

Prepared in cooperation with the U.S. Fish and Wildlife Service and the  
U.S. Environmental Protection Agency

# Chemicals of Emerging Concern in Water and Bottom Sediment in Great Lakes Areas of Concern, 2010 to 2011— Collection Methods, Analyses Methods, Quality Assurance, and Data



Data Series 723

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

**Cover photograph:** U.S. Geological Survey personnel collecting bottom-sediment samples on Superior Bay near Duluth, Minnesota. Photograph taken by Minnesota Pollution Control Employee, 8/4/2010.

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By Kathy E. Lee, Susan K. Langer, Michael A. Menheer, William T. Foreman, Edward T. Furlong, and Steven G. Smith

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

**U.S. Department of the Interior**  
KEN SALAZAR, Secretary

**U.S. Geological Survey**  
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2012

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## Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
Volume		
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
liter (L)	61.02	cubic inch (in <sup>3</sup> )
milliliter (mL)	0.0338	ounce, fluid (fl. oz)
microliter (μL)	0.0000338	ounce, fluid (fl. oz)
Flow rate		
liter per minute (L/min)	0.2642	gallon per minute (gal/min)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
Pressure		
megapascal (MPa)	145.0	pounds per square inch (lb/in <sup>2</sup> )

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:  
 $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$ .

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

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 grams per kilogram (g/kg) or nanograms per gram (ng/g).

## Abbreviations and Symbols

<	less than
AOC	area of concern
ASE	accelerated solvent extraction
BHA	3- <i>tert</i> -butyl-4-hydroxy anisole
<sup>13</sup> C	carbon-13
CEC	chemical of concern
C <sub>f</sub>	value in dataset that was flagged because of detections in field blank samples
C <sub>l</sub>	value in dataset that was flagged because of detections in laboratory blank samples
DEET	<i>N,N</i> -diethyl- <i>meta</i> -toluamide
E	estimated
EAC	endocrine-active chemical
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
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
TIC	tentatively identified chemical
USEPA	U.S. Environmental Protection Agency
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
v/v	volume per volume
WLSSD	Western Lake Sanitary Sewer District
WWTP	wastewater-treatment plant





# Chemicals of Emerging Concern in Water and Bottom Sediment in Great Lakes Areas of Concern, 2010 to 2011—Collection Methods, Analytical Methods, Quality Assurance Analyses, and Data

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## Abstract

Synoptic surveys of surface-water quality across the United States have detected a large group of organic chemicals associated with agricultural, household, and industrial waste. 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.

The U.S. Geological Survey (USGS) cooperated with the U.S. Environmental Protection Agency and the U.S. Fish and Wildlife Service on a study to identify the occurrence of CECs in water and bottom-sediment samples collected during 2010–11 at sites in seven areas of concern (AOCs) throughout the Great Lakes. This report documents the collection methods, analyses methods, quality-assurance data and analyses, and provides the data for this study.

Field measurements and sample collections were completed from September 19, 2010, to September 6, 2011, by a combination of U.S. Geological Survey, U.S. Fish and Wildlife Service, and U.S. Environmental Protection Agency personnel. Study sites include tributaries to the Great Lakes in AOCs located near Duluth, Minn.; Green Bay, Wis.; Rochester, N.Y.; Detroit, Mich.; Toledo, Ohio; Milwaukee, Wis.; and Ashtabula, Ohio. Water and bottom-sediment samples were analyzed at the USGS National Water Quality laboratory in Denver, Colo., for a broad suite of chemicals that are indicators of industrial, domestic, and agricultural wastewaters.

During this study, 135 environmental and 23 field duplicate samples of surface water and wastewater effluent, 10 field blank water samples, and 11 field spike water samples were collected or prepared during 2010–11 and analyzed at the USGS National Water Quality Laboratory for a wide variety of CECs. Sixty-one of the 69 chemicals analyzed were detected at concentrations ranging from 0.002 to 11.2 micrograms per

liter using laboratory method 4433 for wastewater indicators in water. Twenty-eight of the 48 chemicals analyzed were detected at concentrations ranging from 0.0029 to 22.0 micrograms per liter using research method 8244 for pharmaceuticals in water. Ten of the 20 chemicals analyzed were detected at concentrations ranging from 0.16 to 10,000 nanograms per liter using research method 4434 for steroid hormones.

During this study, 75 environmental, 13 field duplicate samples, and 9 field spike samples of bottom sediment were collected and analyzed for a wide variety of CECs at the USGS National Water Quality Laboratory using laboratory method 5433 for wastewater indicators, research method 6434 for steroid hormones, and research method 9008 for human-use pharmaceuticals and antidepressants. Forty-seven of the 57 chemicals analyzed were detected at concentrations ranging from 0.921 to 25,800 nanograms per gram using laboratory method 5433 for wastewater indicators. Seventeen of the 20 chemicals analyzed were detected at concentrations ranging from 0.006 to 8,921 nanograms per gram using research method 6434 for steroid hormones. Twelve of the 20 chemicals analyzed were detected at concentrations ranging from 2.35 to 453.5 nanograms per gram using research method 9008 for human-use pharmaceuticals. Six of the 11 chemicals analyzed were detected at concentrations ranging from 2.79 to 91.6 nanograms per gram using research method 9008 for antidepressants.

During 2010, environmental water samples were analyzed to determine the occurrence of non-target CECs at the USGS National Water Quality Laboratory using custom method 2753. This analysis method was selected to identify non-target chemicals, is not considered quantitative, and is in a preliminary format. The estimated concentrations reported for tentatively identified chemicals analyzed by using custom method 2753 are qualitative and should not be considered quantitative.

## Introduction

A large group of 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 waters 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, 2008). These CECs include endocrine-active chemicals (EACs) capable of inducing endocrine disruption, as well as pharmaceuticals designed for human or animal consumption.

After these CECs enter streams and lakes, most are detected at low concentrations in 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 under long-term (greater than 1 year) exposure to water or sediment contaminated with these chemicals. Various research studies have indicated that fish and other wildlife can be adversely affected by some EACs at environmentally relevant concentrations, producing developmental and reproductive problems. For example, feminization of male fish has been documented (Iguchi and others, 2001), and intersex fish have been documented in areas (Hinck and others, 2006) with known EACs (Vjada and others, 2008; Lee and others, 2010). Throughout the United States, endocrine disruption has been observed in wild fish (Bjerrgaard and others, 2006; Hinck and others, 2009; Brown and others, 2011; Blazer and others, 2012), and within Minnesota, endocrine disruption has been observed in the effluent of large wastewater-treatment plants (WWTPs), including vitellogenin induction in male carp (*Cyprinus carpio*) and walleye (*Sander vitreus*) (Folmar and others, 1996, 2001; Lee and others, 2000). Vitellogenin in male carp also was observed at numerous sites downstream from WWTP discharges throughout central Minnesota (Lee and others, 2000; Lee, Schoenfuss, and others, 2008; Lee, Yaeger and others, 2008). When considered together, the results from these studies indicate a substantial potential for the occurrence of endocrine disruption from these contaminants; however, our current understanding of the distribution and concentration of these contaminants is incomplete. Although these studies establish the presence of organic CECs in selected surface waters throughout the United States, including the Great Lakes Basin, and identified the presence of

endocrine disruption in wild fishes, only a small percentage of the surface waters in the Great Lakes Basin have been sampled specifically to determine these chemicals. In addition, little is known about the persistence and fate of these chemicals, including the nature and extent of partitioning between water, biota, and sediment in complex hydrological settings, such as the Great Lakes tributaries.

To better define CEC occurrence in Great Lakes areas of concern (AOCs), defined by the International Joint Commission (2012), 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) cooperated with the U.S. Environmental Protection Agency (USEPA) and the USFWS on a study to identify the occurrence of CECs, including EACs, pharmaceuticals, synthetic and biogenic hormones, and other chemicals in water and bottom-sediment samples collected during 2010–11 at sites selected by the USFWS throughout the Great Lakes AOCs.

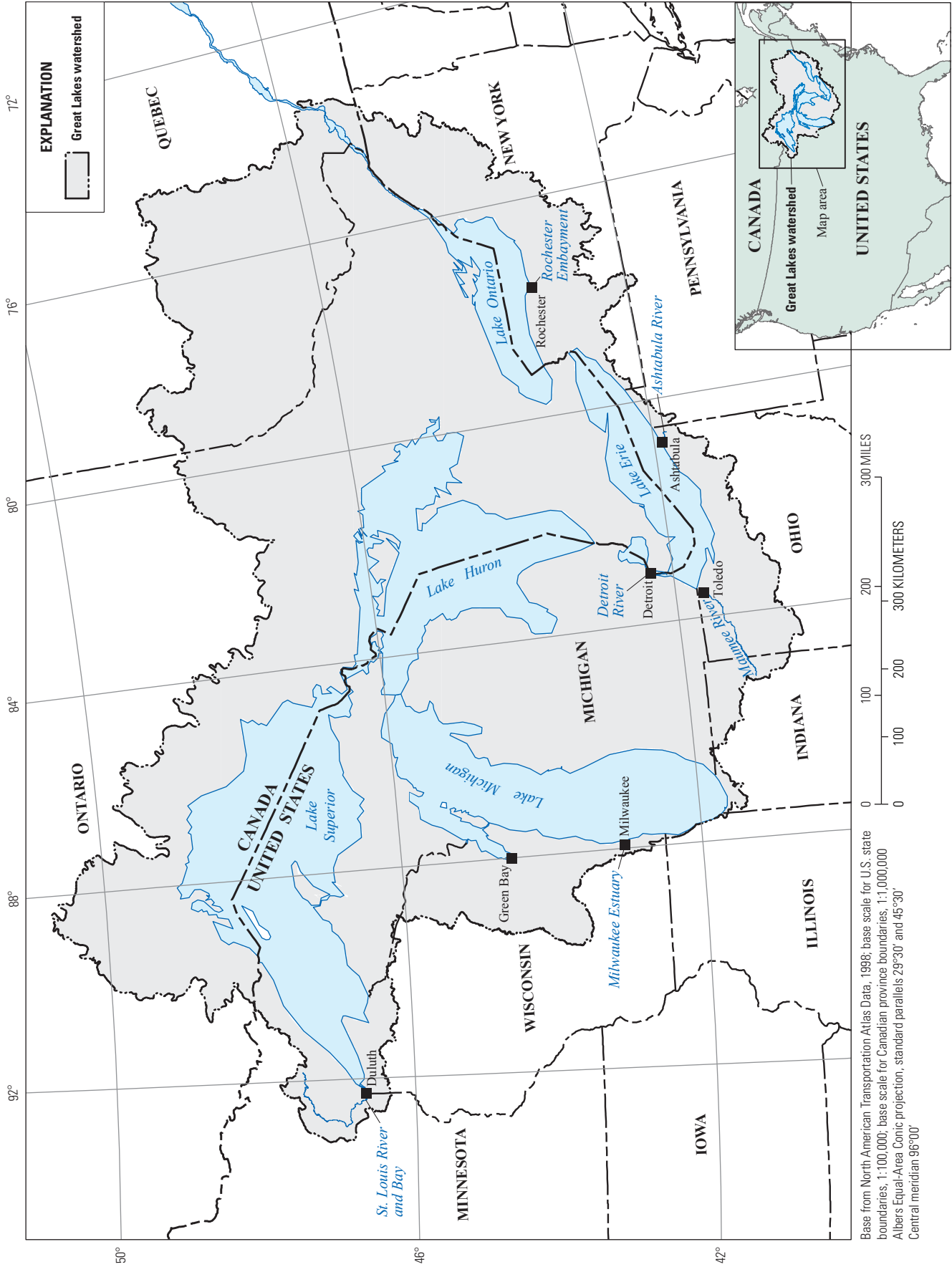
The purposes of this report are to document the collection and analytical methods, provide the quality-assurance data and analyses, and provide the water and bottom-sediment data for this study of CECs in the Great Lakes AOCs. A concurrent biological effects study with wild fishes was undertaken at the study sites by USGS and USFWS, and a concurrent biological effects study using caged fish was undertaken by the USEPA. Results from the biological effects studies are not included in this report.

## Study Locations

The USFWS selected seven AOCs throughout the Great Lakes for study during 2010–11. The specific sampling locations within each AOC were selected in the field by USFWS, USEPA, and USGS personnel during 2010 and 2011. Study sites include tributaries to the Great Lakes in AOCs located near Duluth, Minn.; Green Bay and Milwaukee, Wis.; Detroit, Mich.; Toledo and Ashtabula, Ohio; and Rochester, N.Y. (table 1, fig. 1).

## Sample Collection

During this study, measurements or sample collections were completed from September 19, 2010, to September 6, 2011. The types of samples collected and collection procedures are described in this section. Water and bottom-sediment samples were collected by a combination of USGS, USFWS, and USEPA personnel during 2010 and 2011. The water samples included collection of surface-water samples from lakes and rivers, and wastewater-effluent samples. The first sampling period occurred from September to November 2010. The second sampling period occurred from April to



**Figure 1.** Locations of Great Lakes areas of concern where samples were collected during 2010–11.

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**Table 1.** List of sampling sites, station identifiers, field identifiers, latitude, longitude, and sampling year for water and bottom-sediment samples.

[USGS, U.S. Geological Survey; Areas of concern are defined at <http://www.epa.gov/glnpo/aoc/>; GLRI, Great Lakes Restoration Initiative; SW, surface water; WWTP, wastewater-treatment plant; WLSSD, Western Lake Sanitary Sewer District]

USGS station identifier	Station name	Field identifier	Latitude	Longitude	Year sampled
Area of concern, Ashtabula River					
415352080473601	Ashtabula River (GLRI site1) at Ashtabula, Ohio	ASH-1	415352	804736	2011
415345080474601	Ashtabula River (GLRI site2) at Ashtabula, Ohio	ASH-2	415345	804746	2011
415328080475301	Ashtabula River (GLRI site3) at Ashtabula, Ohio	ASH-3	415328	804753	2011
Area of concern, Detroit River					
421738083055601	Detroit River (site 1) at Detroit, Mich.	DTR-1	421737.6	830555.6	2010–11
421625083063601	Detroit River (site 2) near River Rouge, Mich.	DTR-2	421624.6	830636.2	2010
421219083084601	Detroit River (site 3) near Wyandotte, Mich.	DTR-3	421218.7	830845.6	2010
420650083110001	Detroit River (site 4) near Trenton, Mich.	DTR-4	420649.8	831059.7	2010–11
420509083103901	Detroit River (site 5) near Gibraltar, Mich.	DTR-5	420509	831038.8	2010
420424083110401	Detroit River (site 6) near Gibraltar, Mich.	DTR-6	420423.9	831104	2010
421209083083201	Detroit River (site 7) above Point Hennipin near Wyandotte, Mich.	PTHENN-1	421209	830832	2011
421100083080801	Detroit River (site 8) below Mamajuda Island near Wyandotte, Mich.	WYAND-2	421100	830808	2011
420738083102301	Detroit River (site 9) at Grosse Ile Parkway in Grosse Ile, Mich.	GROSIL-3	420738	831023	2011
420714083104801	Detroit River (site 10) above Trenton WWTP, Trenton, Mich.	TRENTN-4	420714	831048	2011
421104083090201	Detroit River (site 11) by Downriver WWTP at Wyandotte, Mich.	DTR-11	421104	830902	2011
Area of concern, Rochester Embayment					
431400077370601	Genesee River above Rattlesnake Point in Rochester, New York, N.Y. site 1	GNR-1	431400.1	773705.9	2010–11
431205077372601	Genesee River below Veterans Bridge at Rochester, New York, N.Y. site 2	GNR-2	431204.8	773725.8	2010–11
431226077373501	Genesee River at Seneca Park in Rochester, New York, N.Y. site 3	GNR-3	431226.2	773735.4	2010
431340077365901	Genesee River at Genesee Dock in Rochester, New York, N.Y. site 4	GNR-4	431339.9	773659.1	2010
431403077370501	Genesee River at Rattlesnake Point in Rochester, New York, N.Y. site 5	GNR-5	431402.5	773704.5	2010
431524077362201	Genesee River above mouth at Rochester, New York, N.Y. site 6	GNR-6	431523.6	773621.5	2010–11
Area of concern, Maumee River					
413813083341401	Swan Creek (QW site 1) near Toledo, Ohio	SWC-1	413812.7	833414.4	2010
413813083341001	Swan Creek (QW site 2) near Toledo, Ohio	SWC-2	413812.7	833410.2	2010
413813083340601	Swan Creek (QW site 3) near Toledo, Ohio	SWC-3	413813	833405.5	2010
413812083340101	Swan Creek (QW site 4) near Toledo, Ohio	SWC-4	413811.7	833400.5	2010
413814083334701	Swan Creek (QW site 5) near Toledo, Ohio	SWC-5	413814.4	833347.3	2010
413829083334601	Swan Creek (QW site 6) near Toledo, Ohio	SWC-6	413828.5	833345.9	2010
413835083334401	Swan Creek (QW site 7) near Toledo, Ohio	SWC-7	413834.9	833344.1	2010–11
413829083332601	Swan Creek (QW site 8) near Toledo, Ohio	SWC-8	413829.4	833326.3	2010–11
413833083330701	Swan Creek (QW site 9) near Toledo, Ohio	SWC-9	413833.4	833307.4	2010



**Table 1.** List of sampling sites, station identifiers, field identifiers, latitude, longitude, and sampling year for water and bottom-sediment samples.—Continued

[USGS, U.S. Geological Survey; Areas of concern are defined at <http://www.epa.gov/glnpo/aoc/>; GLRI, Great Lakes Restoration Initiative; SW, surface water; WWTP, wastewater-treatment plant; WLSSD, Western Lake Sanitary Sewer District]

USGS station identifier	Station name	Field identifier	Latitude	Longitude	Year sampled
Area of concern, Maumee River—Continued					
413835083325901	Swan Creek (QW site 10) near Toledo, Ohio	SWC-10	413834.5	833258.7	2010
413831083324401	Swan Creek (QW site 11) near Toledo, Ohio	SWC-11	413830.7	833244.2	2010–11
413840083323501	Swan Creek (QW site 12) near Toledo, Ohio	SWC-12	413840.2	833235.1	2010
413852083320301	Swan Creek (site 5) near mouth at Toledo, Ohio	SWANC-5	413852	833203	2011
414059083290500	Maumee River (site 6) above Toledo WWTP at Toledo, Ohio	CLARKO-6	414059	832905	2011
414119083283001	Maumee River (site 7) below Toledo WWTP at Toledo, Ohio	TOLEDO-7	414119	832830	2011
Area of concern, St. Louis River and Bay					
463934092170101	St. Louis River (site 1) near Fond Du Lac, Minn.	STR-FDL-1	463933.5	921701.2	2010–11
463937092170001	St. Louis River (site 2) near Fond Du Lac, Minn.	STR-FDL-2	463936.7	921659.7	2010
463939092170701	St. Louis River (site 3) near Fond Du Lac, Minn.	STR-FDL-3	463938.8	921706.9	2010–11
463932092170101	St. Louis River (site 4) near Fond Du Lac, Minn.	STR-FDL-4	463931.5	921701	2010
463935092170901	St. Louis River (site 5) near Fond Du Lac, Minn.	STR-FDL-5	463934.7	921709.2	2010–11
463937092171201	St. Louis River (site 6) near Fond Du Lac, Minn.	STR-FDL-6	463937.1	921712.3	2010
463931092165701	St. Louis River, north channel, at Highway 23 near Fond Du Lac, Minn.	FDL	463931	921657	2010
464404092090901	St. Louis Bay (site 1) near Minnesota Power, Duluth, Minn.	STB-MP-1	464404.2	920908.5	2010–11
464359092091901	St. Louis Bay (site 2) near Minnesota Power, Duluth, Minn.	STB-MP-2	464359	920919	2010
464352092091801	St. Louis Bay (site 3) near Minnesota Power, Duluth, Minn.	STB-MP-3	464351.5	920918	2010–11
464349092091001	St. Louis Bay (site 4) near Minnesota Power, Duluth, Minn.	STB-MP-4	464349.3	920909.9	2010–11
464352092090401	St. Louis Bay (site 5) near Minnesota Power, Duluth, Minn.	STB-MP-5	464351.6	920903.5	2010
464357092090601	St. Louis Bay (site 6) near Minnesota Power, Duluth, Minn.	STB-MP-6	464356.6	920905.7	2010–11
464517092071401	St. Louis Bay (site 1) near WLSSD WWTP, Duluth, Minn.	STB-WLSSD-1	464517.3	920713.9	2010–11
464521092071001	St. Louis Bay (site 2) near WLSSD WWTP, Duluth, Minn.	STB-WLSSD-2	464520.8	920710.9	2010
464522092071601	St. Louis Bay (site 3) near WLSSD WWTP, Duluth, Minn.	STB-WLSSD-3	464522.8	920716.9	2010
464524092070901	St. Louis Bay (site 4) near WLSSD WWTP, Duluth, Minn.	STB-WLSSD-4/ WLSSD-distal	464519	920716	2010–11
464527092071601	St. Louis Bay (site 5) near WLSSD WWTP, Duluth, Minn.	STB-WLSSD-5	464527.3	920716.6	2010
464527092071301	St. Louis Bay (site 6) near WLSSD WWTP, Duluth, Minn.	STB-WLSSD-6/ WLSSD-proximal	464528	920712	2010–11
464343092040601	Duluth Harbor Basin near WWTP at Superior, Wis.	SMTF	464343	920406	2010
464538092072601	WLSSD - WWTP effluent at Duluth, Minn.	WLSSD-EFF	464538	920726	2010
Area of concern, Lower Fox River/Green Bay					
443219088001401	Fox River at mouth (site 1), in Green Bay, Wis.	FXR-1	443218.9	880014.2	2010
443228087593001	Fox River at mouth (site 2), in Green Bay, Wis.	FXR-2	443228.1	875930.5	2010
443248087573401	Fox River at mouth (site 3), in Green Bay, Wis.	FXR-3	443248.2	875733.8	2010–11
443424087584401	Fox River at mouth (site 4), in Green Bay, Wis.	FXR-4	443423.7	875844.3	2010
443527087595701	Fox River at mouth (site 5), in Green Bay, Wis.	FXR-5	443526.9	875957	2010–11
443202088002401	Fox River at mouth (site 6), in Green Bay, Wis.	FXR-6	443201.9	880024	2010–11

**Table 1.** List of sampling sites, station identifiers, field identifiers, latitude, longitude, and sampling year for water and bottom-sediment samples.—Continued

[USGS, U.S. Geological Survey; Areas of concern are defined at <http://www.epa.gov/glnpo/aoc/>; GLRI, Great Lakes Restoration Initiative; SW, surface water; WWTP, wastewater-treatment plant; WLSSD, Western Lake Sanitary Sewer District]

USGS station identifier	Station name	Field identifier	Latitude	Longitude	Year sampled
Area of concern, Lower Fox River/Green Bay—Continued					
04085060	Fox River at Fox River Sewage Treatment Plant at De Pere, Wis.	DPERE-9	442743	880334	2011
040851378	Fox River at Monroe Street at Green Bay, Wis.	EASTR-10	443102	880024	2011
040851385	Fox River at Oil Tank Depot at Green Bay, Wis.	PRGAM-11	443143	880036	2011
04085139	Fox River at mouth at Green Bay, Wis.	GRBAY-12	443222	880016	2011
Area of concern, Milwaukee Estuary					
04087143	Menomonee River at North Emmber Lane at Milwaukee, Wis.	MENMR-13	430157	875545	2011
04087013	Milwaukee River at St. Paul Avenue at Milwaukee, Wis.	MILWR-14	430204	875437	2011
430123087533801	Milwaukee Harbor (site 15) at Jones Island WWTP, Milwaukee, Wis.	JONESI-15	430123	875338	2011
04087162	Kinnickinnic River above South Kinnickinnic Avenue at Milwaukee, Wis.	KINNI-17	430029	875433	2011
040870122	Milwaukee River at Wisconsin Avenue Bridge, Milwaukee, Wis.	MILWR-WABR	430217	875435	2011
430143087551501	Burnham Canal at South 7th Street, Milwaukee, Wis.	MIL-2	430143	875515	2011
040870104	Milwaukee River below North Avenue Dam, Milwaukee, Wis.	MIL-NAVDAM	430326	875350	2011

September 2011. The 2010 sampling included collection of at least six water and six bottom-sediment samples at each AOC; water was sampled at additional caged fish deployment locations by USEPA. During 2010 and 2011, 179 water samples (135 environmental and 23 field duplicate samples of surface water and wastewater effluent, 10 field blank water samples, and 11 field spike water samples) and 97 bottom-sediment samples (75 environmental, 13 field duplicate, and 9 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 (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 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 WWTP by USEPA 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; 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 glass, or stainless steel. All collection and processing equipment was cleaned between sampling sites with a succession of 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).

## 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 other 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 stainless steel bowl and homogenized with a stainless steel spoon. Approximately 100–200 grams (g) of unsieved wet material were placed in wide-mouth, glass containers, and frozen. Collection containers were washed with soap and water, rinsed with water, baked at 450 degrees Celsius (°C) for 4 hours, and sealed with a Teflon®-lined lid before use. All collection and processing equipment was cleaned between sampling sites with a succession of soapy (liquinox) tap water, tap water, deionized water, methanol, and organic-free water rinses. Frozen bottom-sediment samples were shipped to the USGS NWQL.

## Sample Analyses

Water and bottom-sediment samples were analyzed at the NWQL for a broad suite of chemicals ([table 2](#), link to Excel spreadsheet) that are indicators of industrial, domestic, and agricultural sources. 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 method availability. A combination of laboratory production methods and research methods were used to analyze study samples. Laboratory research methods included pharmaceuticals in unfiltered water (method 8244), tentatively identified chemicals in water (method 2753, not listed in [table 2](#)), steroid hormones in unfiltered water (method 4434), steroid hormones in bottom sediment (method 6434), and human-use pharmaceuticals and antidepressants in bottom sediment (method 9008).

### Water Chemical Analyses

The surface-water and wastewater-effluent samples (water samples) were split into numerous parts for analyses. Unfiltered samples were analyzed for boron, total nitrogen, and total phosphorus (NWQL methods 2354, 2333, and 2756, respectively) using standard analytical techniques described in Patton and Truitt (1992), U.S. Environmental Protection Agency (1993), and Fishman and others (1994).

Unfiltered samples were analyzed for organic chemicals typically present in domestic and industrial wastewater and nonpoint sources using NWQL method 4433 (Zaugg and others, 2006) ([table 2](#)). The method targets chemicals that are indicators of wastewater or have endocrine-disrupting potential in unfiltered samples. Chemical types or uses include alkylphenol ethoxylate nonionic surfactants, food additives, fragrances, antioxidants, flame retardants, plasticizers, industrial solvents, disinfectants, animal and plant sterols, polycyclic aromatic hydrocarbons, and selected pesticides. A suite of 48 pharmaceuticals also was added to method 4433 (research method 8244). Chemicals analyzed using laboratory method 4433/8244 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°C. The holding-time limit 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 NWQL research method 4434 (Foreman and others, 2012) ([table 2](#)). Isotope dilution standards (IDSs), which are isotopically labeled analogs of the method analytes, 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). Analyte concentrations were calculated using isotope-dilution quantification, which automatically corrects for any laboratory procedural losses in the reported chemical concentration. Absolute (non-corrected) recoveries were reported for the IDS compounds that are comparable to surrogate compound recoveries in other NWQL methods.

Unfiltered samples collected during 2010 were analyzed at the NWQL for tentatively identified chemicals (TICs) using research method 2753. Chemicals were tentatively identified by matching their mass spectrum to a reference mass spectrum in the National Institute of Standards and Technology's NIST05a mass spectral reference library; however, the mass spectrometer was not calibrated to determine the concentration for any of the reported TICs. Thus, although TIC concentrations are provided in this report, these results are most suitable as indicators of likely compound presence/absence and not as being a quantitatively reliable concentration.

### Bottom-Sediment Chemical Analyses

Bottom-sediment samples were split into portions and analyzed for three carbon types (total, inorganic, and organic) using laboratory method 2503 described in Wershaw and others (1987), organic wastewater indicators (method 5433), steroid hormones (research method 6434), and human-use pharmaceuticals and antidepressants (research method 9008) at the NWQL ([table 2](#)). A subset of each sample also was analyzed for particle size using the dry-sieve method of analysis at the USGS Iowa Water Science Center Sediment Laboratory, which closely follows the recommendations of Guy (1969) and Tyler Industrial Products (1976).

Bottom-sediment samples were analyzed for wastewater indicators (method 5433) according to Burkhardt and others (2006). The method used pressurized liquid extraction (PLE) using an accelerated solvent extraction instrument (ASE®; Dionex Corp., Sunnyvale, Calif.), 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* using NWQL research method 6434. Similar to water method 4434, 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 steroid hormone analyses 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 sub-sampling for extraction or for separate dry-weight determination. Dry weight was obtained by weighing a sample aliquot, contained in a tarred aluminum pan, before and after heating at 130°C for at least 16 hours. Amounts used for extraction of samples in this study ranged from 1.04 to 13.2 g of sediment (dry weight), with lesser amounts used for matrices anticipated to have high organic matter or method chemical concentrations. A subsample was placed in a tarred 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°C and water:isopropanol (20:80 v/v) at 200°C 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 pH 7 potassium phosphate buffer solution and sequentially passed through an OASIS® hydrophilic-lipophilic-balanced reversed-phase sorbent (Waters Corp., Milford, Mass.) SPE column 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 by using 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 analyzed by GC/MS/MS using procedures similar to water method 4434 (Foreman and others, 2012).

Bottom-sediment samples were analyzed for two suites of pharmaceuticals using NWQL research method 9008. One suite encompasses a range of prescription and non-prescription pharmaceuticals and is referred to as human-use pharmaceuticals. The second suite measures antidepressants and is referred to as such. For the analysis of both suites of pharmaceuticals

in bottom sediment, a method described by Kinney and others (2006) was used for extraction and 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 (bupropion, carbamazepine, citalopram, duloxetine, fluoxetine, fluvoxamine, norfluoxetine, nortriptyline, 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 ([table 2](#)) for human-use pharmaceuticals and antidepressants are considered provisional limits of quantitation.

## Quality Assurance

This section of the report presents the quality-assurance data collected for the study. Data are presented for water samples (surface water and wastewater effluent) and bottom-sediment samples. The USGS Minnesota District Quality Assurance Plan and the USGS National Field Manual (U.S. Geological Survey, 2010) were used to guide data-collection activities for the study. USGS guidelines and standard procedures for water and bottom-sediment collections were used for this study to assure quality data collection. All field personnel were familiarized with study design and sampling protocols before field sampling or data processing to assure sample integrity.

## Database Integrity

The first tier of quality assurance was dataset confirmation, which included a comparison of field sheets to the data stored in the USGS National Water Information System (NWIS) database to assure that sample coding was correct. This step was particularly important given the complexity of site selection and that multiple agencies collected the data. The USGS station identifiers, station names, and other parameters (sample time, sample type, sample medium) were confirmed. These variables are essential to catalog the data in the NWIS database and to transfer the samples to the NWQL.

## Laboratory Reporting Levels

Laboratory reporting levels (LRLs) used by the NWQL are designed to minimize the reporting of false positive results and, under specific data reporting conventions, false negative results (see additional information in appendix C in U.S. Geological Survey, 2010). A false positive occurs when a chemical



is reported present when, in fact, none is present in a sample, whereas a false negative occurs 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 chemical identifications are determined by mass spectrometry. 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 for most analytes. The intention is to provide as much information as possible for complex samples, 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 LRL 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 noise levels, or, for those methods using mass spectrometry, when mass spectral qualifying criteria are not met and the response is less than the LRL concentration. The LRL values are re-evaluated annually based on the most current quality-control data and, therefore, might change (Childress and others, 1999).

The NWQL uses remark codes to provide information about the analyses. Because concentration data less than the LRL have a greater risk of false positives, the reported concentrations should be carefully compared to laboratory and field blank data for evaluation. The “E” (estimated remark) code is applied to analyte data by the NWQL for a variety of reasons (Childress and others, 1999), including, for example, (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 bottom-sediment data have multiple LRLs for a given chemical. Methods 5433 and 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. This 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 (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 raised reporting levels can occur because of matrix interference with the instrument’s ability 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. Laboratory quality-assurance samples included reagent-water blanks and spikes that are collected for all USGS methods as part of ongoing performance assessment and evaluation of potential interferences and contamination sources, and are used to set or adjust LRLs. Surrogate compounds were added before extraction to all samples for organic methods to monitor sample-specific procedural performance.

## Laboratory Blank Samples

For the analyses in this report, data for laboratory reagent blank samples of water and bottom sediment analyzed with environmental samples at the NWQL during the 2 years of this study were considered. Concentrations in environmental samples were compared to concentrations in the companion laboratory blank sample that was analyzed with the environmental sample. If an environmental sample concentration was less than three times the laboratory blank sample concentration, the concentration was flagged in the dataset with a “C<sub>1</sub>” qualifier to indicate potential sample contamination in laboratory blank samples.

For method 4433 for analyses of wastewater indicators in unfiltered water, 13 laboratory blank samples in 2010 and 13 in 2011 were analyzed along with environmental samples. During 2010 and 2011, all reported concentrations in environmental samples were greater than three times the concentration in the companion laboratory blank samples.

For research method 8244 for analyses of pharmaceuticals in unfiltered water, 13 laboratory blank samples in 2010 and 12 in 2011 were analyzed along with environmental samples. Methocarbamol was detected in one environmental sample in 2010 at a concentration less than three times laboratory blank concentrations, and this concentration was flagged with a “C<sub>1</sub>” qualifier code in [appendix 1](#) (link to Excel spreadsheet) to indicate potential contamination in laboratory blank samples. During 2011, all reported concentrations in environmental concentrations were greater than three times the concentration in the companion laboratory blank samples.

For research method 4434 for analyses of steroid hormones in unfiltered water, 14 laboratory blank samples in 2010 and 13 in 2011 were analyzed along with environmental samples. During 2010 and 2011, all reported concentrations in environmental samples were greater than three times the concentration in the companion laboratory blank samples.

The NWQL analyzed laboratory bottom-sediment sample blanks consisting of a baked reagent-sand matrix. 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 nanograms) of an analyte that results in a 0.14 nanograms per gram (ng/g) or 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 analyte's concentration in the given sample by the weight of the sample.

All bottom-sediment samples were analyzed in 2011, and 14 laboratory blank samples were analyzed with companion environmental samples. The total mass of all reported chemicals in bottom-sediment environmental samples analyzed using method 5433, method 6434, and research method 9008 were greater than three times the total mass of that chemical detected in laboratory reagent blank samples. Chemicals frequently detected in laboratory blanks generally have raised LRLs to ensure that false positives are not reported.

## 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 selected 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. 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. Acceptable chemical performance is described as having mean laboratory reagent spike recoveries between 60 and 120 percent (Foreman and Green, 2008). The number of laboratory reagent spike samples analyzed with environmental water samples ([table 3](#), link to Excel spreadsheet) and bottom-sediment samples ([table 4](#), link to Excel spreadsheet) varied by the chemical analyzed and laboratory method.

There were 25 laboratory reagent-water spikes (13 in 2010 and 12 in 2011) for all chemicals analyzed using method 4433 ([table 3](#)). The mean percent recovery (mPR) of laboratory reagent-water spikes for chemicals analyzed using method 4433 ranged from 2 to 105 ([table 3](#)). The mPRs were greater during 2011 than 2010 for 84 percent of the chemicals analyzed using method 4433 ([table 3](#)); however, in most cases, the mPRs for both years fell within the acceptable limits range of 60 to 120 percent.

The mPRs for 1,4-dichlorobenzene; 3-*beta*-coprostanol; 3,4-dichlorophenyl isocyanate; 3-*tert*-butyl-4-hydroxy anisole (BHA); 5-methyl-1H-benzotriazole; *beta*-sitosterol; *beta*-stigmastanol; cholesterol; cotinine; *d*-limonene; isopropylbenzene; pentachlorophenol; and tetrachloroethene were relatively lower than mPRs for other chemicals in method 4433 (mPRs less than 60 percent for one or both years). Chemicals with

PRs 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).

As many as 5 to 24 laboratory reagent-water spike samples (mean of 23) were analyzed for chemicals using research method 8244 during both years. No clear pattern in the mPRs was evident by year for method 8244 ([table 3](#)). The pharmaceuticals 2-ethyl-2-phenylmalonamide, acetaminophen, amitriptyline, chirald, codeine, dihydrocodeine, fluoxetine, hydrocodone, methocarbamol, norpropoxyphene, oxcarbazepine, oxycodone, and primidone had relatively lower recoveries than other chemicals analyzed by method 8244 (mPRs less than 60 percent) during one or both years. Meperidine, methylphenidate, temazepam, and venlafaxine had the highest mPRs (greater than 120 percent) during one or both years.

For research method 4434, 27 laboratory reagent-water spike samples were analyzed for each chemical—11 in 2010 and 16 in 2011. The mPRs for all chemicals on method 4434 were between 65 and 100 percent, and a pattern of mPRs by year was not apparent.

The NWQL analyzed laboratory reagent spike samples consisting of an ashed sand matrix fortified with low concentrations of selected chemicals. All laboratory reagent sediment spike samples were analyzed in 2011. Thirteen laboratory reagent spike samples were analyzed using laboratory method 5433 along with companion environmental samples ([table 4](#)). The mPRs for all chemicals analyzed in laboratory reagent spike samples for method 5433 ranged from 18 to 116 percent. The chemicals 3-*tert*-butyl-4-hydroxy anisole (BHA), atrazine, bisphenol A, chlorpyrifos, *d*-limonene, indole, isopropylbenzene, triphenyl phosphate, and tris(dichlorisopropyl)phosphate had relatively lower mPRs in laboratory reagent spike samples (less than 60 percent) than other method 5433 chemicals.

The number of laboratory reagent-sand spike samples ranged from 18 to 21 among chemicals analyzed using research method 6434 for bottom sediment ([table 4](#)). The mPRs for chemicals analyzed in laboratory spike samples using method 6434 ranged from 71 to 116 percent. All of the chemicals on method 6434 had mPRs greater than 80 percent with the exception of equilin, which had an mPR of 71 percent.

The NWQL analyzed 15 laboratory reagent-sand spikes for chemicals on research method 9008 for human-use pharmaceuticals and antidepressants in bottom sediment. The mPRs ranged from 4 to 81 percent among all chemicals analyzed in method 9008 ([table 4](#)). Most of the chemicals had mPRs less than 60 percent except for carbamazepine, warafin, citalopram, nortriptyline, sertraline, and venlafaxine, which had mPRs ranging from 63 to 81 percent.

## 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 method. In addition, all samples were fortified with surrogate compounds that are similar to the chemicals of interest but do not interfere with the analyses of the chemicals, and were used to comparatively assess method performance in the presence of the sample matrix.

## Field Blank Water Samples

Field blank water samples were prepared at selected sampling sites where corresponding environmental samples were 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, Penn.) through the same sampling equipment, using the same procedure as used for collection of the environmental and duplicate water samples.

None of the analyzed chemicals were detected in five of the seven blank water samples collected during 2010 ([appendix 1](#)). During 2010, concentrations near or less than the reporting level were reported for naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene in one blank sample, and for tetrachloroethene in the other blank sample. These chemicals were not detected in the companion environmental samples.

During 2011, two chemicals [tetrachloroethene and tris(2-butoxyethyl)phosphate] were detected in one blank sample, four chemicals [*N,N*-diethyl-*meta*-toluamide (DEET), phenol, triphenyl phosphate, and tris(2-butoxyethyl) phosphate] were detected in a second blank sample, and one chemical (isophorone) was detected in a third blank sample. Tetrachloroethene and isophorone concentrations in the companion environmental samples were greater than three times the concentration in the blank sample, indicating that contamination is not an issue. Concentrations of DEET, phenol, triphenyl phosphate, and tris(2-butoxyethyl)phosphate in one of the companion environmental samples were less than three times the concentration in the field blank water sample; therefore, the concentrations in those environmental samples were flagged with a “C<sub>f</sub>” qualifier code to indicate possible contamination from field collection and subsequent sample processing.

## 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 an analyte in an environmental sample should vary little, if any, from its concentration in the corresponding duplicate sample. If the two do not agree, the

absolute relative percent difference (RPD) determines to what extent the concentrations vary. The equation for calculating absolute RPD is as follows:

$$RPD = \left| \frac{ENV - FDUP}{\left( \frac{ENV + FDUP}{2} \right)} \right| * 100 \quad (1)$$

where

ENV is the concentration in an environmental sample, and  
FDUP is the concentration in the corresponding field duplicate sample.

RPDs were calculated for chemicals in sample pairs where both samples had detections. The mean RPDs among all chemicals for the 22 duplicate water samples for 2010 and 2011 ranged from 1.5 to 82.7 percent ([table 5](#), link to Excel spreadsheet). The mean RPD was greatest (greater than 50 percent) for 3-*beta*-coprostanol, *beta*-sitosterol, hydrocodone, *p*-cresol, pentachlorophenol, piperonyl butoxide, and tetrachloroethene ([table 5](#)). A chemical detected in an environmental and duplicate sample pair may have a small absolute difference from an environmental context, but that difference may be magnified by the calculation of the RPD. For example, the environmental and duplicate sample at the Fox River Sewage Treatment Plant at De Pere, Wis., sampled on June 1, 2011 ([appendix 1](#)), with *p*-cresol concentrations of 0.066 and 0.036 micrograms per liter (µg/L), respectively, would yield a high RPD of 59 percent. The consistency in analyte detection between the environmental and duplicate water samples for individual chemicals ranged from no inconsistency (all chemicals had either detections or non-detections in both samples) to 7 of the 22 pairs having inconsistent detections for some chemicals ([table 5](#)).

The mean RPDs for all chemicals analyzed in the 13 bottom-sediment samples collected during 2010 and 2011 ranged from 6.2 to 78.6 percent with a mean of 25 percent. Bisphenol A, camphor, and *cis*-androsterone had the greatest RPDs (greater than 50 percent) among all chemicals analyzed ([table 5](#)). The consistency in detection between the environmental and duplicate bottom-sediment samples for individual chemicals ranged from no inconsistency (all samples had either detections or non-detections in both samples) to 7 of the 13 pairs having inconsistent detections. The steroid hormones analyzed using research method 6434 had the greatest number of chemicals with inconsistent detections. It was not possible to calculate the RPDs for many chemicals analyzed using research method 9008 for human-use pharmaceuticals and antidepressants in bottom sediments because there were few detections. Cotinine was the only pharmaceutical detected in both pairs with a mean RPD of 42.6 percent.

## Field Matrix Spike Samples

The recoveries of chemicals determined from field matrix spike samples are useful for evaluation of method performance



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. Matrix spike samples were prepared in the laboratory by adding (fortifying) a known (theoretical) concentration of a chemical to the environmental sample, and the percent recovery (PR) was determined using the following equation:

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

The PR was computed by substituting zero for the environmental chemical concentration if that concentration was coded with a less than (<) remark code and the measured spiked sample concentration was coded as estimated or was without a remark code.

Spiked water samples were prepared for laboratory method 4433, research method 8244, and research method 4434 ([table 3](#)); spiked bottom-sediment samples were prepared for laboratory method 5433, research method 6434, and research method 9008 ([table 4](#)). An important consideration for field matrix spike recoveries is the fortification concentrations; that is, theoretical concentrations relative to the concentrations in the unspiked (environmental) samples. If the unspiked sample concentration is much less than the theoretical concentration, then the unspiked sample concentrations will make a trivial contribution to the total concentration in the spiked sample. In this case, the percent recoveries ideally should be in the 60 to 120 range, assuming no procedural or analysis issues (Foreman and Green, 2008). As the unspiked sample concentrations approach the theoretical concentrations, the amount spiked (theoretical concentration) becomes a smaller portion of the total determined concentration, and the unspiked concentrations have a greater (bias) effect on the calculated chemical recovery. If the unspiked concentrations are much greater than the theoretical concentrations, the spiked amount is too low compared to the unspiked concentration. In this case, the recoveries often are substantially biased (positive or negative), highly variable, and typically not reliable. The spiked samples with unspiked concentrations equal to or greater than the spiked amount were coded "NR" or not reported in [table 3](#).

The PRs are useful to identify matrix effects on procedural performance, and are an indication of possible differential biases in reported sample concentrations within and between sites. 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 in a sample due to matrix interference or other analytical issues.

The mPR for field matrix spike water samples among all chemicals analyzed using method 4433 ranged from 20 to 113 percent ([table 3](#)) with an overall mean of 70 percent for all spiked samples. The mPR among all chemicals analyzed

using research method 8244 ranged from 25 to 382 percent with an overall mean of 86 percent for all spiked samples. The mPR for all chemicals analyzed using research method 4434 ranged from 32 to 118 with an overall mean of 88 percent for all spiked samples.

Percent recoveries for field matrix spike water samples varied among sites ([table 3](#)). Site SWC-11 [Swan Creek Site (site 11) near Toledo, Ohio] and site STR-FDL-1 [St. Louis River (site 1) near Fond du Lac, Minn.] had the lowest overall mPRs (less than 52 percent) for all samples by method 4433. Sites SWC-11 and STB-WLSSD-6/WLSSD-proximal [St. Louis Bay Site (site 6) near Western Lake Sanitary Sewer District (WLSSD) WWTP, Duluth, Minn.] had the lowest overall mPRs (less than 53 percent) for all samples by research method 8244. The overall mPRs for all samples analyzed using research method 4434 were similar (ranging from 89 to 98 percent) among sampling sites, with the exception of site STB-WLSSD-2 [St. Louis Bay (site 2) near WLSSD WWTP, Duluth, Minn.], which had relatively greater mPRs (mean of 125 percent).

The mPRs for field matrix spike water samples varied among chemicals analyzed ([table 3](#)). The mPRs for 1,4-dichlorobenzene, 2,2',4,4'-tetrabromodiphenyl ether (PBDE congener 47); 3-*beta*-coprostanol; 3,4-dichloro-phenyl isocyanate, 3-*tert*-butyl-4-hydroxyanisole (BHA); 5-methyl-1H-benzotriazole; benzo[*a*]pyrene; *beta*-sitosterol; *beta*-stigmastanol; chlorpyrifos; cholesterol; cotinine; *d*-limonene; indole; isopropyl benzene; and tetrachloroethene were relatively lower (less than 60 percent) compared with mPRs for other chemicals on method 4433. The chemicals 2-ethyl-2-phenylmalonamide, celecoxib, dihydrocodeine, metaxalone, methylphenidate, oxcarbazepine, oxycodone, and primidone had relatively lower mPRs (less than 60 percent) than other chemicals on research method 8244. Fluconazole, ibuprofen, and methocarbamol had relatively higher (greater than 120 percent) mPRs compared to other chemicals on research method 8244. All of the mPRs for chemicals on research method 4434 were greater than 60 percent with the exception of progesterone, which had an mPR less than 35 percent.

The mPRs for chemicals analyzed in the field matrix spike bottom-sediment samples using laboratory method 5433 ranged from 7 to 162 percent, with an overall mean for all chemicals of 71 percent ([table 4](#)). The mPRs for chemicals analyzed using research method 6434 for spiked bottom-sediment samples ranged from 29 to 121 percent, with an overall mean for all chemicals of 84 percent. The mPRs for chemicals analyzed using research method 9008 for human-use pharmaceuticals in the spiked bottom-sediment samples ranged from 0 to 48 percent, with an overall mean for all chemicals of 13 percent. The mPR for all chemicals analyzed using research method 9008 for antidepressants in the spiked bottom-sediment samples ranged from 1 to 43 percent, with an overall mean for all samples of 7 percent.

The mPRs differed among sites for the field matrix spike samples for some chemicals in bottom sediment. The mPRs

for the spiked samples prepared for site STB-WLSSD-3 [St. Louis Bay (site 3) near WLSSD WWTP, Duluth, Minn.] were relatively lower than spiked samples for other sites, with an overall mPR less than 31 percent for all chemicals analyzed using method 5433 ([table 4](#)). The mPRs for all chemicals at each site were greater than 70 percent for chemicals analyzed using research method 6434. The mPRs for all chemicals at each site were less than 20 percent for chemicals analyzed using research method 9008.

The mPRs for individual chemicals analyzed using laboratory method 5433 were less than 40 percent for 1,4-dichlorobenzene; 3-*tert*-butyl-4-hydroxyanisole (BHA), diethyl phthalate; *d*-limonene; isophorone; isopropylbenzene; and prometon, and less than 60 percent for an additional 14 chemicals ([table 4](#)). The mPRs for all chemicals analyzed using research method 6434 were greater than 60 percent with the exception of equilin and progesterone, which had relatively lower mPRs (less than 40 percent). The mPRs for individual chemicals analyzed using research method 9008 were less than 50 percent for all chemicals.

## Surrogate and Isotope Dilution Standard Recoveries

All samples were fortified with surrogate standards or IDSs (used in research methods 4434 and 6434). Surrogates typically are similar in structure to (or are isotopic analogs of) at least several of the method analytes. 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 analytes for the sample.

IDS recoveries also are indicators of absolute analyte recovery (total analyte mass recovered through the procedure); however, for research methods 4434 and 6434 that use IDS compounds, analyte concentrations (or analyte method recoveries for spiked samples) are corrected for procedural losses by use of the isotope-dilution quantification procedure. Thus, IDS recoveries typically will be somewhat (or substantially) lower than chemical method recoveries reported for spiked samples. Although low IDS recoveries in a sample are an indication of reduced analyte total 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 15 surrogate standards or IDSs were determined for water samples analyzed using method 4433 and research method 4434. The mPRs for the 15 surrogate standards or IDSs for water ranged from 43 to 88 percent ([table 6](#)). The mPRs for decafluorobiphenyl, medroxyprogesterone-*d*<sub>3</sub>, and *trans*-diethyl-1,1,1',1'-*d*<sub>4</sub>-stilbesterol-3,3',5,5'-*d*<sub>4</sub> were relatively lower (less than 60 percent) than other surrogate standards or IDSs in water samples. The recoveries of

surrogate standards or IDSs did not differ appreciably between sites within an AOC or among AOCs.

The mPRs for the 14 surrogate standards or IDSs analyzed using laboratory method 5433 or research method 6434 in bottom-sediment samples ranged from 26 to 94 percent. Bisphenol *A-d*<sub>3</sub>; cholesterol-25,26,26,26,27,27,27-*d*<sub>7</sub>; decafluorobiphenyl; and *trans*-diethyl-1,1,1',1'-*d*<sub>4</sub>-stilbesterol-3,3',5,5'-*d*<sub>4</sub> had relatively lower mPRs (less than 40 percent) than other standards analyzed. The mPRs for the five surrogate standards in bottom-sediment samples analyzed using research method 9008 for pharmaceuticals and antidepressants ranged from 8 to 47 percent.

## Study Data

This section of the report presents the environmental and field quality-assurance data collected for the study of CECs in the Great Lakes AOCs. The results from this study are published as a USGS Data Series Report to ensure adequate documentation of the original results and provide a single citable source of original results. This report contains no interpretations of the study data. These data were collected during 2010–11 by USGS, USFWS, and USEPA 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. Quality-assurance analyses described in the “Laboratory Blank Samples” and “Field Blank Water Samples” sections indicated that laboratory or field contamination was limited during sample collection for this study. The variability determined for chemicals between duplicate and environmental samples ([table 5](#)) provides a benchmark for comparison of data among sites. The spike ([tables 3 and 4](#)), surrogate standard, and IDS recoveries ([table 6](#)) indicate that some methods and some chemicals within a method perform better than others. Equally important, matrix spike recoveries indicate differences in the data that are in some cases likely due to matrix complexities that interfere with analytical determinations that complicate comparisons of data from different sites.

## Water-Quality Properties

Field water-quality properties, including dissolved oxygen, pH, specific conductance, and water temperature, were measured at the study sites during 2010–11. Field water-quality properties are presented in [appendix 1](#). Water-quality properties varied among AOCs and among sites within an AOC. For example, specific conductance was lowest at sites within the Ashtabula River AOC ([appendix 1](#); ranged from 101–150 microsiemens per centimeter at 25°C) and greatest at the Maumee River AOC ([appendix 1](#); ranged from 282–1,068 microsiemens per centimeter at 25°C).

**Table 6.** Summary of surrogate or isotope dilution standard chemical recoveries in water and bottom-sediment samples.

[USGS, U.S. Geological Survey; --, not applicable]

USGS parameter code	Surrogate or isotope dilution standard	Mean percent recovery	Standard devia- tion of percent recovery	Number of sur- rogate samples analyzed
Surrogate standards analyzed in water samples submitted for laboratory method 4433				
62839	Bisphenol <i>A</i> - <i>d</i> <sub>3</sub>	76	22	111
62840	Caffeine- <sup>13</sup> C <sub>6</sub>	76	15	131
62841	Decafluorobiphenyl	53	12	131
62842	Fluoranthene- <i>d</i> <sub>10</sub>	80	16	131
Isotope dilution standards analyzed in water samples submitted for research method 4434				
91680	16-Epiestriol-2,4- <i>d</i> <sub>2</sub>	71	9	130
90827	17- <i>alpha</i> -Ethinylestradiol-2,4,16,16- <i>d</i> <sub>4</sub>	76	9	130
91755	17- <i>beta</i> -Estradiol-13,14,15,16,17,18- <sup>13</sup> C <sub>6</sub>	74	9	130
67309	Bisphenol <i>A</i> - <i>d</i> <sub>16</sub>	88	12	130
90781	Cholesterol-25,26,26,26,27,27,27- <i>d</i> <sub>7</sub>	75	8	130
91616	Estriol-2,4,16,17- <i>d</i> <sub>4</sub>	84	8	60
91756	Estrone-13,14,15,16,17,18- <sup>13</sup> C <sub>6</sub>	79	9	130
91682	Medroxyprogesterone- <i>d</i> <sub>3</sub>	43	23	130
90836	Mestranol-2,4,16,16- <i>d</i> <sub>4</sub>	77	8	130
91683	Nandrolone-16,16,17- <i>d</i> <sub>3</sub>	65	15	130
90832	<i>trans</i> -Diethyl-1,1,1',1'- <i>d</i> <sub>4</sub> -stilbestrol-3,3',5,5'- <i>d</i> <sub>4</sub>	50	15	130
Surrogates standards analyzed with bottom-sediment samples submitted for laboratory method 5433				
90735	Bisphenol <i>A</i> - <i>d</i> <sub>3</sub>	32	9	73
90737	Decafluorobiphenyl	29	9	73
90738	Fluoranthene- <i>d</i> <sub>10</sub>	94	23	73
Isotope dilution standards analyzed with bottom-sediment samples submitted for research method 6434				
91684	16-Epiestriol-2,4- <i>d</i> <sub>2</sub>	63	27	75
91805	17- <i>alpha</i> -Ethinylestradiol-2,4,16,16- <i>d</i> <sub>4</sub>	56	17	75
91757	17- <i>beta</i> -Estradiol-13,14,15,16,17,18- <sup>13</sup> C <sub>6</sub>	51	22	75
67310	Bisphenol <i>A</i> - <i>d</i> <sub>16</sub>	62	28	75
90772	Cholesterol-25,26,26,26,27,27,27- <i>d</i> <sub>7</sub>	28	14	75
91617	Estriol-2,4,16,17- <i>d</i> <sub>4</sub>	65	21	27
91758	Estrone-13,14,15,16,17,18- <sup>13</sup> C <sub>6</sub>	69	26	75
91686	Medroxyprogesterone- <i>d</i> <sub>3</sub>	45	26	75
91813	Mestranol-2,4,16,16- <i>d</i> <sub>4</sub>	63	19	75
91687	Nandrolone-16,16,17- <i>d</i> <sub>3</sub>	44	20	75
91809	<i>trans</i> -Diethyl-1,1,1',1'- <i>d</i> <sub>4</sub> -stilbestrol-3,3',5,5'- <i>d</i> <sub>4</sub>	26	15	75
Surrogates standards analyzed with bottom-sediment samples submitted for research method 9008 for human-use pharmaceuticals				
--	Ethyl nicotinoate- <i>d</i> <sub>4</sub>	17	10	82
--	Carbamazepine- <i>d</i> <sub>10</sub>	29	13	82
Surrogates standards analyzed with bottom-sediment samples submitted for research method 9008 for antidepressants				
--	Carbamazepine- <i>d</i> <sub>10</sub>	47	28	82
--	Fluoxetine- <i>d</i> <sub>5</sub>	8	8	82
--	Norfluoxetine- <i>d</i> <sub>5</sub>	11	11	82

## Water Data

During this study, 135 environmental and 23 field duplicate samples of surface water and wastewater effluent, 10 field blank water samples, and 11 field spike water samples were collected during 2010–11. The samples were analyzed at the USGS NWQL for a wide variety of chemicals.

Boron, nitrogen, and phosphorus were analyzed in a few water samples during 2010 as general indicators of wastewater ([appendix 1](#)). A broad suite of CECs were detected among all water samples. Sixty-one of the 69 chemicals analyzed were detected at concentrations ranging from 0.002 to 11.2 µg/L using method 4433 for wastewater indicators in water. Twenty-eight of the 48 chemicals analyzed were detected at concentrations ranging from 0.0029 to 22.0 µg/L using research method 8244 for pharmaceuticals in water. Ten of the 20 chemicals analyzed were detected at concentrations ranging from 0.16 to 10,000 nanograms per liter (ng/L) using research method 4434 for steroid hormones. The chemicals *N,N*-diethyl-*meta*-toluamide (DEET); cholesterol; isophorone; tris(2-butoxyethyl)phosphate; bisphenol *A*; and caffeine were the most frequently detected chemicals among all water samples (detected in greater than 60 percent of the samples). Analytical results are presented in [appendix 1](#) for the environmental and field quality-assurance water samples.

## Bottom-Sediment Data

During this study, 75 environmental samples, 13 field duplicate samples, and 9 field spike samples of bottom sediment and laboratory matrix spike samples were analyzed for a wide variety of CECs at the NWQL using method 5433 for wastewater indicators, research method 6434 for steroid hormones, and research method 9008 for human-use pharmaceuticals and antidepressants. Forty-seven of the 57 chemicals analyzed were detected at concentrations ranging from 0.921 to 25,800 ng/g using method 5433 for wastewater indicators. Seventeen of the 20 chemicals analyzed were detected at concentrations ranging from 0.006 to 8,921 ng/g using research method 6434 for steroid hormones, sterols, and bisphenol *A*. Twelve of the 20 chemicals analyzed were detected at concentrations ranging from 2.35 to 453.5 ng/g using research method 9008 for human-use pharmaceuticals. Six of the 11 chemicals analyzed were detected at concentrations ranging from 2.79 to 91.6 ng/g using research method 9008 for antidepressants. Analytical results are presented in [appendix 2](#) (link to Excel spreadsheet) for the environmental and field quality-assurance bottom-sediment samples.

## Tentatively Identified Chemicals in Water Samples

During 2010, environmental water samples were analyzed to determine the occurrence of non-target CECs at the NWQL by using custom method 2753. Concentration data

from the custom method 2753 analysis are presented in a preliminary format in [appendix 3](#) (link to Excel spreadsheet) for the environmental and field quality-assurance samples. The estimated concentrations reported for tentatively identified chemicals (TICs) analyzed by using custom method 2753 are qualitative.

## Summary

Synoptic surveys of surface-water quality across the United States have detected a large group of organic chemicals associated with agricultural, household, and industrial waste. These contaminants 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. Research indicates that fish and wildlife can be affected by some of these CECs at environmentally relevant concentrations, producing developmental and reproductive problems.

The U.S. Geological Survey (USGS) cooperated with the U.S. Environmental Protection Agency (USEPA) and the U.S. Fish and Wildlife Service (USFWS) on a study to identify the occurrence of CECs in water and bottom-sediment samples collected during 2010–11 at sites in seven areas of concern (AOCs) throughout the Great Lakes. This report documents the collection methods, analyses methods, quality-assurance data and analyses, and provides the data for environmental samples collected for this study.

Field measurements and sample collections were completed from September 19, 2010, to September 6, 2011, by a combination of USGS, USFWS, and USEPA personnel. Study sites included tributaries to the Great Lakes in AOCs located near Duluth, Minn.; Green Bay, Wis.; Rochester, N.Y.; Detroit, Mich.; Toledo, Ohio; Milwaukee Wis.; and Ashtabula, Ohio. Water and bottom-sediment samples were analyzed at the USGS National Water Quality Laboratory in Denver, Colo., for a broad suite of chemicals that are indicators of industrial, domestic, and agricultural wastewaters using a variety of laboratory and research methods.

Few concentrations of chemicals analyzed in laboratory reagent blank samples were greater than environmental water and bottom-sediment sample concentrations. Almost all of the environmental sample concentrations were greater than three times the laboratory blank concentrations, indicating that laboratory contamination was not affecting environmental concentrations. Chemicals frequently detected in laboratory reagent blanks generally have raised laboratory reporting levels to ensure that false positives are not reported. Data from the field blank water samples generally indicate that field cleaning and sampling protocols were sufficient to avoid most contamination of environmental samples; however, three chemicals—phenol, triphenyl phosphate, and 2-(butoxyethyl)phosphate in field blank water samples had concentrations that were



greater than three times the concentration in the environmental samples. Therefore, the concentrations in those environmental samples were flagged in the dataset.

The combination of results from laboratory reagent spikes samples and field matrix spike samples provides information about laboratory performance with time, site-to-site differences due to matrix-specific analytical performance issues, and potentially differential bias in sample concentrations. Relatively higher percent recoveries for spike samples indicate that sample concentrations might be biased high, whereas relatively lower percent recoveries indicate that sample concentrations might be biased low in a sample due to matrix interference or other analytical issues. Acceptable chemical performance in a method generally is described as having mean percent recoveries between 60 and 120 percent. Percent recoveries for most of the chemicals analyzed in laboratory reagent spiked and field matrix spiked water samples were in this acceptable range; however, some chemicals had low percent recoveries, which might indicate that the reported concentrations in the environmental samples also are biased low, or that the risk is higher for false negatives (that is, that the true concentration exceeds the reported “less than”).

Most of the mean percent recoveries for chemicals analyzed in laboratory reagent and field matrix spike samples for bottom sediment were in the acceptable range for method 5433 for analyses of wastewater indicators in bottom sediment and research method 6434 for analyses of steroid hormones in bottom sediment; however, the mean percent recoveries in the field matrix spike sample of chemicals analyzed using research method 9008 for analyses of for human-use pharmaceuticals and antidepressants were all less than 50 percent, indicating poor recovery of method chemicals.

During this study, 135 environmental and 23 field duplicate samples of surface water and wastewater effluent, 10 field blank water samples, and 11 field spike water samples were collected during 2010–11 and analyzed at the USGS National Water Quality Laboratory for a wide variety of CECs. Sixty-one of the 69 chemicals analyzed were detected at concentrations ranging from 0.002 to 11.2 micrograms per liter using laboratory method 4433 for wastewater indicators in water. Twenty-eight of the 48 chemicals analyzed were detected at concentrations ranging from 0.0029 to 22.0 micrograms per liter using research method 8244 for pharmaceuticals in water. Ten of the 20 chemicals analyzed were detected at concentrations ranging from 0.16 to 10,000 nanograms per liter using research method 4434 for steroid hormones in water. The chemicals *N,N*-diethyl-*meta*-toluamide (DEET); cholesterol; isophorone; tris(2-butoxyethyl)phosphate; bisphenol *A*; and caffeine were the most frequently detected chemicals among all water samples (detected in greater than 60 percent of the samples). During 2010, environmental water samples also were analyzed to determine the occurrence of non-target CECs at the USGS National Water Quality Laboratory using custom laboratory method 2753. Data for the environmental and field quality-assurance samples from this analysis of tentatively

identified chemicals are presented in a preliminary format and are not considered quantitative.

During this study, 75 environmental, 13 field duplicate samples, and 9 field spike samples of bottom sediment were collected and analyzed for a wide variety of organic chemicals at the National Water Quality Laboratory using laboratory method 5433 for wastewater indicators, research method 6434 for steroid hormones, and research method 9008 for human-use pharmaceuticals and antidepressants. Forty-seven of the 57 chemicals analyzed in bottom-sediment samples were detected at concentrations ranging from 0.92 to 25,800 nanograms per gram using method 5433 for wastewater indicators. Seventeen of the 20 chemicals analyzed were detected at concentrations ranging from 0.006 to 8,921 nanograms per gram using research method 6434 for steroid hormones. Twelve of the 20 chemicals analyzed were detected at concentrations ranging from 2.35 to 453.5 nanograms per gram using research method 9008 for human-use pharmaceuticals. Six of the 11 chemicals analyzed were detected at concentrations ranging from 2.79 to 91.6 nanograms per gram using research method 9008 for antidepressants.

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## Appendixes 1–3

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These data files are included with the U.S. Geological Survey (USGS) Data Series 723 and are available for download at <http://pubs.usgs.gov/ds/723/downloads>. See report text for details about the study. The data tables are available for download in Microsoft® Excel (.xlsx) format. The [read me](#) contains information about the data. There are three appendixes included in this report.

## **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 “[Appendix\\_1.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 boron, total nitrogen, and total phosphorus (laboratory methods 2354, 2333, and 2756, respectively); 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 “[Appendix\\_2.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 carbon; 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. This spreadsheet also contains particle-size analyses for bottom-sediment samples.

## **Appendix 3. Occurrence and estimated concentrations of tentatively identified chemicals in water samples and quality-assurance samples analyzed at the U.S. Geological Survey National Water Quality Laboratory using custom laboratory method 2753.**

The Excel spreadsheet “[Appendix\\_3.xlsx](#)” contains estimated concentrations of non-target chemicals of emerging concern analyzed at the U.S. Geological Survey’s National Water Quality Laboratory using custom method 2753. The data from this analysis are presented in a preliminary format and are not considered quantitative. Reported compounds were identified by matching their mass spectrum to a reference mass spectrum in the National Institute of Standards and Technology NIST05a mass spectral reference library. The mass spectrometer was not calibrated for the quantitative determination of any of the analytes reported by this analysis. Thus, the results presented are compounds analyzed by using custom method 2753 are qualitative, and should not be considered quantitative rather than quantitative because the provided concentrations could not be accurately determined. Tentatively identified chemicals are reported as approximate concentrations and are most suitable as indications of the chemical presence.

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