

Prepared in cooperation with the Minnesota Pollution Control Agency and the Wisconsin Department of Natural Resources

Presence of Selected Chemicals of Emerging Concern in Water and Bottom Sediment from the St. Louis River, St. Louis Bay, and Superior Bay, Minnesota and Wisconsin, 2010



Scientific Investigations Report 2012–5184

Front cover. Bottom-sediment collection on Superior Bay, Minnesota, August 2010.

Back cover. Bottom-sediment collection on Superior Bay, Minnesota, August 2010.

Photographs by Minnesota Pollution Control Agency personnel.

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Conversion Factors and Datums

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	milliliter (mL)
Flow rate		
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m ³ /s)
Mass		
ounce, avoirdupois (oz)	28.35	gram (g)
pound avoirdupois (lb)	0.4536	kilogram (kg)

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 ($\mu\text{S}/\text{cm}$ at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$). Concentrations of chemical constituents in bottom sediment are given in micrograms per kilogram ($\mu\text{g}/\text{kg}$) or nanograms per gram (ng/g).

Acronyms and Abbreviations

CEC	chemical of concern
DEET	<i>N,N</i> -diethyl- <i>meta</i> -toluamide
E	estimated
EAC	endocrine active chemical
GC/MS/MS	gas chromatography/tandem quadrupole mass spectrometry
HHCB	hexahydrohexamethyl cyclopentabensopyran
HPLC/MS/MS	high-performance liquid chromatography/tandem mass spectrometry
IDS	isotope dilution standard
IJC	International Joint Commission
MDL	method detection limit
MPCA	Minnesota Pollution Control Agency
NWQL	National Water Quality Laboratory
PAH	polycyclic aromatic hydrocarbon
PhAC	pharmaceutically active compound
RL	reporting level
RPD	relative percent difference
SQT	sediment-quality target
TPAH ₇	total concentration of 7 PAHs analyzed in this study for which sediment-quality targets exist
TPAH ₁₃	total concentration of 13 PAHs identified by the U.S. Environmental Protection Agency as priority pollutants
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
WIDNR	Wisconsin Department of Natural Resources
WWTP	wastewater treatment plant

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Abstract

The St. Louis Bay of Lake Superior receives substantial urban runoff, wastewater treatment plant effluent, and industrial effluent. In 1987, the International Joint Commission designated the St. Louis Bay portion of the lower St. Louis River as one of the Great Lakes Areas of Concern. Concerns exist about the potential effects of chemicals of emerging concern on aquatic biota because many of these chemicals, including endocrine active chemicals, have been shown to affect the endocrine systems of fish.

To determine the occurrence of chemicals of emerging concern in the St. Louis River, the St. Louis Bay, and Superior Bay, the U.S. Geological Survey in cooperation with the Minnesota Pollution Control Agency and the Wisconsin Department of Natural Resources collected water and bottom-sediment samples from 40 sites from August through October 2010. The objectives of this study were to (1) identify the extent to which chemicals of emerging concern, including pharmaceuticals, hormones, and other organic chemicals, occur in the St. Louis River, St. Louis Bay, and Superior Bay, and (2) identify the extent to which the chemicals may have accumulated in bottom sediment of the study area. Samples were analyzed for selected wastewater indicators, hormones, sterols, bisphenol *A*, and human-health pharmaceuticals.

During this study, 33 of 89 chemicals of emerging concern were detected among all water samples collected and 56 of 104 chemicals of emerging concern were detected in bottom-sediment samples. The chemical *N,N*-diethyl-*meta*-toluamide (DEET) was the most commonly detected chemical in water samples and 2,6-dimethylnaphthalene was the most commonly detected chemical in bottom-sediment samples. In general, chemicals of emerging concern were detected at a higher frequency in bottom-sediment samples than in water samples.

Estrone (a steroid hormone) and hexahydrohexamethyl cyclopentabensopyran (a synthetic fragrance) were the most commonly detected endocrine active chemicals in water samples; *beta*-sitosterol (a plant sterol), estrone, and 4-*tert*-octylphenol (an alkylphenol) were the most commonly detected endocrine active chemicals in bottom-sediment samples. The greater detection frequency of chemicals in bottom-sediment samples compared to the detection frequency in water samples indicates that bottom sediment is an important sink for chemicals of emerging concern. At least one polycyclic aromatic hydrocarbon was detected in every sample; and in most samples, all nine polycyclic aromatic hydrocarbons included in analyses were detected. Bottom sediment collected from Superior Bay had the most polycyclic aromatic hydrocarbon detections of the sediment sampling locations.

Introduction

A broad group of chemicals of emerging concern (CECs) [also called contaminants of emerging concern in the literature] including prescription drugs, over-the-counter medications, reproductive hormones, personal-care products, surfactants, plastic components, flame retardants, and an array of other chemicals have been identified in surface waters from many states, including Minnesota (Loper and others, 2007; Fono and others, 2006; Brown and others, 2006; Sando and others, 2005; Lee and others, 2004; Kolpin and others, 2002; Buser and others, 1999; Barber and others, 2000, 2007; Lee, Schoenfuss, and others, 2008; Lee, Yaeger, and others, 2008; Martinovic and others, 2008; Lee and others, 2010, 2011). Streams receiving municipal and industrial wastewaters appear to be the most affected (Kolpin and others, 2002; Lee and others, 2004; Barber and others, 2000, 2007; Lee and others, 2010), but other sources have been identified, including on-site septic systems (Carrara and others, 2008; Godfrey and others, 2007). From a functional standpoint, CECs include endocrine active chemicals (EACs) capable of endocrine

¹ U.S. Geological Survey.

² University of St. Thomas.

disruption and pharmaceutically active compounds (PhACs) designed for human or animal consumption. Although PhACs are designed to benefit humans or animals when ingested, PhACs may have an unwanted biological effect in the environment (Halling-Sorenson and others, 1998). Most CECs occur at low concentrations in water (Kolpin and others, 2002; Lee and others, 2004; Lee and others, 2010) and evidence indicates that adverse effects at low doses are common (Vandenberg and others, 2012). Many CECs also have been detected in bottom sediment (Mayer and others, 2007; Pojana and others, 2007; Kim and Carlson, 2007; Lee and others, 2010; Writer and others, 2010).

Current research indicates that EACs cause developmental and reproductive problems that affect fish and wildlife. For example, changes in fish endocrine systems have been documented (Iguchi and others, 2001; Barber and others, 2007; Schoenfuss and others, 2001), and intersex fish have been found in areas with known EACs (Hinck and others, 2006; Woodling and others, 2006). In 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 (*Stizostedion vitreum*) (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) and in fathead minnows (*Pimephales promelas*) exposed to wastewater in Minnesota (Barber and others, 2007; Martinovic and others, 2008). Ecological disruption potential from EACs and other CECs is substantial, and the current understanding of their distribution in the St. Louis River is incomplete.

Previous work in Minnesota streams and rivers has documented the occurrence of CECs downstream from WWTPs. One of the earliest studies by Lee and others (2004) analyzed samples from 65 sites for the presence of 91 CECs, including pharmaceuticals, surfactants, fragrances, plastic components, and disinfectants. In that study, surface-water samples from across the State of Minnesota (and in waters shared with the States of Wisconsin, North Dakota, and South Dakota) identified 56 CECs from 32 surface-water sites. Some of the more commonly detected compounds included caffeine, cholesterol, and acetaminophen. Sites located on small streams with an upstream WWTP had the highest average number of chemicals detected, but small streams draining urban land without WWTP effluent contributions also had detections of organic wastewater contaminants. This study also identified the St. Louis Bay of Lake Superior as having detectable concentrations of 13 CECs (Lee and others, 2004).

In 1987, the International Joint Commission (IJC) designated the St. Louis Bay portion of the lower St. Louis River as one of the Great Lakes Areas of Concern originally because of large loads of suspended solids, nutrients, and biochemical oxygen demand directly discharged into the river by various industries and communities (St. Louis River Alliance, 1992). In 1989, the Minnesota Pollution Control Agency (MPCA) and the Wisconsin Department of Natural Resources

(WIDNR) collaborated on an effort to address those issues in an area that focuses on the lower 39 river miles (mi) of the St. Louis River and the entire Nemadji River basin. Although much is known about the presence of polycyclic aromatic hydrocarbons (PAHs) and metals in the St. Louis River (Crane and Schubauer-Berigan, 1997a, b), little is known about the presence, persistence, or fate of CECs in hydrological settings like the lower St. Louis River and Bay complex.

To determine the occurrence of chemicals of emerging concern in the St. Louis River, the St. Louis Bay, and Superior Bay, the U.S. Geological Survey (USGS) cooperated on a study with the MPCA and the WIDNR to collect water and bottom-sediment samples during 2010. The objectives of this study were to (1) identify the extent to which CECs, including pharmaceuticals, hormones, and other organic chemicals, occur in the St. Louis River, St. Louis Bay, and Superior Bay, and (2) identify the extent to which the chemicals may have accumulated in bottom sediment of the study area. Water and bottom-sediment samples were collected at 40 sites from August through October 2010. Samples were analyzed for selected wastewater indicators, human-health pharmaceuticals, hormones, sterols, and a plastic component (bisphenol A).

This study contributes to an integrated framework for understanding the distribution and fate of CECs in rivers and lakes in the Great Lakes area. The information from this study assists the States of Wisconsin and Minnesota in their efforts to assess the nature and scope of this issue. This study also allows further assessment of progress towards the Lake Superior Zero Discharge Demonstration Program (Lake Superior Binational Program, 2007).

Description of Study Area

The St. Louis River flows 179 mi from its headwaters in northern Minnesota to the southwestern part of Lake Superior between Duluth, Minnesota, and Superior, Wisconsin. The St. Louis River forms a large freshwater estuary at its entry to Lake Superior, and this estuary forms part of the border between Minnesota and Wisconsin (figs. 1, 2). The St. Louis River drains 3,634 mi² of predominantly forested and wetland area, including State and National Forest and drains the Mesabi Iron Range, noted for rich deposits of iron ore (Lindholm and others, 1979; Wisconsin Department of Natural Resources, 2010).

Much of the St. Louis River drainage basin is sparsely populated, but as the river meanders to the northeast, it flows into the relatively densely populated cities of Duluth, Minnesota, and Superior, Wisconsin (Lindholm and others, 1979). Near Duluth and Superior, the river takes on the characteristics of a freshwater estuary, with a lower estuary characterized by urban development (U.S. Environmental Protection Agency, 2012). The lower estuary includes St. Louis Bay and Superior Bay. Finally, the river enters Lake Superior where it is affected by multidirectional flow between Superior Bay and Lake Superior.

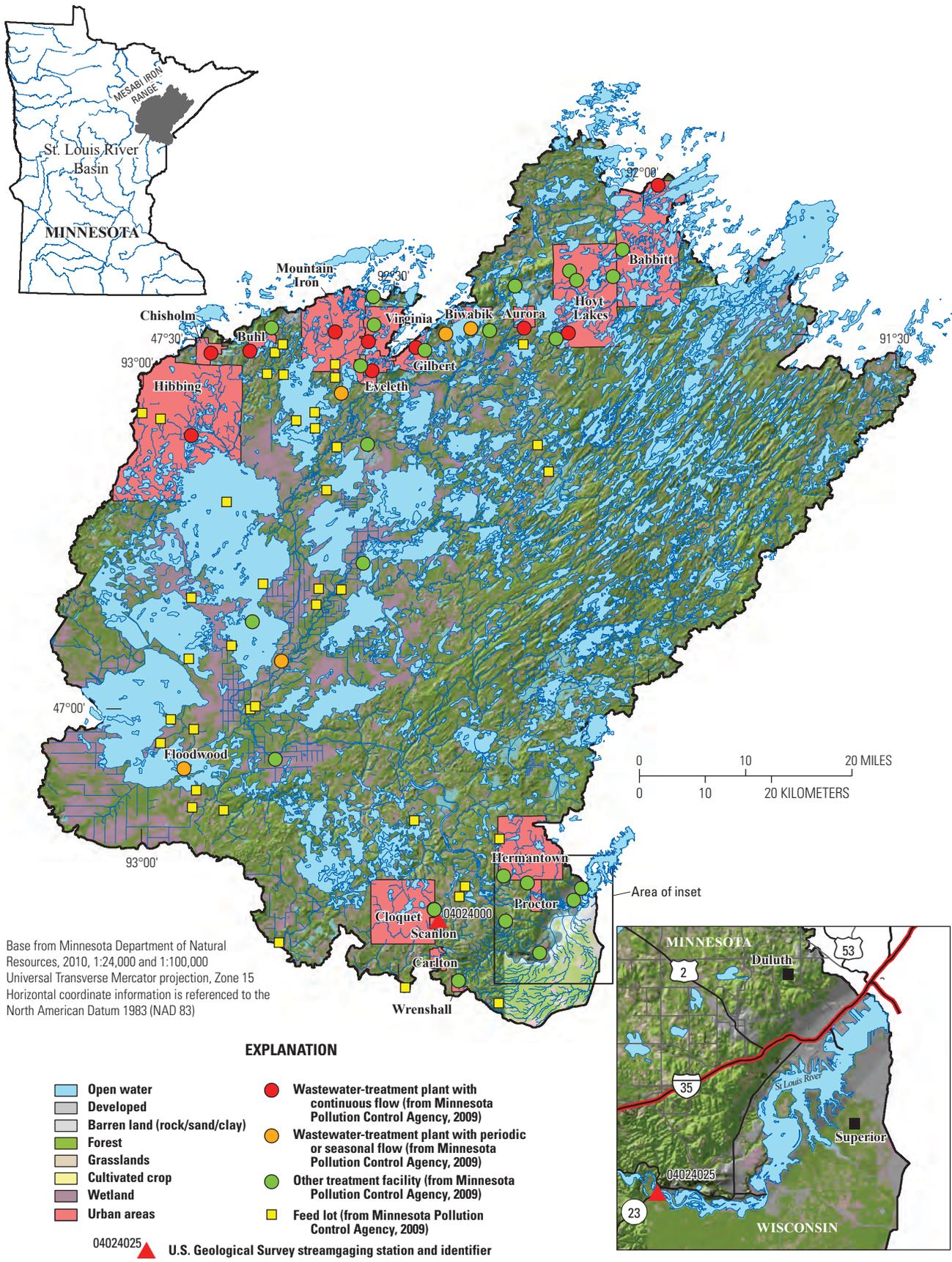


Figure 1. Characteristics of the drainage basin upstream from the St. Louis River, St. Louis Bay, and Superior Bay study area, Minnesota and Wisconsin.

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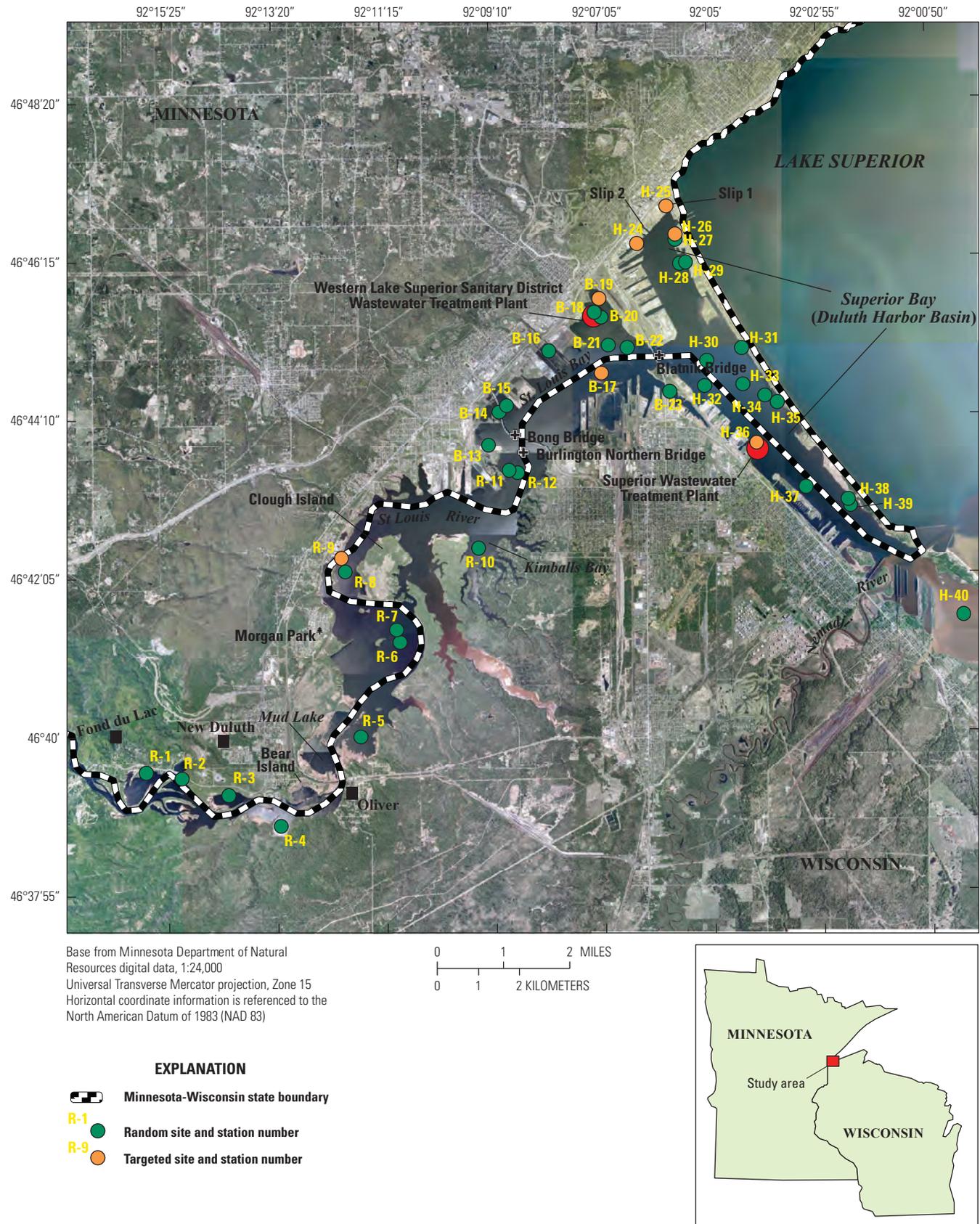


Figure 2. St. Louis River, St. Louis Bay, and Superior Bay study area and sampling sites, Minnesota and Wisconsin.

Urban land uses, industrial land uses, shipping facilities, and two WWTPs affect water quality in the St. Louis Bay and Superior Bay parts of the study area. The Western Lake Superior Sanitary District WWTP in Duluth has an average daily flow of 37.8 million gallons per day (Mgal/d), and the Superior WWTP has an average flow of 0.93 Mgal/d (U.S. Environmental Protection Agency, 2010).

Purpose and Scope

The purpose of this report is to describe the presence of selected CECs in water and bottom-sediment samples collected from 40 sites from August through October 2010 from the St. Louis River, St. Louis Bay, and Superior Bay, in Minnesota and Wisconsin. Analytical results of water and bottom-sediment samples are presented in this report and include physical properties and CECs in water and CECs in bottom sediment.

This report also presents a comparison between water and bottom-sediment chemistry. Furthermore, CEC concentrations in water and sediment are compared to aquatic-life criteria and sediment-quality targets, respectively.

Methods

The sampling approach for this study was designed to expand the results of previous studies. The following sections describe the methods used for site selection, sample collection, laboratory analyses, and quality assurance in this study.

Site Selection and Approach

The sampling design included randomly distributed samples and targeted samples. The MPCA randomly selected 25 sampling sites in non-dredged parts of the study area; MPCA also selected five targeted sites in the vicinity of large point and non-point discharges into Minnesota waters. The five MPCA targeted sites (table 1) were selected because of their proximity to known or possible sources of contamination—station R-9 near the Spring Street Marina, station B-19 near the Western Lake Superior Sanitary District WWTP, station H-24 near Slip 2, station H-25 near Slip 1, and station H-26 (fig. 2). The WIDNR selected 10 sites to provide an even coverage of the study area on the Wisconsin side of the border. For this report, the two Wisconsin sites that are considered targeted are the site across the St. Louis River from the Western Lake Superior Sanitary District WWTP (station B-17) and the site near the Superior WWTP (station H-36; table 1, fig. 2). Although the WIDNR targeted station B-17 is upstream from the Western Lake Superior Sanitary District WWTP, the area is affected by a strong seiche effect, which complicates the transport of chemicals in the system. The USGS and MPCA sampled water and sediment from 40 locations (table 1). All

sampling sites were assigned a station and map identifier (table 1) in downstream order and indicating whether the site is located in the lower St. Louis River (designated by “R”), in the St. Louis Bay (designated by “B”), or in Superior Bay, also called Duluth Harbor Basin (designated by “H”). For the purpose of this report, the division between the St. Louis Bay and St. Louis River is the Burlington Northern Railroad Bridge, and the division between St. Louis Bay and Superior Bay is the Blatnik Bridge (fig. 2).

Sample Collection and Analyses

Sampling followed previously developed sampling protocols (Lee and others, 2004, 2010, 2011) for comparison to previous studies. All samples were collected using protocols and procedures that were designed to obtain a representative sample and avoid sample contamination. Specific protocols and methods are documented for the collection and processing of water-quality and bottom-sediment samples (U.S. Geological Survey, variously dated). All samples were collected with inert materials, such as Teflon, glass, or stainless steel. A multi-parameter probe was used to measure field properties (dissolved oxygen, pH, specific conductance, and water temperature) at each site.

All collection and processing equipment was cleaned between sites/samples with a succession of soapy water, tap water, de-ionized water, methanol and organic contaminant free water. The clean equipment was then double bagged in single use polyethylene bags and transported to the next sample site. The equipment was rinsed with native water at the sample site before samples were collected (U.S. Geological Survey, variously dated). To avoid contamination of samples, use of certain personal-care items (such as insect repellent, cologne, aftershave, and perfume) was avoided by personnel collecting and processing samples. The only exception to this was that field personnel used sunscreen during sampling. Powderless, disposable gloves were worn during collection of water-quality and bottom-sediment samples to avoid contamination of samples. Standard labeling and packing techniques (for example, foam sleeves placed around bottles) were used to prevent breakage and ensure sample integrity. When not in use, sample processing equipment was covered with clear plastic bags.

Water and bottom-sediment samples were analyzed at the USGS National Water Quality Laboratory (NWQL) for a broad suite of organic compounds (table 2) that are indicators of industrial, domestic, and agricultural wastewaters. These compounds, that may have multiple uses, were placed into categories based on Zaugg and others (2006). The specific compounds analyzed were selected on the basis of usage, toxicity, potential estrogenic activity, and persistence in the environment (Barnes and others, 2002; Kolpin and others, 2002). A combination of USGS approved methods and custom methods were used to analyze study samples. Laboratory methods for steroid hormones in water (laboratory

method 4434), for steroid hormones in bottom sediment (laboratory method 6434), and for pharmaceuticals in bottom sediment (laboratory method 9008) are considered custom analyses.

Surface-Water Samples

A modified depth-integrated sampling technique was used to collect water from streams and lakes (U.S. Geological Survey, variously dated). A baked amber glass 1-liter bottle or a 250-milliliter (mL) bottle was lowered into the water column with a weighted bottle sampler at one location at each site to collect the depth-integrated sample. Water samples were chilled immediately and then processed within 1 to 2 hours of collection before being shipped to the NWQL for analyses.

The water samples were split into numerous fractions for analyses. Filtered-water samples were analyzed for organic chemicals typically found in domestic, industrial, wastewater, and nonpoint sources using laboratory schedule 1433 at the NWQL (Zaugg and others, 2006). The method focuses on the determination of compounds that are indicators of wastewater or that have endocrine disrupting potential in water samples. The compounds analyzed include the alkylphenol ethoxylate nonionic surfactants, food additives, fragrances, antioxidants, flame retardants, plasticizers, industrial solvents, disinfectants, fecal sterols, PAHs, and pesticides. Compounds were isolated using liquid-liquid extractions and methylene chloride solvent, and concentrations were determined by capillary-column gas chromatography/mass spectrometry (Zaugg and others, 2006).

Filtered-water samples were analyzed at the NWQL for pharmaceutical compounds using laboratory schedule 2080. This method uses a chemically modified styrene-divinylbenzene resin-based solid-phase extraction cartridge for analyte isolation and concentration. High-performance liquid chromatography/mass spectrometry was used for detection and quantification (Furlong and others, 2008).

Whole-water (unfiltered) samples were analyzed for steroid hormones, sterols, and bisphenol *A* using laboratory method 4434 (Foreman and others, 2012) at the NWQL. Method compounds were identified and quantified using an isotope dilution method by gas chromatography/tandem quadrupole mass spectrometry (GC/MS/MS).

Bottom-Sediment Samples

Bottom-sediment samples were collected with a stainless steel Eckman grab sampler according to established protocols (U.S. Geological Survey, variously dated). Bottom-sediment samples were collected using techniques that were designed to obtain the most recent bottom-sediment deposition [top 4 inches (10 centimeters) of bottom sediment]. At least five bottom-sediment samples were composited for each sample site. The bottom-sediment sample was discarded if a large amount of vegetation was present. A stainless steel spoon was used to carefully collect sediment that was not touching the

sampler. The sediment was placed in a stainless steel bowl and homogenized for 5 minutes. Approximately 4–7 ounces (100–200 grams) of unsieved wet material were placed in wide-mouth glass containers and frozen before shipment to the NWQL.

Bottom-sediment samples were split into fractions and analyzed for organic wastewater-indicator chemicals (laboratory method 5433), steroid hormones (custom method 6434), and pharmaceuticals (laboratory code 9008) at the NWQL. The wastewater-indicator chemicals were extracted from sediment into a water/isopropanol solution using pressurized solvent extraction, and then extracted from the solution by polystyrene-divinylbenzene solid-phase extraction. Wastewater-indicator chemicals were analyzed using gas chromatography/mass spectrometry operated in electron-impact mode with full-scan ion monitoring. Compounds were identified using chromatographic retention times and mass spectral matches; compounds were quantified using multi-point standard calibration curves. Steroid hormones, sterols, and bisphenol *A* were analyzed in bottom-sediment samples at the NWQL using a custom method (6434). Compounds were extracted from sediment into a water/isopropanol solution using pressurized solvent extraction and then extracted from the solution by polystyrene-divinylbenzene solid-phase extraction. Compounds were identified then quantified using an isotope-dilution method by GC/MS/MS.

Bottom-sediment samples were analyzed for two suites of pharmaceuticals using a custom research laboratory method (laboratory method 9008) at the NWQL. One suite of pharmaceuticals encompasses a range of prescription and non-prescription pharmaceuticals referred to as human-use pharmaceuticals. The second suite of pharmaceuticals are the antidepressants. For the analysis of both suites of pharmaceuticals in bed sediment, a method described by Kinney and others (2006) was used for extraction and quantification. For all extractions, a solvent consisting of 70-percent acetonitrile and 30-percent water was used to extract the samples using pressurized liquid extraction. 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, 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).

Quality-Assurance Analyses

The USGS National Field Manual (U.S. Geological Survey, variously dated) was used to guide data-collection activities for the study. Standard USGS procedures for collecting water and bottom-sediment samples were used to assure quality data collection, processing, and shipment. Personnel

were familiarized with the study design and sampling protocols before field sampling to assure sample integrity. Laboratory and field quality-assurance samples were collected and analyzed to validate the environmental sample data.

Laboratory Quality Assurance

Water and bottom-sediment samples analyzed in 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 chemicals using the presence of characteristic mass spectral ions with correct ion ratios. Because qualitative identification is completed before a concentration is reported, these information-rich methods are not censored at the reporting level (RL) or the method detection limit (MDL). The intention is to produce as much information as possible for complex samples, for which qualitative identification can be made. If the concentration is less than either the RL or the lowest calibration standard, results are reported by using the “E” code to indicate that it has been estimated. Other cases where it is appropriate to use the “E” code include matrix interferences, method compounds that have been permanently assigned an “E” code, and those compounds that do not meet quality-control criteria, such as being out of calibration by more than plus or minus 20 percent. Chemical concentrations less than the RL do not have decreased confidence in qualitative identification. However, because the concentration data that are less than the RL have a greater risk of false positives, reported concentrations were carefully compared to laboratory and field blank data for evaluation.

Laboratory quality-control samples included laboratory blanks, reagent spikes, and surrogate compounds that were added to each sample. Because sample concentrations commonly are less than RLs, the comparison of environmental sample concentrations to laboratory blank concentrations is the first step in validating the environmental data. The laboratory blank samples that were analyzed concurrently with the environmental samples were used for these analyses.

There were 14 compounds detected in laboratory blanks and corresponding environmental samples using laboratory schedule 1433. Compound concentrations in environmental samples were 5 to 33 times greater than the concentrations in corresponding laboratory blank samples analyzed using laboratory schedule 1433. Few pharmaceutical compounds were detected in laboratory-blank samples analyzed using laboratory schedule 2080, and no pharmaceutical compounds were detected in the eight laboratory-blank samples that coincided with environmental samples that had a detection. No steroid hormones were detected in the six laboratory blanks that were analyzed concurrently with environmental samples using custom laboratory method 4434. The two sterols (*3-beta*-coprostanol and cholesterol) were detected in all six blank samples and all corresponding environmental samples. However, concentrations in environmental samples were 3 to 104 times greater than those in the corresponding blank samples.

The NWQL analyzed laboratory blank bottom-sediment samples consisting of an ashed-sand matrix with environmental samples. Environmental bottom-sediment sample sizes varied, and thus the RLs are scaled on the basis of sample-weight extracted relative to RLs 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 differed from each other, a comparison of these samples was made on total mass of a chemical rather than on dry mass-normalized concentrations, which can be misleading. For example, a sample concentration of 0.14 nanograms per gram (ng/g) for a 1-g environmental sample is the same mass as a concentration of 0.014 ng/g for a 10-g laboratory-blank sample. The mass of each chemical in laboratory-blank samples and environmental samples was calculated by multiplying the concentration of the sample by the weight of the sample.

In laboratory blanks, 26 chemicals were detected using laboratory schedule 5433. The concentrations of all compounds in the environmental samples were at least three times greater—and on average 99 times greater—than concentrations in corresponding laboratory blank samples. Cholesterol, *17-beta*-estradiol, and *3-beta*-coprostanol were detected in seven laboratory-blank samples using custom laboratory method 6434, but the concentrations of these chemicals in the environmental samples were all greater than three times the concentrations in the corresponding laboratory-blank samples.

Laboratory reagent matrix spikes were analyzed with environmental samples to assess compound recovery. The satisfactory range of percent recoveries for matrix spikes typically is between 50 and 120 percent (Sando and others, 2006). The average recoveries for nine laboratory reagent spikes for water samples analyzed using schedule 1433 ranged from 14.5–105.4 percent for each chemical. The chemicals with the lowest average percent recoveries in laboratory reagent spikes (less than 60 percent) were bromoform, 1,4-dichlorobenzene, 5-methyl-1H-benzotriazole, bisphenol *A*, carbaryl, cotinine, *d*-limonene, indole, isopropylbenzene, and tetrachloroethene. Average recoveries for all pharmaceuticals in eight laboratory reagent blank samples analyzed using laboratory schedule 2080 ranged from 30–103 percent for each chemical. Diltiazem, sulfamethoxazole, and warfarin had recoveries less than 45 percent, and the rest of the chemicals had recoveries ranging from 66–103 percent. Average recoveries for all chemicals in six laboratory spikes analyzed using custom method 4434 ranged from 68–113 percent. Average recoveries for each chemical in seven laboratory bottom-sediment reagent spike samples analyzed using laboratory schedule 5433 ranged from 39–129 percent. The average recoveries for target analytes (1,4-dichlorobenzene, *beta*-sitosterol, bisphenol *A*, chlorpyrifos, isoquinilone, isopropyl benzene, triphenyl phosphate, and tris(dichlorisopropyl)phosphate) were less than 60 percent (39 to 57 percent). The low percent recoveries (less than 60 percent) indicate that the concentrations in environmental samples may be biased low for those chemicals.

Most methods had either surrogate chemicals or isotope dilution standards (IDSs) added to samples before extraction

to monitor method performance. Surrogates are chemicals that have similar properties to the analytes of interest but do not interfere with quantitation of the chemicals of interest. An IDS is an isotopically labeled analog of the analytes that is added to the sample just before sample extraction. Average recoveries were between 25 and 95 percent for the 10 surrogates or IDSs analyzed in water samples (table 3). Average recoveries were between 6 and 89 percent for the 13 surrogates or IDSs analyzed in bottom-sediment samples (table 3). For water samples, average percent recovery was lowest for medroxyprogesterone-*d3*. For bottom-sediment samples, percent recoveries were lowest for the IDSs cholesterol-25,26,26,26,27,27,27, -*d7*, medroxyprogesterone-*d3*, and nandrolone-16,16,17-*d3*. Surrogates or IDSs with low percent recoveries indicate that the concentrations in the paired environmental samples may be greater than the reported values.

The sediment data have multiple RLs. Both the laboratory schedules 5433 and 6434 use RL scaling based on the amount of sediment that is extracted. The RL values associated with these sample results in the USGS National Water Information System database are scaled based on the sample's extracted dry weight. If more sample weight is extracted relative to the default weight, lower RLs result. If less weight is used relative to the default weight, higher RLs result. In addition, raised RLs can be associated with chemical-specific cases because matrices may interfere with the instrument's ability to identify or quantify target compounds correctly.

Field Quality Assurance

Field quality-assurance samples were used to assess sample collection and processing. Field quality-assurance samples included 1 water field-blank sample, 5 water field-replicate samples, and 1 bottom-sediment field-replicate sample.

Potential contamination of samples during collection and sample processing was assessed with the field-blank sample. The field-blank sample was prepared at station B-18 (fig. 2) on August 25, 2010, at 10:35 a.m. following the collection of the scheduled environmental sample. The field-blank sample was prepared by processing high-performance liquid-chromatography (HPLC) grade organic-free water through the same clean equipment used to collect and process field samples. The field-blank sample was analyzed by the NWQL for chemicals on laboratory schedule 1433 (wastewater indicators), laboratory schedule 2080 (human-health pharmaceuticals), and custom laboratory schedule 4434 (hormones, sterols, and bisphenol *A*). Of the 92 analytes determined in the field-blank sample, two had detectable concentrations (table 4). Caffeine and pyrene were detected in the field blank at concentrations less than the RL and less than any concentration detected in an environmental sample (appendix 1), therefore verifying the quality-assurance procedures adopted for sample collection.

Field-replicate samples were used to determine detection and concentration variabilities resulting from sample processing techniques. Field-replicate samples consisted of a split of the field sample so the field and replicate samples were nearly equal in composition. Replicate water samples were collected at five sites (stations R-2, R-6, R-9, B-11, and R-9, table 1, fig. 2), and a replicate bottom-sediment sample was collected at one site (station R-23, table 1, fig. 2).

The relative percent difference (RPD) is a measure of variability within a particular site. RPDs were calculated using the following equation:

$$RPD = \left[\frac{|sample2 - sample1|}{\left(\frac{sample1 + sample2}{2} \right)} \right] \times 100$$

where

- sample1* is the concentration in the environmental sample, and
- sample2* is the concentration in the replicate sample.

RPDs were not calculated when only one paired concentration was greater than the RL or when both paired sample concentrations were less than the RL.

The RPDs among chemical concentrations in the water replicate and corresponding environmental samples were less than 20 percent, which is an objective for precision according to Taylor (1987). For replicates in bottom-sediment samples, 10 of 47 wastewater analytes (laboratory schedule 5433) had an RPD greater than 20 percent (table 5). None of the 17 hormone analytes (laboratory schedule 6434) had an RPD greater than 20 (table 5), as only 1 of 17 analytes (estrone) had detections in both samples. For pharmaceuticals in bottom sediment (custom laboratory code 9008), no analytes with the exception of diphenhydramine were detected in either the environmental sample or its replicate. The high RPD (73.3 percent) of diphenhydramine must be considered when interpreting the results for this chemical in bottom-sediment.

Presence of Chemicals of Emerging Concern in Water and Bottom Sediment

Physical properties and concentrations of chemicals of emerging concern (CECs) in water samples collected from the St. Louis River, St. Louis Bay, and Superior Bay are described in this section. This section also describes the concentrations of CECs determined for bottom-sediment samples collected from the same locations.

Physical Properties

Physical properties were measured using a water-quality sonde at all 40 sites immediately before collecting water samples. Dissolved-oxygen concentrations ranged from 3.22 to 12.19 milligrams per liter (mg/L; median=7.54, standard deviation=1.39, table 6) and reflected the difference in collection time during the day and the date of collection from early August through early October. One site (station R-3, fig. 2) had a dissolved-oxygen concentration (3.22 mg/L, table 6) less than the Minnesota State standard of 5 mg/L (Minnesota Pollution Control Agency, 2008). The range in pH values was not large (standard deviation=0.3) as most pH values were close to neutral (median 7.9). Specific conductance values generally were low [median=212 microsiemens per centimeter at 25°C (mS/cm)] and water temperatures ranged from 12.83 to 25.94°C based on collection time and date. When comparing August sampling data (eliminating the seven samples collected in October), the only noticeable difference between the lower St. Louis River, St. Louis Bay, and Superior Bay was that the Superior Bay specific conductance values were more consistent and values were slightly lower (range 162–192 μS/cm) than August St. Louis River or St. Louis Bay values (range 150–285 μS/cm).

Hydrologic Characteristics

A USGS streamgage (04024000) on the St. Louis River at Scanlon, Minn. (fig. 1), provides a 103-year period of record (U.S. Geological Survey, 2012) to compare with hydrologic conditions in 2010. The Scanlon streamgage is approximately 25 miles upstream from Lake Superior. In general, streamflow was low in 2010 based on streamflow conditions during the previous 103 years (fig. 3). However, during a peak in streamflow in early August 2010, when some samples were collected, streamflow was greater than the 75th percentile for the 103-year record (fig. 3). The Scanlon streamgage is upstream from the sampling sites, so different factors may affect the hydrology in the study area in comparison to those at the Scanlon streamgage. For example, minor tributaries may affect conditions in the lower St. Louis River, St. Louis Bay, and Superior Bay.

The St. Louis Bay and Superior Bay also are affected by seiches, waves, and ship traffic from Lake Superior. Seiches occur when water levels oscillate up and down (Wetzel, 2001). In Lake Superior small seiches are common and these can generate currents within the lake’s water column and can affect lake biology (Korgen, 2000). Seiches can reverse the flow of tributary rivers of Lake Superior and flush sediments

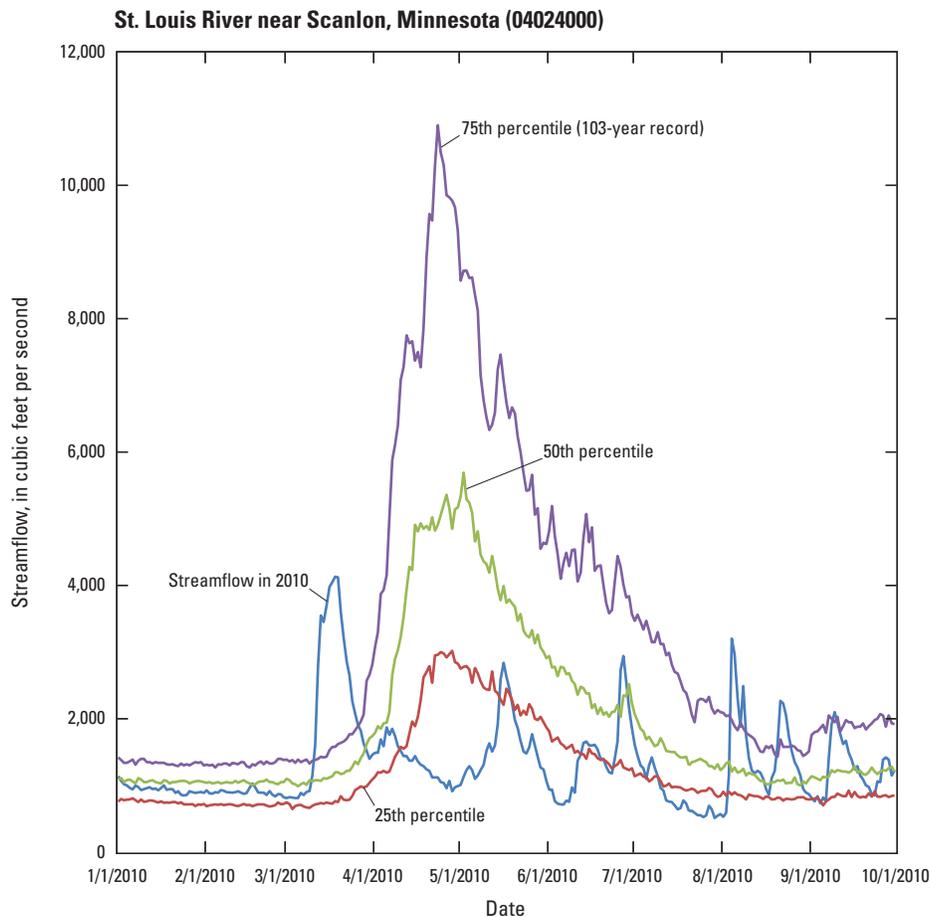


Figure 3. Streamflow at the St. Louis River near Scanlon, Minnesota, in 2010 and the 25th-, 50th-, and 75th-percentile streamflows for the 103-year record (1908–2010).

and nutrients back upstream (Minnesota Department of Natural Resources, 2012). In addition, bottom sediments can be resuspended by ship traffic (Story and Sydor, 1980). Seiches, waves, and ship traffic may move resuspended sediment and related contaminants.

Chemicals of Emerging Concern in Water

During this study, 33 out of 89 CECs were detected among all water samples collected (table 7). The number of detections of CECs in individual water samples ranged from 1 to 12 (appendixes 1, 2, and 3). The water sample collected at Howards Bay below Blatnik Bridge at Superior, Wisc. (station B-23, fig. 2) had the most CEC detections (12), whereas the water samples from the St. Louis River above Bear Island near New Duluth, Minn. (station R-4, fig. 2) had one detection (*N,N*-diethyl-*meta*-toluamide, a mosquito repellent also called DEET, appendix 1).

The most frequently detected chemicals (detected in at least 25 percent of the samples, fig. 4) have a wide variety of uses and sources. DEET was detected in water samples from every site, and cholesterol was detected in samples from 98 percent of the sites. Other frequently detected CECs include a wastewater indicator (caffeine, 28 detections), an ultraviolet inhibitor (benzophenone, 26 detections), a pharmaceutical (carbamazepine, 24 detections), a plasticizer and fire retardant (tris(2-butoxyethyl) phosphate, 21 detections), a steroid hormone (estrone, 21 detections), a nicotine metabolite (cotinine, 21 detections), PAHs (pyrene, 19 detections and fluoranthene, 9 detections), and a fragrance (hexahydrohexamethyl cyclopentabenzopyran or HHCB, 9 detections).

The number of detections of hormones in individual water samples ranges from one to four (appendix 3). Generally, sites in the St. Louis Bay or Superior Bay had 2 to 3 hormone detections. Five pharmaceuticals were detected: cotinine, 1,7-dimethylxanthine, acetaminophen, caffeine, and carbamazepine. The number of detections of pharmaceuticals in individual water samples ranged from zero to five (appendix 2). Duluth Harbor Basin samples (stations H-38 and H-39) had the largest number of detections (five). Dimethylxanthine was detected in two samples, and acetaminophen was detected in four samples.

Nine of the chemicals analyzed during this study were PAHs. The number of PAHs detected per site ranged from 0 to 3, and 56 percent of the sites had a detection of at least one PAH. Water collected from the St. Louis River below Mud Lake near Oliver, Wisconsin (station R-5, fig. 2) had the greatest number of PAH detections (3 of 9 chemicals) and the greatest PAH concentrations among all sites (appendix 1). The PAHs (1-methylnaphthalene, 2-methylnaphthalene, and naphthalene) detected at this site had low molecular weights. Naphthalene and its alkylated homologues represent a proportion of total PAH composition in fossil fuels, such as petroleum or crude oil, with low molecular weights (Boehm, 2006). In contrast, the PAHs detected at the remaining sites were fluoranthene and pyrene, which have high molecular weights, indicate wood or fossil fuel combustion (Boehm, 2006). The presence of these two PAHs and the lack of low molecular weight chemicals at the remaining sites indicate that wood or fossil fuel combustion may act as an important PAH source throughout the study area. These results highlight the complexity of the river system and indicate that while some

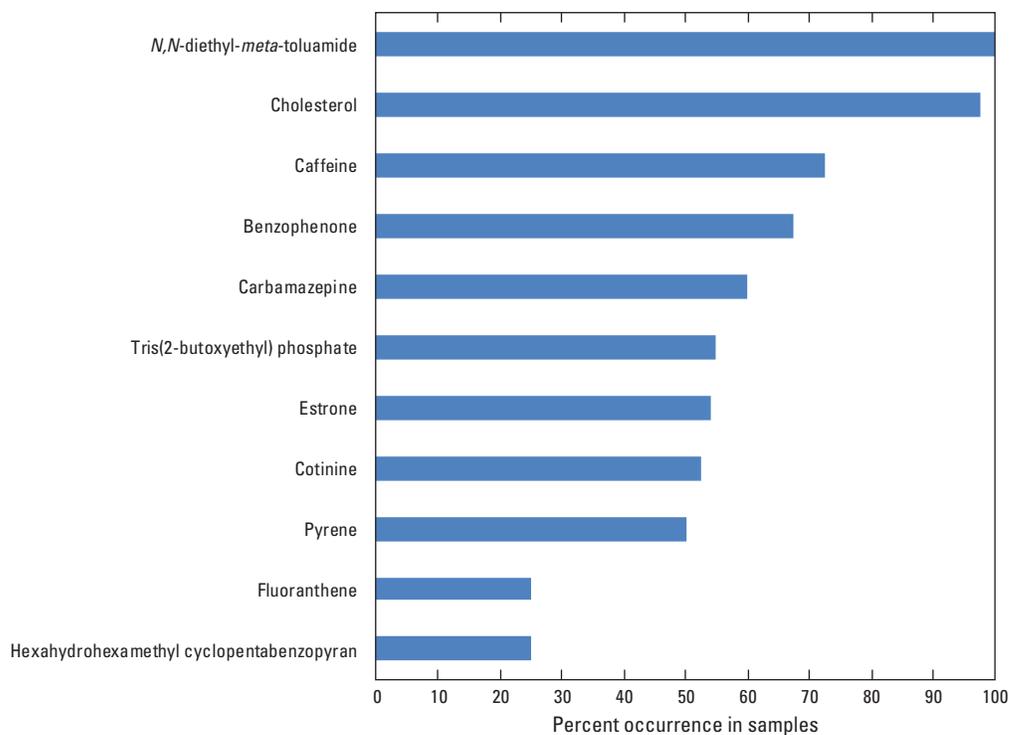


Figure 4. Occurrence of selected chemicals of emerging concern detected in at least 25 percent of water samples from the St. Louis River, St. Louis Bay, and Superior Bay sites, Minnesota and Wisconsin, 2010.

PAH sources may affect the entire river, some specific sources may only affect localized areas. Source identification was not within the scope of this study, and due to the few PAHs that were analyzed, source identification would not be feasible; however, general trends can provide an indication of source types that may be important contributors of PAHs.

In the lower St. Louis River (stations R-1 through R-12), 16 CECs were detected with a median of 4 chemicals per sample. The types of chemicals detected most frequently in this upstream reach include PAHs and isophorone (a solvent). The types and numbers of chemicals detected changed beginning at station B-13 near the Burlington Northern railroad bridge. The number of chemicals detected among all samples was greater in the St. Louis Bay and Superior Bay areas than in the St. Louis River (fig. 5A). More chemicals were detected downstream from station B-13 than upstream—including surfactants (4-nonylphenol, 4-*tert* octylphenol), a fragrance (HHCB), plasticizers and fire retardants (bisphenol *A* and tris(2-butoxyethyl) phosphate), a wastewater indicator (caffeine), pharmaceuticals (cotinine and carbamazepine), triethyl citrate (used in cosmetics and pharmaceuticals), a UV inhibitor (benzophenone), estrone (steroid hormone), and 3-*beta*-coprostanol (a fecal sterol). Although some of these chemicals can originate from natural sources such as estrone and 3-*beta*-coprostanol, the combination of industrial and personal-care products indicates domestic waste sources.

The concentrations also varied among chemicals and among the St. Louis River, St. Louis Bay, and Superior Bay. For example, the pharmaceuticals carbamazepine and cotinine were not detected in the lower St. Louis River, but they were detected in the St. Louis Bay and Superior Bay (fig. 5B and C) indicating domestic water sources. In contrast, the coal-derivative pyrene has a wider distribution among all three areas (fig. 5D).

Nonylphenol, nonylphenol diethoxylate, and estrone (known EACs), pharmaceuticals (cotinine and carbamazepine), and fire retardants were detected more frequently in samples from the St. Louis Bay and Superior Bay sites than in samples from the lower St. Louis River sites, indicating a larger influence of domestic wastewater in samples from sites in the two bays. Although DEET was detected in samples from all of the sites reflecting sources in addition to domestic waste sources, the concentrations were greater in the St. Louis Bay and Superior Bay areas (fig. 5E).

To put the results of this study into perspective, other studies conducted on CECs in streams across the United States (Buxton and Kolpin, 2002) and on wastewater in Wisconsin (Karthikeyan and Bleam, 2003) were reviewed. Buxton and Kolpin (2002) reported low CEC concentrations in areas downstream from intense urbanization and animal production. Steroids, nonprescription drugs, and insect repellent were the chemical groups most frequently detected. Detergent metabolites, steroids, and plasticizers generally were measured at the highest concentrations. Karthikeyan and Bleam (2003) reported 8 of 25 samples contained antibiotics.

Because of the similar datasets, the detections and concentrations of CECs in this study were compared to those in water samples reported by Ferrey and others (2010), Lee and others (2011), and Tomasek and others (2012). Samples from Ferrey and others (2010) and Lee and others (2011) were collected throughout the State of Minnesota, whereas samples from Tomasek and others (2012) were collected from the St. Croix River Basin in both Minnesota and Wisconsin. Many samples from all three studies did not have detectable concentrations of selected chemicals from stream and lake sites. All three studies also included WWTP effluent.

Because none of these studies analyzed the exact same suite of CECs, a comparison was made between percent detection overall for the studies where similar methods were used. The detection rate (the total number of detections divided by the product of number of analytes and number of sites) for all CECs in water samples from the St. Louis River, St. Louis Bay, and Superior Bay (this study) was about 8 percent. For the studies in which WWTP effluent was sampled in addition to stream and lake water samples, the detection rates were 33 percent (Ferrey and others, 2010), 20 percent (Lee and others, 2011), and 18 percent (Tomasek and others, 2012). For water, average concentrations for many CECs in this study of the St. Louis Bay complex were larger than those reported by Tomasek and others (2012) and smaller than those reported by Ferrey and others (2010) or Lee and others (2011).

Chemicals of Emerging Concern in Bottom Sediment

Bottom-sediment samples were analyzed for 104 CECs (table 8; app. 4, 5, and 6). Fifty-six of these chemicals were detected in at least one sample (table 8). Samples from St. Louis Bay above Blatnik Bridge in Duluth, Minn. (stations B-18 and B-19, fig. 2) had the most detections (31), whereas samples from Duluth Harbor Basin near Barkers Island at Superior, Wisc. (station H-37, fig. 2) had the fewest detections (5). Station B-19, St. Louis Bay above the Blatnik Bridge, was a site targeted by the MPCA for its proximity to the Western Lake Superior Sanitary District WWTP outfall. Station H-37 was a site targeted by the WIDNR and is in proximity of the Superior WWTP.

A wide variety of CECs were detected among all bottom-sediment samples. PAHs, sterols, and a steroid hormone were among the most frequently detected categories of chemicals. PAHs (identified in table 2) were detected in 31 of 40 samples (appendixes 4 and 5). The most commonly detected PAHs were dimethylnaphthalene, fluoranthene, pyrene, and anthracene; occurring in greater than 90 percent of samples. The chemical 2,6-dimethylnaphthalene was detected in all 40 bottom-sediment samples followed by 3-methyl-1H-indole (skatole-fragrance or odor of feces), which was detected in 39 of 40 samples. Cholesterol was detected in 36 samples, and 3-*beta*-coprostanol was detected in 24 samples. Six hormones were detected in at least one bottom-sediment sample. The

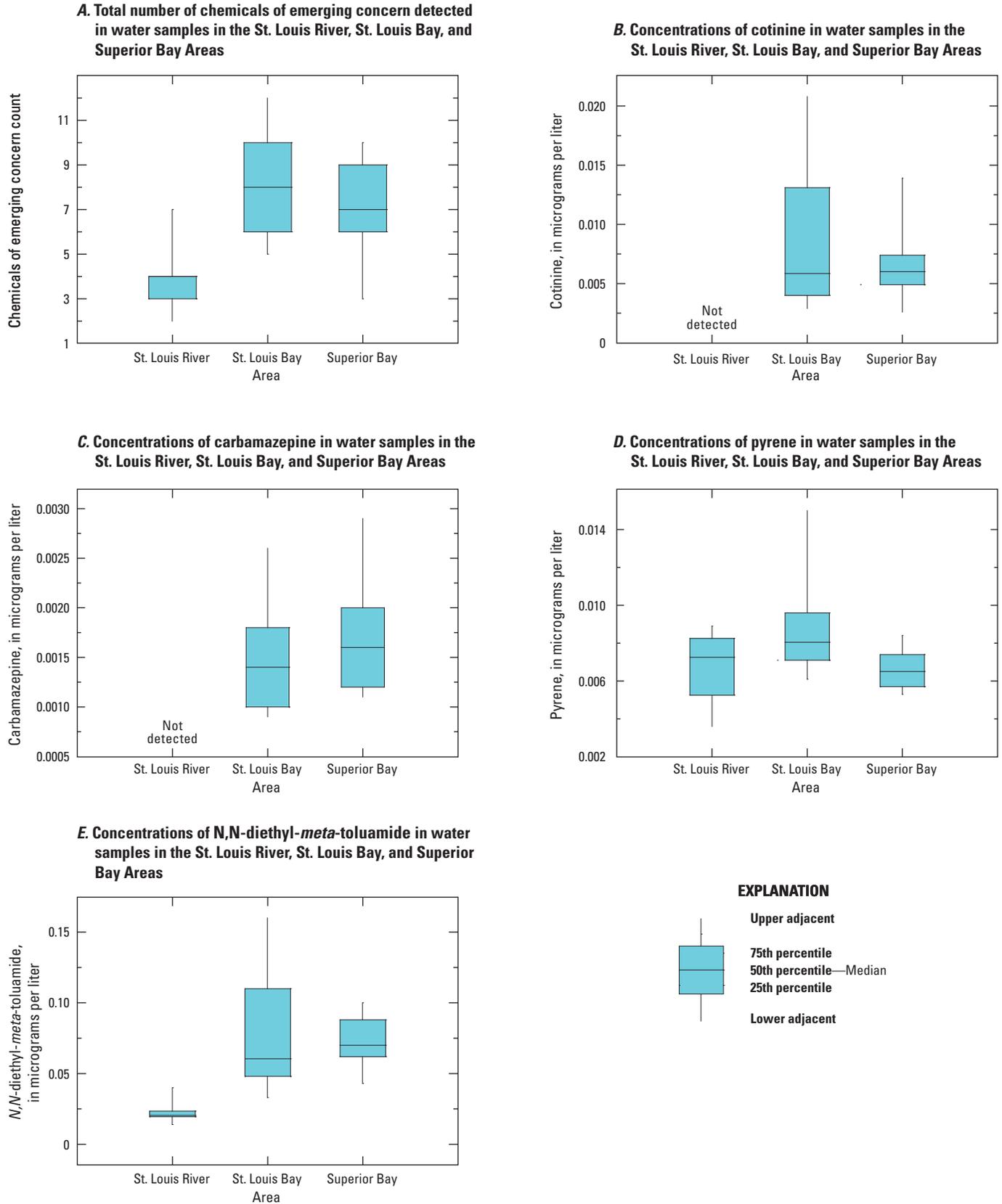


Figure 5. Detections and distributions of (A) chemicals of emerging concern, (B) cotinine, (C) carbamazepine, (D) pyrene, and (E) *N,N*-diethyl-*meta*-toluamide (DEET), in samples from the St. Louis River, St. Louis Bay, and Superior Bay.

number of hormones detected in individual samples ranged from zero to four. Twenty-two CECs were detected in more than 35 percent of the samples (fig. 6).

The number of CECs detected per sample varied only slightly among the three areas. However, the types and concentrations of chemicals detected varied among sites and areas. For example, samples collected in St. Louis Bay and Superior Bay had a greater number of detections of fire retardants, bisphenol *A*, diethylphthalate, and bis(2-ethylhexyl) phthalate than the St. Louis River sites. Alkylphenols, such as nonylphenol, 4-*tert*-octylphenol, and nonylphenol monoethoxylate, also were more prevalent in the Superior Bay and St. Louis Bay areas compared to the St. Louis River area. In contrast, detections of the most frequently detected steroid hormone (estrone) were similar among the areas; however, the concentrations of estrone were greater in the St. Louis Bay and Superior Bay areas than in the St. Louis River area (appendixes 4 and 5).

The detections and concentrations of CECs in bottom-sediment samples were compared with data from two other recent studies of streams across Minnesota (Lee and others, 2011) and of the St. Croix River, bordering southern Minnesota and Wisconsin (Tomasek and others, 2012). The detection rate for wastewater indicators (laboratory schedule 5433, table 8) and hormones (laboratory schedule 6434, table 8) in bottom-sediment samples from the St. Louis River, St. Louis Bay, and Superior Bay was 23 percent. The detection rates were 52 percent for bottom-sediments from Minnesota streams (Lee and others, 2011) and 15 percent for bottom sediments from the St. Croix River (Tomasek and others, 2012). Many average CEC concentrations were greater in this study than those for samples reported by Tomasek and others (2012) and less than those for samples reported by Lee and others (2011). Exceptions occurred, however, and these included fluoranthene (a PAH) and epitestosterone (a hormone), in which average concentrations were greater for this study than for sites sampled by Lee and others (2011).

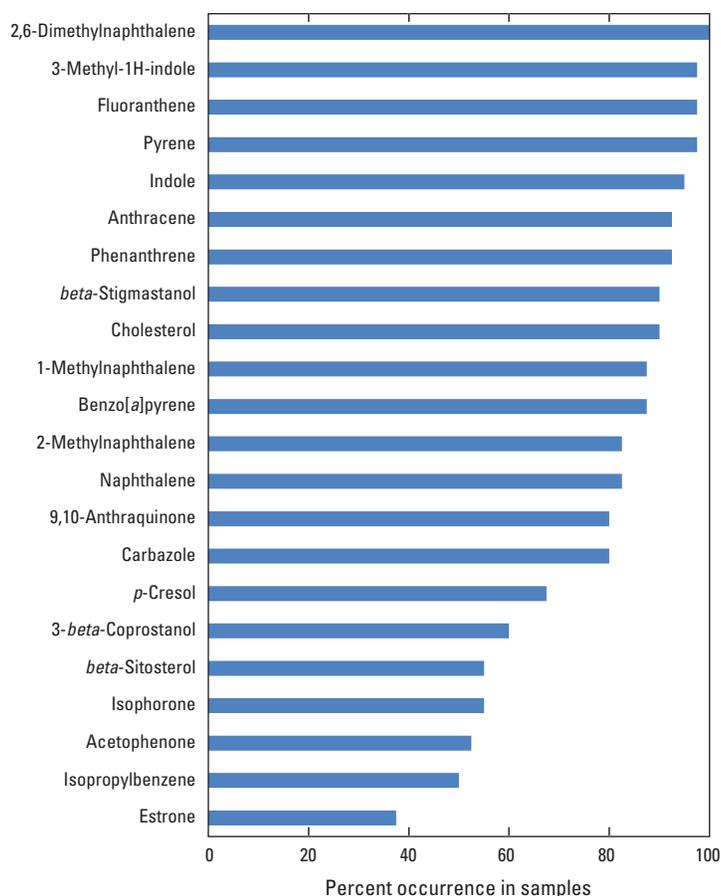


Figure 6. Occurrence of selected chemicals of emerging concern detected in at least 35 percent of bottom-sediment samples, 2010.

Comparison of Water and Bottom-Sediment Chemistry

In general, CECs were detected more frequently in bottom-sediment samples than in surface-water samples (fig. 7). Ferrey and others (2010) found similar results in that much higher concentrations of contaminants occurred in lake bottom-sediment than in lake water across the state of Minnesota. Although surface-water samples had higher detection rates of CECs in the St. Louis Bay and Superior Bay than in the St. Louis River, the percentage of CECs detected in bottom-sediment samples were distributed throughout the St. Louis River, St. Louis Bay, and Superior Bay (fig. 7). Steroid hormones were detected throughout the study area at a lower frequency (fig. 8) than other CECs.

The concentration and types of compounds varied between water and bottom-sediment samples. Compounds that were analyzed in both water and sediment were compared in figure 9. PAHs, pharmaceuticals, fragrances, flavors, sterols, alkylphenols, and steroid hormones, were detected at a higher frequency in bottom-sediment samples than in water samples. Fire retardants, plasticizers, and pesticides were detected more frequently in water samples than in bottom-sediment samples. Endocrine active chemicals were detected in 58 percent of the water samples and 90 percent of bottom-sediment samples. The greater detection rate of both chemicals of emerging concern and endocrine active chemicals in bottom sediment compared to the detection rates in water samples indicates that bottom sediment is an important sink for these chemicals.

14 Chemicals of Emerging Concern from the St. Louis River, St. Louis Bay, and Superior Bay, 2010

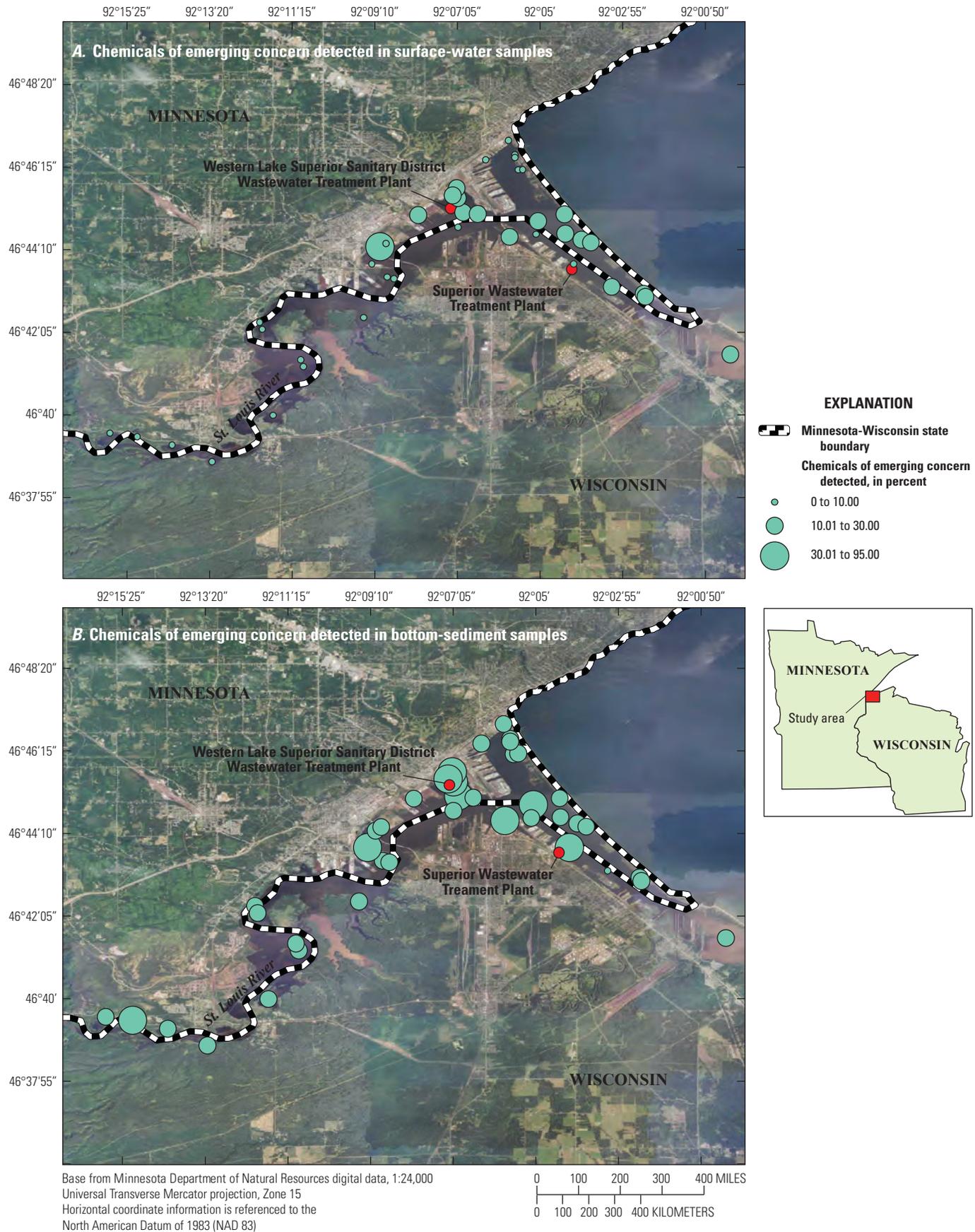


Figure 7. Percentage of chemicals of emerging concern detected in (A) surface-water, and (B) bottom-sediment samples, St. Louis River, St. Louis Bay, and Superior Bay, Minnesota and Wisconsin, 2010.

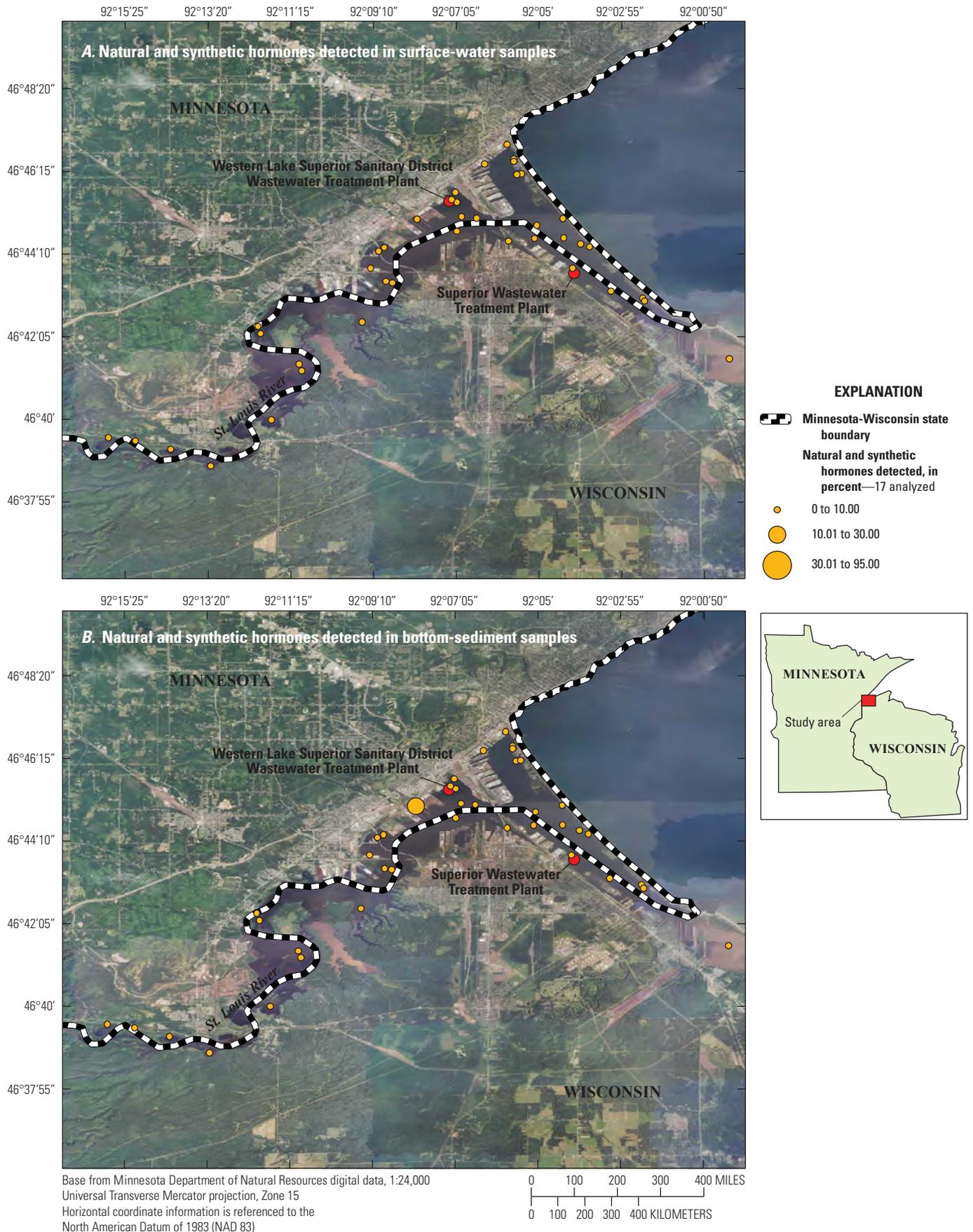


Figure 8. Percentage of natural and synthetic hormones detected in (A) surface-water, and (B) bottom-sediment samples from the St. Louis River, St. Louis Bay, and Superior Bay sites, Minnesota and Wisconsin, 2010.

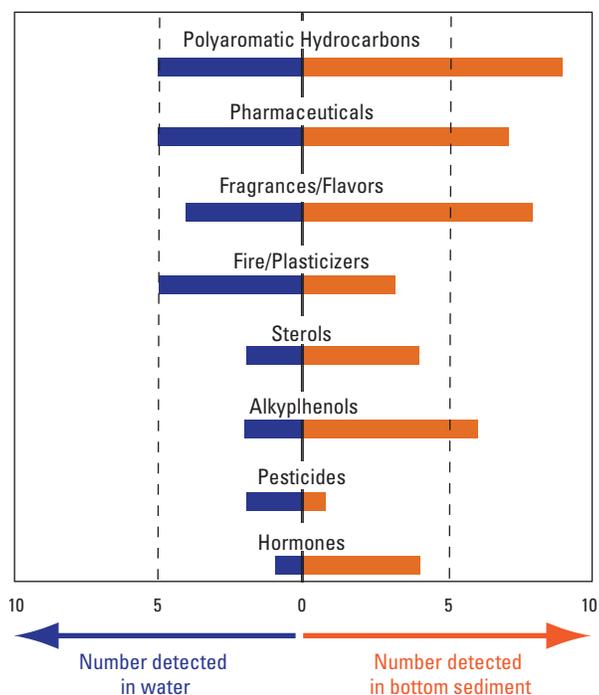


Figure 9. Distribution of selected chemicals of concern among chemical classes in water and bottom-sediment samples from the St. Louis River, St. Louis Bay, and Superior Bay sites, Minnesota and Wisconsin, 2010.

Aquatic-Life Criteria and Sediment-Quality Targets

Many of the compounds analyzed for this study are newly recognized contaminants, and thus very few criteria or standards exist for these compounds. A few chemicals measured have U.S. Environmental Protection Agency (USEPA) aquatic-life criteria in surface water. Nonylphenol, diazinon, and chlorpyrifos have USEPA Chronic Criterion Continuous Concentrations of 6.6, 0.17, and 0.041 micrograms per liter ($\mu\text{g/L}$), respectively (U.S. Environmental Protection Agency, 2005). Nonylphenol was detected in one water sample (from station B-23, estimated concentration of $0.22 \mu\text{g/L}$). Diazinon and chlorpyrifos were not detected in any water samples.

Few guidelines exist for CEC concentrations in bottom sediment for protection of aquatic organisms. However, sediment-quality targets (SQTs) have been established to assess the degree of contamination of bottom sediment (MacDonald and others, 2000; Crane and others, 2002; Crane and MacDonald, 2003) by selected chemicals measured in this study. SQTs exist for the 13 USEPA priority PAHs individually, as well as for the sum total concentration of those 13 PAHs (TPAH₁₃) (Crane and others, 2002). Although SQTs are

not standards, SQTs provide a reference to which concentrations in environmental samples can be compared. SQTs are not intended to assess human-health risks and do not take into account bioaccumulation. Two levels exist for each SQT: Level I targets are based on threshold-effect concentrations, and Level II targets are based on probable-effect concentrations adopted from benthic macroinvertebrate toxicity test results (Crane and others, 2002). Seven of the nine PAHs analyzed in bottom-sediment samples for this study have associated SQTs and are included in the TPAH₁₃: 2-methylnaphthalene, naphthalene, anthracene, fluoranthene, phenanthrene, pyrene, benzo[*a*]pyrene (table 9). As a result, the following description of individual and TPAH₁₃ SQTs in the context of this study is in reference to those seven compounds.

Many bottom-sediment samples had concentrations of at least one compound that exceeded SQTs; many times numerous SQTs were exceeded. Only 6 of the 40 samples (15 percent) did not exceed any SQT for individual compounds or TPAH₁₃. Level I SQTs of $200 \mu\text{g/kg}$ for pyrene and of $20 \mu\text{g/kg}$ for 2-methylnaphthalene were exceeded in more than one-half of samples. Level II SQTs were exceeded for every PAH in at least one sample. Most of the Level II exceedances occurred in sediment collected from St. Louis Bay sites. Duluth Harbor Basin in Allouez Bay at Superior, Wisc. (H-40, a site targeted by WIDNR, fig. 2) exceeded the Level II SQT for 6 of 7 PAHs.

For this study, the total concentration of the seven PAHs analyzed in this study for which SQTs exist (TPAH₇) was calculated for each sample by summing concentrations for those seven PAHs. Concentrations reported as less than the MDL were taken as zero. The TPAH₇ values ranged from not detected to $33,530 \mu\text{g/kg}$ (table 10).

Although TPAH₇ was calculated using only seven compounds, 16 of the 40 samples exceeded the TPAH₁₃ Level I SQT of $1,600 \mu\text{g/kg}$, and two samples exceeded the Level II SQT of $23,000 \mu\text{g/kg}$ (tables 9 and 10). Generally, samples collected upstream from the Burlington Northern Railroad Bridge had TPAH₁₃ values less than the Level I SQT, with the exception of three sites: St. Louis River above Bong Bridge at Duluth, Minn. (stations R-11 and R-12, fig. 2) and St. Louis River at Spring Street in Duluth, Minn. (station R-9, a site targeted for its proximity to the Spring Street Marina, fig. 2). Samples collected from Duluth Harbor Basin at Duluth, Minn. (station H-25, a site targeted for its proximity to Slip 1, fig. 2), and from Duluth Harbor in Allouez Bay at Superior, Wisc. (station H-40, fig. 2) had TPAH₇ values that exceeded the TPAH₁₃ Level II SQT. In contrast, 11 of the 17 sites located within Superior Bay did not exceed the TPAH₁₃ Level I SQT. This highlights the variability in the presence of PAHs within Superior Bay and indicates that sources of PAH compounds may be localized. Although total PAH calculations within this report are underestimates based on only seven compounds, TPAH₁₃ SQTs based on 13 PAHs were exceeded, highlighting the persistence of these chemicals within the system.

Ecosystem Implications

The presence of CECs in both the water and bottom-sediment samples collected within the St. Louis River complex indicated that aquatic organisms are likely to be exposed to CECs. The greater frequency of detection, types of chemicals detected, and greater concentrations in the St. Louis Bay and Superior Bay indicate that wastewater effluent is a likely source of some of the CECs in combination with other undocumented sources such as surface runoff, atmospheric deposition, or unknown sources. CECs enter sewage collection systems from domestic, commercial, and industrial use, and chemicals not removed through treatment and are discharged to the environment (Ahel and others, 1994; Ternes and others, 1999; and Barber and others, 2000). CECs typically are present at low concentrations in surface waters; however, the continuous discharge of wastewater effluent into rivers results in potential continuous exposure of aquatic organisms.

The consequences of aquatic organism exposure to most CECs measured in this study are likely non-lethal. Because some pharmaceuticals and other CECs are naturally, inadvertently, or intentionally designed to modify physiological processes in humans and livestock, exposed aquatic organisms may be affected by exposure to these chemicals. For example, certain classes of chemicals including natural and synthetic hormones, pesticides, metals, alkylphenols, alkylphenol ethoxylates, plastic components, phthalates, and phytoestrogens affect the endocrine systems of fish through biochemical, structural, and behavioral disruption (Jobling and Sumpter, 1993; Jobling and others, 1996; Ankley and others, 1998; Kime, 1998; Miles-Richardson and others, 1999; Bistodeau and others, 2006; Barber and others, 2007; Schoenfuss and others, 2008).

The presence of priority pollutants such as PAHs in the bottom sediment and exceedance of SQTs indicates that priority pollutants such as PAHs remain a concern. Comparison of PAH concentrations to SQTs alone does not provide enough evidence of sediment toxicity; however, when used as a screening criteria, it does highlight areas that may have toxic effects on benthic organisms. Based on Level II SQT exceedances, several sites throughout the study area could potentially have toxic effects to benthic invertebrates. Additional evaluation of other contaminants present at those sites, along with toxicity tests and invertebrate assessments, would be required to fully understand the degree of contamination and effects on invertebrates. Additionally, although concentrations of some PAHs only exceeded Level I SQTs, the cumulative effects of these chemicals in the presence of other contaminants is not well understood. Effects on benthic organisms may be greater than expected solely based on data from this study.

Results from this study provide information useful for characterizing organic contaminants; however, a combined multidisciplinary approach is necessary to better understand the potential effects these compounds may have on aquatic and benthic organisms. Multiple interacting factors control whether these chemicals occur in the aquatic

environment—including the sources and natural conditions that affect in-stream processing and degradation and cycling between bottom sediment and water. Although concentrations generally were low for CECs and pharmaceuticals in water, the combined effects of numerous organic contaminants on aquatic organisms are largely unknown.

Summary

Pharmaceutical compounds, including prescription drugs, antibiotics, over-the-counter medications, reproductive hormones, and an array of other compounds including personal-care products, detergent metabolites, and flame retardants have been identified in surface waters from many states, including Minnesota and Wisconsin. These chemicals of emerging concern include endocrine active chemicals (EACs) capable of endocrine disruption as well as pharmaceutically active compounds (PhACs) designed for human or animal consumption. In Minnesota, endocrine disruption has been observed in the effluent of large wastewater treatment plants, including vitellogenin induction in male carp (*Cyprinus carpio*) and walleye (*Sander vitreus*). The potential ecological disruption from EACs and PhACs is substantial, and our current understanding of their distribution incomplete.

The St. Louis Bay of Lake Superior receives substantial urban runoff, wastewater treatment plant effluent, and industrial effluent. In 1987, the International Joint Commission designated the St. Louis Bay portion of the lower St. Louis River as one of the Great Lakes Areas of Concern because of the accumulation of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in sediment over time.

From August through October of 2010, the U.S. Geological Survey in cooperation with the Minnesota Pollution Control Agency and the Wisconsin Department of Natural Resources collected and analyzed water and bottom-sediment samples from 40 sites for pharmaceuticals, hormones, and other wastewater indicators from the St. Louis River, St. Louis Bay, and Superior Bay in Minnesota and Wisconsin. The objectives of this study were to (1) identify the extent to which chemicals of emerging concern occur in the St. Louis River, St. Louis Bay, and Superior Bay, and (2) identify the extent to which the chemicals may have accumulated in bottom sediment of the study area.

During this study, 33 of 89 CECs were detected among all water samples collected. The number of detections of chemicals of concern in individual water samples ranged from 1 to 12. The wastewater compound detected most frequently was *N,N*-diethyl-*meta*-toluamide (DEET), which was detected at every site, followed by caffeine (28 detections) and benzophenone (26 detections). Cholesterol, 3-*beta*-coprostanol, bisphenol *A*, and estrone were detected in at least one water sample. The number of detections of hormones in individual water samples ranges from one to four. Generally, sites in the St. Louis Bay or Superior Bay had 2 to 3 hormone detections.

Five pharmaceuticals were detected: cotinine, 1,7-dimethylxanthine, acetaminophen, caffeine, and carbamazepine. The number of detections of pharmaceuticals in individual water samples ranged from zero to five. Duluth Harbor Basin samples (stations H-38 and H-39) had the largest number of detections (five). Dimethylxanthine was detected in two samples, and acetaminophen was detected in four samples.

Fifty-six of 104 chemicals of concern were detected in at least one bottom-sediment sample. The number of detections of wastewater compounds in individual bottom-sediment samples ranged from 5 to 31. Dimethylnaphthalene was detected in all 40 bottom-sediment samples. This chemical was followed (in frequency of detection) by 3-methyl-1H-indole, which was detected in 39 of 40 samples. Twenty-two chemicals of concern were detected in more than 35 percent of the samples. Six hormones were detected in at least one bottom-sediment sample. The number of hormones detected in individual samples ranged from zero to four. The largest number of detections was for cholesterol, which was detected in 36 samples and 3-*beta*-coprostanol, which was detected in 24 samples.

An assessment of the presence of polycyclic aromatic hydrocarbons (PAHs) and the frequency at which concentrations in bottom-sediment samples exceeded established sediment-quality targets (SQTs) indicates these chemicals continue to persist in the sediment of the St. Louis River, St. Louis Bay, and Superior Bay. PAHs were detected in 31 of 40 samples. Bottom sediment collected from Superior Bay had the most detections and 7 of 11 samples exceeded the Level I SQT for total PAHs. Samples from two sites exceeded the Level II SQT for total PAHs; both sites were in the Duluth Harbor.

Chemicals of concern, including hormones, were detected at a higher frequency in bottom-sediment samples than in water samples. Endocrine active chemicals were detected in 58 percent of the water samples and 90 percent of bottom-sediment samples. The greater detection rate of both chemicals of concern and endocrine active chemicals in bottom sediment compared to the detection rates in water samples indicates that bottom sediment is an important sink for these chemicals.

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Tables and Appendixes

Tables 1 through 10 and appendixes 1 through 6 are presented in a single Microsoft® Excel spreadsheet available for download at http://pubs.usgs.gov/sir/2012/5184/downloads/tables_appendixes.xlsx.

Tables

Table 1. St. Louis River, St. Louis Bay, and Superior Bay sampling sites, Minnesota and Wisconsin, 2010.

Table 2. Analytical schedules of properties and chemicals analyzed in water or bottom-sediment samples.

Table 3. Surrogate chemicals and isotope dilution standards analyzed in water and bottom-sediment samples, St. Louis River, St. Louis Bay, and Superior Bay, Minnesota and Wisconsin, 2010.

Table 4. Analyte concentrations detected in blank sample, collected at St. Louis Bay (site 25) above Blatnik Bridge, Duluth, Minnesota (station and map identifier B-18, fig. 2), August 25, 2010.

Table 5. Summary of relative percent differences for replicate water and bottom-sediment samples collected from St. Louis River, St. Louis Bay, and Superior Bay, Minnesota and Wisconsin, 2010.

Table 6. Physical properties in water at the St. Louis River, St. Louis Bay, and Superior Bay sites, Minnesota and Wisconsin, 2010.

Table 7. Detection frequency and maximum concentration for chemicals of emerging concern analyzed in water samples from the St. Louis River, St. Louis Bay, and Superior Bay sites, Minnesota and Wisconsin, 2010.

Table 8. Detection frequency and maximum concentration of chemicals of emerging concern analyzed in bottom-sediment samples from the St. Louis River, St. Louis Bay, and Superior Bay sites, Minnesota and Wisconsin, 2010.

Table 9. Sediment-quality targets for selected polycyclic aromatic hydrocarbons.

Table 10. Occurrence of concentrations in bottom-sediment samples exceeding total polycyclic aromatic hydrocarbon sediment-quality targets.

Appendixes

Appendix 1–1. Concentrations of chemicals in water samples and quality-assurance samples analyzed at the U.S. Geological Survey National Water Quality Laboratory using laboratory schedule 1433 for analysis of wastewater-indicator chemicals.

Appendix 2–1. Concentrations of chemicals in water samples and quality-assurance samples analyzed at the U.S. Geological Survey National Water Quality Laboratory using laboratory schedule 2080 for analysis of human health pharmaceuticals.

Appendix 3–1. Concentrations of chemicals in water samples and quality-assurance samples analyzed at the U.S. Geological Survey National Water Quality Laboratory using laboratory schedule 4434 for analysis of hormones.

Appendix 4–1. Concentrations of chemicals in bottom-sediment samples and quality-assurance samples analyzed at the U.S. Geological Survey National Water Quality Laboratory using laboratory schedule 5433 for analysis of wastewater compounds.

Appendix 5–1. Concentrations of chemicals in bottom-sediment samples and quality-assurance samples analyzed at the U.S. Geological Survey National Water Quality Laboratory using laboratory schedule 6434 for analysis of hormones.

Appendix 6–1. Concentrations of chemicals in bottom-sediment samples and quality-assurance samples analyzed at the U.S. Geological Survey National Water Quality Laboratory using laboratory code 9008 for analysis of pharmaceuticals.

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2280 Woodale Drive
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(763) 783-3100

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