Prepared in cooperation with the Minnesota Pollution Control Agency

Wastewater Indicators, Hormones, Sterols, Antibiotics, and Pharmaceuticals in Soil at an Agricultural Field Irrigated with Domestic Septage, Central Minnesota, September 2014

Scientific Investigations Report 2018–5100

U.S. Department of the Interior
U.S. Geological Survey

Cover. Collecting soil from an agricultural field in central Minnesota, September 2014. Photograph by Sarah M. Elliott, U.S. Geological Survey.

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Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
	Volume	
milliliter (mL)	0.033814	ounce, fluid (fl. oz)
liter (L)	0.2642	gallon (gal)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as

$$°F = (1.8 \times °C) + 32.$$

Supplemental Information

Septage application rates are given in liters per hectare (L/ha).

Concentrations of wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals are given in micrograms per kilogram (µg/kg), or milligrams per kilogram (mg/kg).

Wastewater Indicators, Hormones, Sterols, Antibiotics, and Pharmaceuticals in Soil at an Agricultural Field Irrigated with Domestic Septage, Central Minnesota, September 2014

By Sarah M. Elliott,[1] Melinda L. Erickson,[1] Aliesha L. Krall,[1] and Byron A. Adams[2]

Abstract

Treated domestic septage can be used to irrigate agricultural fields as a disposal method or as a means to reuse water. Because traditional on-site treatment systems are not designed to remove wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals, land application of septage potentially results in soil contamination. Soils were collected and analyzed from four sites in a central Minnesota agricultural field irrigated with domestic septage. Soil samples were analyzed for 111 unique contaminants, including wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals. In total, 32 contaminants were detected in soil samples. Several wastewater indicators were detected in soil, including fragrances, alkylphenols, and flame-retardants, at concentrations ranging from 1 (2,6-dimethylnaphthalene at soil site 4) to 1,550 (β-sitosterol at soil site 1) micrograms per kilogram. Relative to the number of contaminants analyzed, steroid hormones had the most frequent detections in soil samples (33 percent), and androgens were more prevalent compared to estrogens (50 and 22 percent, respectively). Androgens and estrogens were detected at concentrations ranging from 0.21 (estrone at soil site 3) to 3.9 (dihydrotestosterone at soil site 1) micrograms per kilogram. Quantifiable concentrations of antibiotics and pharmaceuticals ranged from 1.4 (carbamazepine at soil site 1) to 540 (azithromycin at soil site 3) micrograms per kilogram. Two antibiotics, ciprofloxacin and ofloxacin, were detected at concentrations above the limit of quantification (greater than 1,000 micrograms per kilogram at soil sites 2 and 3). This pilot sampling indicates that soils may be a repository for some contaminants introduced to the environment through land application of domestic septage.

Introduction

Domestic septage is a potential source of contaminants to soil when used for irrigation. Even after treatment, domestic septage is known to contain various pharmaceuticals, hormones, alkylphenols, and fragrances (Carrara and others, 2008; Katz and others, 2009; Lapworth and others, 2012). The practice of irrigating with domestic septage is an efficient reuse of water, especially in arid regions. However, the fate, transport, and ecological effects of septage-associated contaminants after application to the land surface are not well understood. Contaminants may accumulate in soils resulting in alterations to the microbial community, uptake by crops, or transport to underlying aquifers.

Unlike wastewater treatment plants that typically discharge into surface waters as a point source, agricultural lands can act as nonpoint sources of contaminants to the environment through runoff and infiltration. Herbicides, insecticides, and fungicides may be introduced to the environment through direct application to crops, whereas hormones and antibiotics may be introduced through animal excretion directly onto the land surface or through application of manure on a broad scale. Antibiotics commonly detected in stream waters and sediments in agricultural settings include sulfonamides and tetracyclines (Arikan and others, 2008; Bartelt-Hunt and others, 2011); however, most studies mainly focus on establishments that land apply or store livestock manure and less on sources such as treated domestic septage used for irrigation.

Irrigation using treated septage may accumulate contaminants in the soil (Chen and others, 2011). The affinity of organic chemicals to bind to soils depends on many factors including the physical properties of the chemical, soil carbon content, soil texture, and, in agricultural settings, field practices (Rodvang and Simpkins, 2001; Xu and others, 2009). For example, carbamazepine has a high affinity to sorb to soil with a high organic matter content, which often is present in the topmost layers of soil (Arye and others, 2011). However, depending on the type of tillage practices used, the

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organic-rich layer can be incorporated into deeper depths, affecting the chemical profile of the soil and environmental risks.

In addition to the potential ecological risks associated with applying domestic septage to land, potential human-health risks exist, such as contamination of downgradient drinking water and exposure through consumption (in agricultural settings). More than 15 million households in the United States rely on groundwater from private wells for domestic water use (U.S. Environmental Protection Agency, 2017); some of these wells are located downgradient and within the same aquifers as sites where domestic septage is applied to land. Pharmaceuticals, perfluorinated chemicals, and flame-retardants represent some of the types of chemicals that may contaminate drinking water sources (Schaider and others, 2016); furthermore, domestic wells near a septic system and in shallow, thin aquifers are more vulnerable compared to others (Verstraeten and others, 2005). Another potential human-health risk is associated with consumption of produce grown on lands irrigated with domestic septage. Specifically, carbamazepine, carbamazepine metabolites, and lamotrigine can accumulate in certain vegetables (Malchi and others, 2014; Paz and others, 2016). As further evidence, carbamazepine and its metabolites were excreted from humans that consumed produce grown on lands irrigated with reclaimed wastewater (Paltiel and others, 2016).

The quantity of septage removed from septic tanks or applied to land in Minnesota is not tracked. However, based on the current estimate of 542,000 septic systems in the State, an approximate volume of septage pumped from tanks and other sanitation devices may be as high as 275 million gallons per year (Jensen, 2015). More than 400 licensed businesses (maintainers) pump and apply septage from septic tanks, holding tanks, and other sanitation devices from domestic and nondomestic sources in the State to land. Some maintainers apply septage to land at one site, whereas others may have many sites within their service areas, bringing the possible number of land application sites scattered across the State to more than 1,000 (Minnesota Pollution Control Agency, 2006). Given the estimated volume of septage that is applied to land in Minnesota, it is important to understand potential effects to the environment. A pilot study was completed to characterize the presence of wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals in soil collected from a central Minnesota agricultural field that irrigates with treated domestic septage.

Purpose and Scope

The purpose of this report is to present an assessment on the presence of wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals in soil collected from a Minnesota agricultural field that irrigates with treated domestic septage. The assessment was based on analyses of 111 unique contaminants in four soil samples collected in September 2014. Wastewater indicator, hormone, and sterol data are available in the USGS National Water Information System and can be searched by the following station numbers: 451700093430001 (soil site 1), 451700093440001 (soil site 2), 451700093430003 (soil site 3), 451700093430002 (soil site 4; U.S. Geological Survey, 2017). Antibiotic and pharmaceutical data are provided in this report.

Study Area

The study area is a 14-hectare agricultural field in central Minnesota, northwest of the Twin Cities Metropolitan Area (fig. 1). The field contains gently rolling, glacially deposited materials that extend to a depth of nearly 30 meters. Geologic materials identified during drilling of the four on-site monitoring wells included intermittent layers of sand and clays, sandy clays and sand, and gravel; no confining layers were identified. The depth to the water table at time of well installation was 12 to 15 meters below land surface (Minnesota Department of Health, 2016). Crops alternate between soybeans and corn on an annual basis, and tillage practices consist mainly of chisel plowing to a depth of 10 to 15 centimeters after corn harvest.

The agricultural field has been irrigated with treated domestic septage for more than 40 years. The septage, consisting almost entirely of residential wastewater from septic and holding tanks, is sprayed from a tanker truck onto the soil and row crops. Septage is applied year round, mostly during the growing season and fall before winter freezeup. An average of 2.25 million liters is applied every year across the field at a rate of about 160,000 liters per hectare. About 50 percent of the septage receives a lime stabilization treatment for 30 minutes to raise the pH of the wastewater to about 12 to control pathogens before it is applied to land. Biosolids have been applied to the field previously; however, this practice has not been used for at least two decades. Other sources of irrigation water have not been applied to the field.

Methods

The methods section describes field procedures used to collect soil samples, laboratory analytical methods, and laboratory quality-assurance and quality-control samples and analyses.

Soil Sample Collection Methods

Soil samples were collected from four soil sites around the perimeter of the agricultural field (fig. 1). Soil representative of the top 15 centimeters was scooped into a stainless steel bowl using a stainless steel scoop. Once enough soil was collected to fill a 500 milliliter jar, the sample was manually

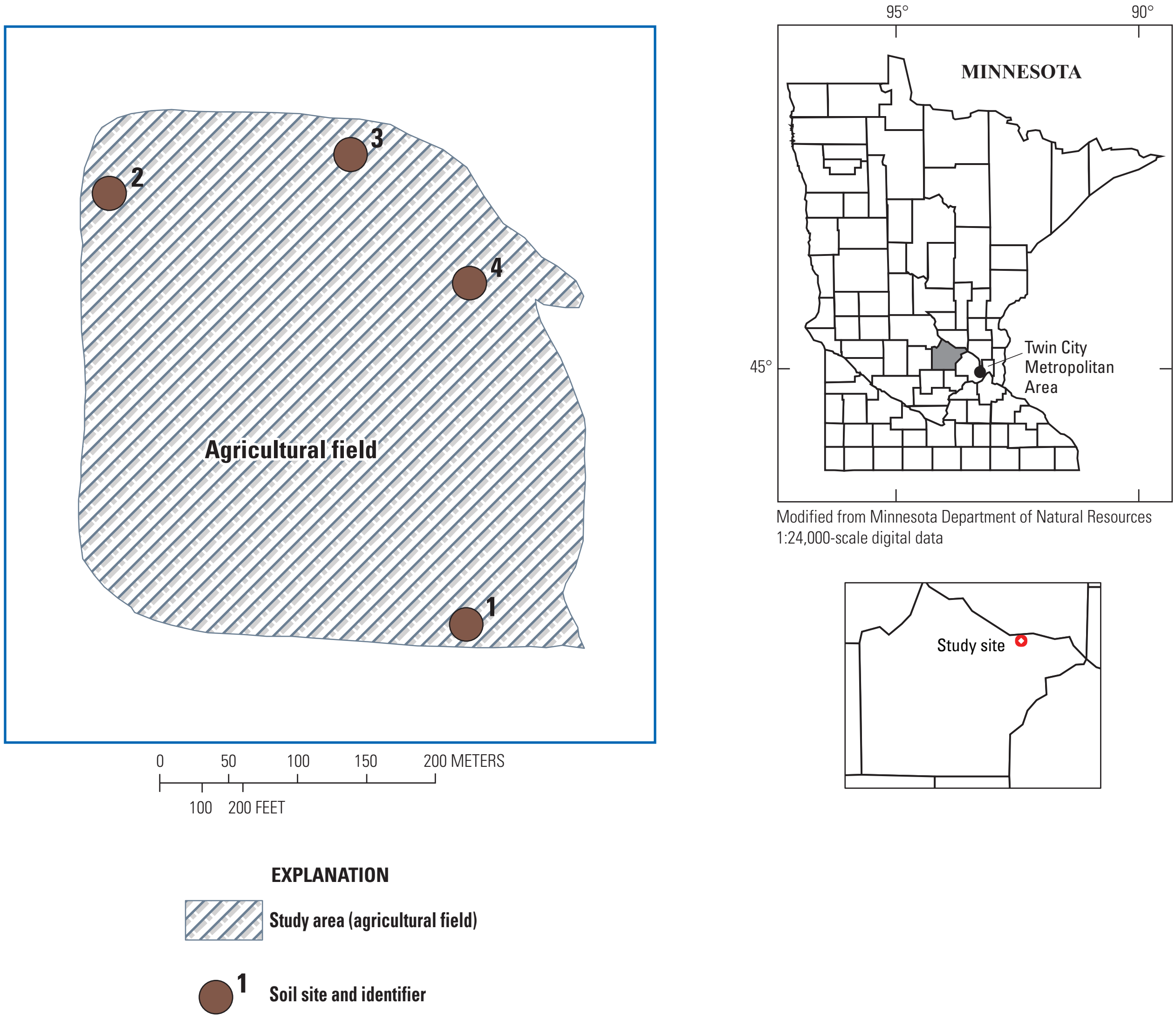


Figure 1. Location of soil sites on an agricultural field sampled for wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals, central Minnesota, September 2014.

stirred with the stainless steel scoop to homogenize it before dispensing it into a glass amber jar. The stainless steel bowl and scoop were cleaned following USGS protocols for organic chemical sampling (Wilde, 2004). Briefly, the bowl and scoop were washed with, in succession, Liquinox® + tap water solution, tap water, methanol, and organic-blank water obtained from the USGS National Water Quality Laboratory in Lakewood, Colorado, prior to initial sample collection and in between collection of soil from different sites. Soil samples were frozen at -4 degrees Celsius until shipped to the analyzing laboratories.

Laboratory Analytical Methods

Soil samples were analyzed for 60 wastewater indicators (including 3 surrogate standards) and 33 hormones and sterols (including 13 surrogate standards) at the U.S. Geological Survey National Water Quality Laboratory in Lakewood, Colorado, and 37 antibiotics and pharmaceuticals at the U.S. Geological Survey Organic Geochemistry Research Laboratory in Lawrence, Kansas. Wastewater indicators were determined by gas chromatography/mass spectrometry (Burkhardt and others, 2006), and hormones and sterols were determined by gas chromatography/tandem mass spectrometry by an adaptation of the method of Foreman and others (2012) for solid samples (Yang and others, 2012). Antibiotics and pharmaceuticals were determined by a research method previously described by Gibs and others (2013), Massey and others (2010), McKinney and others (2010), and Watanabe and others (2010). Briefly, samples were thawed and freeze-dried to remove moisture. Antibiotics and pharmaceuticals were extracted from the freeze-dried samples with a citric acid buffer adjusted to pH 6.0 with sodium hydroxide and mixed 50/50 (volume/volume) with methanol. Extracts were evaporated to about 50 percent of their original volume using a TurboVap LV nitrogen evaporator. Chemical determinations were made by using a liquid chromatography method with tandem mass spectrometry in electrospray positive and negative mode (for two compounds) with scheduled multiple reaction monitoring and negative multiple reaction monitoring modes. A complete list of antibiotics and pharmaceuticals included in analysis is provided in table 1. The reporting level for most antibiotics and pharmaceuticals was 1 microgram per kilogram (µg/kg). Reporting levels for ibuprofen and virginiamycin were 50 and 5 µg/kg, respectively.

Laboratory Quality-Assurance Methods and Results

Several quality-assurance measures were done with analyses including laboratory reagent-spike samples, laboratory-blank samples, one laboratory duplicate sample, and one matrix-spike sample in which a baked reagent-sand matrix was spiked with chemicals of interest. Additional quality assurance was provided by surrogates, isotope dilution standards, or both, which were added to all samples before analysis. Relative percent difference between the laboratory duplicate samples was calculated as:

$$RPD=(|C_1-C_2|/[(C_1+C_2)/2])\times 100 \qquad (1)$$

where

RPD is the relative percent difference;

C_1 is the measured concentration in sample 1, in micrograms per kilogram; and

C_2 is the measured concentration in sample 2, in micrograms per kilogram.

Similarly, the percent recovery of the laboratory baked reagent-sand matrix-spike sample was calculated as:

$$PR=(C_{sp}-C_{env}/C_{exp})\times 100 \qquad (2)$$

where

PR is the percent recovery,

C_{sp} is the measured concentration, in micrograms per kilogram, in the spiked environmental sample,

C_{env} is the measured concentration, in micrograms per kilogram, in the unspiked environmental sample, and

C_{exp} is the nominal concentration, in micrograms per kilogram, added to the unspiked environmental sample.

Average percent recovery of 19 wastewater indicators was below 60 percent. Additionally, 4-nonylphenol, 4-nonylphenol diethoxylate, and 4-nonylphenol monoethoxylate had a percent recovery of zero. Additionally, average percent recovery of the antibiotics doxycycline and ofloxacin was 50 percent. Measurable concentrations of 10 analytes were detected in laboratory-blank samples; most maximum concentrations ranged from 3 to 9 times less than the respective reporting levels. However, the maximum concentration of phenol, 78.2 µg/kg, detected in laboratory-blank samples was above the reporting level of 50 µg/kg. All environmental detections of phenol in soil samples were coded with a "v" to reflect elevated concentrations found in laboratory blanks and were not included in counts of detections. The percent recovery of all analytes in the laboratory matrix-spike sample varied greatly, ranging from 1.1 to 418 percent. Average laboratory matrix-spike percent recoveries for antibiotics and pharmaceuticals were less than wastewater indicator chemicals, which were less than hormones, sterols, and bisphenol A. Average percent recovery of surrogate or isotope dilution standards was often below 60 percent, suggesting that reported concentrations not corrected for isotope dilution standards potentially underestimated environmental concentrations in the samples.

Presence of Wastewater Indicators, Hormones, Sterols, Antibiotics, and Pharmaceuticals in Soil Irrigated with Domestic Septage

A total of 32 contaminants were detected among the 4 soil samples (table 2). Quantifiable concentrations ranged from 0.21 to about 2,460 µg/kg; concentrations of the antibiotics ciprofloxacin and ofloxacin were greater than the limit of quantification (1,000 µg/kg) for soil sites 2 and 3. Detectable concentrations of hormones, sterols, and wastewater indicators generally were comparable to ranges reported in bottom sediments collected from Minnesota streams and rivers downstream from wastewater treatment plant effluent discharge (fig. 2; Lee and others 2011; Elliott and others 2016). Of the detected contaminants, 56 percent were detected in at least two samples, and 37 percent were detected in all four. A greater percentage of hormones and sterols were detected (47 percent) compared to wastewater indicators (29 percent) or antibiotics and pharmaceuticals (19 percent). Given the high soil adsorption coefficients for 4-androstene-3,17-dione, *cis*-androsterone, and 3β-coprostanol, these chemicals are more likely to adsorb to soils and have lower mobility to deeper depths or groundwater and may help to explain their presence in all the soil samples.

Of the hormones analyzed, three androgens (4-androstene-3,17-dione, *cis*-androsterone, and dihydrotestosterone) and two estrogens (estrone and progesterone) were detected. Total androgen and estrogen concentrations in each soil sample ranged from 1.5 to 10.6 and 0.2 to 0.9 µg/kg, respectively. All detectable concentrations of *cis*-androsterone in this study were greater than the 75th percentile of those reported for river bottom sediments in Minnesota (fig. 2; Lee and others 2011; Elliott and others 2016). In addition to the detected biogenic estrogens, several other contaminants were

Table 1. Antibiotics and pharmaceuticals analyzed in soil samples collected from a Central Minnesota agricultural field, September 2014.

[CASRN, Chemical Abstracts Service Registry Number; µg/kg, micrograms per kilogram; USGS, U.S. Geological Survey; OGRL, Organic Geochemistry Research Laboratory; --, no data]

Chemical	CASRN[1]	Reporting level,[2] in µg/kg
Antibiotics and pharmaceuticals analyzed at USGS OGRL		
Azithromycin	117772-70-0	1
Carbamazepine	298-46-4	1
Chloramphenicol	56-75-7	1
Chlorotetracycline	64-72-2	1
Ciprofloxacin	85721-33-1	1
Doxycycline	564-25-0	1
Enrofloxacin	93106-60-6	1
Epichlorotetracycline	--	1
Epiisochlorotetracycline	--	1
Epioxytetracycline	--	1
Epitetracycline	79-85-6	1
Erythromycin	114-07-8	1
Erythromycin-H_2O	23893-13-2	1
Ibuprofen	15687-27-1	50
Isochlorotetracycline	514-53-4	1
Lincomycin	154-21-2	1
Lomefloxacin	98079-51-7	1
Norfloxacin	70458-96-7	1
Ofloxacin	82419-36-1	1
Ormetoprim	6981-18-6	1
Oxytetracycline	6153-64-6	1
Roxithromycin	80214-83-1	1
Sarafloxacin	98105-99-8	1
Sulfachloropyridazine	80-32-0	1
Sulfadiazine	68-35-9	1
Sulfadimethoxine	122-11-2	1
Sulfamethazine	57-68-1	1
Sulfamethoxazole	723-46-6	1
Sulfathiazole	72-14-0	1
Tetracycline	60-54-8	1
Total chlorotetracycline	--	1
Total erythromycin	--	1
Total oxytetracycline	--	1
Total tetracycline	--	1
Trimethoprim	738-70-5	1
Tylosin	1401-69-0	1
Virginiamycin	11006-76-1	5

[1] This report contains Chemical Abstracts Service Registry Numbers (CASRN)®, which is a Registered Trademark of the American Chemical Society. The CASRN online database provides the latest registry number information: http://www.cas.org/. Chemical Abstracts Service recommends the verification of the CASRNs through Chemical Abstracts Service Client Services^{SM}.

[2] U.S. Geological Survey Organic Geochemistry Research Laboratory.

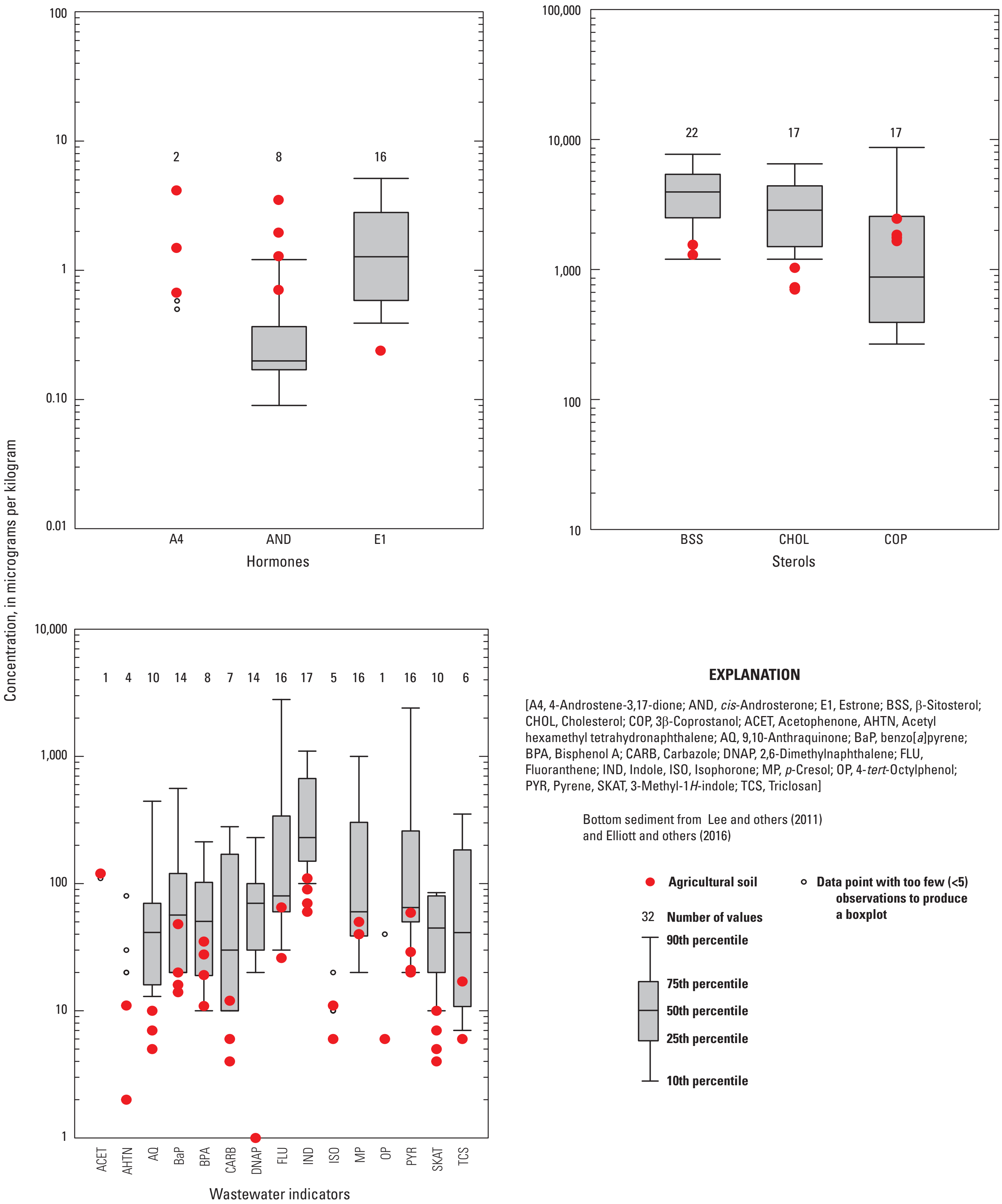
Table 2. Concentrations of wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals in soil samples collected from a Minnesota agricultural field that applies domestic septage to the land, central Minnesota, September 2014.

[Table only includes chemicals that were detected in at least one sample. See figure 1 for soil site locations. na, not applicable; nr, not reported—sample potentially affected by laboratory contamination; <, less than; E, estimated; >, greater than]

Chemical	Reporting level[1]	Sample concentration, in micrograms per kilogram			
		Soil site 1	Soil site 2	Soil site 3	Soil site 4
Wastewater indicators					
Sample weight (grams)	na	9.9	10	10	10
p-Cresol	250	50	40	40	nr
4-*tert*-Octylphenol	50	<50	<50	6	<50
BDE congener 47	50	<50	<50	3	<50
Tributyl phosphate	50	<50	10	<50	<50
3-Methyl-1*H*-indole	50	7	10	5	4
Acetyl hexamethyl tetrahydronaphthalene	50	<50	<50	11	2
Indole	100	60	110	90	70
Isophorone	50	<50	<50	11	6
Carbazole	50	<50	12	6	4
9,10-Anthraquinone	50	<50	10	7	5
Acetophenone	150	nr	nr	120	nr
2,6-Dimethylnaphthalene	50	<50	<50	<50	1
Benzo[*a*]pyrene	50	16	48	14	20
Fluoranthene	50	26	65	<50	<50
Pyrene	50	21	59	20	29
Triclosan	50	<50	nr	17	6
Bisphenol A[2]	50	<50	13	nr	nr
3β-Coprostanol[2]	500	1,140	1,470	nr	nr
β-Sitosterol	500	1,550	1,300	<500	<500
Hormones, sterols, and bisphenol A					
Sample weight (grams)	na	4.99	4.83	4.97	4.98
4-Androstene-3,17-dione	0.1	3.65	1.31	0.59	<0.43
cis-Androsterone	0.25	3.08	1.72	1.13	0.62
Dihydrotestosterone	0.1	3.9	1.82	1.13	0.9
Estrone	0.1	<0.36	<0.34	<0.20	0.21
Progesterone	0.5	<1.05	<1.45	0.91	<1.01
Bisphenol A[2]	10	E 35	E 27.7	E 10.9	E 36.3
3β-Coprostanol[2]	50	E 1,850	E 2,460	E 1,655	1,352
Cholesterol	50	702	E 1,031	731	326
Antibiotics and pharmaceuticals					
Sample weight (grams)	na	1	1	1	1
Carbamazepine	1.0	1.4	4.3	6.3	3.9
Norfloxacin	1.0	<1	10	24	<1
Ciprofloxacin	1.0	380	>1,000	>1,000	540
Ofloxacin	1.0	400	>1,000	>1,000	310
Epitetracycline	1.0	<1	3.1	5.7	1.8
Tetracycline	1.0	<1	3.3	6.6	2.2
Azithromycin	1.0	<1	180	540	<1

[1] Determined by the U.S. Geological Survey National Water Quality Laboratory or Organic Geochemistry Research Laboratory.

[2] Analyzed by two different analytical methods.



[A4, 4-Androstene-3,17-dione; AND, *cis*-Androsterone; E1, Estrone; BSS, β-Sitosterol; CHOL, Cholesterol; COP, 3β-Coprostanol; ACET, Acetophenone, AHTN, Acetyl hexamethyl tetrahydronaphthalene; AQ, 9,10-Anthraquinone; BaP, benzo[*a*]pyrene; BPA, Bisphenol A; CARB, Carbazole; DNAP, 2,6-Dimethylnaphthalene; FLU, Fluoranthene; IND, Indole, ISO, Isophorone; MP, *p*-Cresol; OP, 4-*tert*-Octylphenol; PYR, Pyrene, SKAT, 3-Methyl-1*H*-indole; TCS, Triclosan]

Figure 2. Comparison of concentrations for wastewater indicators, hormones, and sterols detected in a central Minnesota agricultural soil with bottom sediments collected from receiving streams, downstream from effluent inputs from wastewater treatment plants. Data for bottom sediments are from Elliott and others (2016) and Lee and others (2011).

detected that exhibit estrogenic properties: 4-*tert*-octylphenol, tributyl phosphate, acetyl hexamethyl tetrahydronaphthalene, and bisphenol A. Although these contaminants have relatively weak estrogenic properties by themselves, the additive estrogenicity of weak estrogens in a mixture may increase the effective estrogenicity of the soil (Silva and others, 2002).

Six antibiotics and one anticonvulsant were detected at least once among all soil samples. Carbamazepine, ciprofloxacin, and ofloxacin were detected in all soil samples; the sum of concentrations ranged from 201 to greater than 2,500 µg/kg per sample. Two fluoroquinolones (ciprofloxacin and oflaxacin) were present in all four soil samples at concentrations ranging from 310 to greater than 1,000 µg/kg. Azithromycin (antibiotic) was present in two soil samples at concentrations of 180 and 540 µg/kg. Ciprofloxacin and ofloxacin tend to have high sorption to soils, even soils with low organic carbon and high sand contents (Leal and others, 2013; Peng and others, 2014). Additionally, ofloxacin can inhibit microbial growth by more than 50 percent at concentrations of 5,000 µg/kg (Peng and others, 2014). Carbamazepine is detected frequently in soils from fields irrigated with wastewater at concentrations similar to those observed in this study (Durán-Alvarez and others, 2009; Kinney and others, 2006). Compared to other studies, soil concentrations of tetracycline in this study are relatively low (2–6 compared to 3–20 µg/kg; Chen and others, 2011).

Fluoroquinolones and other antibiotics persist in agricultural soils and earthworms amended with biosolids (which often contain the same contaminants as septage) with the potential for accumulation over time (Golet and others, 2003; Kinney and others, 2008). The presence of antibiotics in soils also may lead to shifts in microbial communities dominated by resistant organisms (Thiele-Bruhn, 2003) or favor particular bacteria, altering the microbial activity of soils (Córdova-Kreylos and Scow, 2007). Microbial abundance and diversity can shift when exposed to ciprofloxacin concentrations as low as 200 µg/kg (Girardi and others, 2011). Ciprofloxacin concentrations in the soil in the current study were all greater than 200 µg/kg; two were an order of magnitude greater, indicating the potential for an altered microbial community.

Hydraulic factors such as overlying soil properties and degree of aquifer confinement are important factors in the transport of organic contaminants to groundwater (Lapworth and others 2012); for example, carbamazepine is more likely to sorb to soils with high clay or organic matter content (Arye and others, 2011). The soil organic matter content was not analyzed, but the Natural Resources Conservation Service provides estimates of less than 2 percent organic matter at sites 1–3 and 6 percent at site 4 (Natural Resources Conservation Service, U.S. Department of Agriculture, 2017). Sorption to soils has been an important mechanism for removal of contaminants such as carbamazepine and sulfamethoxazole from water (Martínez-Hernández and others, 2016); in fact, carbamazepine was detected in all the soil samples (table 2).

Summary

Traditional on-site wastewater treatment systems are not designed to remove wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals, yet treated domestic septage can be used to irrigate agricultural fields. Soil collected from a central Minnesota agricultural field irrigated with domestic septage was analyzed for a variety of contaminants composed of 60 wastewater indicators (including 3 surrogate standards) and 33 hormones and sterols (including 13 surrogate standards) at the U.S. Geological Survey National Water Quality Laboratory in Lakewood, Colorado, and 37 antibiotics and pharmaceuticals at the U.S. Geological Survey Organic Geochemistry Research Laboratory in Lawrence, Kansas. A total of 32 contaminants were detected among the samples collected from four soil sites. In total, 19 wastewater indicators were detected at concentrations ranging from 1 (2,6-dimethylnaphthalene at soil site 4) to 1,550 (β-sitosterol at soil site 1) micrograms per kilogram (µg/kg). Considering the number of individual compounds analyzed within each chemical group (wastewater indicators; hormones, sterols, and bisphenol A; and antibiotics and pharmaceuticals), hormones and sterols were detected the most frequently (47 percent). Quantifiable concentrations of androgens and estrogens ranged from 0.21 (estrone at soil site 3) to 3.9 (dihydrotestosterone at soil site 1) µg/kg, and androgens were more prevalent than estrogens. A total of seven antibiotics and pharmaceuticals were detected at concentrations ranging from 1.4 µg/kg (carbamazepine at soil site 1) to above the limit of quantification, 1,000 µg/kg (ciprofloxacin and ofloxacin at soil sites 2 and 3). Results from this pilot sampling indicate that contaminants may be accumulating in soil that is lacking a high organic content. Further research needs to be done to assess fate and transport of wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals through the soil column that may potentially reach groundwater, as well as effect soil health.

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Appendix 1

The appendix consists of one table listing wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals analyzed (table 1.1), and five tables summarizing laboratory quality-assurance data for reagent-spike samples (table 1.2), laboratory-blank samples (table 1.3), duplicate samples (table 1.4), matrix-spike samples (table 1.5), and surrogate and isotope dilution standards (table 1.6).

Table 1.1 Wastewater indicators, hormones, and sterols analyzed in soil samples collected from an agricultural field, central Minnesota, September 2014.

[CASRN, Chemical Abstracts Service Registry Number; µg/kg, micrograms per kilogram; USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory; --, no data; na, not applicable; d, deuterium]

Chemical	CASRN[1]	Reporting level,[2] in µg/kg
Wastewater indicators analyzed at USGS NWQL		
1,4-Dichlorobenzene	106-46-7	100
1-Methylnaphthalene	90-12-0	100
2,6-Dimethylnaphthalene	581-42-0	100
2-Methylnaphthalene	91-57-6	100
3β-Coprostanol	360-68-9	1,000
3-Methyl-1*H*-indole (Skatole)	83-34-1	100
3-*tert*-Butyl-4-hydroxyanisole (BHA)	121-00-6	300
4-Cumylphenol	599-64-4	100
4-*n*-Octylphenol	1806-26-4	100
4-Nonylphenol (sum of all isomers)	--	1,500
4-Nonylphenol diethoxylate (sum of all isomers; NP2EO)	20427-84-3	2,000
4-Nonylphenol monoethoxylate (sum of all isomers; NP1EO)	68412-54-4	1,000
4-*tert*-Octylphenol	140-66-9	100
4-*tert*-Octylphenol diethoxylate (OP2EO)	2315-61-9	100
4-*tert*-Octylphenol monoethoxylate, (OP1EO)	2315-67-5	500
9,10 Anthraquinone	84-65-1	100
Acetophenone	98-86-2	300
Acetyl hexamethyl tetrahydro naphthalene (AHTN)	21145-77-7	100
Anthracene	120-12-7	100
Atrazine	1912-24-9	200
BDE congener 47	5436-43-1	100
Benzo[*a*]pyrene	50-32-8	100
Benzophenone	119-61-9	100
β-Sitosterol	83-46-5	1,000
β-Stigmastanol	19466-47-8	1,000
Bis(2-ethylhexyl) phthalate	117-81-7	500
Bisphenol A	80-05-7	100
Bromacil	314-40-9	1,000
Camphor	76-22-2	100
Carbazole	86-74-8	100
Chlorpyrifos	2921-88-2	100
Cholesterol	57-88-5	500
Diazinon	333-41-5	100
Diethyl phthalate	84-66-2	200
D-Limonene	5989-27-5	100
Fluoranthene	206-44-0	100
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)	1222-05-5	100
Indole	120-72-9	200
Isoborneol	124-76-5	100
Isophorone	78-59-1	100

Table 1.1 Wastewater indicators, hormones, and sterols analyzed in soil samples collected from an agricultural field, central Minnesota, September 2014.—Continued

[CASRN, Chemical Abstracts Service Registry Number; µg/kg, micrograms per kilogram; USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory; --, no data; na, not applicable; d, deuterium]

Chemical	CASRN[1]	Reporting level,[2] in µg/kg
Wastewater indicators analyzed at USGS NWQL—Continued		
Isopropylbenzene	98-82-8	200
Isoquinoline	119-65-3	200
Menthol	89-78-1	100
Metolachlor	51218-45-2	100
Naphthalene	91-20-3	100
N,N-Diethyl-*m*-toluamide (DEET)	134-62-3	200
p-Cresol	106-44-5	500
Phenanthrene	85-01-8	100
Phenol	108-95-2	100
Prometon	1610-18-0	100
Pyrene	129-00-0	100
Tributyl phosphate	126-73-8	100
Triclosan	3380-34-5	100
Triphenyl phosphate	115-86-6	100
Tris(2-butoxyethyl) phosphate	78-51-3	300
Tris(2-chloroethyl) phosphate	115-96-8	200
Tris(dichloroisopropyl) phosphate	13674-87-8	200
Bisphenol A-d_{14} (surrogate)	--	na
Decafluorobiphenyl (surrogate)	434-90-2	na
Fluoranthene-d_{10} (surrogate)	93951-69-0	na
Steroid hormones, sterols, and bisphenol A analyzed at USGS NWQL		
11-Ketotestosterone	564-35-2	0.52
17α-Estradiol	57-91-0	0.2
17α-Ethynylestradiol	57-63-6	0.2
17β-Estradiol	50-28-2	0.4
3β-Coprostanol	360-68-9	50
4-Androstene-3,17-dione	63-05-8	0.5
Bisphenol A	80-05-7	20
Cholesterol	57-88-5	120
cis-Androsterone	53-41-8	0.5
Dihydrotestosterone	521-18-6	1
Epitestosterone	481-30-1	1
Equilenin	517-09-9	0.52
Equilin	474-86-2	4
Estriol	50-27-1	0.52
Estrone	53-16-7	0.5
Mestranol	72-33-3	0.4
Norethindrone	68-22-4	0.4
Progesterone	57-83-0	3
Testosterone	58-22-0	0.4

Table 1.1 Wastewater indicators, hormones, and sterols analyzed in soil samples collected from an agricultural field, central Minnesota, September 2014.—Continued

[CASRN, Chemical Abstracts Service Registry Number; µg/kg, micrograms per kilogram; USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory; --, no data; na, not applicable; d, deuterium]

Chemical	CASRN[1]	Reporting level,[2] in µg/kg
Steroid hormones, sterols, and bisphenol A analyzed at USGS NWQL—Continued		
trans-Diethylstilbestrol	56-53-1	0.33
16-Epiestriol-*2,4*-d_2 (surrogate)	366495-94-5	na
17α-Ethynylestradiol-*2,4,16,16*-d_4 (surrogate)	350820-06-3	na
17β-Estradiol-*13,14,15,16,17,18*-$^{13}C_6$ (surrogate)	--	na
Bisphenol A-d_{16} (surrogate)	96210-87-6	na
Cholesterol-*25,26,26,26,27,27,27*-d_7 (surrogate)	83199-47-7	na
cis-Androsterone-*16,16*-d_2(surrogate)	89685-22-3	na
Estriol-*2,4,16,17*-d_4 (surrogate)	--	na
Estrone-*13,14,15,16,17,18*-$^{13}C_6$(surrogate)	--	na
Medroxyprogesterone-d_3 (surrogate)	162462-69-3	na
Mestranol-*2,4,16,16*-d_4 (surrogate)	--	na
Nandrolone-*16,16,17*-d_3 (surrogate)	120813-22-1	na
Progesterone-*2,3,4*-$^{13}C_3$ (surrogate)	327048-87-3	na
trans-Diethyl-*1,1,1’,1’*-d_4-stilbesterol-*3,3’,5,5’*-d_4 (surrogate)	--	na

[1] This report contains Chemical Abstracts Service Registry Numbers (CASRN)®, which is a Registered Trademark of the American Chemical Society. The CASRN online database provides the latest registry number information: http://www.cas.org/. Chemical Abstracts Service recommends the verification of the CASRNs through Chemical Abstracts Service Client Services^{SM}.

[2] Determined by the U.S. Geological Survey National Water Quality Laboratory.

Table 1.2 Recovery of method analytes in laboratory reagent-spike samples analyzed at the U.S. Geological Survey National Water Quality Laboratory and Organic Geochemistry Research Laboratory.

[CASRN, Chemical Abstracts Service Registry Number; USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory; m, highly variable chemical using this method, questionable precision and (or) accuracy; E, estimated value; v, chemical detected in laboratory blank; --, no data; Organic Geochemistry Research Laboratory]

Chemical	CASRN[1]	Percent recovery	
		Analyzed March 3, 2015	Analyzed February 19, 2015
Wastewater indicator compounds analyzed at USGS NWQL			
1,4-Dichlorobenzene	106-46-7	61.6 m	64.9 m
1-Methylnaphthalene	90-12-0	69	89
2,6-Dimethylnaphthalene	581-42-0	73	93
2-Methylnaphthalene	91-57-6	67	90
3β-Coprostanol	360-68-9	0 m	E105 vm
3-Methyl-1*H*-indole (Skatole)	83-34-1	83	98
3-*tert*-Butyl-4-hydroxy anisole (BHA)	121-00-6	19 m	12 m
4-Cumylphenol	599-64-4	105	117
4-*n*-Octylphenol	1806-26-4	94	90
4-Nonylphenol (sum of all isomers)	--	0 m	0 m
4-Nonylphenol diethoxylate (NP2EO, all isomers)	20427-84-3	0 m	0 m
4-Nonylphenol monoethoxylate (NP1EO, all isomers)	68412-54-4	0 m	E154 vm
4-*tert*-Octylphenol	140-66-9	87	102
4-*tert*-Octylphenol diethoxylate (OP2EO)	2315-61-9	E126 vm	E119 m
4-*tert*-Octylphenol monoethoxylate (OP1EO)	2315-67-5	E60 vm	E64 vm
Acetophenone	98-86-2	E63 vm	108 m
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	21145-77-7	108	118
Anthracene	120-12-7	E91 vm	102
Anthraquinone	84-65-1	41	84
Atrazine	1912-24-9	62	126
BDE congener 47	5436-43-1	108 m	111 m
Benzo[*a*]pyrene	50-32-8	97	112
Benzophenone	119-61-9	E91 v	E112 v
β-Sitosterol	83-46-5	0 m	0 m
β-Stigmastanol	19466-47-8	0 m	0 m
Bis(2-ethylhexyl) phthalate	117-81-7	E126 v	E104 v
Bisphenol A	80-05-7	E74 m	62 m
Bromacil	314-40-9	48 m	105 m
Camphor	76-22-2	51.4	101
Carbazole	86-74-8	100	119
Chlorpyrifos	2921-88-2	62 m	52 m
Cholesterol	57-88-5	0 m	0 m
Diazinon	333-41-5	2	2
Diethyl phthalate	84-66-2	0	E58 v
D-Limonene	5989-27-5	E53 vm	60 m
Fluoranthene	206-44-0	E103 v	114
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)	1222-05-5	109	113
Indole	120-72-9	62	64

Table 1.2 Recovery of method analytes in laboratory reagent-spike samples analyzed at the U.S. Geological Survey National Water Quality Laboratory and Organic Geochemistry Research Laboratory.—Continued

[CASRN, Chemical Abstracts Service Registry Number; USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory; m, highly variable chemical using this method, questionable precision and (or) accuracy; E, estimated value; v, chemical detected in laboratory blank; --, no data; Organic Geochemistry Research Laboratory]

Chemical	CASRN[1]	Percent recovery	
		Analyzed March 3, 2015	Analyzed February 19, 2015
Wastewater indicator compounds analyzed at USGS NWQL—Continued			
Isoborneol	124-76-5	0 m	0 m
Isophorone	78-59-1	36 m	75 m
Isopropylbenzene	98-82-8	0 m	0 m
Isoquinoline	119-65-3	23 m	86 m
Menthol	89-78-1	54 m	108 m
Metolachlor	51218-45-2	92	119
Naphthalene	91-20-3	75	93
N,N-Diethyl-*m*-toluamide (DEET)	134-62-3	56 m	118 m
p-Cresol	106-44-5	59	113
Phenanthrene	85-01-8	96	105
Phenol	108-95-2	0 m	--
Prometon	1610-18-0	0 m	104 m
Pyrene	129-00-0	102	112
Tributyl phosphate	126-73-8	E79	117
Triclosan	3380-34-5	90	120
Triphenyl phosphate	115-86-6	41 m	22 m
Tris(2-butoxyethyl) phosphate	78-51-3	17 m	120 m
Tris(2-chloroethyl) phosphate	115-96-58	43 m	65 m
Tris(dichloroisopropyl) phosphate	13674-87-8	42 m	17 m
Hormones, sterols, and bisphenol A analyzed at USGS NWQL			
11-Ketotestosterone	564-35-2	91	106
17α-Estradiol	57-91-0	111	110
17α-Ethynylestradiol	57-63-6	100	104
17β-Estradiol	50-28-2	107	104
3β-Coprostanol	360-68-9	107	104
4-Androstene-3,17-dione	63-05-8	113	109
Bisphenol A	80-05-7	E135	E130
Cholesterol	57-88-5	113	109
cis-Androsterone	53-41-8	101	98
Dihydrotestosterone	521-18-6	108	108
Epitestosterone	481-30-1	116	113
Equilenin	517-09-9	114	104
Equilin	474-86-2	100 m	88 m
Estriol	50-27-1	E95	109
Estrone	53-16-7	113	107
Mestranol	72-33-3	99	105
Norethindrone	68-22-4	116	98

Table 1.2 Recovery of method analytes in laboratory reagent-spike samples analyzed at the U.S. Geological Survey National Water Quality Laboratory and Organic Geochemistry Research Laboratory.—Continued

[CASRN, Chemical Abstracts Service Registry Number; USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory; m, highly variable chemical using this method, questionable precision and (or) accuracy; E, estimated value; v, chemical detected in laboratory blank; --, no data; Organic Geochemistry Research Laboratory]

Chemical	CASRN[1]	Percent recovery	
		Analyzed March 3, 2015	Analyzed February 19, 2015
Hormones, sterols, and bisphenol A analyzed at USGS NWQL—Continued			
Progesterone	57-83-0	105 m	97 m
Testosterone	58-22-0	108	101
trans-Diethylstilbestrol	58-63-1	E123	E111
Antibiotics and pharmaceuticals analyzed at USGS OGRL			
Azithromycin	117772-70-0	100	--
Carbamazepine	298-46-4	96	--
Chloramphenicol	56-75-7	82	--
Ciproflaxacin	85721-33-1	69	--
Doxycycline	564-25-0	50	--
Enrofloxacin	93106-60-6	60	--
Erythromycin	114-07-8	67	--
Erythromycin-H_2O	23893-13-2	83	--
Ibuprofen	15687-27-1	89	--
Lincomycin	154-21-2	87	--
Lomefloxacin	82419-36-1	120	--
Norfloxacin	70458-96-7	69	--
Ofloxacin	82419-36-1	50	--
Ormetoprim	6981-18-6	98	--
Roxithromycin	80214-83-1	91	--
Sarafloxacin	98105-99-8	130	--
Sulfachloropyridazine	80-32-0	82	--
Sulfadiazine	68-35-9	100	--
Sulfadimethoxine	122-11-2	70	--
Sulfamethazine	57-68-1	91	--
Sulfamethoxazole	723-46-6	90	--
Sulfathiazole	72-14-0	87	--
Total chlorotetracycline	--	81	--
Total oxytetracycline	--	110	--
Total tetracycline	--	100	--
Trimethoprim	738-70-5	100	--
Tylosin	1401-69-0	85	--
Virginiamycin	11006-76-1	82	--

[1] This report contains Chemical Abstracts Service Registry Numbers (CASRN)®, which is a Registered Trademark of the American Chemical Society. The CASRN online database provides the latest registry number information: http://www.cas.org/. Chemical Abstracts Service recommends the verification of the CASRNs through Chemical Abstracts Service Client Services^{SM}.

Table 1.3 Concentrations of wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals in laboratory-blank soil samples analyzed at the U.S. Geological Survey National Water Quality Laboratory.

[Table only includes chemicals that were detected in blank samples; µg/kg, micrograms per kilogram]

Chemical	Reporting level, in µg/kg	Maximum concentration, in µg/kg
4-*tert*-Octylphenol diethoxylate (OP2EO)	100	14.6
Anthracene	100	10.5
Benzophenone	100	5.5
β-Sitosterol	1,000	79
β-Stigmastanol	1,000	51
Cholesterol	500	56
D-Limonene	100	5.9
Fluoranthene	100	12
Phenanthrene	100	9.2
Phenol	100	78.2

Table 1.4 Relative percent difference between environmental (U.S. Geological Survey station 451700093430001, sampled September 8, 2014) and laboratory duplicate samples analyzed at the U.S. Geological Survey Organic Geochemistry Laboratory.

Chemical	Relative percent difference
Azithromycin	0
Carbamazepine	3
Ciproflaxacin	20
Norfloxacin	0
Ofloxacin	0
Total tetracycline	16

Table 1.5 Percent recovery of study analytes in a laboratory matrix-spike soil sample (U.S. Geological Survey station 451700093430001, sampled September 8, 2014).

[USGS, U.S. Geological Survey; OGRL, Organic Geochemistry Research Laboratory; --, no data—not included in spiked sample; NWQL, National Water Quality Laboratory]

Chemical	Percent recovery
Antibiotics and pharmaceuticals analyzed at the USGS OGRL	
Azithromycin	3.2
Carbamazepine	93
Chloramphenicol	100
Ciproflaxacin	1.8
Doxycycline	73
Enrofloxacin	1.1
Ibuprofen	100
Lincomycin	88
Lomefloxacin	15
Norfloxacin	2.0
Ofloxacin	2.3
Ormetoprim	87
Roxithromycin	66
Sarafloxacin	16
Sulfachloropyridazine	89
Sulfadiazine	86
Sulfadimethoxine	90
Sulfamethazine	94
Sulfamethoxazole	94
Sulfathiazole	86
Total chlorotetracycline	94
Total erythromycin	44
Total oxytetracycline	45
Total tetracycline	71
Trimethoprim	87
Tylosin	66
Virginiamycin	--
Wastewater indicator compounds analyzed at the USGS NWQL	
1,4-Dichlorobenzene	56
1-Methylnaphthalene	92
2,6-Dimethylnaphthalene	95
2-Methylnaphthalene	96
3-Methyl-1*H*-indole (Skatole)	26
3β-Coprostanol	80
3-*tert*-Butyl-4-hydroxy anisole (BHA)	--
4-Cumylphenol	87
4-*n*-Octylphenol	65
4-Nonylphenol (sum of all isomers)	114
4-Nonylphenol diethoxylate (NP2EO, all isomers)	161
4-Nonylphenol monoethoxylate (NP1EO, all isomers)	190

Table 1.5 Percent recovery of study analytes in a laboratory matrix-spike soil sample (U.S. Geological Survey station 451700093430001, sampled September 8, 2014).—Continued

[USGS, U.S. Geological Survey; OGRL, Organic Geochemistry Research Laboratory; --, no data—not included in spiked sample; NWQL, National Water Quality Laboratory]

Chemical	Percent recovery
Wastewater indicator compounds analyzed at the USGS NWQL—Continued	
4-*tert*-Octylphenol	255
4-*tert*-Octylphenol diethoxylate (OP2EO)	67
4-*tert*-Octylphenol monoethoxylate (OP1EO)	70
Acetophenone	37
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	95
Anthracene	130
Anthraquinone	139
Atrazine	109
BDE congener 47	74
Benzo[*a*]pyrene	132
Benzophenone	137
β-Sitosterol	42
β-Stigmastanol	61
Bis(2-ethylhexyl) phthalate	87
Bisphenol A	62
Bromacil	69
Camphor	83
Carbazole	137
Chlorpyrifos	59
Cholesterol	122
Diazinon	--
Diethyl phthalate	87
D-Limonene	25
Fluoranthene	245
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)	80
Indole	75
Isoborneol	--
Isophorone	25
Isopropylbenzene	--
Isoquinoline	50
Menthol	79
Metolachlor	130
Naphthalene	100
N,N-Diethyl-*m*-toluamide (DEET)	50
p-Cresol	12
Phenanthrene	180
Prometon	89
Pyrene	220
Tributyl phosphate	145
Triclosan	122

Table 1.5 Percent recovery of study analytes in a laboratory matrix-spike soil sample (U.S. Geological Survey station 451700093430001, sampled September 8, 2014).—Continued

[USGS, U.S. Geological Survey; OGRL, Organic Geochemistry Research Laboratory; --, no data—not included in spiked sample; NWQL, National Water Quality Laboratory]

Chemical	Percent recovery
Wastewater indicator compounds analyzed at the USGS NWQL—Continued	
Triphenyl phosphate	66
Tris(2-butoxyethyl) phosphate	130
Tris(2-chloroethyl) phosphate	31
Tris(dichloroisopropyl) phosphate	62
Hormones, sterols, and bisphenol A analyzed at the USGS NWQL	
11-Ketotestosterone	213
17α-Estradiol	--
17α-Ethynylestradiol	116
17β-Estradiol	--
3β-Coprostanol	116
4-Androstene-3,17-dione	418
Bisphenol A	103
Cholesterol	124
cis-Androsterone	98
Dihydrotestosterone	136
Epitestosterone	207
Equilenin	--
Equilin	60
Estriol	--
Estrone	141
Mestranol	102
Norethindrone	249
Progesterone	107
Testosterone	158

Table 1.6 Percent recovery of surrogate and isotope dilution standards analyzed at the U.S. Geological Survey National Water Quality Laboratory.

Standard	Percent recovery at U.S. Geological Survey station, sampled September 8, 2014			
	451700093430001	**451700093440001**	**451700093430003**	**451700093430002**
Wastewater indicator surrogate standards				
Bisphenol A-d_{14}	10	20	20	40
Decafluorobiphenyl	24	17	36	25
Fluoranthene-d_{10}	62	65	83	84
Steroid hormone, sterol, and bisphenol A isotope dilution standards				
16-Epestriol-*2,4*-d_2	6	19	36	29
17α-Ethynylestradiol-*2,4,16,16*-d_4	6	28	48	43
17β-Estradiol-*13,14,15,16,17,18*-$^{13}C_6$	3	18	34	36
Bisphenol A-d_{16}	5	18	40	28
Cholesterol-*25,26,26,26,27,27,27*-d_7	33	23	26	59
cis-Androsterone-*16,16*-d_2	94	43	57	18
Diethyl-*1,1,1’,1’*-d_4-stilbestrol-*3,3’,5,5’*-d_4	1	3	5	2
Estriol-*2,4,16,17*-d_4	3	10	10	3
Estrone-*13,14,15,16,17,18*-$^{13}C_6$	8	35	53	48
Medroxyprogesterone-d_3	27	59	88	94
Mestranol-*2,4,16,16*-d_4	47	54	67	77
Nandrolone-*16,16,17*-d_3	19	40	66	87
Progesterone-*2,3,4*-$^{13}C_3$	16	42	58	53
trans-Diethyl-*1,1,1’1’*-d_4-stilbestrol-*3,3’,5,5’*-d_4	2	3	5	1

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