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Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant

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Abstract

In a study conducted by the US Geological Survey and the Centers for Disease Control and Prevention, 24 water samples were collected at selected locations within a drinking-water-treatment (DWT) facility and from the two streams that serve the facility to evaluate the potential for wastewater-related organic contaminants to survive a conventional treatment process and persist in potable-water supplies. Stream-water samples as well as samples of raw, settled, filtered, and finished water were collected during low-flow conditions, when the discharge of effluent from upstream municipal sewage-treatment plants accounted for 37–67% of flow in stream 1 and 10–20% of flow in stream 2. Each sample was analyzed for 106 organic wastewater-related contaminants (OWCs) that represent a diverse group of extensively used chemicals. Forty OWCs were detected in one or more samples of stream water or raw-water supplies in the treatment plant; 34 were detected in more than 10% of these samples. Several of these compounds also were frequently detected in samples of finished water; these compounds include selected prescription and non-prescription drugs and their metabolites, fragrance compounds, flame retardants and plasticizers, cosmetic compounds, and a solvent. The detection of these compounds suggests that they resist removal through conventional water-treatment processes. Other compounds that also were frequently detected in samples of stream water and raw-water supplies were not detected in samples of finished water; these include selected prescription and non-prescription drugs and their metabolites, disinfectants, detergent metabolites, and plant and animal steroids. The non-detection of these compounds indicates that their concentrations are reduced to levels less than analytical detection limits or that they are transformed to degradates through conventional DWT processes. Concentrations of OWCs detected in finished water generally were low and did not exceed Federal drinking-water standards or lifetime health advisories, although such standards or advisories have not been established for most of these compounds. Also, at least 11 and as many as 17 OWCs were detected in samples of finished water. Drinking-water criteria currently are based on the toxicity of individual compounds and not combinations of compounds. Little is known about potential human-health effects associated with chronic exposure to trace levels of multiple OWCs through routes such as drinking water. The occurrence in drinking-water supplies of many of the OWCs analyzed for during this study is unregulated and most

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of these compounds have not been routinely monitored for in the Nation's source- or potable-water supplies. This study provides the first documentation that many of these compounds can survive conventional water-treatment processes and occur in potable-water supplies. It thereby provides information that can be used in setting research and regulatory priorities and in designing future monitoring programs. The results of this study also indicate that improvements in water-treatment processes may benefit from consideration of the response of OWCs and other trace organic contaminants to specific physical and chemical treatments.

Keywords: Pharmaceuticals; Wastewater contaminants; Water treatment

1. Introduction

During the 1990s, pharmaceutically active compounds such as lipid-regulating drugs, analgesics, antibiotics, antiseptics, hormones, and chemotherapy and beta-blocking heart drugs were detected in wastewaters, streams, and ground-water resources across Europe (Heberer and Stan, 1997; Buser et al., 1998a,b, 1999). Although pharmaceutically active compounds had been detected previously in effluent from landfills (Turner et al., 1993; Holm et al., 1995) and sewage-treatment plants (STPs) (Hignite and Azarnoff, 1977), these more recent investigations indicated that some pharmaceutically active compounds are nearly ubiquitous at low concentrations in water bodies that receive STP effluent. Reviews of the occurrence, fate, and effects of pharmaceutically active compounds in the environment are available (Richardson et al., 1985; Halling-Sorensen et al., 1998; Daughton, 2001; Ternes, 2001).

During 1999–2000, Kolpin et al. (2002) conducted a reconnaissance of pharmaceuticals and other wastewater-related contaminants in susceptible streams across the United States, expanding the scope of previous investigations and providing the first nationwide data set of this type. Results of this reconnaissance survey document that a wide variety of organic compounds are frequently detected in streams that receive agricultural, domestic, and (or) industrial wastewater effluent. These contaminants include antibiotics, other prescription drugs, non-prescription drugs, animal and plant steroids, reproductive hormones, personal-care products, detergent metabolites, flame retardants, products of oil use and combustion, and other extensively used chemicals, collectively referred to as organic wastewater contaminants (OWCs).

Measures to conserve and reuse water commonly are initiated in areas with growing urban populations and constraints on the development of new water sources. These measures include the use of treated municipal wastewater to augment raw-water supplies—a process referred to as indirect potable water reuse (IPWR) (National Research Council, 1998). The presence of OWCs in wastewater effluent is one of the most challenging aspects of IPWR because of the large number of compounds that may be present, the inability to determine all of these compounds, and the lack of toxicity information and drinking-water standards for many of them (National Research Council, 1998). The frequent occurrence of these compounds in streams (Kolpin et al., 2002), some of which are used as sources of drinking water, gives rise to concern over the potential for these compounds to occur in drinking water and, thus, to affect human health through chronic exposure.

To date, few studies have been published concerning the occurrence of OWCs in drinking-water supplies (Kümmerer, 2001). Notable exceptions include the detection of the pharmaceuticals phenazone and propiphenazone and the drug metabolites clofibric acid and 1-acetyl-1-methyl-2-dimethyl-oxamoyl-2-phenylhydrazide in samples of potable water collected in the vicinity of Berlin, Germany (Heberer and Stan, 1997; Reddersen et al., 2002), and the detection of three widely used non-prescription drugs—caffeine, cotinine, and acetaminophen—in samples of potable water collected near Atlanta, Georgia (Frick et al., 2001).

The objective of this study, conducted by the US Geological Survey (USGS) and the Centers for Disease Control and Prevention, was to build

on the above-mentioned investigations by examining a wider variety of OWCs in order to further assess the potential for these compounds to survive conventional water treatment and occur in finished-water supplies. The occurrence of many of these compounds in drinking water is unregulated and most of them have not been routinely monitored for in the Nation's source- and potable-water supplies. By documenting the occurrence of a broad suite of OWCs in source- and potable-water supplies, results of this study can be used in setting monitoring, research, and regulatory priorities, and in designing appropriate chemical and toxicological studies and risk assessments to address more fully the potential health effects associated with IPWR.

This paper documents the occurrence of select OWCs in 24 samples of stream, raw, settled, filtered, and finished water associated with a drinking-water-treatment (DWT) facility. Although these OWCs represent a diverse group of chemicals with a wide variety of uses, they account for only a fraction of the thousands of organic compounds that currently are manufactured and used for therapeutic purposes or that occur in various consumer and household, industrial and commercial, or agricultural products. This study, therefore, does not provide information on all of the OWCs that may occur in source- or potable-water supplies; rather, it documents the occurrence of selected organic contaminants representing a wide variety of uses and origins in environmental waters and in potable-water supplies.

2. Description of site and sampling methods

The DWT facility from which samples were collected during this study is in a heavily populated, highly urbanized drainage basin. More than 50 STPs discharge effluent to the two streams from which the DWT facility withdraws its raw-water supplies or to tributaries of these streams. Samples of stream water were collected from the streams that provide raw water to the DWT facility (Fig. 1a). USGS personnel collected all stream samples using standard depth- and width-integrating techniques (Shelton, 1994) and water-quality sampling field protocols (US Geological Survey, 1998). At each site, a composite sample of unfiltered water was collected from approximately 10 vertical profiles and then split into baked, 1-liter (l) amber glass bottles that were immediately chilled and shipped to participating laboratories. The sampling site on stream 2 was located approximately 30 meters (m) upstream from a source-water intake (Fig. 1a). Stream 2 flows into stream 1 approximately 6175 m upstream from a source-water intake on stream 1. In order to distinguish the chemical signature of each stream, the sampling site for stream 1 was located just upstream from their confluence (Fig. 1a). This design allows for the identification of differences in chemical occurrence associated with each stream but does not account for sources that may be present between their confluence and the source-water intake on stream 1. A STP located along this reach of stream 1 discharges an average of 7 million gallons per day (Mgal/d) (Fig. 1a).

The DWT facility treats an average of 62 Mgal/d, providing potable water to an estimated 850 000 people. The facility utilizes a conventional treatment process that consists of the following sequence of physical and chemical treatments: (1) raw-water screening – the movement of raw water past a stationary bar rack and two traveling screens to remove coarse debris; (2) the addition of powdered activated carbon to remove taste- and odor-causing compounds as well as organic chemicals; (3) the addition of sulfuric acid or caustic for pH control; (4) coagulation – the addition of coagulant salts and polymers to destabilize colloidal particles and facilitate their flocculation with other suspended particles; (5) primary disinfection – the addition of Na hypochlorite to inactivate pathogenic microorganisms; (6) flocculation – the agitation of coagulated water to promote the aggregation of suspended materials; (7) sedimentation – the stilling of flocculated water to promote the settling of suspended solids and floccules; (8) filtration – the movement of water through tanks that contain sand and either bituminous granular activated carbon (GAC), lignite GAC, or anthracite to retain remaining fine solids and bacteria; (9) secondary disinfection – the addition of Na hypochlorite to

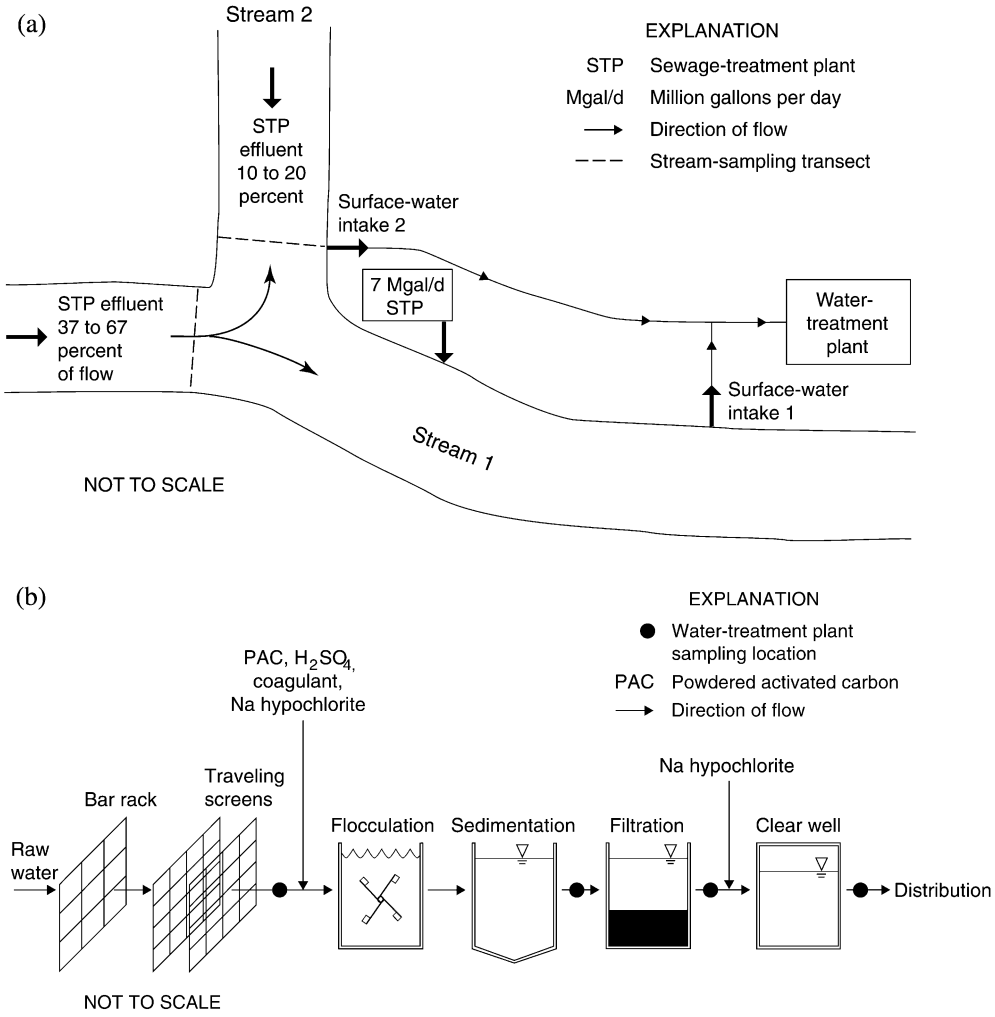

Fig. 1. Schematic diagram showing (a) location of stream sampling sites, surface-water intakes, and drinking-water-treatment plant, and (b) physical and chemical processes used in drinking-water-treatment plant.

maintain a chlorine residual in the distribution system; and (10) the addition of caustic soda to maintain a pH of 7.8 to 8.2 for corrosion control (Fig. 1b).

Samples of unfiltered water were collected at selected locations in the DWT facility; raw water, settled water, filtered water, and finished water were collected (Fig. 1b). Plant personnel collected the DWT-facility samples by filling baked, 1-l amber glass bottles from spigots. These samples were chilled immediately and sent to participating laboratories.

All samples were collected over 4 consecutive weeks during November and December 2001. Stream samples were collected later than samples of raw water in the DWT facility and the collection of samples in the DWT facility did not completely account for expected retention times associated with each treatment process. To the extent that the occurrence of some OWCs in raw-water supplies may be transient in nature, the timing of sample collection may introduce some degree of uncertainty into the results of this study. Nonetheless, the design of this study allows for an initial

assessment of the occurrence and concentration of OWCs in water at various points before, during, and after treatment.

3. Analytical methods and quality assurance

One hundred six compounds were analyzed for in each sample using three analytical methods recently developed by the USGS (Table 1). Four compounds (sulfamethoxazole, trimethoprim, caffeine, and cotinine) were measured by more than one method. Descriptions of the analytical methods and method performance characteristics are provided elsewhere (Barber et al., 2000; Kolpin et al., 2002; Cahill et al., 2004). The list of analytes and their reporting levels reported herein differ slightly from those in Kolpin et al. (2002) as a result of additions to the list of analytes and increases in method reporting levels for the wastewater-related compounds by continuous liquid–liquid extraction and gas chromatography/mass spectrometry (CLLE GC/MS). Twenty-five antibiotic compounds were extracted and analyzed by tandem solid-phase extraction (SPE) and single quadrapole, liquid chromatography/mass spectrometry with electro-spray ionization set in positive mode and selected-ion monitoring (SIM). Reporting levels for the antibiotic method range from 0.02 to 2.0 μg/l (Table 1). Twenty-two human prescription and non-prescription drugs and selected metabolites were extracted by SPE and measured by high performance liquid chromatography/electrospray-ionization mass spectrometry (HPLC/ESI-MS) using a reverse-phase octylsilane (C8) HPLC column (Cahill et al., 2004). Reporting levels for the prescription and non-prescription drugs method range from 0.001 to 0.24 μg/l (Table 1). Sixty-three other OWCs were extracted from whole-water using CLLE GC/MS (Barber et al., 2000). Reporting levels for the wastewater-related compounds method range from 0.5 to 5.0 μg/l (Table 1). For each method, concentrations of constituents with confirmed detections below the reporting level are provided. The uncertainty associated with concentrations reported below the reporting limit is greater than concentrations reported above the reporting limit; therefore, concentrations below the reporting limit are reported as estimates. Method recovery and precision data are reported in Barber et al. (2000) and Cahill et al. (2004).

One field and 27 laboratory blanks were analyzed for target compounds during the course of this study. Blank samples were derived from laboratory-grade organic-free water and were used to determine whether sampling procedures, sampling equipment, field conditions, or sample shipment procedures introduced the target analytes to environmental samples (field blank) or to assess the potential for sample contamination in the laboratory (laboratory blanks). Carbamazepine, sulfamethoxazole, and trimethoprim were each detected in the field blank at 0.0001 μg/l for trimethoprim, 0.0003 μg/l for carbamazepine, and 0.0009 μg/l for sulfamethoxazole. These concentrations are well below the reporting levels for these compounds (Table 1) and reflect (1) the sensitivity for detecting these compounds by HPLC/ESI-MS; and (2) possible low-level carryover between instrumental analysis. Carbamazepine was detected in the associated environmental sample, but at a concentration more than 100 times that measured in the field blank. Sulfamethoxazole and trimethoprim were not detected in the associated environmental sample. Moreover, sulfamethoxazole was detected in only one of the 24 samples collected. Although carbamazepine and trimethoprim were detected more frequently, concentrations of these compounds in stream samples and samples from the DWT facility were at least 20 times greater than concentrations observed in the field blank.

Indole and diphenhydramine were each detected in one laboratory blank. Indole was not detected in any of the associated environmental samples, whereas diphenhydramine was detected in one associated environmental sample, but at a concentration 10 times that measured in the laboratory blank. Erythromycin-H_2O was detected at concentrations less than 0.01 μg/l in laboratory blanks. Erythromycin is a low-level contaminant in the ^{13}C-erythromycin surrogate standard and is converted to erythromycin-H_2O when the sample is acidified. Environmental concentrations of erythromycin-H_2O reported herein are more than three times the observed background concentration in laboratory blanks. The remaining target analytes

Table 1
Wastewater-related compounds analyzed for in all samples and highest concentration detected in samples of finished water

Chemical	CAS number	General use	Reporting level (μg/l)	Detection frequency in stream and raw-water samples ($n=12$)	Drinking water standards and health advisories (μg/l)	Cancer group	Highest concentration in sample of finished water (μg/l)
Antibiotics by LCMS							
Carbadox	6804-07-5	Antibiotic	0.10	0	–	–	ND
Chlortetracycline	57-62-5	Antibiotic	0.05	0	–	–	ND
Ciprofloxacin	85721-33-1	Antibiotic	0.02	0	–	–	ND
Demeclocycline	127-33-3	Antibiotic	0.05	0	–	–	ND
Doxycycline	564-25-0	Antibiotic	0.1	0	–	–	ND
Enrofloxacin	93106-60-6	Antibiotic	0.02	0	–	–	ND
Erythromycin-H_2O	–	Erythromycin metabolite	0.05	67	–	–	ND
Lincomycin	154-21-2	Antibiotic	0.05	0	–	–	ND
Methotrexate	59-05-2	Antibiotic	0.05	0	–	–	ND
Minocycline	10118-90-8	Antibiotic	0.05	0	–	–	ND
Norfloxacin	70458-96-7	Antibiotic	0.02	0	–	–	ND
Oxytetracycline	79-57-2	Antibiotic	0.1	0	–	–	ND
Roxarsone	121-19-7	Antibiotic	2.0	0	–	–	ND
Roxithromycin	80214-83-1	Antibiotic	0.03	0	–	–	ND
Sarafloxacin	98105-99-8	Antibiotic	0.02	0	–	–	ND
Sulfadimethoxine	122-11-2	Antibiotic	0.05	0	–	–	ND
Sulfamerazine	127-79-7	Antibiotic	0.05	0	–	–	ND
Sulfamethazine	57-68-1	Antibiotic	0.05	0	–	–	ND
Sulfamethizole	144-82-1	Antibiotic	0.05	0	–	–	ND
Sulfamethoxazole[1]	723-46-6	Antibiotic	0.05	8	–	–	ND
Sulfathiazole	72-14-0	Antibiotic	0.10	0	–	–	ND
Tetracycline	60-54-8	Antibiotic	0.05	0	–	–	ND
Trimethoprim[1]	738-70-5	Antibiotic	0.03	0	–	–	ND
Tylosin	1401-69-0	Antibiotic	0.05	0	–	–	ND
Virginiamycin	21411-53-0	Antibiotic	0.10	0	–	–	ND
Prescription and non-prescription drugs by HPLC/ESI-MS							
1,7-dimethylxanthine	611-59-6	Caffeine metabolite	0.018	75	–	–	ND
Acetaminophen	103-90-2	Antipyretic	0.009	50	–	–	ND
Albuterol	18559-94-9	Antiasthmatic	0.029	8	–	–	ND
Caffeine[2]	58-08-2	Stimulant	0.014	100	–	–	0.119
Carbamazepine	298-46-4	Anticonvulsant	0.011	100	–	–	0.258
Cimetidine	51481-61-9	Antacid	0.007	0	–	–	ND

Table 1 *(Continued)*

Chemical	CAS number	General use	Reporting level (μg/l)	Detection frequency in stream and raw-water samples ($n=12$)	Drinking water standards and health advisories (μg/l)	Cancer group	Highest concentration in sample of finished water (μg/l)
Codeine	76-57-3	Analgesic	0.24	25	–	–	ND
Cotinine[2]	486-56-6	Nicotine metabolite	0.023	100	–	–	0.025
Dehydronifedipine	67035-22-7	Nifedipine metabolite	0.01	50	–	–	0.004
Digoxigenin	1672-46-4	Digoxin metabolite	0.008	0	–	–	ND
Diltiazem	42399-41-7	Antihypertensive	0.012	0	–	–	ND
Diphenhydramine	58-73-1	Antihistamine	0.0148	25	–	–	ND
Fluoxetine	54910-89-3	Antidepressant	0.018	0	–	–	ND
Furosemide	54-31-9	Diuretic	0.0386	0	–	–	ND
Gemfibrozil	25812-30-0	Antihyperlipidemic	0.015	0	–	–	ND
Ibuprofen	15687-27-1	Antiinflammatory	0.018	0	–	–	ND
Miconazole	22916-47-8	Antifungal	0.0175	0	–	–	ND
Ranitidine	66357-35-5	Antacid	0.01	0	–	–	ND
Sulfamethoxazole[1]	723-46-6	Antibiotic	0.023	8	–	–	ND
Thiabendazole	148-79-8	Fungicide	0.0108	8	–	–	ND
Trimethoprim[1]	738-70-5	Antibiotic	0.014	83	–	–	ND
Warfarin	81-81-2	Anticoagulant	0.001	0	–	–	ND
Other wastewater-related compounds by *CLLE GC/MS*							
1,4-dichlorobenzene	106-46-7	Deodorizer	0.5	0	75[3]; 75[4]; 0.1[5]; 4000[6]	C	ND
1-methylnapthalene	90-12-0	Fuels	0.5	0	–	–	ND
2,6-dimethylnapthalene	581-42-0	Fuels	0.5	0	–	–	ND
2-methylnapthalene	91-57-6	Fuels	0.5	0	–	–	ND
3-β-coprostanol	360-68-9	Fecal steroid	2	33	–	–	ND
3-methyl-1H-indole (skatol)	83-34-1	Fragrance	1	0	–	–	ND
3-*tert*-butyl-4-hydroxyanisole (BHA)	25013-16-5	Antioxidant	5	0	–	–	ND
4-cumylphenol	599-64-4	Detergent metabolite	1	0	–	–	ND
4-*n*-octylphenol	1806-26-4	Detergent metabolite	1	0	–	–	ND
4-nonylphenol diethoxylate (NPEO2-total)	26027-38-3	Detergent metabolite	5	58	–	–	ND
4-octylphenol diethoxylate (OPEO2)	26636-32-8	Detergent metabolite	1	0	–	–	ND
4-octylphenol monoethoxylate (OPEO1)	26636-32-8	Detergent metabolite	1	0	–	–	ND
4-*tert*-octylphenol	140-66-9	Detergent metabolite	1	8	–	–	ND
5-methyl-1H-benzotriazole	136-85-6	Anticorrosive	2	0	–	–	ND
Acetophenone	98-86-2	fragrance	0.5	0	–	–	ND
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN)	21145-77-7	Fragrance	0.5	100	–	–	0.49
Anthracene	120-12-7	PAH	0.5	0	0.3[5]; 10 000[6]	D	ND
Anthraquinone	84-65-1	Manufacturing	0.5	42	–	–	0.072

Table 1 *(Continued)*

Chemical	CAS number	General use	Reporting level (μg/l)	Detection frequency in stream and raw-water samples ($n=12$)	Drinking water standards and health advisories (μg/l)	Cancer group	Highest concentration in sample of finished water (μg/l)
Benzo[*a*]pyrene	50-32-8	PAH	0.5	42	0.2[3]	B2	ND
Benzophenone	119-61-9	Fixative	0.5	58	–	–	0.13
β-sitosterol	83-46-5	Plant steroid	2	83	–	–	ND
β-stigmastanol	19466-47-8	Plant steroid	2	8	–	–	ND
Bisphenol A	80-05-7	Plasticizer	1	100	–	–	0.42
Bromacil	314-40-9	Herbicide	0.5	0	90[4]; 0.1[5]; 5000[6]	C	ND
Bromoform[7]	75-25-2	Trihalomethane	0.5	50	80[3]; 0.02[5]; 700[6]	B2	21
Caffeine[2]	58-08-2	Stimulant	0.5	100	–	–	ND
Camphor	76-22-2	Flavorant	0.5	0	–	–	ND
Carbaryl	63-25-2	Insecticide	1	0	700[4]; 0.1[5]; 4000[6]	D	ND
Carbazole	86-74-8	Insecticide	0.5	17	–	–	ND
Chlorpyrifos	2921-88-2	Insecticide	0.5	0	20[4]; 0.003[5]; 100[6]	D	ND
Cholesterol	57-88-5	Plant/animal steroid	2	83	–	–	ND
Cotinine[2]	486-56-6	Nicotine metabolite	1	0	–	–	ND
Diazinon	333-41-5	Insecticide	0.5	0	–	–	ND
d-dichlorvos	62-73-7	Insecticide	1	0	–	–	ND
d-limonene	5989-27-5	Fungicide	0.5	0	–	–	ND
Fluoranthene	206-44-0	PAH	0.5	8	–	–	ND
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl Cyclopenta-γ-2-benzopyran (HHCB)	1222-05-5	Fragrance	0.5	92	–	–	0.082
Indole	120-72-9	Pesticide inert	0.5	0	–	–	ND
Isoborneol	124-76-5	Fragrance	0.5	0	–	–	ND
Isophorone	78-59-1	Solvent	0.5	0	100[4]; 0.2[5]; 7000[6]	C	ND
Isopropylbenzene (cumene)	98-82-8	Fuels	0.5	0	0.1[5]; 4000[6]	D	ND
Isoquinoline	119-65-3	Flavorant	0.5	0	–	–	ND
Menthol	89-78-1	Fragrance	0.5	0	–	–	ND
Metalaxyl	57837-19-1	Fungicide	0.5	0	–	–	ND
Methyl salicylate	119-36-8	Liniment	0.5	0	–	–	ND
Metolachlor	51218-45-2	Herbicide	0.5	0	100[4]; 0.15[5]; 500[6]	C	ND
N,*N*-diethyl-meta-toluamide (DEET)	134-62-3	Insecticide	0.5	25	–	–	0.066
Naphthalene	91-20-3	PAH	0.5	0	100[4]; 0.02[5]; 700[6]	C	ND
Para-cresol	106-44-5	Wood preservative	1	0	–	–	ND
***Para*-nonylphenol (total, NP)**	84852-15-3	Detergent metabolite	5	0	–	–	ND
Pentachlorophenol	87-86-5	Wood preservative	2	33	1[3]; 0.03[5]; 1000[6]	B2	ND
Phenanthrene	85-01-8	PAH	0.5	0		D	ND
Phenol	108-95-2	Disinfectant	0.5	67	4000[4]; 0.6[5]; 20 000[6]	D	ND
Prometon	1610-18-0	Herbicide	0.5	25	100[4]; 0.015[5]; 500[6]	D	0.096

Table 1 *(Continued)*

Chemical	CAS number	General use	Reporting level (μg/l)	Detection frequency in stream and raw-water samples ($n=12$)	Drinking water standards and health advisories (μg/l)	Cancer group	Highest concentration in sample of finished water (μg/l)
Pyrene	129-00-0	PAH	0.5	8	0.03[5]	D	ND
Tetrachloroethylene	127-18-4	Solvent	0.5	58	5[3]; 10[4]; 0.01[5]; 500[6]	–	0.1
Tri(2-butoxyethyl) phosphate	78-51-3	Plasticizer	0.5	83	–	–	0.35
Tri(2-chloroethyl) phosphate	115-96-8	Flame retardant	0.5	100	–	–	0.099
Tri(dichlorisopropyl) phosphate	13674-87-8	Flame retardant	0.5	100	–	–	0.25
Tributyl phosphate	126-73-8	Flame retardant	0.5	83	–	–	0.1
Triclosan	3380-34-5	Antimicrobial disinfectant	1	67	–	–	ND
Triethyl citrate (ethyl citrate)	77-93-0	Cosmetics	0.5	50	–	–	0.062
Triphenyl phosphate	115-86-6	Plasticizer	0.5	0	–	–	ND

CAS number: chemical abstract service number; B2: probable human carcinogen (US Environmental Protection Agency, 2002); C: possible human carcinogen (US Environmental Protection Agency, 2002); D: not classifiable as to human carcinogenicity (US Environmental Protection Agency, 2002); LCMS: liquid chromatography/electrospray ionization mass spectrometry; HPLC/ESI-MS: high performance liquid chromatography/mass spectrometry; CLLE GC/MS: continuous liquid – liquid extraction with gas chromatography/mass spectrometry; PAH; polycyclic aromatic hydrocarbon; ND: not detected; –: no data; compounds suspected of being hormonally active are in bold.

[1]Compound analyzed by LCMS and HPLC/ESI-MS.

[2]Compound analyzed by HPLC/ESI-MS and CLLE GC/MS.

[3]US Environmental Protection Agency maximum contaminant level (μg/l) (US Environmental Protection Agency, 2002).

[4]US Environmental Protection Agency lifetime health advisory (μg/l) (US Environmental Protection Agency, 2002).

[5]US Environmental Protection Agency reference dose (mg/kg/day) (US Environmental Protection Agency, 2002).

[6]US Environmental Protection Agency drinking water equivalent level (μg/l) (US Environmental Protection Agency, 2002).

[7]1998 final rule for disinfection by-products: the total for trihalomethanes is 80 μg/l (US Environmental Protection Agency, 2002).

were not detected in any of the laboratory blanks. These results indicate that sample-collection procedures, sampling equipment, field conditions, and laboratory procedures did not systematically introduce any of the target compounds into field samples at concentrations relevant to observed environmental concentrations.

4. Results

Stream samples were collected during low-flow conditions. Long-term mean daily flows at three nearby gaging stations on the two source streams were compared to flow rates at the gaging stations at the time of stream-sample collection. On the basis of 22–115 years of record, flow rates at the gaging stations ranged from as little as approximately 3% to no more than approximately 30% of long-term mean daily values. On the basis of average seasonal volumes of STP effluent in each stream and flow rates at the time of sample collection, 37–67% of the flow in stream 1 and 10–20% of the flow in stream 2 consisted of STP effluent (Fig. 1a). Furthermore, during such low-flow conditions, some of the flow in stream 1 is diverted into stream 2 to accommodate the volume of water withdrawn at surface-water intake 2 (Fig. 1a). Results reported here pertain only to these conditions and should not be assumed to be representative of water-quality conditions during higher flow conditions.

Forty compounds were detected in samples of stream water or raw-water supplies in the DWT plant; 34 were detected in more than 10% of these samples (Fig. 2). Seven compounds were detected in each sample of stream water and raw-water supplies: 7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN) (a fragrance compound), bisphenol A (a compound used as a manufacturing intermediate, as a component in flame retardants and rubber chemicals, and as a fungicide), caffeine (a stimulant found in coffee, tea, and other beverages), carbamazepine (an anticonvulsant and specific analgesic for trigeminal neuralgia), cotinine (a metabolite of nicotine), tri(2-chloroethyl) phosphate (a flame retardant and plasticizer), and tri(dichloroisopropyl) phosphate (a flame retardant) (Fig. 2). Compounds detected in 75% or more of these samples are 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-γ-2-benzopyran (HHCB) (a fragrance compound), β-sitosterol and cholesterol (plant and animal steroids), tri(2-butoxyethyl) phosphate (a plasticizer and flame retardant), tributyl phosphate (a plasticizer), trimethoprim (an antibiotic), and 1,7-dimethylxanthine (a metabolite of caffeine) (Fig. 2). Many of these compounds likely are derived from domestic and (or) industrial wastewaters that are processed through municipal STPs. These facilities, however, generally are designed to remove suspended solids and oxygen-demanding substances and, for advanced sewage treatment, to remove dissolved inorganic constituents such as phosphate. STPs are not specifically designed to remove organic contaminants that are likely to be present in domestic and industrial wastewaters at trace levels. Low concentrations of these OWCs, therefore, are likely to be present in effluent from municipal STPs; the incomplete removal of pharmaceuticals from wastewater has previously been documented (Stumpf et al., 1999; Heberer, 2002). Although most of the more frequently detected organic compounds likely are derived from domestic and (or) industrial wastewaters, some compounds could be derived from non-point sources or sources unrelated to human activities.

Several compounds that were frequently detected in samples of stream water and raw-water supplies also were frequently detected in samples collected throughout the DWT plant, indicating that these compounds resist removal through conventional water-treatment processes (Fig. 3). The concentrations of several compounds (e.g. HHCB, tetrachloroethylene, tri(2-chloroethyl) phosphate, and tributyl phosphate) are consistent across sampling events and throughout the treatment process, suggesting temporally constant concentrations in the source streams and little or no removal through conventional water treatment (Fig. 3). The consistent concentrations of these compounds across sampling events corroborate analytical method performance as described elsewhere (Barber et al., 2000; Kolpin et al., 2002; Cahill et al., 2004). The concentrations of other compounds (e.g. AHTN, bisphenol A, caffeine, and carbamazepine) are more variable across sampling events and through-

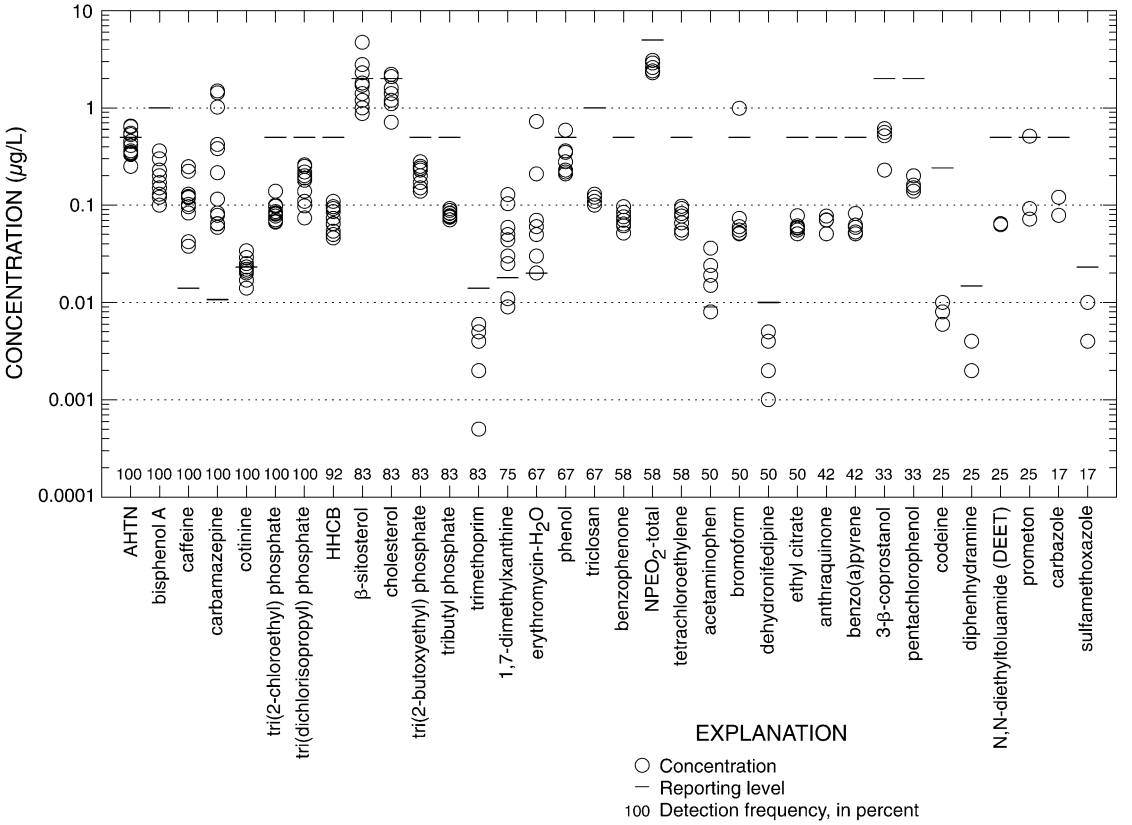

Fig. 2. Concentrations and frequency of detection of compounds detected in more than 10% of samples of stream water and raw-water supplies in the drinking-water-treatment plant.

out the treatment process, indicating that the concentrations of these compounds in the source streams are temporally more variable and, possibly, that the concentrations of these compounds may be reduced through the DWT process (Fig. 3). The concentrations of these compounds in finished water (Fig. 4) generally were similar to or less than concentrations in the associated raw-water sample, indicating that the variability in concentrations of compounds such as AHTN, bisphenol A, caffeine, and carbamazepine throughout the treatment process shown in Fig. 3 is at least partly due to a reduction in concentration along the treatment process.

Other compounds frequently detected in samples of stream water and raw-water supplies (e.g. cholesterol, β-sitosterol, trimethoprim, 1,7-dimethylxanthine, erythromycin-H_2O, triclosan, phenol, 4-nonylphenol diethoxylate, and acetaminophen) were not detected in samples of finished water, indicating that concentrations of these compounds are effectively reduced to levels less than analytical detection limits or that the compounds are transformed through conventional water-treatment processes to degradates not determined by the methods used in this study.

Previous investigators have reported that filtration with GAC is effective in removing carbamazepine from potable-water supplies (Ternes et al., 2002), whereas results of this study indicate that carbamazepine and other hydrophobic compounds such as AHTN and HHCB persist through DWT that includes filtration with GAC. Sorption efficiencies depend on competition with other organic

compounds; therefore, the adsorption capacity for carbamazepine and other OWCs in a DWT facility that processes raw water that contains substantial amounts of many naturally occurring and anthropogenic organic compounds is expected to be smaller than that in laboratory and pilot-scale experiments in which fresh activated carbon and deionized water were used (Ternes et al., 2002). At the time of this study, the GAC filters in the DWT plant were approximately 3 years old and were used primarily to control odor- and taste-causing compounds in chlorinated water, with contact times ranging from approximately 1.5 to 3 min. Because previous investigators did not detect carbamazepine in potable-water supplies (Ternes et al., 2002), the presence of this compound in raw, filtered, settled, and finished water samples was verified using two additional mass spectrometric methods: high-performance liquid chromatography/tandem mass spectrometry with an ion-trap mass spectrometer (HPLC/IT-MS/MS; Bruker Daltonics Esquire) and high-performance liquid chromatography/time-of-flight mass spectrometry (HPLC/TOF-MS; Micromass LCT). In

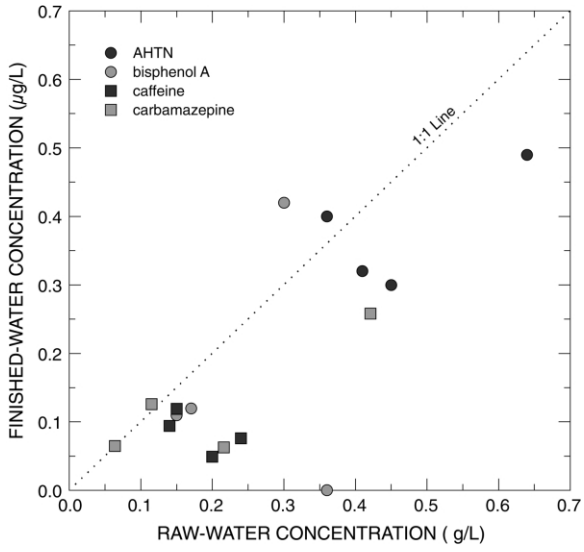

Fig. 4. Concentrations of selected compounds in samples of raw and finished water.

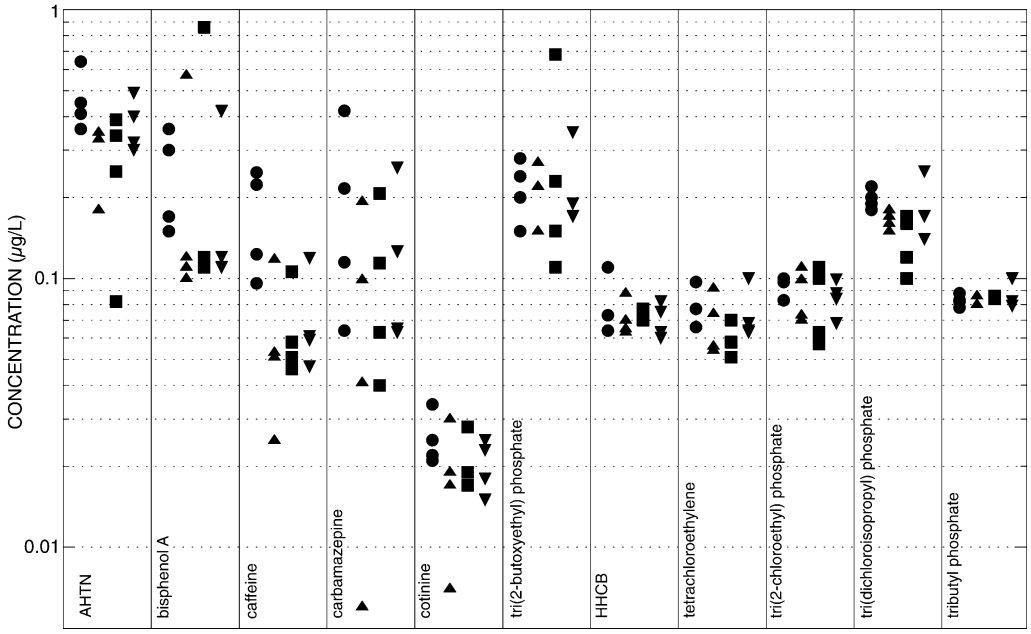

Fig. 3. Concentrations of selected compounds in samples of raw (circles), settled (triangles), filtered (squares), and finished (inverted triangles) water.

all samples, HPLC/IT-MS/MS analysis of the putative carbamazepine peak in samples produced a protonated molecular ion at the retention of a carbamazepine standard. MS/MS analysis of this carbamazepine ion (m/z 237) in all samples resulted in fragmentation yielding an ion of m/z 194, reflecting a loss of CONH, consistent with a loss and rearrangement of the carbamazepine protonated molecular ion. In all samples, the elemental composition of the suspected carbamazepine peak by HPLC/TOF-MS was consistent with the elemental composition of carbamazepine within 1.5 millidaltons. For the protonated molecular ion of carbamazepine, that converts to a mass accuracy error of no greater than 6 parts per million, well within the criteria commonly accepted for accurate mass determination. AHTN and HHCB detections in all samples were verified by full scan mass spectrometry analysis using careful comparison of each samples spectrum to a custom library spectrum made from authentic standards run on the same analytical instrument.

5. Discussion

Results of this study demonstrate that OWCs such as prescription and non-prescription drugs and their metabolites, fragrances, flame retardants, plasticizers, disinfectants, personal care products, detergent metabolites, products of oil use and combustion, and other extensively used chemicals are frequently detected in streams whose flow contains effluent from municipal STPs. These results corroborate those of Kolpin et al. (2002). Furthermore, this study demonstrates that some of these contaminants survive conventional DWT processes and occur in potable-water supplies, whereas others are reduced to non-detectable concentrations through conventional DWT processes. The occurrence of many of these contaminants in drinking water is unregulated and this study provides the first documentation of their occurrence in drinking-water supplies. This information can be used in setting research and regulatory priorities and in designing future monitoring programs.

Concentrations of the OWCs that were detected in finished water during this study generally were low (93% <0.5 μg/l) (Fig. 2), and in the cases where standards have been established, did not exceed Federal drinking-water standards or lifetime health advisories. Most of these compounds, however, do not currently have established drinking-water standards or health advisories (Table 1); therefore, the potential health consequences associated with exposure through drinking water are not known. Concentrations in finished water of OWCs designed for human consumption, such as prescription and non-prescription drugs, were far below doses used in therapy. For example, the maximum possible intake of carbamazepine in finished water in a lifetime (assuming an intake of 2 l per day for 70 years) was 13 mg, whereas a single therapeutic dose generally is 100 mg or greater. Nevertheless, most studies on the therapeutic effects of drugs are based on the short-term ingestion of relatively high doses; little is known about potential health effects associated with long-term chronic ingestion of low concentrations through drinking water (Kümmerer, 2001). Moreover, drinking-water criteria currently are based on the toxicity of individual compounds and not combinations of compounds. The possibility that exposure to multiple organic compounds, even at low concentrations, may have a synergistic human-health consequence is an area of recent research (Birader and Rayburn, 1995; Marinovich et al., 1996), and the co-occurrence of organic compounds in drinking-water supplies has recently been documented (Stackelberg et al., 2001; Squillace et al., 2002). In this study, 11–17 different OWCs were detected in each of the four samples of finished water.

Whereas some frequently detected OWCs, such as pharmaceutical compounds, are designed to be ingested, others (e.g. flame retardants, solvents, and other personal care and industrial chemicals) are not designed for human consumption. The human-health consequence of chronic ingestion of these compounds is even less well understood than that of categories of OWCs such as pharmaceutical compounds. Some of these compounds (e.g. bisphenol A) are known or suspected endocrine disruptors and may be potent reproductive toxins even at low concentrations.

Although only a small number of degradate compounds were analyzed for in this study, several

of the most frequently detected OWCs are degradates (e.g. cotinine, dehydronifedipine, erythromycin-H_2O, and 1,7-dimethylxanthine, degradates of nicotine, nifedipine, erythromycin, and caffeine, respectively); thus, the formation of degradates may represent a substantial component of the total transport of OWCs through DWT processes. This finding demonstrates the importance of analyzing for degradates in order to understand fully the fate of OWCs in a DWT facility as well as the potential human-health issues associated with chronic exposure to these compounds through drinking water. For other classes of organic compounds, such as pesticides, the importance of analyzing for degradates is well established (Thurman et al., 1994; Kolpin et al., 1997; Kalkhoff et al., 1998; Graham et al., 1999; Kolpin et al., 2001). The absence of many OWCs in finished-water supplies, therefore, does not necessarily imply their complete removal from finished water. Rather, the treatment process may transform parent OWCs to unknown and (or) unmeasured degradates. Additional methods development and sample analysis will be required to address these issues.

The limited number of samples ($n=4$) collected at each site for this study and the fact that the collection of grab samples in the DWT plant did not adequately account for expected retention times throughout treatment preclude quantification of the effectiveness of each treatment process in reducing the concentrations of these contaminants. Additional sampling will provide information about (1) temporal variability of OWCs in source waters; (2) effectiveness of specific physical and chemical treatments in reducing the concentrations of the target OWCs; and (3) which primary physical processes and (or) chemical reactions reduce the concentrations of or eliminate OWCs. Only a small subset of the thousands of organic compounds that are currently in use and potentially could occur in domestic and industrial wastewaters were determined; however, this study indicates that at least some organic compounds can enter and persist in environmental waters and also may survive subsequent water-treatment processes. The technology to analyze for all known organic compounds is currently unavailable and, therefore, the complete extent of occurrence of OWCs in drinking-water supplies is unknown. The challenge for future studies is to develop the means to characterize the types and concentrations of these compounds that are likely to co-occur in drinking-water supplies and to assess their potential effects.

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