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A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States — II) Untreated drinking water sources

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ABSTRACT

Numerous studies have shown that a variety of manufactured and natural organic compounds such as pharmaceuticals, steroids, surfactants, flame retardants, fragrances, plasticizers and other chemicals often associated with wastewaters have been detected in the vicinity of municipal wastewater discharges and livestock agricultural facilities. To provide new data and insights about the environmental presence of some of these chemicals in untreated sources of drinking water in the United States targeted sites were sampled and analyzed for 100 analytes with sub-parts per billion detection capabilities. The sites included 25 ground- and 49 surface-water sources of drinking water serving populations ranging from one family to over 8 million people.

Sixty-three of the 100 targeted chemicals were detected in at least one water sample. Interestingly, in spite of the low detection levels 60% of the 36 pharmaceuticals (including prescription drugs and antibiotics) analyzed were not detected in any water sample. The five most frequently detected chemicals targeted in surface water were: cholesterol (59%, natural sterol), metolachlor (53%, herbicide), cotinine (51%, nicotine metabolite), β-sitosterol (37%, natural plant sterol), and 1,7-dimethylxanthine (27%, caffeine metabolite); and in ground water: tetrachloroethylene (24%, solvent), carbamazepine (20%, pharmaceutical), bisphenol-A (20%, plasticizer), 1,7-dimethylxanthine (16%, caffeine metabolite), and tri (2-chloroethyl) phosphate (12%, fire retardant). A median of 4 compounds were detected per site indicating that the targeted chemicals generally occur in mixtures (commonly near detection levels) in the environment and likely originate from a variety of animal and human uses and waste sources. These data will help prioritize and determine the need, if any, for future occurrence, fate and transport, and health-effects research for subsets of these chemicals and their degradates most likely to be found in water resources used for drinking water in the United States.

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1. Introduction

Manufactured and natural organic compounds such as pharmaceuticals, surfactants, flame retardants, plasticizers, steroids, and other trace organics that continue to be synthesized, used, and disposed of by modern society are now widely recognized as environmental contaminants (Daughton and Ternes, 1999; Halling-Sørensen et al., 2002a; Hignite and Azarnoff, 1977). Detection capabilities for these organic compounds in the environment continue to be refined and detection levels are in sub parts per billion to sub parts per trillion levels presently. This has lead to the documented presence of many various targeted compounds in water resources around the world including in sources of public drinking water (Ashton et al., 2004; Kolpin et al., 2002; Metcalf et al., 2003; Stumpf et al., 1999; Ternes, 1998; Wiegel et al., 2004). These detections have been associated with a variety of human and animal sources such as hospitals, septic tanks, wastewater effluents from treatment plants, and livestock activities. Although wastewater treatment plant effluents are only one potential source, human and animal wastewater effluents are among the most important associated source pathways for the majority of these compounds into the aquatic environment (Clara et al., 2005; Glassmeyer et al., 2005; Lindqvist et al., 2005; Miao et al., 2005; Paxeus, 2004; Reiner et al., 2007; Ternes, 1998). For simplicity, we use the collective term "organic wastewater contaminants" (OWCs) for any trace organic compound targeted in this study or any study cited here regardless of potential contaminant source in order to emphasize the variety of waste pathways associated with introduction of these compounds to the environment.

Through a variety of environmental exposure pathways, select OWCs have been found in plant and animal tissue (Brooks et al., 2005, Delepee et al., 2004; Guenther et al., 2002; Boxall et al., 2006), including humans (Adolfsson-Erici et al., 2002; Hovander et al., 2002; Hutter et al., 2005; Kurunthachalam et al., 2005). The relatively small subset of potential OWCs analyzed in these studies typically were targeted because of the large volumes that are manufactured and used, the chemical properties such as water solubility, and(or) the known or suspected toxicity to ecological or human health. In the United States regulatory drinking water standards do not exist for most of these compounds and there are no nationally or internationally standardized methods, therefore, there is little or no consistent infrastructure available to monitor for the presence of OWCs in ambient or drinking water resources on regional or national scales (Focazio et al., 2004). The U.S. Environmental Protection Agency's Unregulated Contaminant Monitoring Rule (UCMR; U.S. Environmental Protection Agency, 1999) is one exception that requires public water suppliers to monitor selected unregulated contaminants in finished drinking water supplies. The UCMR contaminants do not include the OWCs targeted by this study, and consequently, the national-scale occurrence data typically needed by regulators and policy makers to make informed decisions on whether or not to set drinking water standards is minimal or nonexistent for many OWCs in the United States.

Many recent studies have focused on targeted questions concerning the environmental fate and behavior (Loffler et al., 2005), as well as wastewater and drinking water treatment efficacies (Clara et al., 2005; Westerhoff et al., 2005; Stackelberg et al., 2004a; Phillips et al., 2005; Snyder et al., 2007) of some OWCs, and although not providing large-scale occurrence data, these studies are improving our understandings of process-oriented questions regarding the fate and transport of OWCs. In addition, model projections are being used to help provide much needed perspective on the national- and regional-scale questions regarding occurrence and the potential for associated human-health impacts of pharmaceuticals in water bodies receiving wastewater effluent (Anderson et al., 2004; Schwab et al., 2005).

Recognizing the need for additional data at the regional and national scales, the U.S. Geological Survey (USGS) has implemented a series of national reconnaissance efforts targeting a broad suite of OWCs with various potential uses and origins (e.g. pesticides, solvents, pharmaceuticals, personal care products, etc.) in an array of environmental and hydrological settings across the United States. For example, 95 organic compounds were analyzed in samples collected from streams known or suspected to be impacted by human and agricultural waste sources (Kolpin et al., 2002). Subsequently, the USGS has completed a ground-water reconnaissance for OWCs (Barnes et al., 2008-this issue), and methods have recently been developed for assessing OWC occurrence in streambed sediments (Burkhardt et al., 2006). This paper documents results of a national-scale reconnaissance of 100 OWCs in 74 raw, untreated sources of drinking water from targeted surface- and ground-water sources across the United States (Fig. 1).

2. Experimental methods

2.1. Site selection and field sampling

Raw, untreated ground and surface water used as sources of drinking water were targeted for this reconnaissance. Sites were chosen in areas that were known or suspected to have at least some human and(or) animal wastewater sources in upstream or upgradient areas (Fig. 1). The number of people served by drinking water sources was also considered during the site selection process in order to include a range of drinking water system sizes. The sites were selected and sampled by USGS personnel with local knowledge of potential contaminant sources and associated hydrologic conditions in order to be representative of the source waters entering drinking water treatment plants. Water samples were collected in the summer of 2001, and no attempt was made to determine temporal patterns in OWC concentrations (e.g. collecting samples more than once). Therefore, resulting detections and concentrations are indicative of the limited conditions at the time of sampling and the sampling sites chosen and may not be representative of other hydrologic, water quality, and(or) source-input conditions within any particular watershed. At each site, untreated water samples were collected as close to the wellhead, raw-water sampling ports, or surface-water intakes of the public water system as possible and then split into appropriate containers for shipment to the participating laboratories. Although site

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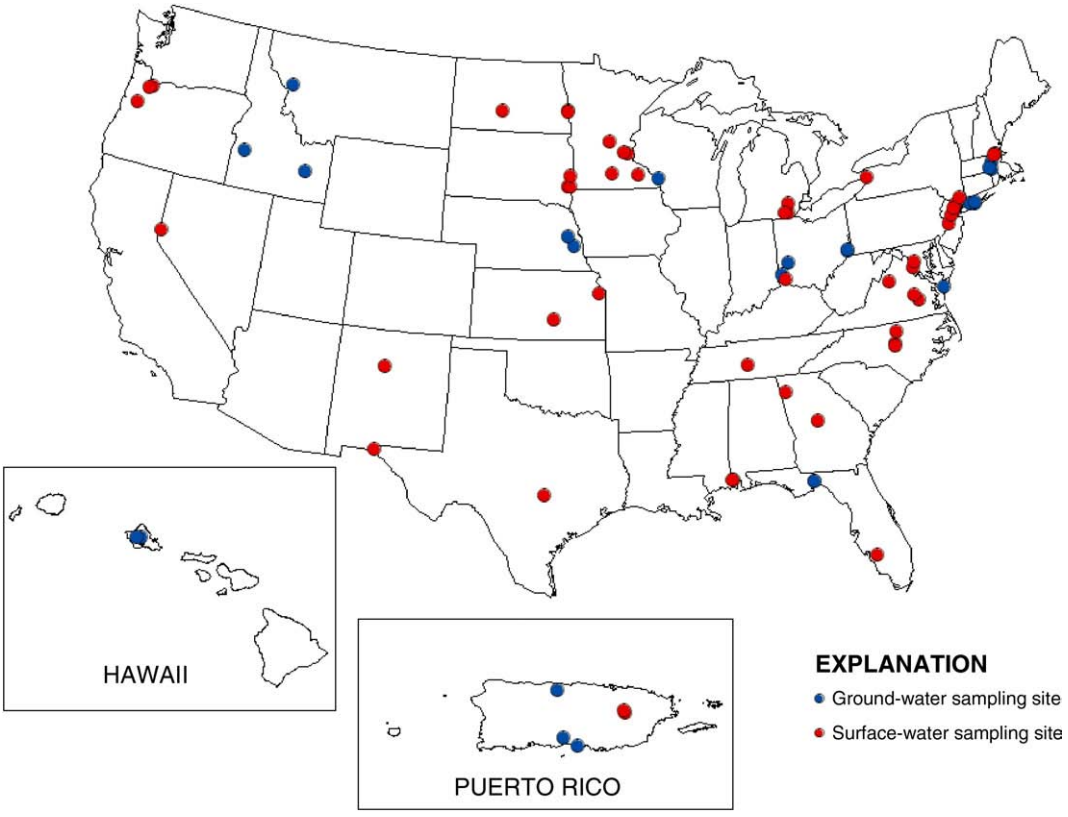

Fig. 1 – Locations of surface- and ground-water sites sampled for the reconnaissance.

selection did not follow a statistically representative design, 25 ground- and 49 surface-water sources for public drinking water systems were selected from 25 states and Puerto Rico (Fig. 1; see Table 1) with populations served ranging from one family to 8 million people. Thus, this reconnaissance sampling network, while not statistically representative of the source waters used by the approximately 52,000 public water systems in the United States, does include a wide range of potential contaminant-source strengths and environmental settings, as well as populations served.

All water samples were collected by USGS personnel using consistent protocols and procedures designed to obtain a grab-sample representative of the untreated (or raw) ground- or surface-water source using standard field protocols for ultra-clean sampling, preparation, preservation, and transportation to the laboratory (U.S. Geological Survey; variously dated). For filtered water samples, a whole-water sample aliquot was passed through a 0.7 μm, baked, glass-fiber filter in the field where possible or filtration was conducted in the laboratory. Water samples for each chemical analysis were stored in precleaned-amber, glass bottles and collected in duplicate. The duplicate samples were used for backup purposes (in case of breakage of the primary sample) and for laboratory replicates. Following collection, samples were immediately chilled and overnight-shipped to the laboratories. To minimize contamination of samples, use of personal care items (e.g. insect repellents, colognes, perfumes, and pharmaceuticals), caffeinated products, and tobacco was discouraged during sample collection and processing and water samples were not stored in proximity to any of these products (U.S. Geological Survey, variously dated).

2.2. *Analytical methods*

The 100 targeted OWCs were selected from the large number of chemical possibilities based upon known or suspected usage, toxicity, potential hormonal activity, persistence in the environment, as well as results from previous studies (Kolpin et al., 2002). Three separate analytical methods were used to assess detections and concentrations of 100 OWCs in untreated sources of public drinking water. Twenty-two antibiotic compounds were extracted from filtered-water samples and analyzed by tandem solid-phase extraction (SPE) and single quadrapole, liquid chromatography/mass spectrometry (LC/MS) with electro-spray ionization set in positive mode and selected-ion monitoring (Meyer et al., 2007; hereafter referred to as ANT LC/MS). Sixteen human prescription and non-prescription drugs and their select metabolites (other than antibiotics) were extracted from filtered-water samples by SPE and analyzed by LC/MS using a polar reverse-phase octylsilane (C8) HPLC column (Cahill et al., 2004; hereafter referred to as PHARM LC/MS). The PHARM LC/MS method also included 3 antibiotics raising the total number of antibiotics analyzed in this study to 25. Fifty-nine compounds were extracted from whole-water samples using continuous liquid–liquid extraction (CLLE) and analyzed by capillary-column gas chromatography/mass spectrometry (Zaugg et al., 2006; hereafter referred to as CLLE GC/MS). Detailed descriptions of each analytical method and its associated quality assurance/quality control measures, calibration procedures, and identification and quantitation approaches are fully described in the original citations.

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Table 1 – Descriptive information for all sampling locations

State	Well depth (m)	Well type/use	Mean daily streamflow/mean daily volume of effluent upstream (m^3/s)	Surrounding land use	Population served	General lithology of aquifer	Watershed area (km^2)	Comment
Ground water sites								
FLorida	59	Community Water Supply	na	Rural/residential	<50	Limestone	na	
FLorida	60	Community Water Supply	na	Rural/residential	<50	Limestone	na	
Hawaii	219	Monitoring	na	Urban/military	na	Basalt	na	Monitoring well in drinking water aquifer
Hawaii	208	Monitoring	na	Urban/military	na	Basalt	na	Monitoring well in drinking water aquifer
Idaho	m	Self-supplied domestic drinking water	na	Rural/residential	na	Unconsolidated sands and gravels	na	
Massachusetts	m	Community Water Supply	na	Mixed	18,000	Glacial outwash/sand and gravel	na	
Massachusetts	m	Community Water Supply	na	Mixed	6600	Glacial outwash/sand and gravel	na	
Massachusetts	m	Community Water Supply	na	Mixed	7000	Glacial outwash/sand and gravel	na	
Montana	15	Self-supplied domestic drinking water	na	Rural/residential	5	Sand and gravel	na	
Nebraska	27	Community Water Supply/collector well	na	Cropland and pasture	220,000	Alluvium/sand and gravel	na	Influenced by Platte River
Nebraska	<15	Self-supplied domestic drinking water	na	Cropland, pasture and residential	5	Alluvium/sand	na	
New York	82	Community Water Supply	na	Urban	22,750	Glacial drift/sand and gravel	na	
New York	107	Community Water Supply	na	Urban	10,000	Glacial drift/sand and gravel	na	
New York	140	Community Water Supply	na	Urban	10,000	Glacial drift/sand and gravel	na	
New York	48	Community Water Supply	na	Urban	231,800	Glacial drift/sand and gravel	na	
Ohio	54	Community Water Supply	na	Industrial/military	250,000	Glacial outwash/clay, sand, and gravel	na	
Ohio	54	Community Water Supply	na	Urban/residential	100,000	Glacial drift/clay, sand, and gravel	na	
Puerto Rico	m	Community Water Supply	na	Industrial	5733	Limestone	na	
Puerto Rico	36	Community Water Supply	na	Urban	1200	Limestone	na	
Puerto Rico	m	Community Water Supply	na	Rural	5200	Coastal Plain Alluvium/ sand and gravel	na	
Texas	m	Community Water Supply	na	Urban	40,000	Limestone	na	Spring
Virginia	<30	Self-supplied domestic drinking water	na	Rural	<10	Coastal Plain/sand and gravel	na	
West Virginia	24	Community Water Supply	na	Residential/mixed	3000	Alluvium/sand and gravel	na	

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West Virginia	36	Community Water Supply	na	Residential/mixed	2100	Alluvium/sand and gravel	na	
Wisconsin	33	Community Water Supply	na	Industrial/airport	51,000	Alluvium/sand and gravel	na	Influenced by surface water
Surface water sites								
Alabama	na	na	0.71/m	Mixed	na	na	m	
Alabama	na	na	m	Forest and agriculture	260,000	na	m	
Florida	na	na	m	Urban and agriculture	<7000	na	m	
Georgia	na	na	76/4.2	Mixed urban	145,900	na	5802	
Georgia	na	na	107/0.8	Mixed urban	50,000	na	5569	
Kansas	na	na	213/1.8	Agriculture	590,000	na	135,343	
Kansas	na	na	11/0.2	Agriculture	400,000	na	3017	
Massachusetts	na	na	m/4.9	Urban	68,000	na	m	
Massachusetts	na	na	m/6.5	Urban	38,000	na	m	
Massachusetts	na	na	m/6.5	Urban	24,300	na	m	
Michigan	na	na	6.4/0.01	Agriculture	22,172	na	171	
Michigan	na	na	<10/0.01	Agriculture	400,000	na	3017	
Michigan	na	na	9.4/0.01	Agriculture	115,000	na	1888	
Minnesota	na	na	m	Agricultural/urban	36,200	na	17,094	
Minnesota	na	na	m	Agricultural/wetland	7500	na	14,763	
Minnesota	na	na	m	Mixed	na	na	33,670	
Minnesota	na	na	m	Mixed	500,000	na	49,210	
Minnesota	na	na	m	Mixed	33,000	na	38,635	Water drawn from Ranney wells
Minnesota	na	na	m	Mixed	415,000	na	m	Water drawn from Mississippi River system
New Jersey	na	na	190/15	Mixed	1,299,251	na	17,581	
New Jersey	na	na	1.1/0.5	Urban	87,443	na	256	
New Jersey	na	na	9.4/6.3	Urban	na	na	1974	
New Jersey	na	na	3.2/1	Urban	101,652	na	181	
New Jersey	na	na	0.5/0.2	Urban	na	na	425	
New Jersey	na	na	17/6.4	Urban	413,682	na	1340	
New Mexico	na	na	17/m	Rangeland	300,000	na	83,416	
New Mexico	na	na	37/m	Rangeland	400,000	na	41,699	
New York	na	na	7.2/m	Urban and residential	<8,000,000	na	979	
New York	na	na	3.7/m	Mixed	290,000	na	682,983	
North Carolina	na	na	m/0.5	Urban	120,000	na	3626	Impoundments
North Carolina	na	na	na	Mixed	170,000	na	433	Impoundments
North Carolina	na	na	83/na	Mixed	20,000	na	8184	
North Dakota	na	na	16/m	Agricultural	75,000	na	17,612	
North Dakota	na	na	47/m	Agricultural	60,000	na	482,776	
Nevada	na	na	29/m	Forested	250,000	na	2764	
Ohio	na	na	2.4/m	Mixed	850,000	na	197,306	
Oregon	na	na	16/m	Mixed	22,060	na	2435	
Oregon	na	na	162/2.8	Mixed	13,000	na	21,756	
Oregon	na	na	96/1.3	Mixed	23,500	na	6812	

(continued on next page)

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Table 1 *(continued)*

State	Well depth (m)	Well type/use	Mean daily streamflow/mean daily volume of effluent upstream (m^3/s)	Surrounding land use	Population served	General lithology of aquifer	Watershed area (km^2)	Comment
Surface water sites								
Puerto Rico	na	na	2.7/m	Urban	145,000	na	189	
Puerto Rico	na	na	0.4/0.1	Rural	41,044	na	21	
South Dakota	na	na	14/0.2	Agricultural/urban	124,000	na	8599	
South Dakota	na	na	17/0.6	Agricultural/urban	na	na	10,437	Not at intake
South Dakota	na	na	8.8/0.2	Agricultural	na	na	7770	
Tennessee	na	na	50/0.2	Agriculture/forest	38,920	na	3129	Flow regulated by impoundment
Virginia	na	na	m	Urban and industrial	25,000	na	3481	
Virginia	na	na	130/m	Mixed	500,000	na	17,503	
Virginia	na	na	199/m	Mixed	<4,600,000	na	29,940	
Virginia	na	na	25/m	Mixed	40,000	na	2808	

[na, not applicable; m, missing]

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All methods reported here have been continuously evaluated, developed, and revised over the past several years as new laboratory and field data have become available throughout the USGS and research objectives have evolved. These evaluations include new information, insights, and focused studies on matrix interferences, laboratory and field contamination, and interlaboratory comparisons all resulting in a limited number of method performance and reporting level changes. For example, Meyer et al. (2007) compares the results of compounds independently determined by each method for the ANT and PHARM LC/MS methods from three separate studies. Accordingly, all environmental data in this study (collected in summer 2001) are reported using the most recent evaluations and determinations regarding these methods and reporting criteria in order to provide consistent and up-to-date analysis across methods and compounds. For example, the CLLE GC/MS selected-ion monitoring mode previously used (Kolpin et al., 2002) was changed to a full-scan monitoring mode at the time of the present study. Although this simple, but important, change to the method decreased detection sensitivity, it enabled detection of a broader suite of compounds; an important tradeoff for reconnaissance occurrence research. Other recent revisions to analytical methods include incorporation of tandem MS, although those revisions were not available at the time of this study. In addition, the antibiotic data from the ANT LC/MS method for this report have been compared to an independent antibiotic on-line SPE LC/MS method (Meyer et al., 2007) also developed at the USGS Organic Research Geochemistry Laboratory. Therefore, the on-line SPE LC/MS method is used only for quality-control data and not for reporting of environmental data. Compounds measured by more than one analytical method were compared and evaluated to determine the most reliable method on a compound-by-compound specific basis. This evaluation yielded "primacy" methods for caffeine, cotinine, azithromycin, sulfamethoxazole, and trimethoprim. For example, cotinine and caffeine are measured by the PHARM LC/MS and the CLLE GC/MS method; however, the detection levels are lower with the PHARM LC/MS method, and therefore, it is used to report environmental data.

2.3. *Qualitative identification criteria and reporting levels*

The three analytical methods used in this study share a common rationale for compound identification and quantitation, despite differences in specific analytical details. All rely on the application of mass spectrometric techniques, which provide compound-specific fragments, and when coupled with chromatographic retention characteristics produce unambiguous identification of each compound. In addition, the specific criteria for the identification of each compound are based on analysis of authentic standards for all compounds (Cahill et al., 2004; Zaugg et al., 2006; Meyer et al., 2007).

Method detection limits (MDLs) were established for the PHARM LC/MS method (Cahill et al., 2004), and CLLE GC/MS method (Zaugg et al., 2006) using a 99-percent confidence interval (U.S. Environmental Protection Agency, 1997). The MDL calculation was performed on reagent water samples that were spiked within five times the estimated MDL. In addition, the MDLs had minimum signal to noise ratios that were three times above background. Method reporting levels (RL's) were established at five times the MDL for each analyte.

For the PHARM LC/MS and CLLE GC/MS methods analytes detected below the MDL that met the full retention time and mass spectral criteria required for confirmation were reported as detects for frequency of detection calculations and were assigned unquantified concentration indicators of "<RL." For graphical purposes maximum concentrations were estimated below the reporting levels in a limited number of instances. All data were blank censored to ensure that the reported compounds were in the sample at the time of collection and not artifacts of sample processing and analysis.

For the ANT LC/MS method the RL was established for each analyte with signal-to-noise ratios of 5 to 10 times above

Table 2 – Summary of detections in field blanks

Compound	Reporting level (μg/L)	Concentration in field blank (μg/L)	Concentration in environmental sample (μg/L)	Method
methyl salicylate	0.5	0.015[a]	ND	CLLE GC/MS
bisphenol A	1.0	0.20[a]	1.9	CLLE GC/MS
triphenyl phosphate	0.5	0.093[a]	ND	CLLE GC/MS
1,4 dichlorobenzene	0.5	0.4[a]	ND	CLLE GC/MS
caffeine	0.014	0.162	0.164	PHARM LC/MS
caffeine	0.014	0.0067	0.239	PHARM LC/MS
caffeine	0.014	0.0033	0.0067[b]	PHARM LC/MS
caffeine	0.014	0.014	0.014[b]	PHARM LC/MS
caffeine	0.014	0.014	0.014[b]	PHARM LC/MS
caffeine	0.014	0.016	0.239	PHARM LC/MS
caffeine	0.014	0.003	0.010[b]	PHARM LC/MS
caffeine	0.014	0.004	0.006[b]	PHARM LC/MS
caffeine	0.014	0.011	0.0242[b]	PHARM LC/MS
1,7 dimethylxanthine	0.018	0.0003	ND	PHARM LC/MS

[ND, not detected; PHARM LC/MS, solid-phase extraction with high-performance liquid chromatography and mass spectroscopy; CLLE GC/MS, continuous liquid–liquid extraction with gas chromatography and mass spectroscopy].

Note: Eleven field blanks were processed for all methods. No detections were found in field blanks for any compound analyzed by ANT LC/MS.

[a] Estimated concentration.

[b] Concentration is less than the 95th percentile concentration in field blanks.

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Table 3 – Summary of occurrence data for all compounds analyzed

Chemical (Method)	CASRN	RL (μg/L)	*n*	Percent detected	Maximum concentration [a] (μg/L)	Typical use [b]	Drinking water standards and health advisories (μg/L)
Veterinary and human antibiotics							
azithromycin (PHARM LC/MS)	83905-01-5	0.023	74	1.4	0.029	antibiotic	
carbodox (ANT LC/MS)	6804-07-5	0.1	73	0	ND	antibiotic	–
chlortetracycline (ANT LC/MS)	57-62-5	0.05	73	0	ND	antibiotic	–
ciprofloxacin (ANT LC/MS)	85721-33-1	0.02	73	1.4	0.03	antibiotic	–
demeclocycline (ANT LC/MS)	127-313-3	0.05	73	0	ND	antibiotic	–
doxycycline (ANT LC/MS)	564-25-0	0.1	73	0	ND	antibiotic	–
enrofloxacin (ANT LC/MS)	93106-60-6	0.02	73	6.8	0.04	antibiotic	–
erythromycin-H_2O (ANT LC/MS)	114-07-8	0.05	73	8.1	0.3	erythromycin metabolite	–
lincomycin (ANT LC/MS)	154-21-2	0.05	73	0	ND	antibiotic	–
methotrexate (ANT LC/MS)	59-05-2	0.05	73	0	ND	antibiotic	–
minocycline (ANT LC/MS)	10118-90-8	0.05	73	0	ND	antibiotic	–
norfloxacin (ANT LC/MS)	70458-96-7	0.02	73	0	ND	antibiotic	–
oxytetracycline (ANT LC/MS)	79-57-2	0.1	73	0	ND	antibiotic	–
roxithromycin (ANT LC/MS)	80214-83-1	0.03	73	0	ND	antibiotic	–
sarafloxacin (ANT LC/MS)	98105-99-8	0.02	73	1.4	0.02	antibiotic	–
sulfadimethoxine (ANT LC/MS)	122-11-2	0.05	72	0	ND	antibiotic	–
sulfamerazine (ANT LC/MS)	127-79-7	0.05	73	0	ND	antibiotic	–
sulfamethazine (ANT LC/MS)	57-68-1	0.05	73	0	ND	antibiotic	–
sulfamethizole (ANT LC/MS)	144-82-1	0.05	73	0	ND	antibiotic	–
sulfamethoxazole (PHARM LC/MS)	723-46-6	0.023	74	2.7	UC	antibiotic	–
sulfathiazole (ANT LC/MS)	72-14-0	0.1	73	0	ND	antibiotic	–
tetracycline (ANT LC/MS)	60-54-8	0.05	73	0	ND	antibiotic	–
trimethoprim (PHARM LC/MS)	738-70-5	0.014	71	6.8	0.02	antibiotic	–
tylosin (ANT LC/MS)	1401-69-0	0.05	73	0	ND	antibiotic	–
virginiamycin (ANT LC/MS)	21411-53-0	0.1	73	0	ND	antibiotic	–
Prescription drugs							
albuterol (PHARM LC/MS)	18559-94-9	0.029	74	0	ND	antiasthmatic	–
cimetidine (PHARM LC/MS)	51481-61-9	0.007	74	0	ND	antacid	–
codeine (PHARM LC/MS)	76-57-3	0.24	74	2.7	<RL	analgesic	–
carbamazepine (PHARM LC/MS)	298-46-4	0.011	74	21.6	0.19	anticonvulsant	–
dehydronifedipine (PHARM LC/MS)	67035-22-7	0.01	74	4.1	0.019	antianginal	–
diltiazem (PHARM LC/MS)	42399-41-7	0.012	74	1.4	<RL	antihypertensive	–
diphenhydramine (PHARM LC/MS)	58-73-1	0.01	74	5.4	0.023	antihistamine	–
fluoxetine (PHARM LC/MS)	54910-89-3	0.018	74	1.4	<RL	antidepressant	–
gemfibrozil (PHARM LC/MS)	25812-30-0	0.015	74	0	ND	antihyperlipidemic	–
ranitidine (PHARM LC/MS)	66357-35-5	0.01	74	0	ND	antacid	–
warfarin (PHARM LC/MS)	81-81-2	0.001	74	0	ND	anticoagulant	–
Non-prescription drugs							
1,7-dimethylxanthine (PHARM LC/MS)	611-59-6	0.018	73	23.0	0.30	caffeine metabolite	–
acetaminophen (PHARM LC/MS)	103-90-2	0.009	74	8.1	0.16	antipyretic	–
caffeine (PHARM LC/MS) [f]	58-08-2	0.014	74	7.5	0.27	stimulant	–

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cotinine (PHARM LC/MS)	486-56-6	0.023	74	35.1	0.10	nicotine metabolite	–
ibuprofen (PHARM LC/MS)	15687-27-1	0.018	74	1.4	0.27	anti-inflammatory	–
Other wastewater-related							
1,4-dichlorobenzene (CLLE GC/MS)	106-46-7	0.5	73	2.7	<RL	fragrance	[1]75; [2]75; [3]0.1; [4]4000
1-*methyl* naphthalene (CLLE GC/MS)	90-12-0	0.5	73	0	ND	PAH, pesticide adjuvant, wall coverings	
2,6-*dimethyl* naphthalene (CLLE GC/MS)	58-14-2	0.5	73	0	ND	PAH, pesticide adjuvant	
2-*methyl* naphthalene (CLLE GC/MS)	91-57-6	0.5	73	0	ND	PAH, pesticide adjuvant, sealant	
3-*methyl*-1(H)-indole (CLLE GC/MS)	83-34-1	1	73	2.7	<RL	fragrance	
3-*tert*-butyl-4-hydroxyanisole (CLLE GC/MS)	25013-16-5	5	73	0	ND	antioxidant	
4-cumylphenol (CLLE GC/MS)	599-64-4	1	73	0	ND	nonionic detergent metabolite, surfactant	
4-*n*-octylphenol (CLLE GC/MS)	1806-26-4	1	73	0	ND	nonionic detergent metabolite, surfactant	
4-nonylphenol diethoxylate (CLLE GC/MS)	26027-38-3	5	73	2.7	UC	nonionic detergent metabolite, surfactant	
4-octylphenol diethoxylate (CLLE GC/MS)	26636-32-8	1	73	1.4	<RL	nonionic detergent metabolite, surfactant	
4-octylphenol monoethoxylate (CLLE GC/MS)	26636-32-8	1	73	0	ND	nonionic detergent metabolite, surfactant	
4-*tert*-octylphenol (CLLE GC/MS)	140-66-9	1	73	8.1	<RL	nonionic detergent metabolite, surfactant	
5-*methyl*-1H-benzotriazole (CLLE GC/MS)	136-85-6	2	73	5.4	<RL	manufacturing additive; anticorrosive	
acetophenone (CLLE GC/MS)	98-86-2	2	73	0	ND	solvent	
acetyl-hexamethyl-tetrahydro-naphthalene [d] (CLLE GC/MS)	1506-02-1	0.5	73	10.8	<RL	fragrance: musk	
anthracene (CLLE GC/MS)	120-12-7	0.5	73	0	ND	PAH, combustion product, used in dyes	[3]0.3; [4]10,000
anthraquinone (CLLE GC/MS)	84-65-1	0.5	73	2.7	<RL	manufacturing of dye/textiles, seed treatment, bird repellant	
benzo(a)pyrene (CLLE GC/MS)	50-32-8	0.5	73	2.7	<RL	PAH, combustion product	[1]0.2
benzophenone (CLLE GC/MS)	119-61-9	0.5	73	2.7	<RL	hair mousse, inks	
bisphenol A (CLLE GC/MS)	80-05-7	1	73	9.5	1.9	manufacturing additive, used in plastics	
bromacil (CLLE GC/MS)	314-40-9	0.5	73	9.5	0.74	herbicide	[2]90; [3]0.1; [4]5000
camphor (CLLE GC/MS)	76-22-2	0.5	73	0	ND	flavor, odorant	
carbaryl (CLLE GC/MS)	63-25-2	1	73	0	ND	insecticide	[2]700; [3]0.1; [4]4000
chlorpyrifos (CLLE GC/MS)	2921-88-2	0.5	73	5.4	<RL	insecticide	[2]20; [3]0.003; [4]100
diazinon (CLLE GC/MS)	333-41-5	0.5	73	18.9	0.51	insecticide	
dichlorvos (CLLE GC/MS)	62-73-7	1.0	73	1.4	<RL	insecticide	
d-limonene (CLLE GC/MS)	5989-27-5	0.5	73	0	ND	fungicide, antimicrobial, antiviral; fragrance in aerosols	
ethanol,2-butoxy-phosphate (CLLE GC/MS)	78-51-3	0.5	73	16.2	0.96	manufacturing additive, plasticizer	
fluoranthene (CLLE GC/MS)	206-44-0	0.5	73	4.1	<RL	PAH, combustion product	
hexahydrohexamethyl-cyclopentabenzopyran [e] (CLLE GC/MS)	1222-05-5	0.5	73	16.2	0.97	fragrance: musk	
indole (CLLE GC/MS)	120-72-9	0.5	73	2.7	<RL	pesticide inert, fragrance in coffee	
isoborneol (CLLE GC/MS)	124-76-5	0.5	73	0	ND	fragrance in perfume, disinfectants	
isophorone (CLLE GC/MS)	78-59-1	0.5	73	1.4	<RL	solvent for lacquers, plastics, oils, silicon, resins	[2]100; [3]0.2; [4]7000
isoproplylbenzene (CLLE GC/MS)	98-82-8	0.5	73	0	ND	fuels	[3]0.1; [4]4000
isoquinoline (CLLE GC/MS)	119-65-3	0.5	73	1.4	<RL	flavors and fragrances	
menthol (CLLE GC/MS)	89-78-1	0.5	73	1.4	<RL	natural mint oil used in cigarettes, cough drops, liniment, mouthwash	
metalaxyl (CLLE GC/MS)	57837-19-1	0.5	73	4.1	<RL	pesticide	
methyl salicylate (CLLE GC/MS)	119-36-8	0.5	73	12.2	<RL	liniment, food, beverage,	

(continued on next page)

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Table 3 (continued)

Chemical (Method)	CASRN	RL (μg/L)	*n*	Percent detected	Maximum concentration [a] (μg/L)	Typical use [b]	Drinking water standards and health advisories (μg/L)
						UV-absorbing lotions	
metolachlor (CLLE GC/MS)	51218-45-2	0.5	73	39.2	0.67	herbicide	[2]100; [3]0.15; [4]500
N-N-diethyltoluamide (CLLE GC/MS)	134-62-3	0.5	73	14	<RL	insect repellant	
naphthalene (CLLE GC/MS)	91-20-3	0.5	73	0	ND	PAH, combustion product, moth repellant	[2]100; [3]0.02; [4]700
para-cresol (CLLE GC/MS)	106-44-5	1	73	2.7	<RL	wood preservative, solvent	
para-nonylphenol (CLLE GC/MS)	84852-15-3	5	73	1.4	UC	nonionic detergent metabolite, surfactant	
pentachlorophenol (CLLE GC/MS)	87-86-5	2	73	5.4	<RL	herbicide, fungicide, wood preservative	[1]1; [3]0.03; [4]1000
phenanthrene (CLLE GC/MS)	85-01-8	0.5	73	1.4	<RL	PAH, combustion product	
phenol (CLLE GC/MS)	108-95-2	2	73	1.4	<RL	disinfectant	
prometon (CLLE GC/MS)	1610-18-0	0.5	73	25.7	<RL	herbicide	[2]100; [3]0.015; [4]500
pyrene (CLLE GC/MS)	129-00-0	0.5	73	2.7	<RL	PAH, combustion product	
tetrachloroethylene (CLLE GC/MS)	127-18-4	0.5	73	9.5	2.4	solvent, degreaser	[1]5; [2]10; [3]0.01; [4]500
tri(2-chloroethyl) phosphate (CLLE GC/MS)	115-96-8	0.5	73	20.3	<RL	manufacturing additive, fire retardant	
tri(dichlorisopropyl) phosphate (CLLE GC/MS)	13674-87-8	0.5	73	12.2	<RL	manufacturing additive, fire retardant	
tributyl phosphate (CLLE GC/MS)	126-73-8	0.5	73	8.1	0.74	antifoaming agent, fire retardant	
triphenyl phosphate (CLLE GC/MS)	115-86-6	0.5	73	1.35	<RL	plasticizer	
triclosan (CLLE GC/MS)	3380-34-5	1	73	8.1	<RL	antimicrobial disinfectant	
triethyl citrate (CLLE GC/MS)	77-93-0	0.5	73	5.4	0.56	cosmetics, food additive	
Biogenic Steroids [c]							
beta-sitosterol (CLLE GC/MS)	83-46-5	2	73	24.3	UC	naturally occurring	
cholesterol (CLLE GC/MS)	57-88-5	2	73	41.9	UC	naturally occurring	
coprostanol (CLLE GC/MS)	360-68-9	2	73	17.6	<RL	naturally occurring	
stigmastanol (CLLE GC/MS)	19466-47-8	2	73	1.4	<RL	naturally occurring	

[RL, reporting level; n, number of analyses; ND, not detected; UC, unquantified concentration estimated to exceed the reporting level; PHARM LC/MS, solid-phase extraction with high-performance liquid chromatography and mass spectroscopy; ANT LC/MS, solid-phase extraction with liquid chromatography and mass spectroscopy; CLLE GC/MS, continuous liquid–liquid extraction with gas chromatography and mass spectroscopy].

Drinking Water Standards and Health Advisories:

[1]U.S. EPA MCL (μg/L).

[2]U.S. EPA Lifetime Health Advisory (μg/L).

[3]U.S. EPA RfD (mg/kg/day).

[4]U.S. EPA Drinking Water Equivalent Level (DWEL) (μg/L).

[5]1998 Final Rule for Disinfection-By-Products: the total for trihalomethanes is 80 μg/L.

[a] Maximum concentrations that are listed <RL represent non-quantitative detections. Maximum concentrations listed as UC are unquantified concentrations but estimated to exceed the reporting level.

[b] A more complete description of compound-use categories can be found in the forthcoming data report (http://toxics.usgs.gov/regional/emc/).

[c] Concentrations were not quantitative for the GC/MS biogenic steroid analyses (see Experimental methods section).

[d] Also known as AHTM or tonalide.

[e] Also known as HHCB or galaxolide.

[f] Concentrations above the 95th percentile concentration found in blanks are reported.

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background using a series of 0.02, 0.05, and 0.10 μg/L reagent water spikes (Meyer et al., 2007). Only concentrations equal to or above the RL were reported for the ANT LC/MS method. Reagent grade water spikes and blanks, matrix spikes, and duplicate samples were analyzed with each set of samples from each method to evaluate recovery, matrix ionization effects, reproducibility, and laboratory contamination.

Laboratory QA/QC including sets of spikes and blanks provided additional insights and qualifications of method performance and subsequent data reporting for samples analyzed during this study. At least one fortified laboratory spike and one laboratory blank was analyzed with each set of 10 environmental samples. All methods had surrogate compounds added to samples prior to extraction to monitor method performance. Recoveries of diltiazem, diphenhydramine, fluoxetine, tetrachloroethylene, and pentachlorophenol were less than 60%, or varied by more than 25% in laboratory spikes over the duration of this and other recent studies by the USGS, consequently all detected but unquantified concentrations were reported as "<RL" for those 5 analytes and so noted in data tables. Environmental results were not corrected for recovery. The laboratory blanks were used to assess potential contamination and sample carryover introduced during sample preparation and analysis. Blank contamination was not subtracted from environmental results but was considered as part of RL adjustments and general QA/QC. During the course of this study, no compounds were routinely or consistently detected in laboratory blanks for any method; however, as mentioned above we include QA/QC considerations and data from other USGS projects and report results accordingly. As a result of the larger database outside this study, phenol and acetophenone, which exhibited chronic and(or) systematic detections in laboratory blanks, were not reported in this paper below their respective reporting levels (this is footnoted in data tables). No analytes were detected in any field or laboratory blanks for the ANT LC/MS method during the course of this study.

Other laboratory QA/QC considerations included evaluations of reference standards and instrument performance. Technical mixtures were used as reference standards for the surfactants *para*-nonylphenol, nonylphenol diethoxylate (NP2EO), octylphenol diethoxylate (OP2EO), and ocytlphenol monoethoxylate (OPEO). Additionally, instability of the GC/MS for the quantitation of the four steroidal compounds (*beta*-sitosterol, cholesterol, coprostanol, stigmostanol) required that the detected concentrations of these compounds be reported as unquantified "UC" because results were not within preset quality assurance limits. More detailed explanations of analytical methods including extraction/recovery, calibration, and other procedures can be found in each method's primary reference.

2.4. *Quality assurance and quality control of field samples*

Laboratory and field blank data collected during various projects and time periods by USGS personnel are consistently incorporated and considered as part of method development and evaluation and are considered, along with other criteria, in setting or adjusting the RL for each compound and making overall decisions on reporting of data. Therefore, all RLs and related reporting decisions were based not only on QA/QC from this project but also included other QA/QC from preceding USGS projects where possible.

Field blanks, made from laboratory-grade organic free water, were submitted for about 15% of the sites (11 out of 74) and analyzed for all analytes during the course of the present study. Field blanks were subject to the same sample processing, handling, and equipment as the environmental samples. As the number of OWCs analyzed by new methods continues to increase, the potential sources of contamination during field sampling, transport, and laboratory analysis also increases. This is particularly important as the range of compound groups include potential contaminant sources from chemicals commonly used by field and laboratory personnel in their personal as well as professional lives and the equipment used to make these measurements. In spite of this, the majority (94%) of the OWCs analyzed were not detected in any laboratory or field blank in this study for any of the methods. Table 2 lists all of the compounds detected in 11 field blanks analyzed in this study. With the exception of caffeine, there was not a chronic (defined as greater than 5% detection frequency) field blank problem for any analyte in this study. Only caffeine by PHARM LC/MS was chronically present in field blanks in this study (detected in 12% of samples), and the results for all environmental samples of caffeine were censored based on a statistical assessment of the blank data (95th percentile; 0.104 μg/L).

2.5. *Statistical tests*

Nonparametric statistical techniques were used for this study. These methods are appropriate because the data did not exhibit normal distributions and because of the presence of censored data (concentrations less than analytical detection limits). The Wilcoxon rank-sum test was used to test for spatial differences in the medians of two groups. A significance level of 0.05 was used for all statistical tests in this study. This acceptable probability of error (α=0.05) means that there was a 1 in 20 chance that the statistical test reported a significant relation when one did not exist. The smaller the *p*-value, the greater the certainty that a reported statistical relation was real.

3. Results

3.1. *Detections*

Of the 100 OWCs analyzed, 63 were detected at least once; however many compounds were never detected in any water sample (Table 3; Fig. 2). The maximum number of compounds detected at any site was 31 and the median number of detections per site was four. No OWCs were detected in water samples collected from six sites. OWCs such as select pesticides, fragrances and flavors, steroids, non-prescription drugs, plasticizers, flame retardants, and detergent metabolites were detected more frequently than pharmaceutical compounds. The most frequently detected compounds are associated with a variety of uses and sources and include: cholesterol (41.9%, biogenic steroid), metolachlor (39.2%, agricultural herbicide), cotinine (35.1%, nicotine degradate), and prometon (25.7%, non-agricultural herbicide). Seventeen OWCs were detected in more than 10% of the sites (Table 3).

Although the reporting levels of all compounds analyzed were parts per billion or lower, 38 compounds were not detected

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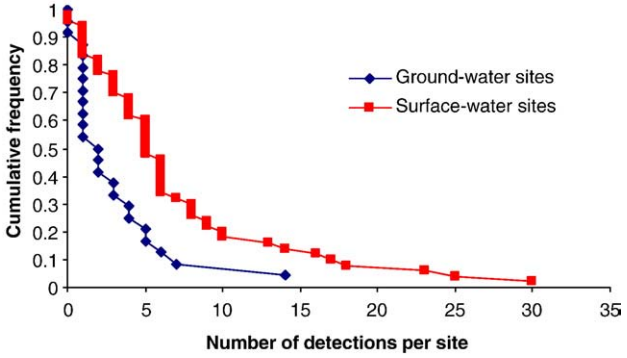

Fig. 2 – Frequency of detection of all compounds analyzed in surface- and ground-water sites.

in any of the samples collected for this study (Table 3). In addition, 60% of the 38 pharmaceuticals (including prescription drugs and antibiotics) analyzed were not detected in any water sample. It is important to note that many of these compounds likely transform or degrade as they are transported into and through the environment as a result of metabolic, photolytic, and other natural attenuation processes (Hignite and Azarnoff, 1977; Sedlak and Pinkston, 2001; Stackelberg et al., 2004a,b, 2007) and many of the possible transformation compounds were not assessed in this reconnaissance due to lack of analytical methods at this time. Therefore it is possible that the parent compounds, though not detected, could have degraded into other compounds that were not targeted. Thus, the absence of detectable concentrations of OWCs may be due to absence of the source, complete attenuation of the compound or attenuation to levels below analytical detection capabilities. The absence of OWCs that have been looked for in the environment at low detection levels is an important, and often overlooked, result of environmental contaminant occurrence assessments which tend to focus only on the detected contaminants.

3.2. *Concentrations*

Concentrations of all detected compounds were typically in the sub-μg/L range with some maximum concentrations above a few μg/L (Table 3). Although many compounds were never detected, others were found in low-concentration mixtures (Fig. 2). The OWCs with the highest maximum concentrations measured in this reconnaissance (greater than or equal to reporting levels) are not necessarily among the most frequently detected compounds (Table 3). For example, although detergent metabolites tend to be detected infrequently, they occur in concentrations greater than 0.5 μg/L. Previous research (Kolpin et al., 2002) has also shown that compound groups found with the highest frequency are not always those found in the highest concentration.

The maximum concentrations of all OWCs other than bisphenol-A, nonylphenol, NP2EO, phenol, tetrachloroethylene, β-sitosterol, cholesterol, and coprostanol were below one part per billion. As previously mentioned, drinking water standards do not exist for most compounds analyzed, and therefore, it is difficult to put these results in a human-health context at this time. Maximum environmental concentrations of 26 pharmaceuticals (including many that were analyzed in this reconnaissance) measured in several previous studies by a variety of investigators were compared with environmental concentrations at selected surface-water sources of drinking water predicted by the PhATE model (Anderson et al., 2004; Schwab et al., 2005). The maximum measured concentrations in the present reconnaissance were lower (and equal for ciprofloxacin) than all previously published maximum measured concentrations for the corresponding pharmaceuticals summarized in that study (Schwab et al., 2005). It is possible however, that some OWCs can be degraded to other compounds with different chemical properties and toxicities as a result of various wastewater treatment and other biotic and abiotic processes as they are transported in the environment. For example, in the presence of chlorine disinfection, naturally occurring as well as some synthetic organic molecules (e.g. triclosan) can be transformed to chloroform or other disinfection by-products (Rule et al., 2005). In addition, the accuracy of models of occurrence and distribution of OWCs depend on the accuracy of the source strength of any given compound. Many factors ranging from off-label uses to uncertainties in the volumes used in consumer products (Reiner and Kannan, 2006) presently limit the accuracy of OWC source strength in environmental modeling efforts, and therefore, measured environmental occurrence data will continue to play a crucial role in model development, maintenance, and validation.

3.3. *Organic wastewater contaminant use categories*

The 100 OWCs were divided into 16 compound groups based on the type of compound or general category of use (Note: uses can vary widely for any given compound. Consequently, the tabulated use categories are presented for illustrative purposes and may not be all inclusive). When summarized as compound groups, non-prescription drugs (including caffeine and its metabolite 1,7 dimethylxanthine, cotinine, ibuprofen, and acetominophen) were detected more frequently than any other group in surface-water samples other than naturally occurring steroids (Fig. 3). Only three groups had individual chemical maximum concentrations exceeding 2 μg/L (biogenic steroids, detergent metabolites, and solvents), whereas seven groups (including antibiotics, non-prescription drugs, and other prescription drugs) had maximum concentrations less than 0.5 μg/L (Table 3).

3.4. *Occurrence in ground water and surface water*

The detection frequencies and total concentrations of all compounds were statistically different between surface-water and ground-water sites (Wilcoxon rank-sum test; $p=0.0015$ and $p=0.001$ respectively; Fig. 2). The five most frequently detected OWCs in samples collected from the 49 surface-water sites were: cholesterol (59%), metolachlor (53%), cotinine (51%), β-sitosterol (37%), and 1,7 dimethylxanthine (27%); and the five most frequently detected from the 25 ground-water sites were: tetrachloroethylene (24%), carbamazepine (20%), bisphenol-A (20%), 1,7-dimethylxanthine (16%), and tri (2-chloroethyl) phosphate (12%). The naturally occurring steroids analyzed in this study can be derived from many potential plant and animal sources. Steroids were detected more frequently at surface-water sites than at ground-water

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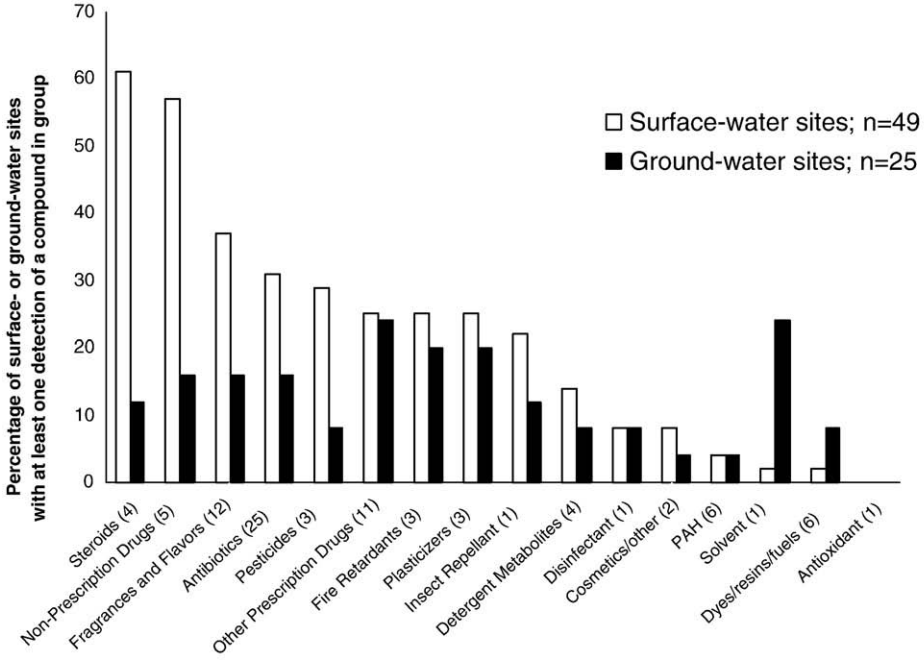

Fig. 3 – Detections of organic wastewater compounds by general use category at surface- and ground-water sites (Note: all steroids analyzed are naturally occurring biogenic steroids).

sites. Lower frequencies of detection were determined at ground-water sites than at surface-water sites for all compound groups except for the solvent tetrachloroethylene and the group of dyes, resins, and fuel additives (Fig. 3).

More frequent detections in surface-water sources than ground-water sources likely reflect the more direct pathways for transport of OWCs into surface waters (e.g. direct discharge of wastewater effluent), as well as other factors such as differences in environmental fate and transport processes (e.g. sorption, volatilization, degradation, etc.) as these contaminants are transported along surface- versus subsurface pathways. Such differences in the occurrence and concentration of OWCs have been previously documented between streams and ground water (Barnes et al., 2008-this issue).

4. Discussion

Because compound detections and concentrations are dependent on source strength, hydrologic condition, timing of sampling and other factors, interpretations of these reconnaissance data are limited. However, many of the same compounds detected in the USGS stream reconnaissance (Kolpin et al., 2002) which targeted streams known or suspected to be susceptible to wastewater inputs, were also detected at surface-water sites in this source-water reconnaissance. The design of these two studies and site selections were not coordinated to assess upstream and downstream transport such as in subsequent research (e.g. Glassmeyer et al., 2005); but it is instructive to qualitatively compare selected results because the range of watershed sizes and streamflows were similar and, more importantly, the sites chosen for the stream reconnaissance (Kolpin et al., 2002) were generally closer to the sources of waste than the surface-water sites chosen for this study. For example, based solely on transport and fate considerations for any environmental water contaminant, it can be expected that detections and concentrations of OWCs are likely to decrease as they are transported away from the contaminant source to downstream locations (e.g. drinking water intakes) due to dilution, sorption, and degradation as long as no other source of the contaminant is present in the watershed (e.g. Glassmeyer et al., 2005; Barber et al., 2006; Gurr and Reinhard, 2006; Fono et al., 2006). This assertion is supported by the observation that detections of compounds with similar reporting levels in both studies (i.e. most antibiotics, and prescription and non-prescription drugs analyzed by the ANT LC/MS and PHARM LC/MS methods) were generally greater in the stream reconnaissance than they were at surface-water sites in the source-water reconnaissance (Fig. 4). This observation should be more

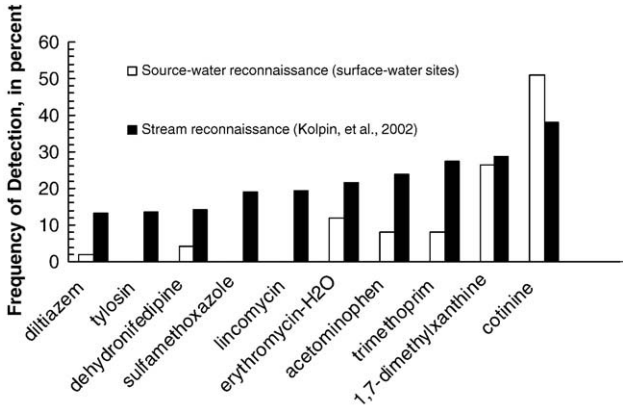

Fig. 4 – Frequently detected compounds with the same reporting levels in the stream reconnaissance (Kolpin et al., 2002) and surface-water sites in this study.

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fully investigated by more rigorously designed fate and transport studies, but indicates the potential for natural attenuation of select OWCs as they are transported within a watershed before reaching drinking water intake locations (Palmer et al., 2008). This finding also highlights questions regarding the potential importance of degradates with different toxicological and ecological significance than the parent compounds (Halling-Sørensen et al., 2002a,b; Isidori et al., 2006; Jensen et al., 2006; Jjemba, 2006) as well as the potential for conjugate forms to be cleaved during wastewater treatment and(or) environmental processes thereby transforming back to the parent compound (Fent et al., 2006).

Results and interpretations of reconnaissance studies also are controlled by the precision, accuracy, and interpretation of the analytical methods. Certainly, an analyte cannot be found in environmental samples unless it is looked for and can be detected by appropriately sensitive methods. The documented presence of a compound in an environmental sample is not only the result of a source of environmental contamination but also limited by measurement capabilities. As shown above many OWCs, particularly the targeted pharmaceuticals, were rarely or not detected in any samples collected from source-water sites. The lack of detections is particularly notable because measurement detection levels were low. Therefore, many of the targeted compounds are either: 1) not being transported to raw sources of drinking water in detectable concentrations due to natural attenuation processes including transformation to other compounds, dilution, and other degradation processes, and(or) 2) there are no, or minimal, sources of these compounds entering the watersheds and aquifers sampled. The results also indicate however, that new analytical methods may be needed to detect the potential compounds as well as their corresponding degradate compounds (Boxall et al., 2004) at lower concentrations if present detection capabilities are shown to be inadequate from ecological and human toxicological perspectives.

Although the analytical methods and associated laboratory and field QA/QC used in this study were the best that resources and capabilities could provide at the time, recent advances in sampling and analysis continue to add refinement to occurrence studies. For example, triple quadrupole (tandem) MS (not available to this study when it was conducted) can help to minimize analytical uncertainties potentially caused by matrix interferences in organic-rich environmental waters and new methods increase the numbers and types of compounds that can be detected in environmental samples (Schultz and Furlong, 2008). Consequently, the results of this present study must be interpreted within the context of the analytical capabilities at the time of sample analysis. For many polar to moderately water-soluble compounds it is difficult to separate the background matrix from the compounds of interest. Recent advances with triple quadrupole MS provides a more robust interface than was used in the present study and also can eliminate ambiguity due to matrix interference should the situation arise for an individual measurement. However, all the mass spectrometry techniques used in this study required the quantitation ion as well as a confirming ion and in many cases two confirming ions were utilized. Several other factors including both field and laboratory QA/QC data significantly decreased the potential for false-positive errors (see Analytical methods and the primary citations for more details). Therefore, all detections in this study are reported with high degrees of analytical rigor and statistical confidence. Additional work to minimize laboratory reporting levels while maintaining data-quality objectives was also integral to this study. However it is possible that some unknown, but likely minimal, subset of our data contain false-positive or false-negative errors.

Natural attenuation processes are likely as OWCs move along subsurface pathways to drinking water wells (Barnes et al., 2004; Barber et al., 2007). The drinking water wells sampled in this study are likely located farther from wastewater inputs than the monitoring wells sampled for the national ground-water reconnaissance, which were targeted near known or suspected wastewater sources (Barnes et al., 2008-this issue). Because of differences in analytical methods, insufficient data to assess sizes and shapes of contributing areas to the sampled wells, and other complications unique to ground-water assessments, qualitative comparison of occurrence at ground-water sites between the two reconnaissance efforts was not attempted. It is important to note, however, that some of the same compounds detected in the ground-water reconnaissance were also detected in drinking water wells in this study.

It is evident from these comparisons and results that natural attenuation processes alone will not likely remove or decrease all OWCs to non-detectable concentrations in surface- and ground-water sources of drinking water. For example, carbamazepine, which has been shown to be resistant to various natural attenuation and treatment processes (Glassmeyer et al., 2005; Clara et al., 2004), was among the most frequently detected compounds for both surface-water (22%) as well as ground-water (20%) sites in this source-water reconnaissance.

Snyder et al. (2007) evaluated the efficacies of a range of drinking water treatment technologies for the removal of several targeted pharmaceuticals, personal care products and other trace contaminants. That study showed through bench as well as full-scale studies that several treatment technologies (e.g. advanced oxidation, granular activated carbon, reverse osmosis) are highly effective in removing most of the target analytes from the water phase. However, a smaller subset of analytes, including some that were found in the present study (e.g. N-N-diethyltoluamide and carbamazepine; Table 3), were not efficiently removed by any of the treatment methods tested.

This source-water reconnaissance study provides new baseline knowledge on a wide range of OWCs in a variety of ground- and surface-water sources of drinking water across the United States. These national-scale reconnaissance data provide preliminary understandings and context to develop and test hypotheses about the environmental occurrence of these and other compounds with similar sources and environmental properties. This will help prioritize and determine the need, if any, for future occurrence, fate and transport, and health-effects research for subsets of OWCs most likely to be found in water resources used for drinking water in the United States. These data also provide needed perspective and comparative information for existing and future models of the occurrence, fate and transport of pharmaceuticals and

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other OWCs in the environment. This is enabling researchers to identify and prioritize environmental research on a smaller targeted list of compounds that likely are resistant to degradation in source waters as well as those that could potentially survive existing drinking water treatment practices and cause human-health concerns.

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