.66	0	ND	0	ND	N
Erythromycin–H <sub>2</sub> O <sup>c</sup>	–	Erythromycin degrade	0.01	NA	58	0.01	0	ND	–
Fluoxetine <sup>a</sup>	54910-89-3	Antidepressant	0.014	2.17	0	ND	0	ND	Y
Lincomycin <sup>c</sup>	154-21-2	Antibiotic	0.01	NA	17	0.01	0	ND	–
Lincomycin <sup>d</sup>	154-21-2		0.05	NA	8	0.06	0	ND	–
Sulfadimethoxine <sup>c</sup>	122-11-2	Antibiotic	0.01	NA	8	0.01	0	ND	–
Sulfadimethoxine <sup>d</sup>	122-11-2		0.05	NA	0	ND	0	ND	–
Sulfamethazine <sup>c</sup>	57-68-1	Antibiotic	0.01	NA	17	0.04	0	ND	–
Sulfamethazine <sup>d</sup>	57-68-1		0.05	NA	0	ND	0	ND	–
Sulfamethoxazole <sup>c</sup>	723-46-6	Antibiotic	0.01	1.58	83	0.06	0	ND	N
Sulfamethoxazole <sup>d</sup>	723-46-6		0.05	1.58	0	ND	0	ND	N
Sulfathiazole <sup>c</sup>	72-14-0	Antibiotic	0.01	NA	8	0.08	8	0.01	–
Sulfathiazole <sup>d</sup>	72-14-0		0.05	NA	0	ND	0	ND	–
<i>Detergent degradates</i>									
4-Nonylphenol (NP) <sup>b</sup>	251-545-23	Detergent degrade	5	500	25	1.4	8	1.1	Y
Diethoxynonylphenol (NP <sub>2</sub> EO) <sup>b</sup>	–	Detergent degrade	5	1000	17	2.6	0	ND	Y
Diethoxyoctylphenol (OP <sub>2</sub> EO) <sup>b</sup>	–	Detergent degrade	1	50	25	0.26	8	0.12	N
Ethoxyoctylphenol (OP <sub>1</sub> EO) <sup>b</sup>	–	Detergent degrade	1	250	8	0.95	0	ND	Y
<i>Flame retardants and plasticizers</i>									
Tributyl phosphate (TBP) <sup>b</sup>	126-73-8	Flame retardant	0.5	50	42	0.14	8	0.18	Y
Triphenyl phosphate (TPP) <sup>b</sup>	115-86-6	Plasticizer	0.5	50	75	0.08	0	ND	Y
Tris(2-butoxyethyl) phosphate (TBEP) <sup>b</sup>	78-51-3	Flame retardant	0.5	100	100	0.57	0	ND	Y
Tris(2-chloroethyl) phosphate (TCEP) <sup>b</sup>	115-96-8	Plasticizer	0.5	100	100	0.12	8	0.05	N
Tris (dichloroisopropyl) phosphate (TDIP) <sup>b</sup>	13674-87-8	Flame retardant	0.5	100	100	0.11	17	0.07	Y
Bisphenol A <sup>b</sup>	80-05-7	Plasticizer	1	100	67	0.36	17	0.22	Y

(continued on next page)

Table 1A (continued)

Compound and method	CAS number	Use/category	RL water (µg/ L)	RL solids (µg/ kg)	DF in source water (%) (N=12)	Max in source water (µg/L)	DF in finished water (%) (N=12)	Max in finished water (µg/L)	Detected in solids samples? (Y/N)
<i>Polycyclic aromatic hydrocarbons (PAH)</i>									
1-Methylnaphthalene <sup>b</sup>	90-12-0	PAH	0.5	50	0	ND	0	ND	Y
2,6-Dimethylnaphthalene <sup>b</sup>	581-42-0	PAH	0.5	50	0	ND	0	ND	Y
2-Methylnaphthalene <sup>b</sup>	91-57-6	PAH	0.5	50	0	ND	0	ND	Y
Anthracene <sup>b</sup>	120-12-7	PAH	0.5	50	17	0.06	0	ND	Y
Benzo[ <i>a</i> ]pyrene <sup>b</sup>	50-32-8	PAH	0.5	50	0	ND	0	ND	Y
Fluoranthene <sup>b</sup>	206-44-0	PAH	0.5	50	83	0.068	0	ND	Y
Naphthalene <sup>b</sup>	91-20-3	PAH	0.5	50	0	ND	0	ND	Y
Phenanthrene <sup>b</sup>	85-01-8	PAH	0.5	50	83	0.034	0	ND	Y
Pyrene <sup>b</sup>	129-00-0	PAH	0.5	50	83	0.059	0	ND	Y
<i>Fragrances and flavorants</i>									
3-Methyl-1 <i>H</i> -indole (skatol) <sup>b</sup>	83-34-1	Fragrance	0.5	50	0	ND	0	ND	Y
Acetyl hexamethyl tetrahydro naphthalene (AHTN) <sup>b</sup>	21145-77-7	Fragrance	0.5	50	100	0.2	58	0.068	Y
Camphor <sup>b</sup>	76-22-2	Flavorant	0.5	50	33	0.014	25	0.017	N
Hexahydrohexamethyl cyclopentabenzopyran (HHCB) <sup>b</sup>	1222-05-5	Fragrance	0.5	50	92	0.085	0	ND	Y
<i>Plant and animal steroids</i>									
<i>b</i> -Sitosterol <sup>b</sup>	83-46-5	Plant sterol	2	500	17	0.93	0	ND	Y
<i>b</i> -Stigmastanol <sup>b</sup>	19466-47-8	Plant sterol	2	500	17	3.0	0	ND	Y
Cholesterol <sup>b</sup>	57-88-5	Fecal indicator/plant sterol	2	250	33	1.7	0	ND	Y
<i>Pesticides, repellents, and adjuvants</i>									
Carbaryl <sup>b</sup>	63-25-2	Insecticide	1	NA	50	0.12	0	ND	–
Carbazole <sup>b</sup>	86-74-8	Insecticide	0.5	50	42	0.072	0	ND	Y
<i>N,N</i> -Diethyltoluamide (DEET) <sup>b</sup>	134-62-3	Repellent	0.5	100	92	0.2	100	0.097	Y
Diazinon <sup>b</sup>	333-41-5	Insecticide	0.5	50	50	0.14	0	ND	N
<i>D</i> -Limonene <sup>b</sup>	5989-27-5	Fungicide	0.5	50	8	0.0018	0	ND	N
Indole <sup>b</sup>	120-72-9	Adjuvant	0.5	50	0	ND	0	ND	Y
Metolachlor <sup>b</sup>	51218-45-2	Herbicide	0.5	50	58	0.11	0	ND	N
<i>Miscellaneous</i>									
1,4-Dichlorobenzene <sup>b</sup>	106-46-7	Deodorizer	0.5	50	17	0.048	0	ND	N
Anthraquinone <sup>b</sup>	84-65-1	Intermediate	0.5	50	58	0.16	0	ND	Y
Benzophenone <sup>b</sup>	119-61-9	Fixative	0.5	50	75	0.087	0	ND	N
Isophorone <sup>b</sup>	78-59-1	Solvent	0.5	50	0	ND	0	ND	Y
4-Cresol <sup>b</sup>	106-44-5	Preservative	1	250	42	0.033	0	ND	Y
Tetrachloroethene <sup>b</sup>	127-18-4	Solvent	0.5	50	83	0.072	8	0.03	Y
Triclosan <sup>b</sup>	3380-34-5	Antimicrobial	1	50	0	ND	0	ND	Y
Triethyl citrate <sup>b</sup>	77-93-0	Cosmetics	0.5	NA	83	0.12	17	0.082	–

RL, reporting level; DF, detection frequency; Max, maximum concentration; ND, not detected; NA, not analyzed; –, no data; Y, yes; N, no.

<sup>a</sup> HPLC/MS–ESI(+).

<sup>b</sup> GC/MS.

<sup>c</sup> HPLC/MS–MS–ESI(+).

<sup>d</sup> LC/MS–ESI(+).

Table 1B  
Compounds not detected in source water or solids samples

Compound	CAS number	Use	RL water ( $\mu\text{g/L}$ )	RL solids ( $\mu\text{g/kg}$ )
<i>Pharmaceuticals</i>				
1,7-Dimethylxanthine <sup>a</sup>	611-59-6	Caffeine degradate	0.144	2.03
Albuterol <sup>a</sup>	18559-94-9	Antiasthmatic	0.023	1.09
Amoxicillin <sup>b</sup>	61336-70-7	Antibiotic	0.20	NA
Ampicillin <sup>b</sup>	69-53-4	Antibiotic	0.10	NA
Anhydrochlorotetracycline <sup>b</sup>	–	Chlorotetracycline degradate	0.10	NA
Anhydrotetracycline <sup>b</sup>	4496-85-9	Tetracycline degradate	0.20	NA
Cefotaxime <sup>b</sup>	63527-52-6	Antibiotic	0.10	NA
Chlorotetracycline <sup>b</sup>	57-62-5	Antibiotic	0.10	NA
Cimetidine <sup>a</sup>	51481-61-9	Antacid	0.012	0.88
Ciprofloxacin <sup>c</sup>	85721-33-1	Antibiotic	0.0005	NA
Ciprofloxacin <sup>b</sup>	85721-33-1		0.05	NA
Clinafloxacin <sup>b</sup>	105956-97-6	Antibiotic	0.05	NA
Cloxacillin <sup>b</sup>	61-72-3	Antibiotic	0.10	NA
Demeclocycline <sup>b</sup>	127-33-3	Antibiotic	0.10	NA
Diltiazem <sup>a</sup>	42399-41-7	Antihypertensive	0.016	1.48
Doxycycline <sup>b</sup>	564-25-0	Antibiotic	0.10	NA
Flumequine <sup>b</sup>	42835-25-6	Antibiotic	0.05	NA
Gemfibrozil <sup>a</sup>	25812-30-0	Antihyperlipidemic	0.013	5.46
Ibuprofen <sup>a</sup>	15687-27-1	Antiinflammatory	0.042	NA
Lomefloxacin <sup>b</sup>	98079-51-7	Antibiotic	0.05	NA
Miconazole <sup>a</sup>	22916-47-8	Antifungal	NA	0.97
Minocycline <sup>b</sup>	10118-90-8	Antibiotic	0.018	NA
Norfloxacin <sup>c</sup>	70458-96-7	Antibiotic	0.005	NA
Norfloxacin <sup>b</sup>	70458-96-7		0.05	NA
Ofloxacin <sup>c</sup>	83380-47-6	Antibiotic	0.01	NA
Ofloxacin <sup>b</sup>	83380-47-6		0.05	NA
Ormetoprim <sup>b</sup>	6981-18-6	Antibiotic	0.05	NA
Oxacillin <sup>b</sup>	66-79-5	Antibiotic	0.10	NA
Oxolinic acid <sup>b</sup>	14698-29-4	Antibiotic	0.05	NA
Oxytetracycline <sup>b</sup>	6153-64-6	Antibiotic	0.10	NA
Penicillin G <sup>b</sup>	61-33-6	Antibiotic	0.10	NA
Penicillin V <sup>b</sup>	87-08-1	Antibiotic	0.10	NA
Ranitidine <sup>a</sup>	66357-35-5	Antacid	0.013	NA
Roxithromycin <sup>b</sup>	80214-83-1	Antibiotic	0.10	NA
Sarafloxacin <sup>c</sup>	98105-99-8	Antibiotic	0.005	NA
Sarafloxacin <sup>b</sup>	98105-99-8		0.05	NA
Sulfachloropyridazine <sup>c</sup>	80-32-0	Antibiotic	0.005	NA
Sulfachloropyridazine <sup>b</sup>	80-32-0		0.05	NA
Sulfadiazine <sup>c</sup>	68-35-9	Antibiotic	0.05	NA
Sulfadiazine <sup>b</sup>	68-35-9		0.05	NA
Sulfamerazine <sup>b</sup>	127-79-7	Antibiotic	0.05	NA
Tetracycline <sup>b</sup>	60-54-8	Antibiotic	0.10	NA
Thiabendazole <sup>a</sup>	148-79-8	Anthelmintic	0.011	1.04
Trimethoprim <sup>c</sup>	738-70-5	Antibiotic	0.05	1.47
Trimethoprim <sup>b</sup>	738-70-5		0.05	1.47
Tylosin <sup>c</sup>	1401-69-0	Antibiotic	0.05	NA
Tylosin <sup>b</sup>	1401-69-0		0.10	NA
Virginiamycin <sup>b</sup>	21411-53-0	Antibiotic	0.10	NA
Warfarin <sup>a</sup>	81-81-2	Anticoagulant	0.012	1.26
<i>Detergent degradates</i>				
4-Cumylphenol <sup>d</sup>	599-64-4	Detergent degradate	1	50
4-Octylphenol <sup>d</sup>	–	Detergent degradate	1	50
4-tert-Octylphenol <sup>d</sup>	–	Detergent degradate	1	50

(continued on next page)

Table 1B (continued)

Compound	CAS number	Use	RL water ( $\mu\text{g/L}$ )	RL solids ( $\mu\text{g/kg}$ )
<i>Fragrances and flavorants</i>				
Isoborneol <sup>d</sup>	124-76-5	Fragrance	0.5	50
Isoquinoline <sup>d</sup>	119-65-3	Flavorant/fragrance	0.5	100
Menthol <sup>d</sup>	89-78-1	Flavorant	0.5	50
<i>Pesticides, repellents, and adjuvants</i>				
Bromacil <sup>d</sup>	314-40-9	Herbicide	0.5	100
Chlorpyrifos <sup>d</sup>	2921-88-2	Insecticide	0.5	50
Dichlorvos <sup>d</sup>	62-73-7	Insecticide	1	NA
Metalaxyl <sup>d</sup>	57837-19-1	Herbicide	0.5	50
Prometon <sup>d</sup>	1610-18-0	Herbicide	0.5	50
<i>Miscellaneous</i>				
3- <i>tert</i> -Butyl-4-hydroxyanisole <sup>d</sup>	121-00-6	Antioxidant	5	NA
5-Methyl-1 <i>H</i> -benzotriazole <sup>d</sup>	136-85-6	Anticorrosive	2	NA
Isopropylbenzene (cumene) <sup>d</sup>	98-82-8	Intermediate	0.5	50
Methyl salicylate <sup>d</sup>	119-36-8	Liniment	0.5	100
Pentachlorophenol <sup>d</sup>	87-86-5	Preservative	2	200

RL, reporting level; DF, detection frequency; NA, not analyzed; –, no data; Y, yes; N, no.

<sup>a</sup> HPLC/MS–ESI(+).

<sup>b</sup> LC/MS–ESI(+).

<sup>c</sup> HPLC/MS–MS–ESI(+).

<sup>d</sup> GC/MS.

sampling (Stackelberg et al., 2004), which were not time-composited nor preserved with ascorbic acid, and in which 63 of the 106 analytes were measured in unfiltered (whole-water) samples.

Two samples of sludge that settled from pre-chlorinated source water after coagulation with ferric chloride, and two samples of solids from the backwashing of GAC filters (Fig. 1) were collected in prebaked, 1-L amber glass bottles. Supernatant water was siphoned off the top of the filter-backwash samples after overnight refrigeration, and all wet-solids samples were chilled on ice and sent overnight to participating laboratories.

### 3. Analytical methods

The water samples were analyzed for 113 compounds, and the sediment samples were analyzed for 71 of these compounds, using methods developed by the USGS (Tables 1A and 1B). Eighteen pharmaceuticals and selected degradates in water samples were measured by solid-phase extraction (SPE) and high-performance liquid chromatography/mass spectrometry positive-ion electrospray ionization [HPLC/MS–ESI(+)] (Tables 1A and 1B) as described in Cahill et al. (2004), and 17 pharmaceuticals and selected degradates were extracted from solids samples by accelerated solvent extraction (ASE) in a manner similar to the approach described in Kinney et al. (2006a). Compounds in these extracts were

identified and quantified by the method described in Cahill et al. (2004). 37 antibiotics and selected degradates in water samples were measured by SPE and LC/MS–ESI(+) (Michael Meyer, USGS, written communication, 2005); 14 of these compounds were also measured by HPLC/MS–MS–ESI(+) (Tables 1A and 1B). The HPLC/MS–MS–ESI(+) method also measured a primary degradate of erythromycin (erythromycin–H<sub>2</sub>O) (Michael Meyer, USGS, written communication, 2005). 59 other OCs in water samples were measured by SPE and gas chromatography/mass spectrometry (GC/MS) (Tables 1A and 1B) (Zaugg et al., 2002); 54 of these OCs also were extracted from solids samples through ASE, as described in Burkhardt et al. (2005) and identified through the method described in Zaugg et al. (2002).

Sixteen OCs in water samples were measured by 2 analytical methods (Tables 1A and 1B). The presence or absence of these compounds was confirmed in all of the paired determinations for 11 of these compounds (ciprofloxacin, cotinine, erythromycin, norfloxacin, sarafloxacin, sulfachloropyridazine, sulfadiazine, sulfadimethoxine, sulfamethoxazole, trimethoprim, and tylosin); and in 98.6% of the paired determinations for sulfamethazine, and 97.2% of the paired determinations for caffeine, lincomycin, ofloxacin, and sulfathiazole. Of these 16 compounds, 14 are antibiotics that were measured by LC/MS–ESI(+) and HPLC/MS–MS–ESI(+). The latter (MS–MS) method is the more sensitive,

and achieves a lower RL, therefore, data from the MS–MS method were used to describe the occurrence and concentration of these antibiotics through the treatment process. Two of the compounds (cotinine and caffeine) were measured by HPLC/MS–ESI(+) and GC/MS; the mean percent recovery for cotinine by the HPLC/MS–ESI(+) method was greater than by the GC/MS method (Cahill et al., 2004; Zaugg et al., 2002); therefore, the data from the HPLC/MS–ESI(+) method were used to describe the occurrence and concentration of cotinine through the treatment process. Mean percent recoveries for caffeine by the HPLC/MS–ESI(+) method were not reported by Cahill et al. (2004), therefore, occurrence and concentration of caffeine through the treatment process are described by data from the GC/MS method.

Analytes detected at low concentrations were assigned estimated values in accordance with conventions described in Oblinger Childress et al. (1999) rather than being censored (set to nondetection) at higher RLs. Providing estimates of low concentrations for analytes that are qualitatively identified by mass spectral methods allowed computation of the average percent removal of these compounds through the DWT process needed for this research (Stackelberg et al., 2006).

#### 4. Quality assurance

Six field blanks and 86 laboratory blanks were analyzed for target compounds. Blank samples were derived from

laboratory-grade organic-free water. Field blanks were used to indicate whether sampling procedures, sampling equipment, field conditions, or sample-shipment procedures introduced target compounds into environmental samples, and laboratory blanks were used to assess the potential for sample contamination in the laboratory. Field blanks were collected at each of the six water-sampling sites (Fig. 1). Six compounds (pyrene, fluoranthene, carbamazepine, acetaminophen, dehydronifedipine, and DEET) were each detected in one field blank and censored in the associated environmental samples, and two compounds (triphenyl phosphate and cotinine) were detected in one field blank, but not in the associated environmental sample and, thus, were not censored. One compound (NP<sub>2</sub>EO) was detected in 10 laboratory blanks, and detections of NP<sub>2</sub>EO in associated environmental samples that were less than 3 times the concentration measured in the laboratory blanks were censored. Two compounds (metformin and acetaminophen) were detected in one laboratory blank. Metformin was not detected in the associated environmental samples and, thus, was not censored; but acetaminophen was detected in one environmental sample at a concentration less than 3 times the laboratory blank concentration, and was censored.

At least one laboratory-reagent spike was processed with each set of 10 environmental samples during this study. Recoveries ranged from 15% for dichlorvos to 183% for 5-methyl-1*H*-benzotriazole, with a median recovery of 92% for all compounds. Matrix spike

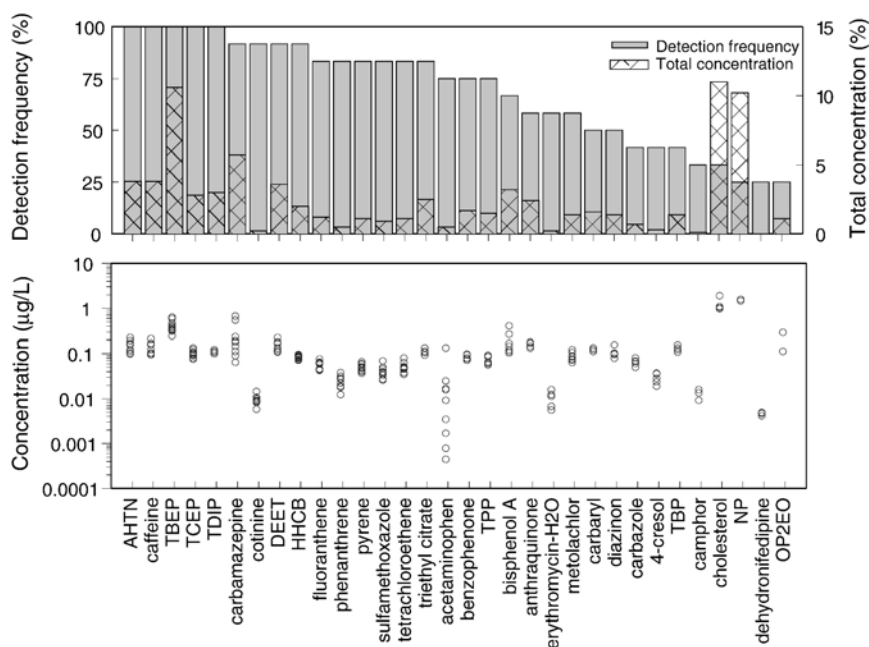


Fig. 2. Compounds detected in 25% or more of source-water samples.

recoveries were not specifically determined in this study; although, matrix spike-recovery samples are collected for a larger USGS research effort, of which this study is a part (Stackelberg et al., 2006). Average recoveries and standard deviations for matrix-free

reagent spikes are similar to those for matrix spikes, even though many matrix samples are from complex wastewater-effluent samples; this indicates that the analytical methods for these compounds were reliable even in the presence of complex interferences.

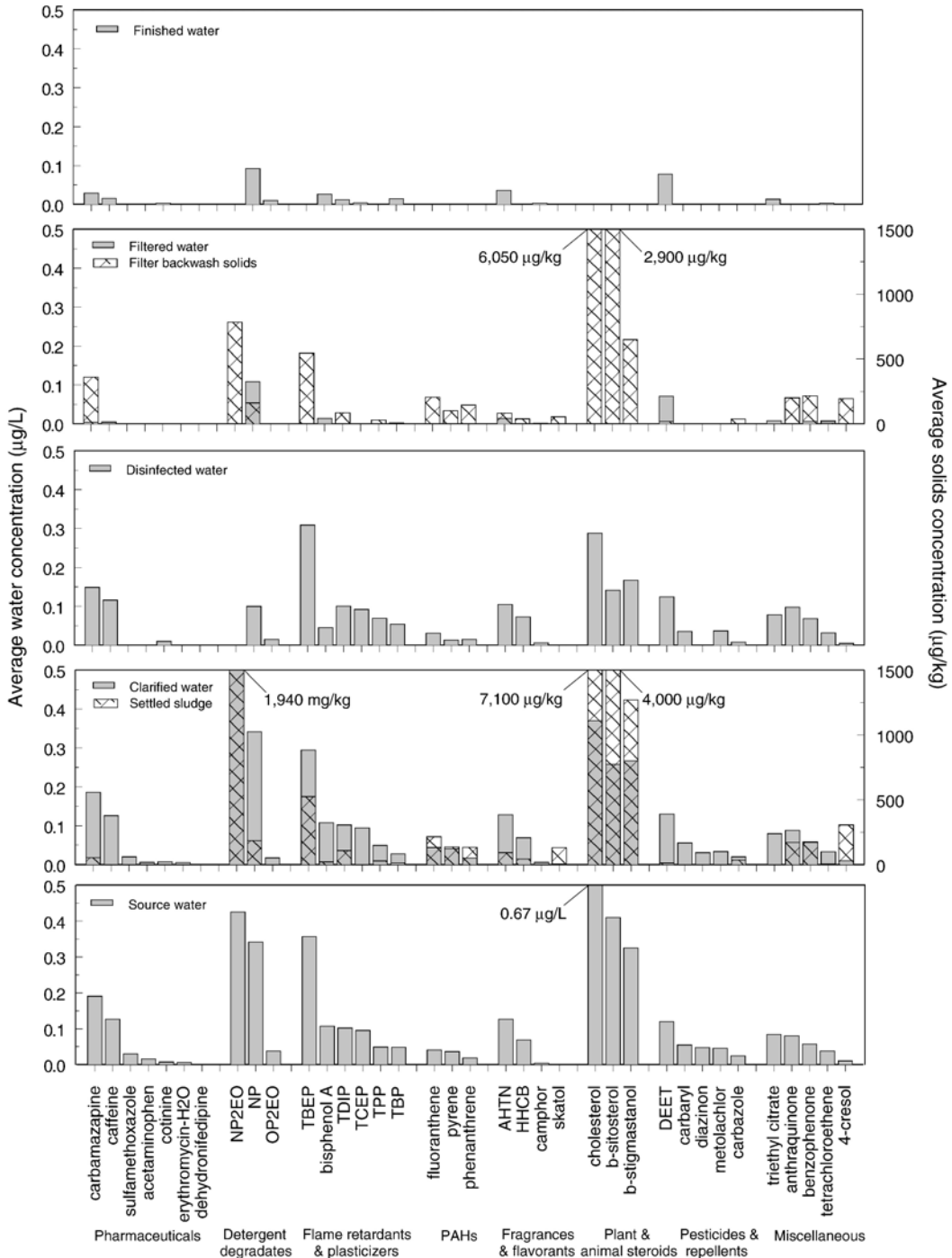


Fig. 3. Compounds detected in 25% or more of source-water samples or in solids samples at 100 µg/kg or greater.

Table 2  
Compounds detected in solids samples or in at least 25% of source-water samples

Constituent	Log $K_{ow}$ (20– 25 °C)	Water solubility (mg/L at 25– 30 °C)	Average concentration (water: µg/L; solids: µg/kg)					
			Source Water	Clarified Water/solids	Disinfected Water	Filtered Water/solids	Finished Water	Percent Removal
<i>Pharmaceuticals</i>								
Erythromycin–H <sub>2</sub> O	–	–	0.01	0.0053/NA	0.0004	ND/NA	ND	100
Sulfamethoxazole	0.89	610	0.030	0.020/ND	ND	ND/ND	ND	100
Acetaminophen	0.46	14,000	0.015	0.006/ND	ND	0.001/ND	.0003	98
Caffeine	–0.07	21,600	0.126	0.126/ND	0.116	0.004/ND	0.015	88
Carbamazepine	2.45	17.7	0.191	0.186/54	0.149	0.004/359	0.029	85
Cotinine	0.07	998,600	0.008	0.0071/ND	0.010	0.0007/ND	0.003	57
Dehydronifedipine	–	–	0.001	0.0007/ND	0.0006	ND/ND	0.0006	40
Fluoxetine	4.05	60.3	ND	ND/49.5	ND	ND/58.6	ND	NC
Diphenhydramine	3.27	3060	ND	ND/26.2	ND	ND/ND	ND	NC
<i>Detergent degradates</i>								
OP <sub>1</sub> EO	6.02	–	0.079	0.0783/65	ND	ND/ND	ND	100
NP <sub>2</sub> EO	5.3	–	1.192	0.858/1940	0.592	ND/785	0.192	84
OP <sub>2</sub> EO	>4.5	–	0.038	0.017/ND	0.015	ND/ND	0.010	74
NP	5.92	5000	0.342	0.342/185	0.100	0.108/160	0.092	73
<i>Flame retardants and plasticizers</i>								
TPP	4.59	1.9	0.049	0.049/27.5	0.069	ND/27	ND	100
TBEP	3.75	1100	0.357	0.294/525	0.309	ND/545	ND	100
TCEP	1.44	7000	0.095	0.094/ND	0.092	ND/ND	0.004	96
TDIP	3.65	7	0.102	0.102/109	0.101	ND/84.5	0.012	88
Bisphenol A	3.32	120	0.107	0.108/19	0.045	.014/ND	0.026	76
TBP	4	280	0.048	0.027/14.5	0.054	ND/7.5	0.015	69
<i>Polycyclic aromatic hydrocarbons</i>								
Anthracene	4.45	0.043	0.010	0.014/30.5	ND	ND/31.5	ND	100
Fluoranthene	5.16	0.26	0.041	0.044/215	0.031	ND/205	ND	100
Phenanthrene	4.46	1.15	0.018	0.017/135	0.015	ND/145	ND	100
Pyrene	4.88	0.135	0.037	0.041/136	0.014	ND/99.5	ND	100
Benzo[ <i>a</i> ]pyrene	6.13	01002	ND	ND/48.5	ND	ND/15	ND	NC
Naphthalene	3.3	31	ND	ND/27.5	ND	.004/39.5	ND	NC
2-Methylnaphthalene	3.86	25	ND	ND/20	ND	ND/22	ND	NC
1-Methylnaphthalene	3.87	26	ND	ND/18.6	ND	ND/17.5	ND	NC
2,6-Dimethylnaphthalene	4.31	2	ND	ND/19.3	ND	ND/14	ND	NC
<i>Fragrances and flavorants</i>								
HHCB	5.9	1.75	0.069	0.069/41.5	0.073	ND/39	ND	100
AHTN	5.7	1.25	0.126	0.128/92	0.105	0.014/83	0.036	71
Camphor	3.04	1600	0.004	0.006/ND	0.006	0.001/ND	0.003	25
Skatol	2.6	498	ND	0.001/129.5	ND	ND/53.5	ND	NC
<i>Plant and animal steroids</i>								
<i>b</i> -Sitosterol	9.65	–	0.411	0.258/4000	0.142	ND/2900	ND	100
<i>b</i> -Stigmastanol	9.73	–	0.325	0.267/1270	0.167	ND/650	ND	100
Cholesterol	8.74	0.1	0.670	0.369/7100	0.288	ND/6050	ND	100
<i>Pesticides, repellents, adjuvants</i>								
Carbaryl	2.36	110	0.055	0.056/NA	0.035	ND/NA	ND	100
Carbazole	3.72	1.8	0.024	0.020/34.5	0.008	ND/36.5	ND	100
Diazinon	3.81	40	0.047	0.031/ND	ND	ND/ND	ND	100
Metolachlor	3.13	530	0.046	0.033/ND	0.037	ND/ND	ND	100
DEET	2.18	912	0.120	0.13/11	0.125	0.071/17	0.078	35
Indole	2.14	3560	ND	0.001/186.5	ND	ND/59	ND	NC

(continued on next page)

Table 2 (continued)

Constituent	Log $K_{ow}$ (20– 25 °C)	Water solubility (mg/L at 25– 30 °C)	Average concentration (water: µg/L; solids: µg/kg)					
			Source Water	Clarified Water/solids	Disinfected Water	Filtered Water/solids	Finished Water	Percent Removal
<i>Miscellaneous</i>								
Anthraquinone	3.39	1.35	0.080	0.088/170	0.098	ND/200	ND	100
Benzophenone	3.18	137	0.057	0.059/170	0.068	0.006/215	ND	100
4-Cresol	1.94	21,500	0.011	0.010/305	0.004	ND/195	ND	100
Tetrachloroethene	3.4	200	0.038	0.032/3.9	0.032	0.007/3.45	0.003	92
Triethyl citrate	0.33	65,000	0.085	0.080/NA	0.078	0.008/NA	0.013	85
Isophorone	1.7	12,000	ND	ND/12	ND	ND/6.5	ND	NC
Triclosan	4.76	10	ND	ND/27	ND	ND/15.5	ND	NC

NC: not calculated; ND: not detected; >, greater than; –, no data.

Table 3

Tukey's multiple comparison test groupings for compounds detected in at least 50% of source-water samples

Constituent	Tukey's multiple comparison test groupings				
	Source	Clarified	Disinfected	Filtered	Finished
<i>Pharmaceuticals</i>					
Erythromycin–H <sub>2</sub> O	A	A	B	B	B
Sulfamethoxazole	A	A	B	B	B
Acetaminophen	A	A	B	B	B
Caffeine	A	A	A	B	B
Carbamazepine	A	A	A	B	B
Cotinine	A	AB	A	C	BC
<i>Flame retardants and plasticizers</i>					
TPP	A	A	A	B	B
TBEP	A	A	A	B	B
TCEP	A	A	A	B	B
TDIP	A	A	A	B	B
Bisphenol A	AB	A	AB	B	AB
<i>Polycyclic aromatic hydrocarbons</i>					
Fluoranthene	A	A	A	B	B
Phenanthrene	A	A	A	B	B
Pyrene	A	A	BC	C	C
<i>Fragrances and flavorants</i>					
HHCB	A	A	A	B	B
AHTN	A	A	A	B	B
<i>Pesticides, repellents, adjuvants</i>					
Carbaryl	A	AB	AB	B	B
Diazinon	A	AB	B	B	B
Metolachlor	A	AB	AB	B	B
DEET	A	A	A	B	B
<i>Miscellaneous</i>					
Anthraquinone	A	A	A	B	B
Benzophenone	A	A	A	B	B
Tetrachloroethene	A	A	A	BC	C
Triethyl citrate	A	A	A	B	B

Sampling locations with one or more letters in common do not differ significantly from one another.

## 5. Data analysis

Analysis of variance (ANOVA) on ranked concentrations was used to evaluate the null hypothesis that mean ranked concentrations were statistically similar among the six sampling points. If the null hypothesis was rejected, Tukey's multiple comparison test was used to indicate which mean ranked concentrations were similar to or significantly different from others (Helsel and Hirsch, 1992). Significance was set at the 95% confidence level for all statistical tests.

Average percent removal by each water-treatment process was calculated for selected OCs by the formula  $(1 - [C/C_o] \times 100)$ , where  $C$  is the average concentration in effluent over twelve 24-h sampling periods from the treatment step, and  $C_o$  is the average concentration in effluent from the preceding treatment step. Total average percent removal was calculated with  $C$  as the average concentration in finished water over twelve 24-h sampling periods, and  $C_o$  the average concentration in source water. Nondetections were set equal to zero for these calculations. Analytical precision associated with trace concentrations may affect the precision of average concentrations and, thus, calculations of their percent differences; therefore, average percent differences in the concentration of OCs between treatment steps are grouped into three categories in the discussions that follow: (1) low (<25% difference), (2) moderate (25–75% difference), and (3) high (>75% difference).

## 6. Results

The effectiveness of a DWT plant in degrading or removing OCs depends on several factors (some of which may change through time), including the quality of the source water, the type and mode of operation of each treatment process, and physiochemical characteristics of the compounds themselves (Volk et al., 2005; Coupe and Blomquist, 2004). The flow of one of the two source streams ranged from about 6 to more than 81 m<sup>3</sup>/s during the sample collection period and the concentrations of some compounds increased during high flows, whereas the concentration of others decreased (Kolpin et al., 2004). Turbidity, a measure of suspended-sediment concentration, ranged from 7.5 to 22.9 NTU in source waters and averaged 11.3 NTU during the 3-week sample collection period. Results presented here pertain only to the source-water characteristics during the sample collection period and the specific manner in which the plant was operated during this time.

The 56 compounds that were detected in source-water or solids samples are listed in Table 1A; the 57

compounds that were not detected are listed in Table 1B. The following sections focus on the average concentration of OCs through the treatment processes, and their occurrence in finished water. To maximize the useful scientific information in our dataset and to improve our understanding of the fate of each OC through the DWT process, the detection frequencies and average concentrations reported for each compound are based on all detections (Stackelberg et al., 2006). Direct comparisons of detection frequencies or average concentrations for OCs with differing RLs, however, would be inappropriate (Table 1A).

ANOVA on ranked concentrations indicates that concentrations of OCs in the source-water and source-and-recycled water samples were statistically similar; therefore, results from the source-and-recycled samples are not discussed further. Furthermore, statistically significant differences in ranked concentrations could be calculated only for OCs that were detected in at least 50% of source-water samples; therefore, ANOVA results are not shown for OCs detected in fewer than 50% of source-water samples.

### 6.1. OCs in source water

The detection of 45 of the 113 OCs in at least 1 sample of source water, and of 32 of these compounds in at least 25% of source-water samples (Fig. 2), is consistent with previous reports of the frequent occurrence of OCs in streams that receive effluent from STPs (Glassmeyer et al., 2005; Kolpin et al., 2002). Compounds detected in at least 75% of the source-water samples include polycyclic musk fragrances (AHTN, HHCb), pharmaceuticals and their degradates (carbamazepine, acetaminophen, cotinine, sulfamethoxazole, and caffeine), the insect repellent *N,N*-diethyltoluamide (DEET), organophosphorus flame retardants and plasticizers [tris(2-butoxyethyl) phosphate (TBEP), tris(2-chloroethyl)phosphate (TCEP), tris(dichloroisopropyl) phosphate (TDIP), and triphenyl phosphate (TPP)], polycyclic aromatic hydrocarbons (PAHs) (fluoranthene, pyrene, phenanthrene), the solvent tetrachloroethene, and the cosmetics triethyl citrate and benzophenone. The concentrations of these frequently detected compounds in source waters were generally low, however, and rarely exceeded 1 µg/L (Fig. 2). A few specific compounds, e.g., TBEP, 4-nonylphenol (NP), and cholesterol, the latter two of which were detected in fewer than half of the source-water samples, account for a large percentage of the total measured concentration of all target analytes (Fig. 2); this underscores the importance of collecting multiple samples over differing flow conditions to adequately reflect the

source-water quality. Certain compounds within specific OC categories accounted for a large percentage of the total average concentration for those categories. For example, carbamazepine and caffeine accounted for most of the total average concentration of pharmaceuticals, NP<sub>2</sub>EO and NP accounted for most of the detergent metabolite concentration, TBEP accounted for most of the flame retardants and plasticizer concentration, AHTN and HHCB accounted for most of the fragrances and flavorant concentration, and DEET accounted for most of the pesticides and repellent concentration (Fig. 3).

### 6.2. Removal through treatment processes

In general, the hydrophobic compounds (as indicated by high  $\log K_{ow}$  and low solubility), such as PAHs and plant and animal steroids, were detected at elevated concentrations in dried-solids samples and were not present at measurable concentrations in finished-water samples. In contrast, the hydrophilic compounds (as indicated by low  $\log K_{ow}$  and high solubility), such as pharmaceuticals, were detected at relatively low concentrations in dried-solids samples and were present in measurable concentrations in finished-water samples. Detection frequency and concentration of OCs in the solids and water phases are highly variable relative to their  $\log K_{ow}$  and water-solubility values, however, as a result of differences in (1) the capability to measure individual OCs in solids and (or) water matrices, (2) the

manner in which individual OCs react to each treatment process, and (or) (3) the use of individual OCs in the watershed. Also, predictors of water–solid distributions, such as  $\log K_{ow}$ , assume that water and solids are in equilibrium, which may not be true in a dynamic DWT process. The following discussion focuses on the clarification, disinfection, and GAC-filtration treatments –the primary processes that govern the fate of OCs through the treatment process, and how the effectiveness of these steps varies among and within the eight classes of compounds. Average concentrations in water and solids samples are presented in Table 2 and shown in Fig. 3.

### 6.3. Clarification

Clarification consists of chemically treating the source water to destabilize colloidal particles (coagulation) and facilitate their flocculation and settling with other suspended sediments. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was added to the source waters prior to clarification to optimize pH levels in the 4.5–5.5 range, and ferric chloride (FeCl<sub>3</sub>) was added as the coagulant agent. Injection of microsand into the clarification tanks to enhance flocculation and settling resulted in retention times of 15–20 min for the clarification process. Two clarification tanks were operated in parallel during this study; the samples of clarified water were collected subsequent to one of these tanks.

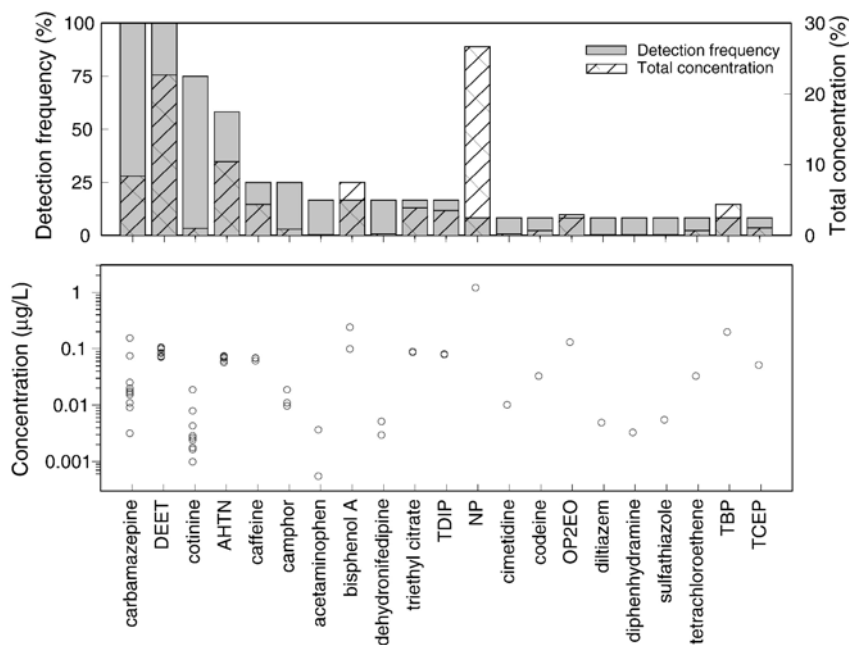


Fig. 4. Compounds detected in 1 or more samples of finished water.

In general, clarification accounted for only 15% of the reduction in average concentration of OCs during the treatment process. Each of the 32 OCs detected in 25% or more of source-water samples (Fig. 2) were also detected in clarified effluent – an indication of incomplete degradation or removal. Ranked concentrations for OCs detected in at least 50% of source-water samples did not differ significantly between source- or clarified-water samples (Table 3), and none of these 32 OCs showed a decrease of 75% or more in average concentration after clarification (Table 2). Clarification, therefore, is generally not a primary route by which OCs in filtered-water samples are degraded or removed.

Clarification decreased the average concentration of eight OCs (sulfamethoxazole, acetaminophen, dehydronifedipine, OP<sub>2</sub>EO, TBP, cholesterol, diazinon, and metolachlor) by 25% to 75% of their concentration in source water – an indication of moderate degradation or removal (Fig. 3). Five of these compounds (OP<sub>2</sub>EO, TBP, cholesterol, diazinon, and metolachlor) are hydrophobic, two of which (TBP and cholesterol) were detected in the dried solids of settled sludge; the high average concentration of 7100 µg/kg for cholesterol ( $\log K_{ow} = 8.74$ ) indicates removal by partitioning onto suspended solids or ferric hydroxide precipitates. The other three of these eight compounds (sulfamethoxazole, acetaminophen, and dehydronifedipine) are hydrophilic ( $\log K_{ow} < 1.0$ ) and, as a result, were not detected in the dried solids of settled sludge. The moderate removal of these hydrophilic pharmaceuticals from the water phase during clarification may be explained by ferric chloride coagulation, which results in base or acid hydrolysis; the potential importance of this removal mechanism could not be verified, however, because the degradates that are potentially formed through hydrolysis were not measured during this study.

The average concentrations of 24 of the 32 OCs that were detected in at least 25% of source-water samples were less than 25% lower in clarified effluent than in source waters – an indication of poor degradation or removal. Minor removal of 10 of these compounds (carbamazepine, caffeine, erythromycin–H<sub>2</sub>O, DEET, TCEP, fluoranthene, pyrene, phenanthrene, metolachlor, and HHCB) is consistent with laboratory-scale simulations of the effect of chemical treatments on these compounds (Ternes et al., 2002; Westerhoff et al., 2005). The analyses of clarified samples in this study provides new information on the limited degradation or removal of additional pharmaceuticals (cotinine), detergent metabolites (NP<sub>2</sub>EO and NP), flame retardants and plasticizers (TBEP, bisphenol A, TDIP, and TPP), the plant sterol  $\beta$ -stigmastanol, and the miscellaneous

compounds triethyl citrate, anthraquinone, benzophenone, tetrachloroethene, and 4-cresol by this process. Several of these OCs (including NP<sub>2</sub>EO,  $\beta$ -stigmastanol, TBEP, and 4-cresol) that were not substantially decreased in the water phase, were detected in the dried solids of settled sludge – a reflection of their hydrophobic nature and their adsorption to suspended sediments. Another 27 OCs that were not substantially decreased in the water phase, or that were not detected in source-water samples, were detected in the dried solids of settled sludge – a further indication of their undetected presence in filtered samples of source waters through sorption to suspended sediments (Table 2).

#### 6.4. Disinfection

The clarified water was disinfected through the addition of sodium hypochlorite (NaClO) to inactivate pathogenic microorganisms (Fig. 1). Contact time for primary disinfection was generally 200 to 300 min. Disinfected-water samples represent water composited from both disinfection basins that were in operation during this study.

In general, disinfection accounted for 32% of the degradation or removal of OCs from the water phase. Of the 32 OCs that were detected in 25% or more of source-water samples and in clarified-effluent samples, 4 (sulfamethoxazole, acetaminophen, erythromycin–H<sub>2</sub>O, and diazinon; Tables 2 and 3) had ranked concentrations that were significantly lowered in disinfected effluent, or average concentrations that decreased by at least 75%, from the values in clarified effluent; this is attributed to reaction with free chlorine. Substantial loss of the first three of these compounds through oxidation with free chlorine is consistent with laboratory-scale simulations of their fates through the disinfection process (Bedner and MacCrehan, 2006; Westerhoff et al., 2005; Dodd and Huang, 2004), and the substantial loss of the fourth (diazinon) corroborates findings of Coupe and Blomquist (2004), Magara (1994), and Aizawa et al. (1994). Chlorinated byproducts likely to form during the reaction of these compounds with NaClO (Pinkston and Sedlak, 2004; Coupe and Blomquist, 2004) were not measured in this study.

Chlorination decreased the average concentration of seven of these 32 OCs (NP, bisphenol A, fluoranthene, pyrene, carbaryl, carbazole, and 4-cresol) by 25% to 75% relative to the concentration in clarified effluent – an indication of moderate reactivity with free chlorine (Table 2; Fig. 3). Loss of two of these seven compounds (NP and bisphenol A) through oxidation with free

chlorine corroborates the findings of Deborde et al. (2004), Petrovic et al. (2003), and Hu et al. (2002a,b). Additional chlorinated byproducts likely form during reaction of NP and bisphenol A with NaClO (Korshin et al., 2006; Petrovic et al., 2003; Hu et al., 2002a,b) but were not measured during this study. Loss of fluoranthene and pyrene corroborates research by Westerhoff et al. (2005) although the effectiveness of oxidation for fluoranthene is less than reported from that study. Data from the present study provide new information on moderate removal or degradation of carbaryl, carbazole, and 4-cresol through oxidation with free chlorine.

The average concentrations of another 21 of the 32 OCs that were detected in 25% or more of source-water samples were decreased by less than 25% in disinfected effluent in relation to clarified effluent – an indication of little or no reactivity of these compounds with free chlorine under ambient pH conditions of the disinfection process. For example, the pharmaceuticals carbamazepine, caffeine, cotinine, and dehydronifedipine were found to have low reactivity with free chlorine which corroborates the findings of Gibs et al. (2007) who examined the stability of OCs in the presence of a free chlorine residual as a function of time. Other investigators (Westerhoff et al., 2005) report more effective oxidation of carbamazepine and caffeine, possibly due to differences in experimental conditions. The decrease in average concentration of five organophosphorus flame retardants (TBEP, TDIP, TCEP, TPP, and TBP), the musk fragrances AHTN and HHCB, the insect repellent DEET, and the pesticide compound metolachlor was less than 25% through oxidation with free chlorine which is consistent with laboratory-scale simulation of the fate of several of these OCs through disinfection with NaClO (Westerhoff et al., 2005). Eight other OCs that were not effectively oxidized by free chlorine in this study were OP<sub>2</sub>EO, phenanthrene, camphor, cholesterol, triethyl citrate, anthraquinone, benzophenone, and tetrachloroethene.

### 6.5. GAC filtration

Chlorinated water from the disinfection process was passed through filters that contained 25.4 cm of sand and 91.4 cm of bituminous granular activated carbon (GAC filters) to retain remaining fine particles and bacteria and to control taste- and odor-causing compounds. Contact time on the GAC filters was generally 1.5 to 3 min. Eight GAC filter banks were in simultaneous operation during this study; samples of GAC-filtered water were collected subsequent to one filter bank.

Despite the short filter-contact times, GAC filtration accounted for 53% of the removal of OCs from the water phase. Of the 29 OCs that were detected in at least 25% of source-water samples and in disinfected effluent, 25 had ranked concentrations that were significantly decreased, and average concentrations that were decreased by 75% or more (Tables 2 and 3), corroborating previous documentation of the effectiveness of GAC filtration in removing OCs from the water phase (Ternes et al., 2002). This process also lowered the concentrations of many OCs – the pharmaceutical degradates erythromycin–H<sub>2</sub>O and dehydronifedipine, the detergent metabolite OP<sub>2</sub>EO, each of the five organophosphorus flame retardants (TBEP, TDIP, TCEP, TPP, and TBP), the three PAHs, i.e. fluoranthene, pyrene, and phenanthrene, the musk fragrance HHCB, the sterol cholesterol, and the five pesticides, i.e. carbaryl, metolachlor, and carbazole, and anthraquinone and 4-cresol – to below analytical detection limits. Average concentrations of carbamazepine, caffeine, cotinine, triethyl citrate, and benzophenone were decreased by 90% or more, and average concentrations of AHTN, camphor, and tetrachloroethene were decreased by 87%, 83%, and 78%, respectively.

GAC filtration decreased the average concentration of two OCs that were detected in at least 25% of source-water samples and in disinfected effluent (bisphenol A and DEET) by 25% to 75%, an indication of moderate removal. Only one compound (NP) showed no response to GAC filtration, an indication of either ineffective removal of NP from the water phase through GAC filtration, or the continuing formation of NP through the break down of NPEOs through the treatment process (Petrovic et al., 2003).

Removal of OCs by GAC filtration was substantiated by the occurrence of 32 compounds in the dried solids of filter-backwash sediments (Table 2). The most hydrophobic compounds (cholesterol,  $\beta$ -sitosterol, and  $\beta$ -stigmastanol;  $\log K_{ow} > 8$ ) were detected at average concentrations of 6050, 2900, and 650  $\mu\text{g}/\text{kg}$ , respectively, and NP<sub>2</sub>EO ( $\log K_{ow} = 5.3$ ), TBEP ( $\log K_{ow} = 3.75$ ) and carbamazepine ( $\log K_{ow} = 2.45$ ) were detected at average concentrations of 785, 545, and 359  $\mu\text{g}/\text{kg}$ , respectively (Fig. 3). Eight OCs that were not detected in samples of source water were detected in the dried solids of filter-backwash sediments (fluoxetine, benzo[*a*]pyrene, naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 2,6-dimethylnaphthalene, skatol, isophorone, and triclosan) (Table 2); this indicates their presence in source-water supplies during time periods not sampled during this study.

## 6.6. Finished water

During this study, GAC-filtered water was diverted to a clear well to which NaClO was added to maintain a chlorine residual of about 1.2 mg/L through the distribution system. Finished-water samples were collected after the clear well and represent the quality of water leaving the treatment plant and entering the distribution system (Fig. 1).

The detection of 21 compounds in at least one sample of finished water, despite the general decrease in average concentration of OCs from source to finished waters, is an indication of incomplete degradation or removal through the treatment process (Fig. 4). Of these 21 compounds, only tetrachloroethene (detected once) is currently regulated in drinking-water supplies. Carbamazepine and DEET were detected in every sample of finished water, and cotinine and AHTN were detected in 75% and 50% of finished-water samples, respectively. Several compounds that were not detected in samples of source water were detected in samples of finished water (for example, cimetidine, diltiazem, and diphenhydramine). One explanation may be their intermittent occurrence in source waters with (1) recycling of OCs that were absorbed on GAC and released during backwashing, (2) desorption from GAC during equilibration with aqueous-phase concentrations, or (3) saturated GAC that does not allow adsorption. Another potential explanation is differing percent recoveries for these compounds in source-water versus finished water matrixes. Several other compounds were detected at higher average concentrations in finished water than in GAC-filtered water. One explanation could be that GAC-filtered samples were collected from only one of eight operating filter banks. The effectiveness of GAC-filter banks in removing OCs depends on the age and condition of the GAC; therefore, effluent from one filter bank might not represent the chemical quality of water composited from all eight filter banks.

Concentrations of individual compounds in finished water were low and mostly less than 0.5 µg/L. Tetrachloroethene was detected at 0.03 µg/L; more than 160 times less than its USEPA MCL of 5 µg/L. Only the detergent-metabolite compound NP was detected at concentrations exceeding 1 µg/L. The majority of the total measured concentration of OCs in finished water represented five compounds (NP, DEET, AHTN, carbamazepine, and BPA) (Fig. 4). The infrequent detection of several of these compounds underscores the need for collection of multiple samples to adequately characterize the quality of finished water.

## 7. Discussion

Results of this study indicate that the combined water treatments (clarification, disinfection, and GAC filtration) were effective at degrading or removing many OCs from source-water supplies to concentrations below analytical detection. Of the 32 compounds that were detected in at least 25% of the source-water samples (Fig. 2), 16 were not detected in samples of finished water (100% degradation or removal), and seven (carbamazepine, caffeine, acetaminophen, bisphenol A, triethyl citrate, TDIP, tetrachloroethene, and TCEP) underwent a 75% or greater decrease in average concentration from source to finished water (Table 2). The most persistent compounds were camphor and DEET, with 25% and 35% removal, respectively. In general, GAC filtration accounted for 53% of the removal of OCs from the water phase, disinfection accounted for 32%, and clarification accounted for 15%. These results corroborate other research on the effectiveness of these treatments in removing OCs from source waters (Ternes et al., 2002; Westerhoff et al., 2005). Results of this study indicate wide variability in the effectiveness of each treatment among and within OCs categories. The primary route of removal for hydrophobic analytes ( $\log K_{ow}$  values >4) that were detected in source waters (e.g., plant and animal steroids, fragrances and flavorants, detergent degradates, and PAHs) was adsorption on GAC, although some hydrophobic compounds were oxidized by free chlorine during disinfection and, thus, unavailable for adsorption on GAC (for example, OP<sub>1</sub>EO, anthracene, diazinon, d-limonene). The most hydrophilic class of compounds detected in source waters was pharmaceuticals (median  $\log K_{ow}$  <1) many of which reacted with free chlorine. GAC filtration removed most of those that were not oxidized by free chlorine (for example, caffeine and cotinine), as well as the most hydrophobic pharmaceutical detected in source waters (carbamazepine;  $\log K_{ow}$  = 2.45). These findings are for filtered samples of effluent from the clarification, disinfection, and GAC-filtration processes. Findings from studies utilizing whole-water (unfiltered) samples from these processes may differ because the amount of suspended solids is significantly reduced through the DWT process.

The detection of 21 compounds in 1 or more samples of finished water (Fig. 4), and from 3 to 13 of these compounds per sample, indicates incomplete removal or incomplete degradation during the water-treatment process. Of these 21 compounds, only tetrachloroethene is currently regulated in drinking-water supplies. By monitoring the occurrence of unregulated contaminants in a drinking-water supply, this study provides valuable

information for potential inclusion in the USEPA's National Contaminant Occurrence Database and Drinking Water Contaminant Candidate List. Data on unregulated contaminants supports decision-making for future drinking-water regulations and helps establish research priorities and future monitoring needs.

Co-occurrence of compounds (3 to 13 per sample of finished water) is of interest because drinking-water regulations are based on the effects of individual compounds, not combinations of compounds. The detection of the known or suspected endocrine disrupters BPA, NP, OP<sub>2</sub>EO, TDIP, and TCEP in finished water could be of concern because the potential human-health effects associated with chronic exposure to trace levels of multiple organic contaminants through routes such as drinking water are poorly understood (Kümmerer, 2001), although Schwab et al. (2005) found no appreciable human-health risk from the presence of trace concentrations of pharmaceuticals in drinking water. The stability of 17 of the 21 compounds detected in samples of finished water in the presence of a free chlorine residual was evaluated by Gibs et al. (2007) (data not available for triethyl citrate, cimetidine, diltiazem, and diphenhydramine). Five compounds (acetaminophen, NP, BPA, codeine, and sulfathiazole) showed a greater than 90% reduction in concentration with residual chlorine indicating the presence of chlorine is an effective means of their removal or degradation. The concentrations of the remaining 12 compounds decreased by no more than 11% in the presence of a free chlorine residual during residence times typical of this DWT plants distribution system and, thus, these compounds are likely present in delivered water.

The occurrence of OCs in finished water may indicate that drinking water is a source of human exposure. Three of the 21 compounds detected in samples of finished water (AHTN, DEET and cotinine), have been monitored and detected in samples of human blood, milk, or urine (Centers for Disease Control and Prevention, 2005; Hutter et al., 2005; Kurunthachalam et al., 2005). Biomonitoring of these compounds indicates environmental exposure to these chemicals, although that exposure could be from sources other than drinking water (Adolfsson-Erici et al., 2002). Degradates of parent compounds that were not detected in samples of finished water (for example, PAHs) have been detected in human blood or urine (Centers for Disease Control and Prevention, 2005). The detection of OC degradates in body fluids underscores the need to measure a complete suite of parent compounds and their degradates to fully characterize their fate through the DWT process and the potential for exposure through drinking water. Finally, classes of OCs that were detected in finished water (for example, pharmaceuticals, detergent

degradates, flame retardants and plasticizers, and fragrances and flavorants) could be candidates for future biomonitoring to assess environmental exposure.

The dried solids of settled sludge and filter-backwash sediments were found to contain 34 OCs. Residual sludge from this DWT plant is transported to a nearby STP for disposal; although residual sludge from many STPs and DWT plants is digested, dewatered, and used as a soil amendment, especially in agricultural areas. Previous research has documented the potential for certain OCs to leach from sludge-amended soils to streams and ground water (Kinney et al., 2006b; Jacobsen et al., 2005; Xia et al., 2005; Difrancesco et al., 2004; LaGuardia et al., 2001; Oppel et al., 2004). Additional research is needed to more fully characterize this potential for a broader suite of constituents such as examined in this study.

### Acknowledgements

This study was conducted cooperatively between the U.S. Geological Survey and the New Jersey Department of Environmental Protection. The authors thank the operators and staff of the drinking-water-treatment plant for allowing access to their facility and assisting our needs. We also thank Richard Coupe and Gregory Delzer of the U.S. Geological Survey and a anonymous reviewer for their helpful comments and suggestions.

### References

- Adams C, Wang Y, Loftin K, Meyer M. Removal of antibiotics from surface and distilled water in conventional water treatment processes. *J Environ Eng* 2002;128:253–60.
- Adolfsson-Erici M, Pettersson M, Parkkonen J, Sturve J. Triclosan, a commonly used bactericide found in human milk and in the aquatic environment in Sweden. *Chemosphere* 2002;46:1485–9.
- Aizawa T, Magara Y, Takagi H, Souna F. Chlorination by-products of pesticides in drinking water. *Water Supply* 1994;12:SS11–6.
- Bedner M, MacCrehan W. Transformation of acetaminophen by chlorination produces the toxicants 1,4-benzoquinone and *N*-acetyl-*p*-benzoquinone imine. *ES&T* 2006;40:516–22.
- Burkhardt M, ReVello R, Smith S, Zaugg S. Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for industrial and anthropogenic waste-indicator compounds in sediment. *Anal Chim Acta* 2005;534:89–100.
- Cahill J, Furlong E, Burkhardt M, Kolpin D, Anderson L. Determination of pharmaceutical compounds in surface- and ground-water samples by solid-phase extraction and high-performance liquid chromatography–electrospray ionization mass spectrometry. *J Chromatogr A* 2004;1040:171–80.
- Centers for Disease Control and Prevention. Third national report on human exposure to environmental chemicals. National center for environmental health pub. no. 05-0570; 2005. accessed online at <http://www.cdc.gov/exposurereport/3rd/pdf/thirdreport.pdf>.
- Coupe R, Blomquist J. Water-soluble pesticides in finished water of community water supplies. *JAWWA* 2004;96:56–68.

- Daughton C. Pharmaceuticals and personal care products in the environment: overarching issues and overview. In: Daughton CG, Jones-Lepp TL, editors. Pharmaceuticals and personal care products in the environment: scientific and regulatory issues 2001. ACS symposium series 791 Washington DC: American Chemical Society; 2001.
- Daughton C, Ternes T. Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environ Health Perspect* 1999;107(Supplement 6).
- Deborde M, Rabouan S, Gallard H, Legube B. Aqueous chlorination kinetics of some endocrine disruptors. *ES&T* 2004;38:5577–83.
- Difrancesco A, Chiu P, Standley L, Allen H, Salvito D. Dissipation of fragrance materials in sludge-amended soils. *ES&T* 2004;38:194–201.
- Dodd M, Huang C. Transformation of the antibacterial agent sulfamethoxazole in reactions with chlorine: kinetics, mechanisms, and pathways. *ES&T* 2004;38:5607–15.
- Focazio M, Kolpin D, Furlong E. Occurrence of human pharmaceuticals in water resources of the United States: a review. In: Kummerer K, editor. Pharmaceuticals in the environment – sources, fate, effects and risks. 2nd ed. Springer; 2004. 527 pp.
- Gibs J, Stackelberg P, Furlong E, Meyer M, Zaugg S, Lippincott R. Persistence of pharmaceuticals and other organic compounds in chlorinated drinking water as a function of time. *Sci Total Environ* 2007;373:240–9.
- Glassmeyer S, Furlong E, Kolpin D, Cahill J, Zaugg S, Werner S, et al. Transport of chemical and microbial compounds from known wastewater discharges: potential for use as indicators of human fecal contamination. *ES&T* 2005;39:5157–69.
- Halling-Sørensen B, Nielsen S, Lanzky P, Ingerslev F, Lutzhoft H, Jørgensen S. Occurrence, fate and effects of pharmaceutical substances in the environment – a review. *Chemosphere* 1998;36:357.
- Heberer TH, Stan H. Determination of clofibric acid and *N*-(phenylsulfonyl)-sarconsine in sewage, river and drinking water. *Int J Environ Anal Chem* 1997;67:113–24.
- Helsel D, Hirsch R. Statistical methods in water resources. Elsevier; 1992. 522 pp.
- Hu J, Xie G, Aizawa T. Products of aqueous chlorination of 4-nonylphenol and their estrogenic activity. *Environ Toxicol Chem* 2002a;21:2034–9.
- Hu J, Aizawa T, Ookubo S. Products of aqueous chlorination of bisphenol A and their estrogenic activity. *ES&T* 2002b;36:1980–7.
- Huber M, Korhonen S, Ternes T, von Gunten U. Oxidation of pharmaceuticals during water treatment with chlorine dioxide. *Water Res* 2005;39:3607–17.
- Hutter H, Wallner P, Moshammer H, Hartl W, Sattelberger R, Lorbeer G, et al. Blood concentrations of polycyclic musks in healthy young adults. *Chemosphere* 2005;59:487–92.
- Jacobsen A, Lorenzen A, Chapman R, Topp E. Persistence of testosterone and 17 $\beta$ -estradiol in soils receiving swine manure and municipal biosolids. *J Environ Qual* 2005;34:861–71.
- Jørgensen S. forward. in Pharmaceuticals in the environment – sources, fate, effects and risks. 2nd ed., ed. Kummerer, K., 2004. Springer, 527 pp.
- Kinney C, Furlong E, Werner S, Cahill J. Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water. *Environ Toxicol Chem* 2006a;25:317–26.
- Kinney C, Furlong E, Zaugg S, Burkhardt M, Werner S, Cahill J, et al. Survey of organic wastewater contaminants in biosolids destined for land application. *ES&T* 2006b;40:7207–15.
- Kolpin D, Furlong E, Meyer M, Thurman E, Zaugg S, Barber L, et al. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. *ES&T* 2002;36:1202–11.
- Kolpin D, Skopec M, Meyer M, Furlong E, Zaugg S. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. *Sci Total Environ* 2004;328:119–30.
- Korshin G, Kim J, Gan L. Comparative study of reactions of endocrine disruptors bisphenol A and diethylstilbestrol in electrochemical treatment and chlorination. *Water Res* 2006;40:1070–8.
- Kümmerer K. In: Kümmerer K, editor. Pharmaceuticals in the environment: sources, fate, effects and risks. Springer; 2001. 265 pp.
- Kurunthachalam K, Reiner J, Hun Yun S, Perrotta E, Tao L, Johnson-Restrepo B, et al. Polycyclic musk compounds in higher tropic level aquatic organisms and human from the United States. *Chemosphere* 2005;61:693–700.
- LaGuardia M, Hale R, Harvey E, Mainor T. Alkylphenol ethoxylate degradation products in land-applied sewage sludge (biosolids). *ES&T* 2001;35:4798–804.
- Loraine G, Pettigrove M. Seasonal variations in concentrations of pharmaceuticals and personal care products in drinking water and reclaimed wastewater in southern California. *ES&T* 2006;40:687–95.
- Magara Y. Degradation of pesticides by chlorination during water purification. *Water Sci Technol* 1994;30:119.
- Metcalfe C, Miao X, Hua W, Letcher R, Servos M. Pharmaceuticals in the Canadian environment. In: Kummerer K, editor. Pharmaceuticals in the environment – sources, fate, effects and risks. 2nd ed. Springer; 2004. 527 pp.
- Oblinger Childress C, Foreman W, Connor B, Maloney T. New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory. U.S. Geological Survey Open-File Report 99-193; 1999. 19 pp.
- Oppel J, Broll G, Löffler D, Meller M, Römbke J, Ternes T. Leaching behavior of pharmaceuticals in soil-testing-systems: a part of an environmental risk assessment for groundwater protection. *Sci Total Environ* 2004;328:265–73.
- Petrovic M, Diaz A, Ventura F, Barcelo. Occurrence and removal of estrogenic short-chain ethoxy nonylphenolic compounds and their halogenated derivatives during drinking water production. *ES&T* 2003;37:4442–8.
- Pinkston K, Sedlak D. Transformation of aromatic ether- and amine-containing pharmaceuticals during chlorine disinfection. *ES&T* 2004;38:4019–25.
- Reddersen K, Heberer T, Dünbnier U. Identification and significance of phenazone drugs and their metabolites in ground- and drinking water. *Chemosphere* 2002;49:539–44.
- Schwab B, Hayes E, Fiori J, Mastrocco F, Roden N, Cragin D, et al. Human pharmaceuticals in US surface waters: A human health risk assessment. *Regul Toxicol Pharmacol* 2005;42:296–312.
- Stackelberg P, Furlong E, Meyer M, Zaugg S, Henderson A, Reissman D. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. *Sci Total Environ* 2004;329:99–113.
- Stackelberg P, Furlong E, Meyer M, Zaugg S, Henderson A, Reissman D. Response to comment on “Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant”. *Sci Total Environ* 2006;354:93–7.
- Ternes T, Meisenheimer M, McDowell D, Sacher F, Brauch H-J, Haist-Gulde B, et al. Removal of pharmaceuticals during drinking water treatment 2002;36:3855–63.

- Volk C, Kaplan L, Robinson J, Johnson B, Wood L, Zhu H, et al. Fluctuations of dissolved organic matter in river used for drinking water and impacts on conventional treatment plant performance. *ES&T* 2005;39:4258–64.
- Westerhoff P, Yoon Y, Snyder S, Wert E. Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *ES&T* 2005;39:6649–63.
- Winslow S, Prakash B, Domino M, Pepich B. Considerations necessary in gathering occurrence data for selected unstable compounds in the USEPA unregulated contaminant candidate list in USEPA method 526. *ES&T* 2001;35:1851–8.
- Xia K, Bhandari A, Das K, Pillar G. Occurrence and fate of pharmaceuticals and personal care products (PPCPs) in biosolids. *J Environ Qual* 2005;34:91–104.
- Zaugg S, Smith S, Schroeder M, Barber L, Burkhardt M. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory – determination of wastewater compounds by polystyrene–divinylbenzene solid-phase extraction and capillary–column gas chromatography/mass spectrometry. U.S. geological survey water-resources investigations report 01-4186; 2002. 37 pp.
- Zwiener C, Frimmel F. Oxidative treatment of pharmaceuticals in water. *Water Res* 2000;34:1881–5.