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A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States — I) Groundwater

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ABSTRACT

As part of the continuing effort to collect baseline information on the environmental occurrence of pharmaceuticals, and other organic wastewater contaminants (OWCs) in the Nation's water resources, water samples were collected from a network of 47 groundwater sites across 18 states in 2000. All samples collected were analyzed for 65 OWCs representing a wide variety of uses and origins. Site selection focused on areas suspected to be susceptible to contamination from either animal or human wastewaters (i.e. down gradient of a landfill, unsewered residential development, or animal feedlot). Thus, sites sampled were not necessarily used as a source of drinking water but provide a variety of geohydrologic environments with potential sources of OWCs. OWCs were detected in 81% of the sites sampled, with 35 of the 65 OWCs being found at least once. The most frequently detected compounds include N,N-diethyltoluamide (35%, insect repellant), bisphenol A (30%, plasticizer), tri(2-chloroethyl) phosphate (30%, fire retardant), sulfamethoxazole (23%, veterinary and human antibiotic), and 4-octylphenol monoethoxylate (19%, detergent metabolite). Although sampling procedures were intended to ensure that all groundwater samples analyzed were indicative of aquifer conditions it is possible that detections of some OWCs could have resulted from leaching of well-construction materials and/or other site-specific conditions related to well construction and materials. Future research will be needed to identify those factors that are most important in determining the occurrence and concentrations of OWCs in groundwater.

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1. Introduction

Increasing standards of living and the continual growth of the human population has led to a growing demand for freshwater. Thus, the protection of this natural resource is an important environmental issue. In the United States in 1995, groundwater withdrawals were estimated at more than 291 million liters per day (Solley et al., 1998). Groundwater not only provides about 40% of the Nation's public water supply, but it also is used by more than 40 million people, including most of

the rural population who supply their own drinking water via domestic wells. Groundwater is also the major source of water used for irrigation (Alley et al., 1999) and is the Nation's principal reserve of freshwater representing much of the potential future water supply. Groundwater is a major contributor to flow in many streams and rivers and thus, has a strong influence on river and wetland habitats for plants and animals.

Tens of thousands of manmade chemicals are used in today's society with all having the potential to enter our water resources. There are a variety of pathways by which these organic contaminants can make their way into the aquatic environment (Heberer, 2002a,b). Such pathways include direct discharge via wastewater treatment plants, landfills, and land application of human and animal waste to farmland. Pharmaceuticals and other organic wastewater contaminants (OWCs) are a set of compounds that are receiving an increasing amount of public and scientific attention. OWCs have been documented in water resources around the world (Ternes, 1998; Stumpf et al., 1999; Heberer et al., 2001; Kolpin et al., 2002; Metcalf et al., 2003; Hohenblum et al., 2004; Moldovan, 2006; Kim et al., 2007). Although some research on OWCs has been conducted in groundwater (Ahel, 1991; Seiler et al., 1999; Sacher et al., 2001; Heberer, 2002a,b; Barnes et al., 2004; Cordy et al., 2004; Scheytt et al., 2004; Hari et al., 2005; Batt et al., 2006; Rabiet et al., 2006), the vast majority of such efforts have been in surface waters. Currently our understanding of the chronic, long-term effects to OWCs is limited. Research is just beginning to untangle this difficult question (Pascoe et al., 2003; Thorpe et al., 2003; Brooks et al., 2005; Flaherty and Dodson, 2005; Johnson et al., 2005; Mills and Chichester, 2005; Oetken et al., 2005; Pomati et al., 2006; Correa-Reyes et al., 2007; Kidd et al., 2007; Nentwig, 2007).

This study represents the first national-scale examination of OWC occurrence in groundwater and provides a baseline from which to proceed with future groundwater investigations and monitoring strategies. This paper summarizes the analytical results from a network of 47 groundwater sites sampled in 2000 (Fig. 1).

2. Experimental design

2.1. Site selection and sampling

Because little information exists on the occurrence of OWCs in groundwater, the 47 groundwater sites sampled in 2000 were selected in areas thought to be susceptible to contamination from either animal or human wastewaters. While this reconnaissance sampling network does represent a variety of land use, climate and hydrogeology, it is not necessarily representative of all groundwaters in the United States. The sampling network consisted of 42 wells, 3 springs, and 2 sumps across 18 states (Fig. 1). The wells sampled in this study were not the same wells sampled in Focazio et al. (2008-this issue). Additional information on the groundwater sites sampled will be available in a forthcoming publication accessible at http://toxics.usgs.gov/regional/emc/. Water samples were collected during 2000 and no attempt was made to determine temporal patterns in OWC concentrations (e.g. samples only collected once from this network). The wells have varied uses with almost half of the wells used for observation purposes. Less than one-third of the wells were used for drinking water supply and the remainder of wells sampled were primarily used for agricultural purposes. Well depths were generally shallow with such depths ranging from 2.4 to 310.9 m with a median depth of 19.2 m. The type of well casing material was known for 36 of the 42 wells with 18 wells having a steel casing and 18 wells having a casing made from poly vinyl chloride (PVC). The sumps sampled were part of a seepage monitoring system in earthen basins used to store livestock waste (Ruhl, 1999).

All samples were collected by U.S. Geological Survey (USGS) personnel using consistent protocols (Koterba et al., 1995; U.S. Geological Survey, variously dated). A composite water sample was collected at each site and split into the appropriate containers for shipment to the various laboratories. For those bottles requiring filtration, water was passed through a 0.7 μm, baked (450 °C for 8 h), glass-fiber filter in the field where

Fig. 1 – Location of groundwater sampling sites.

Table 1 – Summary of analytical results of groundwater sites sampled for 83 organic wastewater contaminants							
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							
carbodox (ANT LC/MS)	6804-07-5	0.1	37	0	ND	Antibiotic	–
chlortetracycline (ANT LC/MS)	57-62-5	0.05	47	0	ND	Antibiotic	–
ciprofloxacin (ANT LC/MS)	85721-33-1	0.02	47	0	ND	Antibiotic	–
doxycycline (ANT LC/MS)	564-25-0	0.1	47	0	ND	Antibiotic	–
enrofloxacin (ANT LC/MS)	93106-60-6	0.02	47	0	ND	Antibiotic	–
erythromycin–H_2O (ANT LC/MS)	114-07-8	0.05	37	0	ND	Erythromycin metabolite	–
lincomycin (ANT LC/MS)	154-21-2	0.05	37	5.4	0.32	Antibiotic	–
norfloxacin (ANT LC/MS)	70458-96-7	0.02	47	0	ND	Antibiotic	–
oxytetracycline (ANT LC/MS)	79-57-2	0.1	47	0	ND	Antibiotic	–
roxithromycin (ANT LC/MS)	80214-83-1	0.03	37	0	ND	Antibiotic	–
sarafloxacin (ANT LC/MS)	98105-99-8	0.02	47	0	ND	Antibiotic	–
sulfadimethoxine (ANT LC/MS)	122-11-2	0.05	37	0	ND	Antibiotic	–
sulfamerazine (ANT LC/MS)	127-79-7	0.05	37	0	ND	Antibiotic	–
sulfamethazine (ANT LC/MS)	57-68-1	0.05	37	2.7	0.36	Antibiotic	–
sulfamethizole (ANT LC/MS)	144-82-1	0.05	37	0	ND	Antibiotic	–
sulfamethoxazole (PHARM HPLC)	723-46-6	0.023	47	23.4	1.11	Antibiotic	–
sulfathiazole (ANT LC/MS)	72-14-0	0.1	37	0	ND	Antibiotic	–
tetracycline (ANT LC/MS)	60-54-8	0.05	47	0	ND	Antibiotic	–
trimethoprim (PHARM HPLC)	738-70-5	0.014	47	0	ND	Antibiotic	–
tylosin (ANT LC/MS)	1401-69-0	0.05	37	0	ND	Antibiotic	–
virginiamycin (ANT LC/MS)	21411-53-0	0.1	37	0	ND	Antibiotic	–
Prescription drugs							
albuterol (salbutamol) (PHARM HPLC)	18559-94-9	0.029	47	0	ND	Antiasthmatic	–
cimetidine (PHARM HPLC)	51481-61-9	0.007	47	0	ND	Antacid	–
codeine (PHARM HPLC)	76-57-3	0.24	46	0	ND	Analgesic	–
dehydronifedipine (PHARM HPLC)	67035-22-7	0.01	47	4.3	0.022	Antianginal	–
diltiazem (PHARM HPLC)	42399-41-7	0.012	47	2.1	0.028	Antihypertensive	–
fluoxetine (PHARM HPLC)	54910-89-3	0.018	47	4.3	0.056	Antidepressant	–
gemfibrozil (PHARM HPLC)	25812-30-0	0.015	47	0	ND	Antihyperlipidemic	–
ranitidine (PHARM HPLC)	66357-35-5	0.01	47	0	ND	Antacid	–
warfarin (PHARM HPLC)	81-81-2	0.001	47	0	ND	Anticoagulant	–
Nonprescription drugs							
1,7-dimethylxanthine (PHARM HPLC)	611-59-6	0.018	47	4.3	0.057	Caffeine metabolite	–
acetaminophen (PHARM HPLC)	103-90-2	0.009	47	6.4	0.38	Antipyretic	–
caffeine (PHARM HPLC)	58-08-2	0.014	47	12.8	0.13	Stimulant	–
cotinine (PHARM HPLC)	486-56-6	0.023	47	2.1	<RL	Nicotine metabolite	–
ibuprofen (PHARM HPLC)	15687-27-1	0.018	47	2.1	3.11	Antiinflammatory	–
Other wastewater-related compounds							
1,4-dichlorobenzene (CLLE SIM GC/MS)	106-46-7	0.5	47	6.4	1.17	Fragrance	[1]75; [2]75; [3]0.1; [4]4000
3-*tert*-butyl-4-hydroxy anisole (CLLE SIM GC/MS)	25013-16-5	5	47	0	ND	Antioxidant	–

4-nonylphenol diethoxylate (CLLE SIM GC/MS)[a]	26027-38-3	5	47	2.1	UC	Nonionic detergent metabolite, surfactant	–
4-octylphenol monoethoxylate (CLLE SIM GC/MS)[a]	–	1	47	19.1	UC	Nonionic detergent metabolite, surfactant	–
4-octylphenol diethoxylate (CLLE SIM GC/MS)[a]	26636-32-8	1	47	4.3	<RL	Nonionic detergent metabolite, surfactant	–
5-*methyl*-1H-benzotriazole (CLLE SIM GC/MS)	136-85-6	2	46	8.7	2.08	Manufacturing additive, anticorrosive	–
acetophenone (CLLE SIM GC/MS)	98-86-2	2	47	4.3	2.67	Solvent	–
anthracene (CLLE SIM GC/MS)	120-12-7	0.5	47	2.1	<RL	PAH, combustion product, used in dyes	[3]0.3; [4]10,000
benzo[a]pyrene (CLLE SIM GC/MS)	50-32-8	0.5	47	0	ND	PAH, combustion product	[1]0.2
bisphenol A (CLLE SIM GC/MS)	80-05-7	1	47	29.8	2.55	Manufacturing additive, used in plastics	–
carbaryl (CLLE SIM GC/MS)	63-25-2	1	47	2.1	<RL	Insecticide	[2]700; [3]0.1; [4]4000
chlorpyrifos (CLLE SIM GC/MS)	2921-88-2	0.5	47	0	ND	Insecticide	[2]20; [3]0.003; [4]100
diazinon (CLLE SIM GC/MS)	333-41-5	0.5	47	0	ND	Insecticide	0.6[2]
ethanol,2-butoxy-phosphate (CLLE SIM GC/MS)	78-51-3	0.5	47	14.9	1.34	Manufacturing additive, plasticizer	–
fluoranthene (CLLE SIM GC/MS)	206-44-0	0.5	47	4.3	<RL	PAH, combustion product	–
N,N-diethyltoluamide (CLLE SIM GC/MS)	134-62-3	0.6	46	34.8	13.5	Insect repellant	–
naphthalene (CLLE SIM GC/MS)	91-20-3	0.5	47	8.5	1.51	PAH, combustion product, moth repellant	[2]100; [3]0.02; [4]700
para-cresol (CLLE SIM GC/MS)	106-44-5	1	47	12.8	<RL	Solvent	–
para-nonylphenol (CLLE SIM GC/MS)	84852-15-3	5	47	0	ND	Nonionic detergent metabolite	
phenanthrene (CLLE SIM GC/MS)	85-01-8	0.5	47	2.1	<RL	PAH, combustion product	–
phenol (CLLE SIM GC/MS)	108-95-2	2	47	0	ND	Disinfectant	400
pyrene (CLLE SIM GC/MS)	129-00-0	0.5	47	2.1	<RL	PAH, combustion product	–
tetrachloroethylene (CLLE SIM GC/MS)	127-18-4	0.5	47	8.5	<RL	Solvent, degreaser	[1]5; [2]10; [3]0.01; [4]500
tri(2-chloroethyl) phosphate (CLLE SIM GC/MS)	115-96-8	0.5	47	29.8	0.737	Manufacturing additive, fire retardant	–
tri(dichlorisopropyl) phosphate (CLLE SIM GC/MS)	13674-87-8	0.5	47	2.1	<RL	Manufacturing additive, fire retardant	–
triphenyl phosphate (CLLE SIM GC/MS)	115-86-6	0.5	47	4.3	<RL	Manufacturing additive, plasticizer	–
triclosan (CLLE SIM GC/MS)	3380-34-5	1	47	14.9	<RL	Antimicrobial disinfectant	–
Sterols							
cholesterol (CLLE SIM GC/MS)	57-88-5	0.01	41	2.1	1.73	Plant/animal steroid	–
coprostanol (CLLE SIM GC/MS)	360-68-9	0.01	41	4.3	1.29	Fecal steroid	–
stigmastanol (CLLE SIM GC/MS)	19466-47-8	2	47	2.1	UC	Plant steroid	–

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

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).

[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/).

possible, or else filtration was conducted in the laboratory. Water samples for each chemical analysis were stored in precleaned-amber, glass bottles. Following collection, samples were immediately chilled and shipped via overnight express to the appropriate laboratory. To minimize contamination, use of personal care items (perfumes, colognes, insect repellents), caffeinated products, and tobacco were discouraged during sample collection and processing (U.S. Geological Survey, variously dated).

2.　Analytical methods

Target compounds within each analytical method 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). The analytical results for each groundwater sample will be available in a forthcoming publication available at http://toxics.usgs.gov/regional/emc/. Three separate analytical methods were used to determine the environmental extent of 65 different OWCs in groundwater samples (Table 1). Descriptions of the analytical methods and method performance characteristics are provided elsewhere (Brown et al., 1999; Cahill et al., 2004; Meyer et al., 2007). Nineteen 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) (Meyer et al., 2007; hereafter referred to as ANT LC/MS). Sixteen human prescription and non-prescription drugs and their select metabolites were extracted by SPE and analyzed by high high-performance liquid chromatography (HP/LC) using a polar reverse-phase octylsilane (C8) HPLC column (Cahill et al., 2004; hereafter referred to as PHARM LC/MS). Thirty OWC-related compounds were extracted using continuous liquid–liquid extraction (CLLE) and analyzed by capillary-column gas chromatography/mass spectrometry with SIM (Brown et al., 1999; hereafter referred to as CLLE SIM GC/MS). A GC/MS/MS derivitization method for a broad suite of biogenic and synthetic hormones was being developed at this time but was unavailable for this study. 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, codeine, cotinine, sulfamethoxazole, and trimethoprim.

2.3.　Reporting levels and identification criteria

The 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 (unless otherwise noted). More details on the development of reporting levels are provided elsewhere (Focazio et al., 2008-

this issue). For the PHARM LC/MS and CLLE SIM 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. The concentration of compounds with <60% recovery, routinely detected in laboratory blanks, or prepared with technical grade mixtures, was also considered estimated (Table 1). For the ANT LC/MS method, the RL was established for each analyte with signal-to-noise ratios of 5 to 10 times above 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.

2.4.　Quality assurance and quality control

The USGS collects and analyzes field and laboratory quality assurance and quality control data for all methods on a continuous basis as part of ongoing research throughout the agency that transcends the groundwater reconnaissance discussed here. Therefore, larger datasets of field and laboratory blanks than were available to this effort were also considered when making decisions on how to report data. As a result of that larger consideration, some compounds (i.e. phenol and acetophenone) which exhibited chronic and systematic detections in field and laboratory blanks are not reported in this paper below their respective reporting levels (as footnoted in Table 1). In addition, a limited number of other compounds (i.e. bisphenol A, N,N-diethyltoluamide, nonyphenol, and 4-nonylphenol diethoxylate, CLLE SIM GC/MS) were detected in field and laboratory blanks randomly and infrequently.

Additional information on method performance is provided by laboratory quality assurance and quality control. At least one fortified laboratory spike and one laboratory blank was analyzed with each set of 10–16 environmental samples. Most methods had surrogate compounds added to samples prior to extraction to monitor method performance. The laboratory blanks were used to assess potential sample contamination. Blank contamination was not subtracted from environmental results. However, environmental concentrations within 10 times the value observed in the set blank were reported as less than the reporting level.

In addition to the laboratory and field blank data collected by USGS personnel during various projects and time periods, a field quality assurance protocol was used for the groundwater reconnaissance study to assist in determining the effect, if any, of field equipment and procedures on the concentrations of OWCs in water samples. Field blanks, made from laboratory-grade organic free water, were submitted for 6% of the sites and analyzed for all of the OWCs. Field blanks were subject to the same sample processing, handling, and equipment as the groundwater samples. Of the three field blanks submitted, two did not have any measurable detection of any
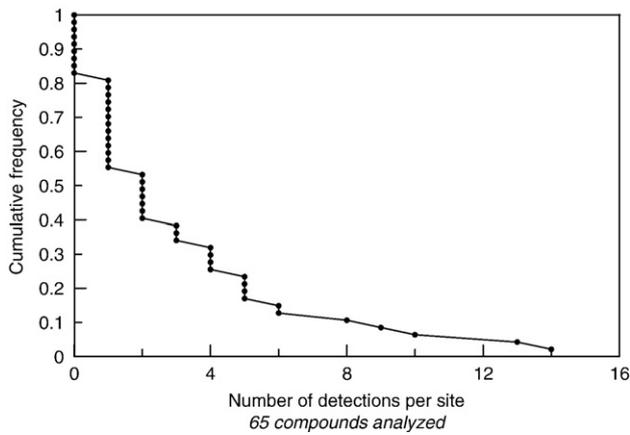
Fig. 2 – Frequency of detection of all compounds analyzed in groundwater samples.

target OWCs. The third field blank had a detection of phenol, 1,4-dichlorobenzene, acetophenone, naphthalene, and 4-octylphenol monoethoxylate. Contamination of this field blank is possibly due to the fact that the water sample was collected within 3 m of a running, gas-powered generator, or improper cleaning of the equipment prior to sampling. The corresponding regular sample showed only a small detection of para-nonylphenol. One duplicate sample was also collected and analyzed. The results from this sample were identical to those from the regular sample and showed no variations in OWC detections.

2.5. Interlaboratory and method comparisons

Five compounds (caffeine, codeine, cotinine, sulfamethoxazole, and trimethoprim) were measured by more than one analytical method and were used to compare and evaluate the most reliable method on a compound compound-by by-compound specific basis. This evaluation yielded "primacy" methods for each compound. For example, cotinine and caffeine were measured by the PHARM LC/MS and the CLLE

SIM GC/MS method; however, the detection capabilities were more sensitive for the PHARM LC/MS method and therefore it was used to report environmental data. In 426 overlapping results, the presence or absence was confirmed in 97.2% of the determinations. More specifically, the overlapping results confirmed the results for 100% of the determinations for caffeine and codeine; 97.3% for sulfamethoxazole and tri-methoprim, and 91.3% for cotinine.

2.6. 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 large number of censored data (concentrations less than the RL). Nonparametric statistical techniques have the advantage of not being overly affected by outliers and censored data because the ranks of the data are used in the statistics rather than the actual concentrations. A Spearman's rank correlation was used to measure the monotonic relation between two continuous variables (Helsel, 2005). A significance level of 0.5 was used for all statistical tests in this study.

3. Results and discussion

At least one OWC was found in 81% of the groundwater sites sampled. The frequent occurrence of OWCs in groundwater is likely due to the design of this study focusing on areas suspected to be susceptible to animal or human wastewater contamination (e.g. sites down gradient of animal feedlots, landfills or unsewered residential developments). As noted previously, not all the groundwater sites sampled were used for drinking water purposes. More than half of the OWCs (35 out of 65) were detected at least once during this study (Table 1). The OWCs detected represent a variety of uses and origins including industrial, residential, and agricultural sources. The five most frequently detected compounds include N,N-diethyltoluamide (insect repellant, 35%),
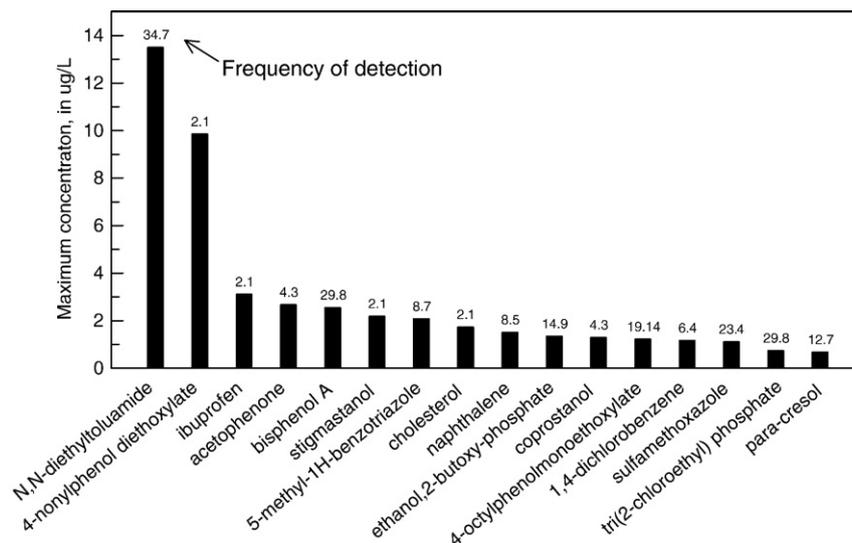

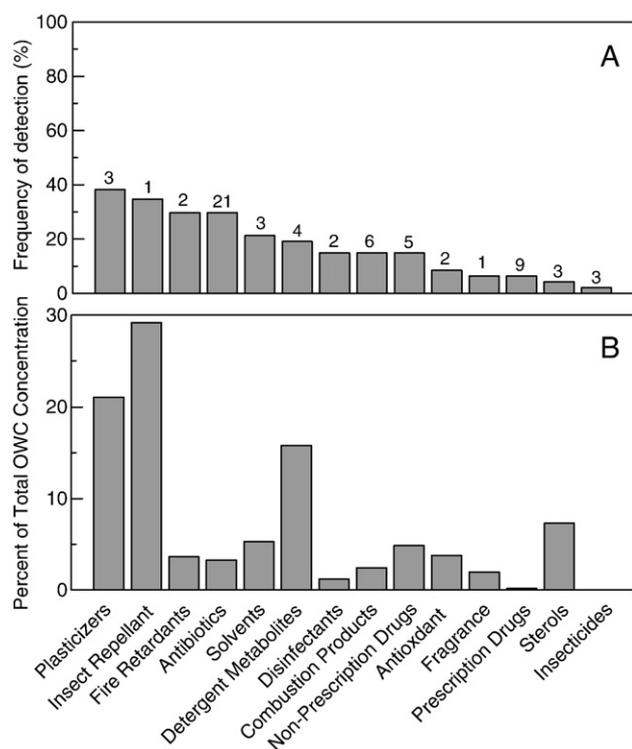**Fig. 3 – Maximum concentrations of all compounds detected at greater than 0.5 µg/L.**

Fig. 4 – Frequency of detection of organic wastewater contaminants by general use category (A), and percent of total measured concentration of organic wastewater contaminants by general use category (B). Number of compounds in each category shown above bar.

bisphenol A (plasticizer, 30%), tri(2-chloroethyl) phosphate (fire retardant, 30%), sulfamethoxazole (veterinary and human antibiotic, 23%), and 4-octylphenol monoethoxylate (detergent metabolite, 19%). Although N,N-diethyltoluamide was the most frequently detected compound for this study, 14 of the 16 detections were estimated concentrations below the RL. Bisphenol A and tri(2-chloroethyl) phosphate were among the most frequently detected compounds in this study and ground water sites from Focazio et al. Eighteen human and veterinary antibiotics, five prescription drugs, and five industrial and wastewater products were not detected in any of 47 samples collected. Nine sites had no OWCs detected in the water samples collected. Of these nine sites, one was a spring located in a mixed agricultural and residential area and the remaining sites were wells located in various land use areas with well depths ranging from almost 8 m to 223 m. It is important to note that many of the target OWCs likely transform or degrade as they are transported into and through the environment as a result of metabolic and other natural attenuation processes (Boxall et al., 2004) 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 analyzed. 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.

Measured concentrations were generally low, with 87% of 137 measured detections being <1 μg/L. None of the compounds exceeded drinking water guidelines, health advisories, or aquatic-life criteria. Only 9 of 65 compounds analyzed, however, have established criteria or guidelines (Table 1). Mixtures were common with more than one compound being detected at 25 of 47 sites and 10 or more compounds detected at three sites. The maximum number of compounds at any particular site was 14 with a median of two (Fig. 2). Little is known about the potential toxicological effects of these compounds either alone or as part of a mixture.

The OWCs with the highest concentrations measured (greater than or equal to 0.5 μg/L) are not necessarily among the most frequently detected compounds (Fig. 3). For example, although several compounds such as ibuprofen and acetophenone were detected infrequently, they had maximum concentrations which exceeded 0.5 μg/L (Table 1; Fig. 3). Previous research (Kolpin et al., 2002) has also shown that compounds found with the highest frequency are not always those found in the highest concentration. The maximum concentrations of 11 OWCs exceeded 1 μg/L (Table 1). 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.

3.1.   Organic wastewater compound groups

The 65 compounds can be divided into 14 contaminant groups based on type of compound or general use category (Fig. 4A and 4B). It should be noted that the uses can vary widely for any given compound. Consequently, the tabulated use categories are presented for illustrative purposes and may not be all inclusive. The plasticizer group, consisting of 3 compounds, had the greatest frequency of detection. Although these groupings are composed of unequal numbers of compounds, it is clear that the detection frequency of any given compound group is not controlled by the number of compounds in the group (i.e. more compounds in a group do not necessarily increase the detection frequency of the group as a whole). Five groups had a detection frequency exceeding 20% and five groups had a detection frequency of less than 10% (Fig. 4A). Three groups (plasticizers, insect repellant, and detergent metabolites) contributed about 66% of the total measured concentration (Fig. 4B). As shown in previous research (Kolpin
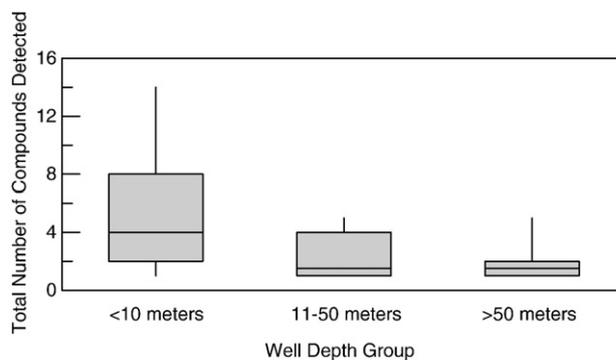

Fig. 5 – Total number of compounds detected by well depth group (<10 meters, 22 sites; 11–50 meters, 13 sites; >50 m, 11 sites).

et al., 2002), compounds found with the highest frequency are not always those found in the highest concentration.

3.2. Relations to well depth

To obtain a better understanding of OWC occurrence in groundwater, a Spearman rank correlation test was calculated to determine potential significant relations between well depth and the number of OWCs detected at each site. For this exercise, the 3 springs and 2 sumps were all given a well depth value = 0. Depth information was not available for one well sampled. Well depths have been shown previously to provide a general indication of the age of groundwater when direct measures of groundwater age are not available (Plummer and Friedman, 1999; Christenson et al., 2006). The total number of compounds detected significantly decreased (p = 0.007, rho = −0.391; Spearman rank correlation test) as well depths increased. To visually display the inverse relation between number of OWCs detected and well depth, sampling sites were divided into 3 groups based on well depth (<10 m, 22 sites; 11–50 m, 13 sites; and >50 m, 11 sites) with the number of wells in each group selected to be as equal as possible given the variance in well depth (Fig. 5). Other studies have indicated that the sources of organic contaminants are commonly near the wellhead, indicating that the shallow seals and gravel packs may provide pathways for contaminants to enter the wells (Christenson, 1998). A similar inverse relation between pesticide detections and well depth has been reported previously in groundwater (Kolpin et al., 1995).

3.3. Comparison to national stream reconnaissance

Data collected for the groundwater reconnaissance can be qualitatively compared to data collected for the national reconnaissance of OWCs in U.S. streams (Kolpin et al., 2002). This comparison is valid because the three analytical methods used for this study of groundwater were also used for the previous study of streams. Although fewer groundwater sites were sampled (47 groundwater sites compared to 139 surface water sites), the design for both studies were similar in that selected sites were known or suspected to be susceptible to contamination from human, industrial, or agricultural wastewater. Overall, fewer numbers of OWCs were detected at groundwater sites, only 35 of 65 as compared to 82 of 95 for surface water sites, with every compound detected at these groundwater sites also being detected in the streams sampled. Although similar compounds were detected in the groundwater reconnaissance, the frequency of detection of OWCs was lower for the groundwater sites compared to the stream sites. The greatest frequency of detection of any compound at groundwater sites was 35% compared to 86% at stream sites. In addition, 12 other compounds had detection frequencies greater than 35% at surface water sites. Measured concentrations of OWCs were generally low for both the groundwater and surface water reconnaissance; however, total concentrations of the OWCs at groundwater sites rarely exceeded 1 μg/L. Only 10 of 38 groundwater sites with detectable concentrations of OWCs had total concentration greater than 1 μg/L, with half of those having a total OWC concentration between 1 and 2 μg/L. The surface water reconnaissance had 111 sites with detectable concentration of OWCs, and of those 111 sites, 60% (67 sites) had a total OWC concentration >1 μg/L, with 23 sites having a total OWC concentration >10 μg/L. Although mixtures were common for both studies (53% in groundwater compared to 75% in streams), the median number of compounds detected was more than 3 times greater in streams compared to groundwater (7 versus 2 compounds). Similar findings between groundwater sites and surface water sites are described in the national reconnaissance of untreated drinking water sources (Focazio et al., 2008-this issue).

This is the first nationwide groundwater reconnaissance study to provide baseline information on the occurrence of OWCs in groundwaters across a variety of land uses, climate, and hydrogeology in the United States. These data will help to provide a better understanding of the environmental occurrence of OWCs across a range of hydrogeological settings. The results of this study will assist in determining the direction and priority of future studies on occurrence, fate and transport, and health-effects research.

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