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Chemicals of Emerging Concern in Water and Bottom Sediment in the Great Lakes Basin, 2012—Collection Methods, Analytical Methods, Quality Assurance, and Study Data

Data Series 910

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

Cover photograph. U.S. Geological Survey hydrologic technician and U.S. Fish and Wildlife Service biologist preparing to collect a bed-sediment sample on the Saginaw River near Essexville, Michigan. Photograph by Lindsay Hastings, U.S. Geological Survey, 2014.

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U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2015

Suggested citation:
Lee, K.E., Langer, S.K., Menheer, M.A., Hansen, D.S., Foreman, W.T., Furlong, E.T., Jorgenson, Z.G., Choy, S.J., Moore, J.N., Banda, JoAnn, and Gefell, D.J., 2015, Chemicals of emerging concern in water and bottom sediment in the Great Lakes Basin, 2012—Collection methods, analytical methods, quality assurance, and study data: U.S. Geological Survey Data Series 910, 14 p., http://dx.doi.org/10.3133/ds910.

ISSN 2327-638X (online)

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(Available at http://pubs.usgs.gov/ds/0910/downloads/tables1-6.xlsx)

Conversion Factors

International System of Units to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
	Volume	
liter (L)	0.2642	gallon (gal)
milliliter (mL)	0.0338	ounce, fluid (fl. oz)
	Flow	
liters per minute	0.2642	gallons per minute
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
nanogram (ng)	0.00000000003527	ounce, avoirdupois (oz)
	Pressure	
megapascal (MPa)	145.0	pounds per square inch (lb/in^2)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
°F=(1.8×°C)+32.

Datum

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L), micrograms per liter (µg/L), or nanograms per liter (ng/L). Concentrations of chemical constituents in bottom sediment are given in micrograms per kilogram (µg/kg) or nanograms per gram (ng/g).

Abbreviations

<	less than
a	value was extrapolated above highest calibration method range or instrument linear range
b	value was extrapolated below highest calibration method range or instrument linear range
®	registered trademark
ASE	accelerated solvent extraction
BHA	3-*tert*-butyl-4-hydroxy anisole
CEC	chemicals of emerging concern
E	estimated
EAC	endocrine-active chemical
EPA	U.S. Environmental Protection Agency
HPLC/MS/MS	high-performance liquid chromatography/tandem mass spectrometry
GC/MS/MS	gas chromatography/tandem mass spectrometry
IDS	isotope dilution standard
LRL	laboratory reporting level
mPR	mean percent recovery
n	value is below laboratory reporting level and above the long-term method detection level
ng	nanogram
NR	not reported
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
PLE	pressurized liquid extraction
PR	percent recovery
RPD	relative percent difference

SPE	solid-phase extraction
t	value is below the long-term method detection level
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
v	value that was flagged because concentration in the environmental sample was greater than three times, but less than 10 times the concentration in laboratory blank samples
v/v	volume per volume
WLSSD	Western Lake Sanitary Sewer District
WWTP	wastewater-treatment plant
x	values that might have additional bias because concentrations in the environmental sample were from 25 to 100 percent of the fortified amount

Chemicals of Emerging Concern in Water and Bottom Sediment in the Great Lakes Basin, 2012—Collection Methods, Analytical Methods, Quality Assurance, and Study Data

By Kathy E. Lee,[1] Susan K. Langer,[1] Michael A. Menheer,[1] Donald S. Hansen,[1] William T. Foreman,[1] Edward T. Furlong,[1] Zachary G. Jorgenson,[2] Steven J. Choy,[2] Jeremy N. Moore,[2] JoAnn Banda,[2] and Daniel J. Gefell[2]

Abstract

In synoptic surveys of surface-water quality across the United States, a large group of organic chemicals associated with agricultural, household, and industrial waste have been detected. These chemicals are referred to collectively as chemicals of emerging concern (CECs) and include prescription drugs and antibiotics, over-the-counter medications, reproductive hormones, personal-care products, detergent metabolites, and flame retardants.

The U.S. Geological Survey (USGS) collaborated with the U.S. Fish and Wildlife Service and the U.S. Environmental Protection Agency on a study to identify the presence of CECs in water and bottom-sediment samples collected during 2012 at 66 sites throughout the Great Lakes Basin. The 2012 effort is part of a long-term study that was initiated in 2010.

The purposes of this report are to document the collection and analytical methods, provide the quality-assurance data and analyses, and provide the water and bottom-sediment data for this study of CECs in the Great Lakes Basin for 2012. A previous report documents data collected during 2010 and 2011. The methods used for chemical analyses were identical between the 2010–11 and 2012 studies, with the exception that a method to determine nontarget chemicals was used during 2010–11. The data from this study are published as a USGS Data Series Report to ensure adequate documentation of the original methods and provide a citable source for study data. This report contains no interpretations of the study data. The chemical data are as reported by the laboratory and have not been censored or adjusted unless otherwise noted.

Field measurements were recorded and samples were collected in April and May and in September 2012, by U.S. Geological Survey, U.S. Fish and Wildlife Service, and U.S. Environmental Protection Agency personnel. Study sites included tributaries to the Great Lakes located near Duluth, Minnesota; King, Wisconsin; Green Bay, Wis.; Detroit, Michigan; Monroe, Mich.; Toledo, Ohio, and Rochester, New York. Water and bottom-sediment samples were analyzed at the USGS National Water Quality Laboratory in Denver, Colorado, for a broad suite of CECs.

During this 2012 study, 140 environmental and 8 field duplicate samples of surface water and wastewater effluent, 1 field blank water sample, and 5 field spike water samples were collected or prepared. Water samples were analyzed at the USGS National Water Quality Laboratory using laboratory schedule 4433 for wastewater indicators, research method 8244 for pharmaceuticals, and laboratory schedule 4434 for steroid hormones, sterols, and bisphenol A. For wastewater indicators in unfiltered water, 61 of the 68 chemicals analyzed using laboratory schedule 4433 had detectable concentrations ranging from 0.002 to 64.4 micrograms per liter. Thirty-eight of the 48 chemicals analyzed using research method 8244 for pharmaceuticals in unfiltered water had detectable concentrations ranging from 0.002 to 3.32 micrograms per liter. Twelve of the 20 chemicals analyzed using laboratory schedule 4434 for steroid hormones, sterols, and bisphenol A in unfiltered water had detectable concentrations ranging from 0.43 to 120,000 nanograms per liter.

During this study, 53 environmental samples, 4 field duplicate samples, and 8 field spike samples of bottom sediment and laboratory matrix-spike samples were analyzed for a wide variety of CECs at the USGS National Water Quality Laboratory using laboratory schedule 5433 for wastewater indicators; research method 6434 for steroid hormones, sterols, and bisphenol A; and research method 9008 for human-use pharmaceuticals and antidepressants. Forty of the 57 chemicals analyzed using laboratory schedule 5433 had detectable concentrations ranging from 1 to 49,000 micrograms per kilogram. Fourteen of the 20 chemicals analyzed using research method 6434 had detectable concentrations ranging from 0.04 to 24,940 nanograms per gram. Ten of the 20 chemicals

[1]U.S. Geological Survey

[2] U.S. Fish and Wildlife Service

analyzed using research method 9008 had detectable concentrations ranging from 0.59 to 197.5 micrograms per kilogram. Five of the 11 chemicals analyzed using research method 9008 had detectable concentrations ranging from 1.16 to 25.0 micrograms per kilogram.

Introduction

Organic chemicals associated with agricultural, household, and industrial waste have been detected in synoptic surveys of surface-water quality across the United States. These chemicals are referred to collectively as chemicals of emerging concern (CECs) and include, for example, prescription drugs and antibiotics, over-the-counter medications, reproductive hormones, personal-care products, detergent metabolites, and flame retardants. CECs have been identified in surface water from many States, including areas surrounding the Great Lakes (Buser and others, 1999; Kolpin and others, 2002; Lee and others, 2004; Sando and others, 2005; Brown and others, 2006; Loper and others, 2007; Lee, Schoenfuss, and others, 2008; Lee, Yaeger, and others, 2008). Streams receiving agricultural, municipal, and industrial wastewaters appear to be the most affected (Kolpin and others, 2002; Lee and others, 2004), but other sources have been identified including on-site septic systems (Conn and others, 2006; Carrara and others, 2008; Godfrey and others, 2007). After these CECs enter streams and lakes, they are detected in surface water (Kolpin and others, 2002; Lee and others, 2004), and also are detected in bottom sediment (for example, Kim and Carlson, 2007; Mayer and others, 2007; Pojana and others, 2007). Questions remain regarding the health of aquatic organisms or humans under exposure to water or sediment contaminated with these chemicals. The understanding of the distribution and concentration of these contaminants in the water and bottom sediment of the Great Lakes Basin is incomplete. Only a small percentage of the surface water in the Great Lakes Basin has been sampled specifically to determine the presence and concentrations of these chemicals and the risks they are posing to fish and wildlife.

Starting in 2010, the U.S. Fish and Wildlife Service (USFWS) initiated a study through the Great Lakes Restoration Initiative as "an early warning program to detect and identify emerging contaminants and to evaluate the effects of these contaminants on fish and wildlife" (U.S. Fish and Wildlife Service, 2012). The U.S. Geological Survey (USGS) collaborated with the USFWS and the U.S. Environmental Protection Agency (EPA) on this study starting in 2010 to identify the presence of CECs, including endocrine active chemicals, pharmaceuticals, synthetic and biogenic hormones, and other chemicals in the Great Lakes Basin.

The purposes of this report are to document the collection and analytical methods, provide the quality-assurance data and analyses, and provide the water and bottom-sediment data for this study of CECs in the Great Lakes Basin for 2012. This report also describes the 2012 sampling effort, which is part of the long-term study that was initiated in 2010. A previous report (Lee and others, 2012) documents work completed during 2010 and 2011. Water and bottom-sediment samples were collected during 2012 at 66 sites throughout the Great Lakes Basin.

Study Locations

Field measurements were recorded and samples were collected at 66 sites throughout the Great Lakes Basin within the United States for study during 2012. Study sites include tributaries to the Great Lakes located near Duluth, Minnesota; King, Wisconsin; Green Bay, Wis.; Detroit, Michigan; Monroe, Mich.; Toledo, Ohio, and Rochester, New York. (fig. 1; table 1, available at http://pubs.usgs.gov/ds/0910/downloads/tables1-6.xlsx).

Sample Collection

For this study, field measurements were recorded and samples were collected during the spring and late summer of 2012. Water and bottom-sediment samples were collected by USGS, USFWS, and EPA personnel during 2012. Water samples were collected from lakes, rivers, and wastewater-effluent discharge. The first sampling period was during April and May of 2012. The second sampling period was in September 2012. During 2012, 154 water samples (140 environmental and 8 field duplicate samples of surface water and wastewater effluent, 1 field blank sample, and 5 field spike samples) and 65 bottom-sediment samples (53 environmental, 4 field duplicate, and 8 field spike samples) were collected.

Water-Sample Collection

Water-quality properties (dissolved oxygen, pH, specific conductance, and temperature) were measured at most sites using a submersible Yellow Springs Instrument Company (YSI) data sonde (Yellow Springs, Ohio). The data sonde was calibrated according to U.S. Geological Survey (variously dated) and manufacturer's specifications before sampling.

A modified depth-integrated sampling technique was used to collect water from streams and lakes (U.S. Geological Survey, variously dated). A weighted bottle sampler with a glass 1-liter bottle was lowered into the water column at one location at each site to collect the depth-integrated sample. Wastewater-effluent samples were collected directly from a wastewater treatment plant (WWTP) by EPA personnel. USGS clean-sampling techniques (U.S. Geological Survey, variously dated) were used to collect samples. To avoid contamination of samples, personnel avoided use of personal-care items, such as insect repellent, cologne, aftershave, and perfume;

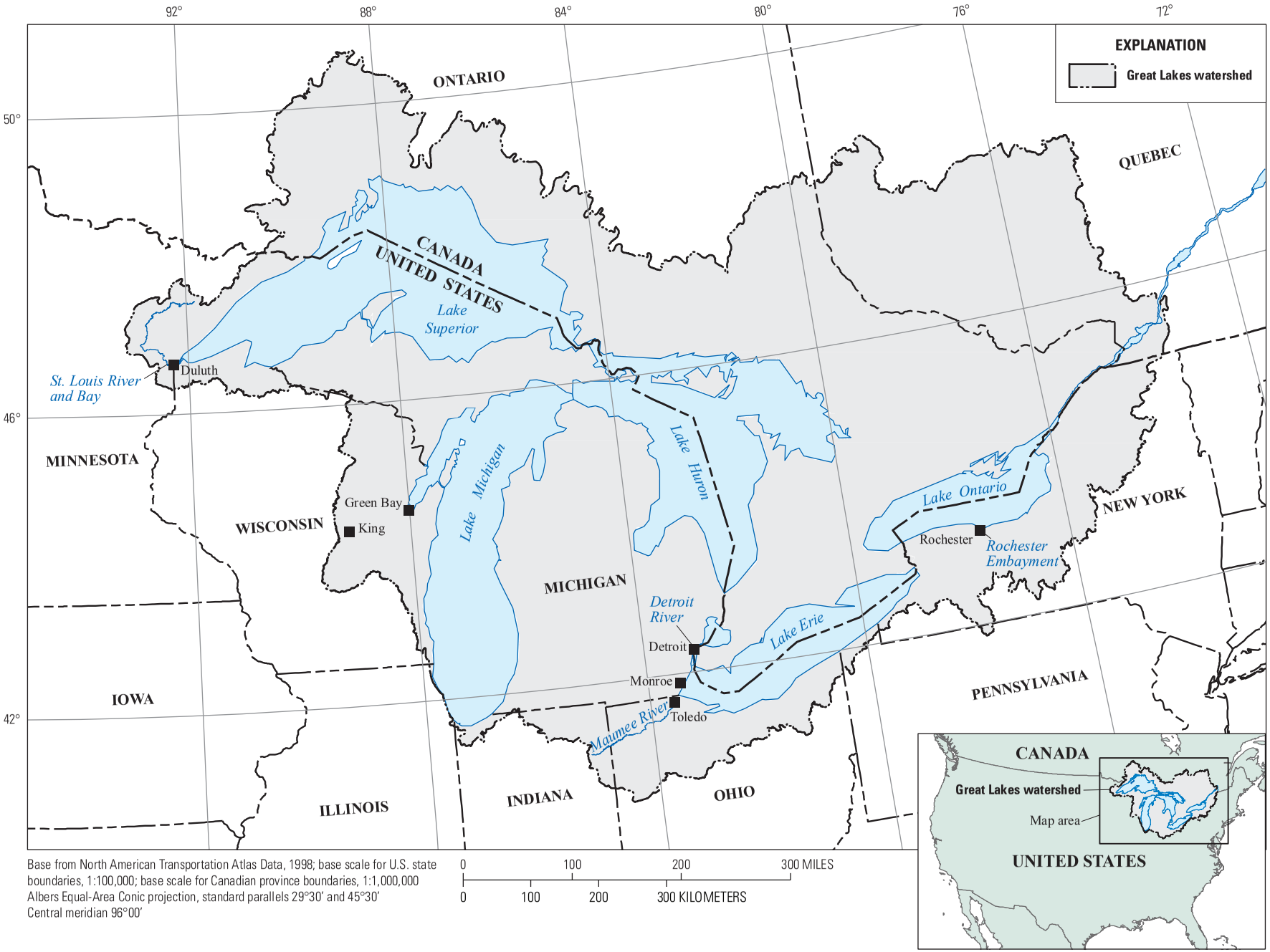

Figure 1. Cities where sampling sites for water and bottom-sediment samples are located, Great Lakes Basin, 2012.

did not consume caffeinated or tobacco products during (or immediately before) collection or processing of samples; and wore powderless, disposable, nitrile gloves during sample collection. All samples were collected with inert materials such as Teflon®, glass, or stainless steel. All collection and processing equipment was cleaned between sampling sites with a succession of native water, soapy (liquinox) tap water, tap water, deionized water, methanol, reagent water, and native water rinses. Chilled water samples were processed within 1 to 2 hours of collection before shipping to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado.

Bottom-Sediment Sample Collection

Bottom-sediment samples were collected from each location according to established protocols (U.S. Geological Survey, variously dated). Bottom sediment was collected using techniques that included the most recent bottom-sediment deposition (top 10 centimeters [cm]). Samples were collected with a stainless steel Eckman grab sampler or stainless steel coring equipment. The bottom-sediment sample was discarded and resampled if it contained a large amount of vegetation or if the sediment layers appeared to be disturbed. Bottom-sediment samples were transferred to a glass or stainless steel bowl and homogenized with a stainless steel spoon for 5 minutes. Approximately 100–200 grams (g) of unsieved wet material were placed in wide-mouth, baked-glass containers with Teflon®-lined lids, and frozen. All collection and processing equipment was cleaned between sampling sites with a succession of native water, soapy (liquinox) tap water, tap water, deionized water, methanol, and organic-free water rinses. Frozen bottom-sediment samples were shipped to the USGS NWQL.

Analytical Methods

Water and bottom-sediment samples were analyzed at the NWQL for a broad suite of chemicals (table 2, available at http://pubs.usgs.gov/ds/0910/downloads/tables1-6.xlsx) that are indicators of industrial, domestic, and agricultural sources of CECs. The specific chemicals analyzed were selected on the basis of usage, toxicity, potential estrogenic activity, persistence in the environment (Barnes and others, 2002; Kolpin and others, 2002), and analytical method availability. A combination of USGS laboratory production and research analysis methods were used to analyze study samples. Laboratory production methods included wastewater indicators in unfiltered water (NWQL laboratory schedule 4433), wastewater indicators in bottom sediment (laboratory schedule 5433), and steroid hormones, sterols, and bisphenol A in unfiltered water (laboratory schedule 4434). Laboratory research methods included pharmaceuticals in unfiltered water (research method 8244), steroid hormones, sterols, and bisphenol A in bottom sediment (research method 6434), and human-use pharmaceuticals and antidepressants in bottom sediment (research method 9008). Laboratory research methods are not established analysis methods. There are fewer quality-assurance analyses available for research methods and greater uncertainty in concentrations.

Water Chemical Analyses

The surface-water and wastewater-effluent samples (water samples) were split into two parts for analyses. Unfiltered samples were analyzed for wastewater indicators by using laboratory schedule 4433 (Zaugg and others, 2006) (table 2). The method targets a wide variety of chemicals including alkylphenol ethoxylate nonionic surfactants, food additives, fragrances, antioxidants, flame retardants, plasticizers, industrial solvents, disinfectants, animal and plant sterols, polycyclic aromatic hydrocarbons, and selected pesticides. The same unfiltered water sample used for schedule 4433, also was used for a suite of 48 pharmaceuticals as research method 8244 (Zaugg and others, 2014). Chemicals analyzed using laboratory schedule 4433 and research method 8244 were extracted using methylene chloride in continuous liquid–liquid extractors, and then determined by capillary-column gas chromatography/mass spectrometry. Samples were preserved before extraction by adding 60 g of sodium chloride and storing at 4 degrees Celsius (°C). The holding time before sample extraction was 14 days from the date of collection.

Unfiltered samples were analyzed for steroid hormones, two sterols (cholesterol and 3-*beta*-coprostanol), and bisphenol A using laboratory schedule 4434 (Foreman and others, 2012) (table 2). Isotope dilution standards (IDSs), which are isotopically labeled analogs of the method chemicals, were added to the sample just before solid-phase extraction (SPE). Derivatized method chemicals were analyzed by gas chromatography/tandem mass spectrometry (GC/MS/MS). Chemical concentrations were calculated using isotope-dilution quantification, which automatically corrects for any laboratory procedural losses in the reported chemical concentration. Absolute (noncorrected) recoveries were reported for the IDS compounds that are comparable to surrogate compound recoveries in other NWQL methods.

Bottom-Sediment Chemical Analyses

Bottom-sediment samples were split into three parts and analyzed for wastewater indicators (laboratory schedule 5433), steroid hormones, sterols, and bisphenol A (research method 6434), and human-use pharmaceuticals and antidepressants (research method 9008) at the NWQL (table 2).

Bottom-sediment samples were analyzed for wastewater indicators (laboratory schedule 5433) according to Burkhardt and others (2006). The method used pressurized liquid extraction (PLE) using an accelerated solvent extraction (ASE) instrument (ASE®; Dionex Corp., Sunnyvale, California), subsequent chemical isolation and extract cleanup by SPE and

analysis by GC/MS/MS operated in electron-impact mode with full-scan ion monitoring. Chemicals analyzed (table 2) include alkylphenol ethoxylate nonionic surfactants and several degradates, food additives, fragrances, antioxidants, flame retardants, plasticizers, industrial solvents, disinfectants, animal and plant sterols, polycyclic aromatic hydrocarbons, and selected pesticides.

Bottom-sediment samples were analyzed for steroid hormones, two sterols, and bisphenol A by using research method 6434. Similar to laboratory schedule 4434 for water, research method 6434 uses an IDS quantification procedure, with IDSs added to the sediment sample before extraction, that automatically corrects any procedural losses in the reported analyte concentration. Following receipt at the NWQL, samples for analyses of steroid hormones, sterols, and bisphenol A were stored in a freezer at -5 °C or less until the day preceding extraction, when allowed to thaw at room temperature. Each sample was homogenized before subsampling for extraction or for separate dry-weight determination. Dry weight was obtained by weighing a sample aliquot, contained in a tared aluminum pan, before and after heating at 130 ºC for at least 16 hours. Amounts used for extraction of samples in this study ranged from 0.8 to 20.6 g of sediment (dry weight), with lesser amounts used for matrices anticipated to have a large amount of organic matter or high chemical concentrations. A subsample was placed in a tared ASE cell and reweighed to determine the aliquot's wet weight before extraction. Reagent sand (cleaned by heating at 450 °C for a minimum of 4 hours) was added to the cell, as needed, based on cell and sample size. The aliquot was fortified with 10–10,000 nanograms (ng, compound dependent) of the IDS compounds. The sample aliquot was extracted by PLE using the ASE instrument with a mixture of water: isopropanol (50:50 volume per volume [v/v]) at 120 ºC and water: isopropanol (20:80 v/v) at 200 ºC using three static cycles (40 minutes total) at each temperature at a pressure of 10.3 megapascals (1,500 pounds per square inch). The resultant PLE extract portions were diluted using 100 milliliters (mL) of a potassium phosphate buffer solution (at pH 7) and sequentially passed through an OASIS® hydrophilic-lipophilic-balanced reversed-phase sorbent SPE column (Waters Corp., Milford, Massachusetts) to isolate the method chemicals on the column using the procedure given in Burkhardt and others (2006). The SPE column was dried with nitrogen gas at a flow of 2 liters per minute for 15 minutes. Method chemicals were eluted from the hydrophilic-lipophilic-balanced column and passed through a cleanup column containing 2 g of Florisil overlain with 2.5 g of sodium sulfate by using 25 mL of a dichloromethane-methanol (95:5 v/v) mixture. The resultant extract was concentrated to 1–2 mL by using nitrogen gas evaporation, and transferred to a silanized 5-mL reaction vial with a 1.5-mL rinse with the dichloromethane-methanol (95:5 v/v) mixture. The extract was evaporated to dryness using nitrogen gas. The method chemicals were derivatized to trimethylsilyl or trimethylsilyl-enol ether analogs and target chemicals analyzed by GC/MS/MS using procedures similar to laboratory schedule 4434 for water (Foreman and others, 2012).

Bottom-sediment samples were analyzed for two suites of pharmaceuticals using research method 9008 (table 2). One suite measured 22 human-use prescription and nonprescription pharmaceuticals and is referred to as human-use pharmaceuticals in this report. The second suite measured 12 antidepressants and is referred to as such in this report. For the analysis of both suites of pharmaceuticals in bottom sediment, a method described by Kinney and others (2006) was used for extraction and concentration of the extract concentration. For all extractions, a solvent consisting of 70-percent acetonitrile and 30-percent water was used to extract the samples using PLE. For human-use pharmaceuticals, the identification and quantification portion of the instrument analysis method of Kinney and others (2006) was modified to take advantage of the superior sensitivity and specificity of high-performance liquid chromatography/tandem mass spectrometry (HPLC/MS/MS). Antidepressants (buproprion, carbamazepine, citalopram, duloxetine, fluoxetine, fluvoxamine, norfluoxetine, norsertraline, paroxetine, sertraline, and venlafaxine) in sediment extracts were identified and quantified by HPLC/MS/MS (Schultz and Furlong, 2008; Schultz and others, 2010). The laboratory reporting levels (LRLs; table 2) for human-use pharmaceuticals and antidepressants (research method 9008) are considered provisional limits of quantitation and are called interim reporting levels, which are temporary reporting levels used for new or custom schedules when long-term method-detection level data are unavailable and a LRL has not yet been established (U.S. Geological Survey, 2003).

Quality Assurance

A combination of standard field sample collection and processing procedures, standardized data handling procedures to maintain database integrity, and analyses of laboratory and field quality-control samples were used to assure the quality of the data generated for this study. The USGS National Field Manual (U.S. Geological Survey, variously dated) was used to guide sample-collection activities for the study. All field personnel were familiarized with study design and sampling protocols before field sampling or data processing to assure sample integrity.

Database Integrity

Site and sample information including USGS station identifiers, station names, and other information (sample time, sample type, sample medium), and USFWS station identifiers were confirmed. This information is required to be in the USGS National Water Information System (NWIS) database and required to transfer the samples to the NWQL. This step was particularly important given the complexity of site selection and that multiple agencies collected the data.

Laboratory Reporting Levels

The LRLs used by the NWQL are designed to minimize the reporting of false positive results and, under specific data reporting conventions, false negative results (W.T. Foreman, written commun., 2010). A false positive happens when a chemical is reported present when, in fact, none is present in a sample, whereas a false negative happens when a chemical is reported as not detected or, more appropriately, as being less than a concentration threshold (the LRL), when it actually is present in a sample above that threshold.

The NWQL methods used for determining organic chemicals for this study are defined as "information-rich" (Childress and others, 1999) because the organic chemicals are determined by mass spectrometry with enhanced analyte identification capabilities. The first step for these methods is qualitative identification of the chemical using chromatographic retention time and the presence of characteristic mass spectral ions with correct ion ratios. Because qualitative identification is completed before a concentration is reported, data from these "information rich" methods are not censored at the LRL. The intention is to provide as much information as possible for complex analytes, but for which qualitative identification can be made. Data from the mass spectrometric-based organic methods applied in this study are reported using a convention that attempts to minimize false negative error at the LRL. A "less than" LRL value is provided when the instrumental signal of the presumed analyte is not detected above background signals from other organic chemicals, or, when mass spectral qualifying criteria are not met and the response is less than the LRL concentration. The LRL values are reevaluated annually based on the most current quality-control data and, therefore, might change (Childress and others, 1999).

The bottom-sediment data have multiple LRLs for a given chemical. Laboratory schedule 5433 and research method 6434 use LRL scaling based on the amount of sediment that is extracted. The LRL values for sample results in the NWIS database are scaled on the basis of the extracted dry weight of the sample. The weight based scaling leads to lower LRLs if more sample weight is extracted relative to the default weight, or higher LRLs if less sample weight is used relative to the default weight; the latter is a more common scenario, especially for "dirtier" samples because a lower sample mass is extracted to minimize matrix interference issues or because high analyte concentrations are anticipated. In addition, chemical-specific cases of higher reporting levels can occur because of matrix interference with the ability of the instrument to identify or quantify target chemicals accurately.

Laboratory and Field Quality-Control Data

Laboratory and field quality-assurance samples were collected as part of the study to assess potential sources of contamination and variability. The combination of laboratory and field-quality assurance data are important for validation and interpretation of the environmental data. Details of USGS quality-control specifications are described in Maloney (2005). Because the NWQL reports estimated values that are at times below stated LRLs, analytical results from laboratory and field quality-control samples were compared to environmental sample results to ensure that reported environmental detections are unlikely to be false positives.

The NWQL uses remark codes to provide information about the analyses. The "E" (estimated remark) code is applied to analyte data by the NWQL for a variety of reasons (Childress and others, 1999) including (1) when there are suspected matrix interferences, (2) if the chemical has a recognized performance limitation, or (3) if only technical mixture and not individual analyte standards are available for use as calibrant materials. The "M" remark code is applied to analyte data by the NWQL if the presence of a chemical was verified but the concentration was low and not verified.

NWQL uses data qualifier codes to indicate data quality. The following list includes data value indicator codes used in this report: "b," value extrapolated below the lowest calibration standard, method range, or instrument linear range; "n," value provided is below the reporting level but at or above the detection level; "t," value provided is below the detection level; and "v," value that was flagged because the concentration in the environmental sample was greater than 3 times, but less than 10 times the concentration in laboratory reagent-blank samples.

Laboratory Quality-Control Data

Laboratory quality-assurance samples included reagent-water blanks and spikes that are collected for all USGS methods as part of ongoing reliability assessment and evaluation of potential interferences and contamination sources, and are used to set or adjust LRLs. Surrogate compounds are added before extraction to all samples for organic methods to monitor sample-specific procedural performance.

Laboratory Reagent Blank Samples

The NWQL analyzed reagent blank samples consisting of organic-free reagent water with each set of samples analyzed using laboratory schedules 4433, 4434, and research method 8244. There were 13, 26, and 13 laboratory reagent blanks analyzed using laboratory schedules 4433, 4434, and research method 8244, respectively.

The USGS Office of Water Quality issued technical guidance to the NWQL in December 2011 for "flagging" environmental analytical results that may have been affected by laboratory contamination with a "v" qualifier code (W.T. Foreman, written commun., 2011). The "v" qualifier code was applied to some analytical results by comparing environmental samples to laboratory blank samples for laboratory schedules 4433, 4434, and research method 8244 in water samples. Environmental sample concentrations greater than three times, but

less than ten times the concentration in the laboratory reagent-blank samples were flagged with a "v" qualifier code in appendix 1 (available at http://pubs.usgs.gov/ds/0910/downloads/appendix1.xlsx). Environmental samples were compared to the laboratory blank sample analyzed with the environmental sample and the previous 10 laboratory blank samples analyzed (W.T. Foreman, written commun., 2011).

The NWQL analyzed laboratory bottom-sediment blank samples consisting of a baked reagent-sand matrix for laboratory schedule 5433 and laboratory research methods 6434 and 9008. There were 9, 10, and 8 bottom-sediment blank samples analyzed using laboratory schedule 5433, and laboratory research methods 6434 and 9008, respectively.

Environmental bottom-sediment sample sizes varied, and, thus, the LRLs are scaled on the basis of sample-weight extracted relative to reporting levels that assume a default 10-g sample size. The laboratory blank samples are composed of a 10-g sample. Because blank-sample and environmental-sample sizes typically differ from each other, a comparison of these samples was made on total mass of the chemical rather than on dry mass-normalized concentrations, which can be misleading. For example, the total mass (0.14 ng) of an analyte that results in a 0.14 nanograms per gram (ng/g) of a 1-g environmental sample is the same total mass that results in an order of magnitude lower concentration of 0.014 ng/g for a 10-g laboratory blank sample. The total mass of the chemical in laboratory blank samples and environmental samples was calculated by multiplying the concentration of the chemical in the given sample by the weight of the sample.

Concentrations for laboratory schedule 5433 and laboratory research methods 6434 and 9008 were flagged with qualifier codes at NWQL to indicate data quality according to (W.T. Foreman, written commun., 2011). Environmental samples of bottom sediment with a total mass greater than three times, but less than ten times the total mass in laboratory reagent-blank samples were flagged with a "v" qualifier code in appendix 2 (available at http://pubs.usgs.gov/ds/0910/downloads/appendix2.xlsx). Environmental samples were compared to the laboratory blank sample analyzed with the environmental sample and the previous 10 laboratory blank samples analyzed (W.T. Foreman, written commun., 2011).

Laboratory Reagent Spike Samples

Laboratory reagent spike recovery data provide information about method performance with time. Laboratory reagent-spike samples are samples spiked (fortified) in the laboratory with a known concentration of all chemicals. The theoretical concentration is a calculated concentration based on the known mass of chemical constituents that are added to a known volume of water:

$$Theoretical\ concentration = \frac{Concentration\ of\ spike\ solution \times Amount\ of\ spike\ added}{Sample\ volume} \quad (1)$$

where

Concentration of the spike soulution is in micrograms per milliliter;

Amount of the spike added is the amount of spike solution added in milliliters;

Sample volume is the spiked sample volume in liters.

The percent recovery (*PR*) of a chemical is the result of a measured concentration in a spiked sample that, when compared to the theoretical concentration, is expressed as a percentage of its theoretical concentration:

$$PR = \frac{Spiked\ sample\ concentration - Environmental\ sample\ concentration}{Theoretical\ concentration} \times 100 \quad (2)$$

where

PR is the percent recovery, in percent;

Spiked sample concentration is the concentration of the spiked sample;

Environmental sample concentration is the concentration of the environmental sample; and

Theoretical concentration is a calculated concentration in equation 1.

The same units are used for the *Theoretical concentration, Environmental sample concentration* and *Spiked sample concentration* in the equation. For water samples, the units could all be nanograms per liter or micrograms per liter; for bottom-sediment samples units are micrograms per kilogram.

Precision of analytical results can be described as having mean laboratory-reagent-spike recoveries between 60 and 120 percent for established methods (NWQL SOP MX0015.2, "Guidelines for Method Validation and Publication;" W.T. Foreman and R.B. Green, U.S. Geological Survey, written commun., 2014).

The number of laboratory reagent-spike samples analyzed with environmental water samples (table 3, available at http://pubs.usgs.gov/ds/0910/downloads/tables1-6.xlsx) and bottom-sediment samples (table 4, available at http://pubs.usgs.gov/ds/0910/downloads/tables1-6.xlsx) varied by the chemical analyzed and laboratory method.

The mean percent recovery (mPR) of laboratory reagent-water spikes for chemicals analyzed using laboratory schedule 4433 ranged from 23 to 113 (table 3). However, in most cases, the mPRs were within the acceptable performance range of 60 to 120 percent. The mPRs for 3,4-dichlorophenyl isocyanate; *beta*-sitosterol, *beta*-stigmastanol, cotinine; *d*-limonene; isopropylbenzene; and tetrachloroethene were less than 60 percent. Chemicals with mPRs less than 60 percent might have environmental sample concentrations that are biased low,

and there is a higher risk for false negatives (not reporting a chemical present when it is in a sample at a concentration near the LRL).

The mPR of laboratory reagent-water spikes for chemicals analyzed using research method 8244 ranged from 3 to 120 (table 3). The pharmaceuticals 2-ethyl-2-phenylmalonamide, acetaminophen, amitriptyline, chlorpheniramine, citalopram, codeine, dihydrocodeine, fluconazole, fluoxetine, hydrocodone, ibuprofen, meperdine, meprobamate, methocarbamol, methylphenidate, oxcarbazepine, oxycodone, phendimetrazine, primidone, tramadol, and venlafaxine had lower recoveries (mPRs less than 60 percent) than other chemicals analyzed using research method 8244.

The mPR of laboratory reagent-water spikes for chemicals analyzed using laboratory schedule 4434 were between 83 and 107 percent (table 3). Thus, the mPRs for all chemicals analyzed using laboratory schedule 4434 were within the acceptable performance range of 60 to 120 percent.

The NWQL analyzed laboratory reagent-spike samples consisting of an ashed sand matrix fortified with low concentrations of selected chemicals. Nine laboratory reagent-spike samples were analyzed using laboratory schedule 5433 along with companion environmental samples (table 4). The mPRs for all chemicals analyzed in laboratory reagent spike samples for laboratory schedule 5433 ranged from 30 to 117 percent. The chemicals 3-*tert*-butyl-4-hydroxy anisole (BHA), *beta*-stigmastanol, bisphenol *A*, *d*-limonene, indole, isophorone, isoquinoline, prometon, triphenyl phosphate, and tris(dichlorisopropyl) phosphate had lower recoveries in laboratory reagent-spike samples (mPRs less than 60 percent) than other chemicals analyzed using laboratory schedule 5433.

The mPRs for chemicals analyzed in laboratory spike samples using research method 6434 ranged from 88 to 110 percent. Thus, the mPRs for all chemicals analyzed using research method 6434 were within the acceptable performance range of 60 to 120 percent.

The mPRs for chemicals analyzed in laboratory spike samples using research method 9008 for human-use pharmaceuticals and antidepressants ranged from 12 to 62 percent (table 4). Most of the chemicals analyzed using research method 9008 had mPRs less than 60 percent except for citalopram and sertraline.

Field Quality-Assurance Data

Field quality-assurance samples were used to assess the effect of sample collection and processing on sample results. Field quality-assurance samples included field blanks, field duplicates, and field matrix spikes. Field blanks were used to assess potential contamination sources introduced during sample collection. Duplicate samples were used to determine variability in determined concentrations resulting from sample processing techniques. Field matrix-spike samples were used to assess the effects of sample composition on recovery performance of the chemicals by the analytical method. In addition, all samples were spiked with surrogate compounds in the laboratory that are similar to the chemicals of interest but do not interfere with the analyses of the chemicals; surrogate compounds also were used to comparatively assess method performance in the presence of the sample matrix.

Field-Blank Water Samples

One field blank water sample was prepared at a site where a corresponding environmental sample was collected. The field blank sample was processed by passing high-performance liquid-chromatography-grade reagent water (J.T. Baker® Analyzed brand, Avantor Performance Materials, Center Valley, Pennsylvania) through the same sampling equipment, using the same procedure as used for processing of the environmental and duplicate water samples. None of the analyzed chemicals were detected in the one blank water sample collected during 2012 (appendix 1).

Field Duplicate Samples

Duplicate samples are used to evaluate the variability introduced during field processing. Field duplicate samples were field processed splits of the environmental samples, so the concentration of a chemical in an environmental sample should vary little, if any, from its concentration in the corresponding duplicate sample. If the two concentrations are not the same, the absolute relative percent difference (*RPD*) determines to what extent the concentrations vary. The equation for calculating absolute *RPD* is as follows:

$$RPD = \left[\frac{ENV - FDUP}{\left(\frac{ENV + FDUP}{2} \right)} \right] \times 100 \qquad (3)$$

where

RPD is the absolute relative percent difference;
ENV is the concentration in an environmental sample; and
FDUP is the concentration in the corresponding field duplicate sample.

The same units are used for environmental sample and field duplicate sample concentrations. For water samples, the concentration units could all be nanograms per liter or micrograms per liter; for bottom sediment samples units are micrograms per kilogram.

The *RPDs* were calculated for chemicals in sample pairs where both samples had detections. The mean *RPDs* among all chemicals for the duplicate water samples for 2012 ranged from 0 to 20.4 percent (table 5, available at http://pubs.usgs.gov/ds/0910/downloads/tables1-6.xlsx) with an average of 5.7 percent. The mean *RPD* was greatest (greater than or equal to 10 percent) for, 5-methyl-1H-benzotriazole, anthracene, tribromomethane (bromoform),

citalopram, diphenhydramine, fluconazole, iminostilbene, and lidocaine, (table 5).

The consistency in analyte detection between the environmental and duplicate water samples for individual chemicals ranged from 100 percent consistency (chemical had either detections or nondetections in both samples) to 63 percent of the pairs having consistent detections or nondetections. The average number of water sample pairs with consistent detections or nondetections was 96 percent indicating good repeatability in analytical methods in terms of presence of a chemical in a given sample (table 5).

The mean *RPDs* for all chemicals analyzed in the bottom-sediment samples collected during 2012 ranged from 0 to 36.0 percent with an average of 8.2 percent (table 5). The consistency in detection between the environmental and duplicate bottom-sediment samples for individual chemicals ranged from 100 percent consistency (all samples had either detections or nondetections in both samples) to 25 percent of the pairs having consistent detections. The average number of bottom-sediment sample pairs with consistent detections or nondetections was 96 percent indicating good repeatability in analytical methods in terms of presence of a chemical in a given sample (table 5).

Field Matrix-Spike Samples

The recoveries of chemicals determined from field matrix-spike samples are useful for evaluation of an analytical method for samples collected at specific study sites, and also to assess whether matrix-induced suppression or enhancement of an analyte's signal might occur during analysis. Field matrix-spike samples were prepared in the laboratory by spiking a known theoretical concentration of a chemical to the environmental sample, and the *PR* was determined using equations 1 and 2.

The *PR* was computed by substituting zero for the environmental chemical concentration if that concentration was coded with a less than (<) remark code. Spiked water samples were prepared for laboratory schedule 4433, research method 8244, and laboratory schedule 4434 (table 3); spiked bottom-sediment samples were prepared for laboratory schedule 5433, research method 6434, and research method 9008 (table 4). An important consideration for field matrix-spike recoveries is the theoretical concentration (equation 1) relative to the concentration in the environmental (unspiked) sample. If the environmental sample concentration is much less than the theoretical concentration, then the environmental sample concentration will make a small contribution to the total concentration in the spiked sample. In this case, the *PR* ideally should range from 60 to 120 percent, assuming no procedural or analysis problems (Foreman and Green, 2008). As the environmental sample concentration approaches the theoretical concentration, the amount spiked (theoretical concentration) becomes a smaller part of the total determined concentration, and the environmental sample concentration has a greater (bias) effect on the calculated chemical recovery. If the environmental sample concentration is much greater than the theoretical concentration, then the spiked amount is too low compared to the environmental sample concentration. In this case, the *PR* often is substantially biased (positive or negative), highly variable, and typically not reliable. The spiked samples with environmental sample concentrations equal to or greater than the spiked amount were coded "NR" for not reported (table 3). The spiked samples with environmental sample concentrations between 25 and 100 percent of the spiked concentration were flagged with an "x" to indicate that recovery calculations may have additional bias.

The *PRs* are useful to identify differences among sites that are due to the differences in matrix complexity. The complexity of water or sediment sample matrices including the type and amount of dissolved organic carbon or the presence of free chlorine (chlorine that has not reacted with inorganic or organic materials, metals, nitrogen compounds, or other compounds) in the sample can affect analytical performance (Winslow and others, 2001; Valder and others, 2011). Relatively high *PRs* (greater than 120 percent) indicate possible positive bias in the reported sample concentrations, whereas relatively low *PRs* (less than 60 percent) indicate possible negative bias in reported concentrations relative to the true sample concentrations because of matrix interference or other analytical problems.

The mPR for field matrix-spike water samples among all chemicals analyzed using laboratory schedule 4433 ranged from 24 to 131 percent (table 3) with a mean of 88 percent for all spiked samples. The mPR among all chemicals analyzed using research method 8244 ranged from 1 to 138 percent with an overall mean of 77 percent for all spiked samples. The mPR for all chemicals analyzed using laboratory schedule 4434 ranged from 76 to 127 with an overall mean of 99 percent for all spiked samples.

The mPRs for field matrix-spike water samples varied among chemicals analyzed (table 3). The mPRs for 3-*beta*-coprostanol; 3,4-dichloro-phenyl isocyanate; *beta*-sitosterol; *beta*-stigmastanol; cholesterol; cotinine; *d*-limonene; and tetrachloroethene were relatively lower (less than 60 percent) compared with mPRs for other chemicals analyzed by using laboratory schedule 4433. The chemical 4-*n*-octylphenol had a relatively higher (greater than 120 percent) mPR compared to other chemicals analyzed by using laboratory schedule 4433. The chemicals 2-ethyl-2-phenylmalonamide, acetaminophen, celecoxib, chlorpheniramine, dihydrocodeine, fluconazole, meprobamate, methocarbamol, methylphenidate, oxcarbazepine, and primidone, and temazepam had relatively lower mPRs (less than 60 percent) than other chemicals analyzed using research method 8244. Diltiazem and verapamil had relatively higher (greater than 120 percent) mPRs compared to other chemicals analyzed using research method 8244. All of the mPRs for chemicals analyzed using laboratory schedule 4434 were greater than 60 percent; one chemical (epitestosterone) had an mPR of 127 percent.

The percent recoveries for chemicals analyzed in the field matrix-spike bottom-sediment sample from the Fox

River sewage treatment plant at De Pere, Wis. (site 04085060 near Green Bay, fig. 1, table 1; sampled April 27, 2012) using laboratory schedule 5433 ranged from 0 to 458 percent (table 4), with an overall mPR for all chemicals of 93 percent. The mPRs for chemicals analyzed using research method 6434 for spiked bottom-sediment samples at this same site (04085060) ranged from 39 to 126 percent, with an overall mPR for all chemicals of 89 percent. The mPRs for chemicals in the eight spiked bottom-sediment samples analyzed using research method 9008 for human-use pharmaceuticals ranged from 11 to 59 percent, with an overall mean for all chemicals of 35 percent. The mPR for all chemicals analyzed using research method 9008 for antidepressants in the eight spiked bottom-sediment samples ranged from 13 to 80 percent, with an overall mean for all samples of 32 percent. The mPRs for individual chemicals analyzed using research method 9008 were less than 60 percent for all chemicals with the exception of carbamazepine (80 percent).

Surrogate and Isotope Dilution Standard Recoveries

All samples were spiked with surrogate standards or IDSs (used in research methods 4434 for unfiltered water and 6434 for bottom sediment). Surrogates typically are similar in structure to (or are isotopic analogs of) at least several of the method chemicals. Surrogate recoveries are used to monitor sample-specific laboratory procedural performance. For example, uniformly low surrogate recoveries typically are an indication of substantial procedural losses and, thus, possible negative bias in reported concentrations of chemicals for the sample.

The IDS recoveries also are indicators of absolute chemical recovery (total chemical mass recovered through the procedure); however, for research methods 4434 and 6434 that use IDS compounds, chemical concentrations (or chemical method recoveries for spiked samples) are corrected for procedural losses by use of the isotope-dilution quantification procedure. Thus, IDS recoveries typically will be lower than chemical method recoveries reported for spiked samples. Although low IDS recoveries in a sample are an indication of reduced total chemical mass recovery, reported chemical concentrations will be less biased and closer to the true sample concentration than indicated by the IDS recovery (see Foreman and others, 2012).

The mPRs of the 16 surrogate standards or IDS compounds were determined for water samples analyzed by using laboratory schedules 4433 and 4434. The mPRs for the 16 surrogate standards or IDS compounds for water ranged from 10 to 88 percent (table 6, available at http://pubs.usgs.gov/ds/0910/downloads/tables1-6.xlsx). The mPRs for decafluorobiphenyl, medroxyprogesterone-d_3, progesterone-2,3,4-$^{13}C_3$, and *trans*-diethyl-1,1,1′,1′-d_4-stilbesterol-3,3′,5,5′-d_4 were relatively lower (less than 60 percent) than other surrogate standards or IDS compounds in water samples. Most recoveries of surrogate standards or IDS compounds did not differ appreciably between sites.

The mPRs for the 15 surrogate standards or IDS compounds analyzed by using laboratory schedule 5433 or research method 6434 in bottom-sediment samples ranged from 14 to 86 percent (table 6). Most of these surrogate standards or IDS compounds had mPRs less than 60 percent with the exceptions of fluoranthene-d_{10}, estriol-2,4,16,17-d_4, and estrone-13,14,15,16,17,18-$^{13}C_6$. The mPRs for the four surrogate standards in bottom-sediment samples analyzed using research method 9008 for pharmaceuticals and antidepressants ranged from 19 to 58 percent.

The combination of laboratory and field-quality assurance data are important for validation and interpretation of the environmental data. Quality-assurance analyses described in the “Laboratory Blank Samples” and “Field Blank Water Samples” sections indicated that laboratory or field contamination was limited to a few instances during sample collection for this study. The relative percent difference determined for chemicals between duplicate and environmental samples (table 5) provides a benchmark for comparison of data among sites. The recoveries of chemicals in spiked (fortified) samples (tables 3 and 4) and the surrogate standard and IDS recoveries (table 6) indicate that some methods and some chemicals analyzed with a method have better reliability than other chemicals or methods. Matrix spike recoveries are different among sites likely because of sample matrix differences that interfere with analytical determinations, which complicate comparisons of data from different sites.

Study Data

This section of the report briefly describes the environmental data for samples collected in 2012 for the study of CECs in the Great Lakes Basin. The data from this study are published as a USGS Data Series Report to document the methods and provide a reference for study data. This report contains no interpretations of the study data. These data were collected during 2012 by USGS, USFWS, and EPA personnel. Data are presented for water samples (surface water and wastewater effluent) and bottom-sediment samples. The data are as reported by the laboratory and have not been censored or adjusted unless otherwise noted.

Water-Quality Properties

Field water-quality properties, including dissolved oxygen, pH, specific conductance, and water temperature, were measured at the study sites during 2012. Field water-quality properties are presented in appendix 1. Water-quality properties varied among sampling sites. For example, specific conductance was lowest at the sites near Detroit, Mich. (appendix 1; from 232 to 367 microsiemens per centimeter at 25 °C) and

greatest at the sites near Toledo, Ohio (appendix 1; from 362 to 1,140 microsiemens per centimeter at 25 °C).

Water Data

During this study, 140 environmental and 8 field duplicate samples of surface water and wastewater effluent, 1 field blank water sample, and 5 field spike water samples (not shown in appendix 1) were collected during 2012. The water samples were analyzed for a wide variety of CECs at the NWQL using laboratory schedule 4433 for wastewater indicators, laboratory schedule 4434 for steroid hormones, sterols, and bisphenol A, and research method 8244 for pharmaceuticals. Analytical results for the environmental, wastewater, and field quality-assurance samples are presented in appendix 1.

A broad suite of CECs were detected among all environmental water samples. For wastewater indicators in unfiltered water using laboratory schedule 4433, 62 of the 69 chemicals analyzed had detectable concentrations ranging from 0.002 to 64.4 µg/L (appendix 1). Thirty-nine of the 48 chemicals analyzed using research method 8244 for pharmaceuticals in unfiltered water had detectable concentrations ranging from 0.002 to 3.32 µg/L. Twelve of the 20 chemicals analyzed using laboratory schedule 4434 for steroid hormones, sterols, and bisphenol A in unfiltered water had detectable concentrations ranging from 0.43 to 120,000 ng/L.

Bottom-Sediment Data

During this study, 53 environmental samples, 4 field duplicate samples, and 8 field spike samples (not shown in appendix 2) of bottom sediment and laboratory matrix-spike samples of bottom sediment were collected in 2012. The bottom sediment samples were analyzed for a wide variety of CECs at the NWQL using laboratory schedule 5433 for wastewater indicators; research method 6434 for steroid hormones, sterols, and bisphenol A; and research method 9008 for human-use pharmaceuticals and antidepressants. Analytical results for the environmental and field quality-assurance samples for are presented in appendix 2.

For wastewater indicators in bottom sediment using laboratory schedule 5433, 40 of the 57 chemicals analyzed had detectable concentrations ranging from 1 to 48,700 micrograms per kilogram (µg/kg) (appendix 2). Thirteen of the 20 chemicals analyzed using research method 6434 for steroid hormones, sterols, and bisphenol A had detectable concentrations ranging from 0.05 to 24,940 ng/g. Eight of the 20 chemicals analyzed using research method 9008 for human-use pharmaceuticals had detectable concentrations ranging from 0.6 to 197.5 µg/kg. Five of the 11 chemicals analyzed using research method 9008 for antidepressants had detectable concentrations ranging from 1.2 to 25.0 µg/kg.

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Appendix 1. Concentrations of Chemicals in Water Samples and Associated Quality-Assurance Samples analyzed at the U.S. Geological Survey National Water Quality Laboratory.

The Excel spreadsheet appendix1.xlsx (available at http://pubs.usgs.gov/ds/0910/downloads/appendix1.xlsx) contains water-quality properties (dissolved oxygen, pH, specific conductance, and water temperature). This spreadsheet also contains chemical concentrations for water samples and associated quality-assurance samples analyzed at the U.S. Geological Survey's National Water Quality Laboratory in Denver, Colo., for laboratory method 4433 for wastewater indicators; research method 8244 for pharmaceuticals; and research method 4434 for steroid hormones, sterols, and bisphenol A. The recoveries of associated surrogate standards or isotope dilution standards also are contained in this spreadsheet.

Appendix 2. Concentrations of Chemicals in Bottom-Sediment Samples and Associated Quality-Assurance Samples analyzed at the U.S. Geological Survey National Water Quality Laboratory.

The Excel spreadsheet appendix2.xlsx (available at http://pubs.usgs.gov/ds/0910/downloads/appendix2.xlsx) contains chemical concentrations for bottom-sediment samples and associated quality-assurance samples analyzed at the U.S. Geological Survey's National Water Quality Laboratory in Denver, Colo., for wastewater indicators using laboratory method 5433; steroid hormones, sterols, and bisphenol A using research method 6434; and human-use pharmaceuticals and antidepressants using research method 9008. The recoveries of associated surrogate standards or isotope dilution standards also are contained in this spreadsheet.

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ISSN 2327-638X (online)
http://dx.doi.org/10.3133/ds910