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Wastewater Indicator Compounds in Wastewater Effluent, Surface Water, and Bed Sediment in the St. Croix National Scenic Riverway and Implications for Water Resources and Aquatic Biota, Minnesota and Wisconsin, 2007–08

Scientific Investigations Report 2011–5208

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

Cover. St. Croix River above Rock Island near Franconia, Minn. (station 05340540) looking upstream. Photograph by Donald S. Hansen, U.S. Geological Survey.

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
acre	4,047	square meter (m^2)
	Volume	
ounce, fluid (fl. oz.)	29.57	milliliter (mL)
gallon (gal)	3.785	liter (L)
million gallons (Mgal)	3,785	cubic meter (m^3)
	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)

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

$$°F = (1.8 \times °C) + 32$$

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

Abbreviations and Acronyms

<	less than
AHTN	acetyl hexamethyl tetrahydronaphthalene
DEET	*N,N*-diethyl-*meta*-toluamide
E	estimated concentration because unacceptably low-biased recovery (less than 60 percent) or highly variable method performance (greater than 25-percent relative standard deviation), unstable instrument response, or reference standards prepared from technical mixtures
e	estimated concentration because the spike recovery or expected continuing calibration verification concentrations for each set of samples were not within control limits
EAC	endocrine active compound
HHCB	hexahydrohexamethyl cyclopentabenzopyran
MDL	method detection limit
MRL	minimum reporting level
NPS	National Park Service
NWQL	National Water Quality Laboratory
OWC	organic wastewater compound
PAH	polycyclic aromatic hydrocarbon
PBDE	polybrominated diphenyl ether
PR	percent recovery
RPD	relative percent difference
SCF-WWTP	St. Croix Falls wastewater-treatment plant
SPE	solid-phase extraction
TF-WWTP	Taylors Falls wastewater-treatment plant
USGS	U.S. Geological Survey
WWTP	wastewater-treatment plant

Acknowledgments

Bill Neska from the Taylors Falls wastewater-treatment plant and Mike Bryant from the St. Croix Falls wastewater-treatment plant provided a thorough description of the plant operations and provided access for collection of effluent samples. Becky Haass from the National Park Service provided assistance with geographic information system data, and Brenda Moraska LaFrancois from the National Park Service provided assistance with study design and site selection. Daniel Hornbach from Macalester College provided information concerning the location of mussel communities.

Wastewater Indicator Compounds in Wastewater Effluent, Surface Water, and Bed Sediment in the St. Croix National Scenic Riverway and Implications for Water Resources and Aquatic Biota, Minnesota and Wisconsin, 2007–08

By Abigail A. Tomasek, Kathy E. Lee, and Donald S. Hansen

Abstract

The U.S. Geological Survey and the National Park Service cooperated on a study to determine the occurrence of wastewater indicator compounds including nutrients; organic wastewater compounds (OWCs), such as compounds used in plastic components, surfactant metabolites, antimicrobials, fragrances, and fire retardants; and pharmaceuticals in the St. Croix National Scenic Riverway in Minnesota and Wisconsin. Samples of treated wastewater effluent from two wastewater-treatment plants (WWTPs), located in St. Croix Falls, Wisc. (SCF-WWTP) and Taylors Falls, Minn. (TF-WWTP), were collected from 2007 to 2008. During this time, surface-water and bed-sediment samples from the St. Croix River below Sunrise River near Sunrise, Minn., upstream from the two WWTPs (Sunrise site), and from the St. Croix River above Rock Island near Franconia, Minn., downstream from the WWTPs (Franconia site), also were collected. The Franconia site was selected because of the two large WWTP discharge points and the presence of mussel beds in this area of the St. Croix River.

A variety of OWCs and pharmaceuticals were detected in wastewater effluent from both WWTPs. Compounds detected varied between the two WWTPs and varied over time from samples collected at each site. The concentration and numbers of OWCs detected were greater in the wastewater effluent samples from SCF-WWTP (38 OWCs and 7 pharmaceuticals detected) than from TF-WWTP (20 OWCs and 3 pharmaceuticals detected). Four endocrine active compounds, compounds known to affect the endocrine systems of fish—4-nonylphenol, 4-nonylphenol diethoxylate, acetyl hexamethyl tetrahydronaphthalene, and hexahydrohexamethyl cyclopentabenzopyran—also were detected in effluent samples from both WWTPs. Concentrations of phosphate flame retardants were greater in effluent from SCF-WWTP than from TF-WWTP with the concentration of tris(2-butoxyethyl) phosphate greater than 200 micrograms per liter.

Seven OWCs, including one endocrine active compound, and two pharmaceuticals were detected in surface-water samples from the Sunrise site. Twelve OWCs and three pharmaceuticals were detected in surface-water samples from the Franconia site. Eighteen OWCs were detected in bed-sediment samples from the Sunrise site, whereas 21 OWCs were detected in bed-sediment samples from the Franconia site. Eight pharmaceuticals were detected in bed-sediment samples from both sites.

The results of this study indicate that aquatic biota in the St. Croix River are exposed to a wide variety of organic contaminants that originate from diverse sources including WWTP effluent. The data on wastewater indicator compounds indicate that exposures are temporally and spatially variable and that OWCs may accumulate in bed sediment. These results also indicate that OWCs in water and bed sediment increase downstream from discharges of wastewater effluent to the St. Croix River; however, the presence of OWCs in surface water and bed sediment at the Sunrise site indicates that potential sources of compounds, such as WWTPs or other sources, are upstream from the Taylors Falls-St. Croix Falls area.

Introduction

The St. Croix River Basin drains 7,790 square miles (mi^2) in Minnesota and Wisconsin (fig. 1). The St. Croix River Basin contains more than 15 major tributaries of the Namekagon and St. Croix Rivers, which together form the St. Croix National Scenic Riverway (referred to as “the Riverway” in this report), a National Wild and Scenic Riverway managed by the National Park Service (NPS) and the States of Minnesota and Wisconsin.

The St. Croix River is classified as an Outstanding Resource Water by Minnesota and Wisconsin. In Wisconsin, this classification requires that discharge to the river meets certain criteria (State of Wisconsin, 2008); in Minnesota, it

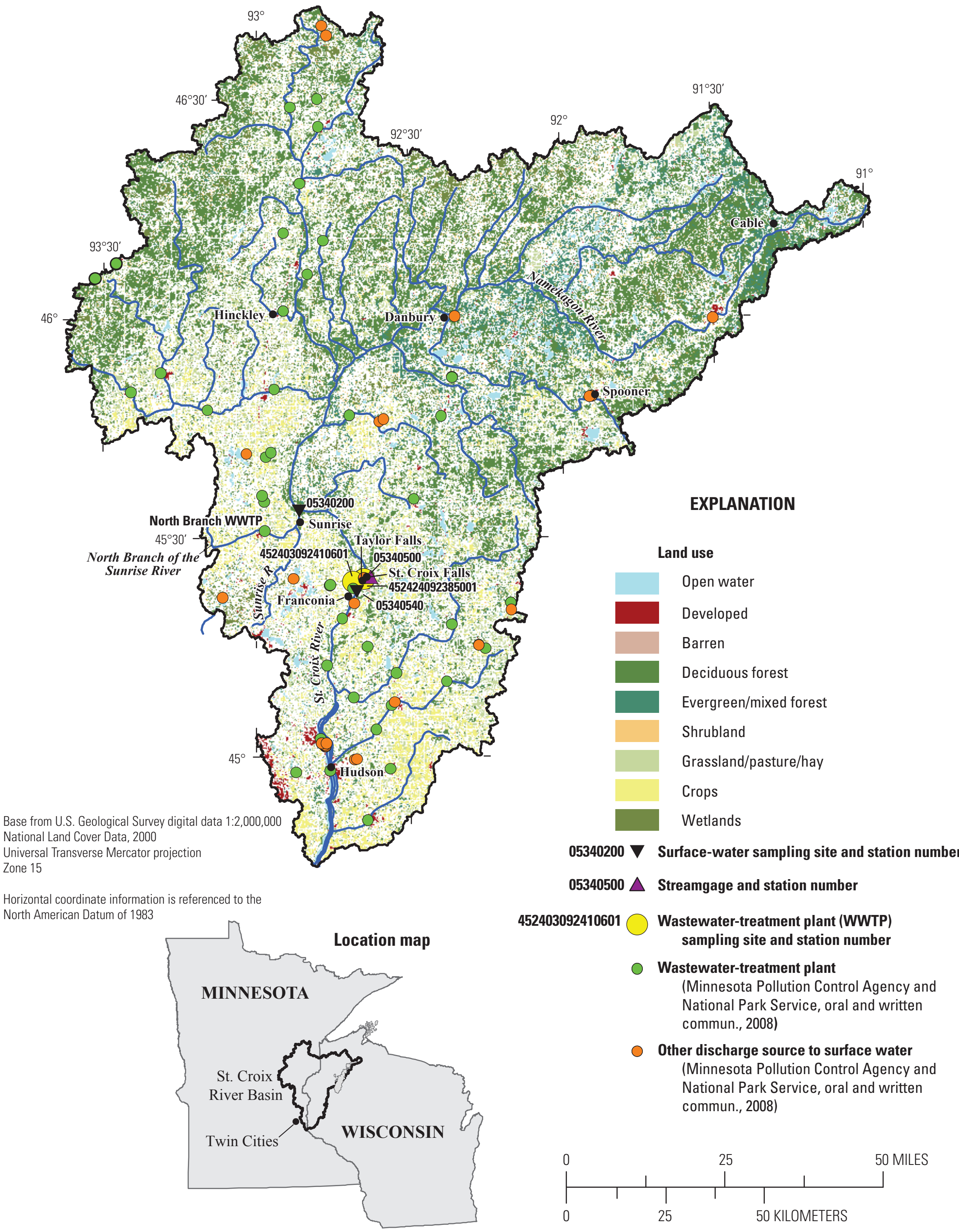

Figure 1. Sites sampled during 2007–08 and wastewater-treatment plants in the St. Croix River Basin, Minnesota and Wisconsin.

requires that all feasible and practical alternatives be implemented before a new or increased discharge is permitted (State of Minnesota, 2008). The St. Croix River has good water quality when compared to other large rivers in the Upper Mississippi River Basin, with low nutrient concentrations, relatively clear water, and low suspended-sediment and pesticide concentrations (Fallon, 1998; Fallon and others, 1997; Kroening, 2000). An indication of the Riverway's resource quality is the presence of numerous State and federally listed endangered and threatened species in the St. Croix River Basin. There are 110 fish species in the basin; 1 species, the crystal darter (*Crystallaria asprella*), is on Wisconsin's endangered species list and 8 others are on Wisconsin's threatened species list (Fago and Hatch, 1993). Large and diverse mussel colonies also are present in the Riverway. Of the 41 native species of freshwater mussels found in the Riverway, numerous species are listed as endangered by the State of Minnesota or Wisconsin (Hornbach, 2001), and 2 species, the Higgins eye pearly mussel (*Lampsilis higginsii*) and the winged mapleleaf mussel (*Quadrula fragosa*), are federally listed as endangered (Code of Federal Regulations, 1993). One of the world's few known, reproducing populations of the winged mapleleaf mussel is located in the St. Croix River Basin (Hornbach and others, 1996). Two introduced mussels, the zebra mussel (*Dreissena polymorpha*) and the Asian clam (*Corbicula fluminea*), are beginning to populate lengths of the St. Croix River and its tributaries (Hornbach, 2001), threatening the sensitive native mussel populations.

Land use and population growth in the St. Croix River Basin has changed and has caused concerns for the health of the aquatic ecosystem. Nutrient and suspended-sediment loads and yields increase in a downstream direction as land use along the St. Croix River changes from predominately forested areas at Danbury, Wisc., to a mixture of forested and agricultural land use at St. Croix Falls, Wisc. (Kroening and others, 2003). Urbanization in the St. Croix River Basin is increasing, and because of its proximity to the Twin Cities, the St. Croix River Basin is expected to experience increased use and developmental pressure (Wenger and Devault, 2000). For example, Washington County, a Minnesota county north of the Twin Cities and bordering the St. Croix River, has experienced a 13.9 percent increase in population from 2000 to 2008, whereas the whole State of Minnesota has only experienced a 6.1 percent increase (U.S. Census Bureau, 2009). As development and population growth continues, more wastewater will be generated, resulting in greater discharges of wastewater effluent into the St. Croix River and its tributaries. More than 30 municipal and industrial wastewater-treatment plants (WWTPs) discharge into the St. Croix River and its tributaries (Minnesota Pollution Control Agency and National Park Service, oral and written commun., 2008; fig. 1).

Numerous pharmaceuticals and other organic wastewater compounds (OWCs) such as plastic components, antimicrobial compounds, detergent metabolites, antioxidants, fragrances, flavors, and flame retardants have been measured in WWTP effluent (Lee and others, 2004; Lee and others, 2011). The removal efficiency of pharmaceuticals and other OWCs is variable (Schwätter and others, 2007), and therefore, treated wastewater effluent is a potential continuous source of these contaminants to streams. Pharmaceuticals and other OWCs have been detected in surface and groundwater throughout the world for more than a decade (Barnes and others, 2008; Halling-Sørensen and others, 1998; Heberer, 2002; Sacher and others, 2001; Ternes, 1998; Weigel and others, 2004). In the United States, Kolpin and others (2002) detected pharmaceuticals and other OWCs in 80 percent of 139 streams analyzed nationwide. Regional studies in Minnesota and Wisconsin have identified pharmaceuticals and other OWCs in wastewater effluent and wastewater receiving streams (Lee and others, 2004; Karthikeyan and Meyer, 2006; Lee and others, 2010). A study by Vajda and others (2008) indicated that downstream from a WWTP in Colorado, the frequency of male fish was one-half of the frequency upstream from the WWTP, and intersex white suckers, which were not found upstream from the WWTP, composed 18 to 22 percent of the downstream population. In a study by Hinck and others (2008), fish were labeled as intersex when individual or small clusters of undeveloped oocytes were observed within testicular tissue or when speractocytes were observed within ovarian tissue, and oocytes were identified in 42 percent of male bass from 12 sites in the United States, including two sites in Minnesota.

The occurrence of pharmaceuticals and other OWCs in the water and sediments of the St. Croix Riverway and the contributions of pharmaceuticals and other OWCs from WWTPs discharging to the river are not well understood, and little is known about the effects of these compounds on aquatic biota. Although pharmaceuticals and other OWCs typically are present at low concentrations, the continuous discharge of wastewater effluent into rivers results in potential continuous exposure of aquatic organisms. Because some pharmaceuticals and other OWCs are naturally, inadvertently, or intentionally designed to modify physiological processes in humans and livestock, exposed aquatic organisms, such as mussel populations, may be unintentionally affected. Refuge and National Park managers have expressed concern about whether aquatic populations in their management areas are adversely affected by these compounds.

One area of particular concern is the St. Croix River near Taylors Falls, Minn., and near St. Croix Falls, Wisc., because of wastewater effluent discharge from the WWTPs of both cities. Both WWTPs are located in the vicinity of concentrated mussel populations (fig. 2), including the federally endangered Higgins eye pearly mussel and winged mapleleaf mussels. Within the past decade, the number of juvenile mussels has decreased by 96 percent downstream from the dam at St. Croix Falls (Kushner and others, 2006). Zebra mussels are threatening native mussel communities (Baker and Hornbach, 2000), and chronic exposures to pharmaceuticals and other OWCs are potentially threatening those mussel communities (Canesi and others, 2007; Gagné and others, 2004; Gagné and others, 2007). The two river sites near Franconia and Sunrise, Minn.,

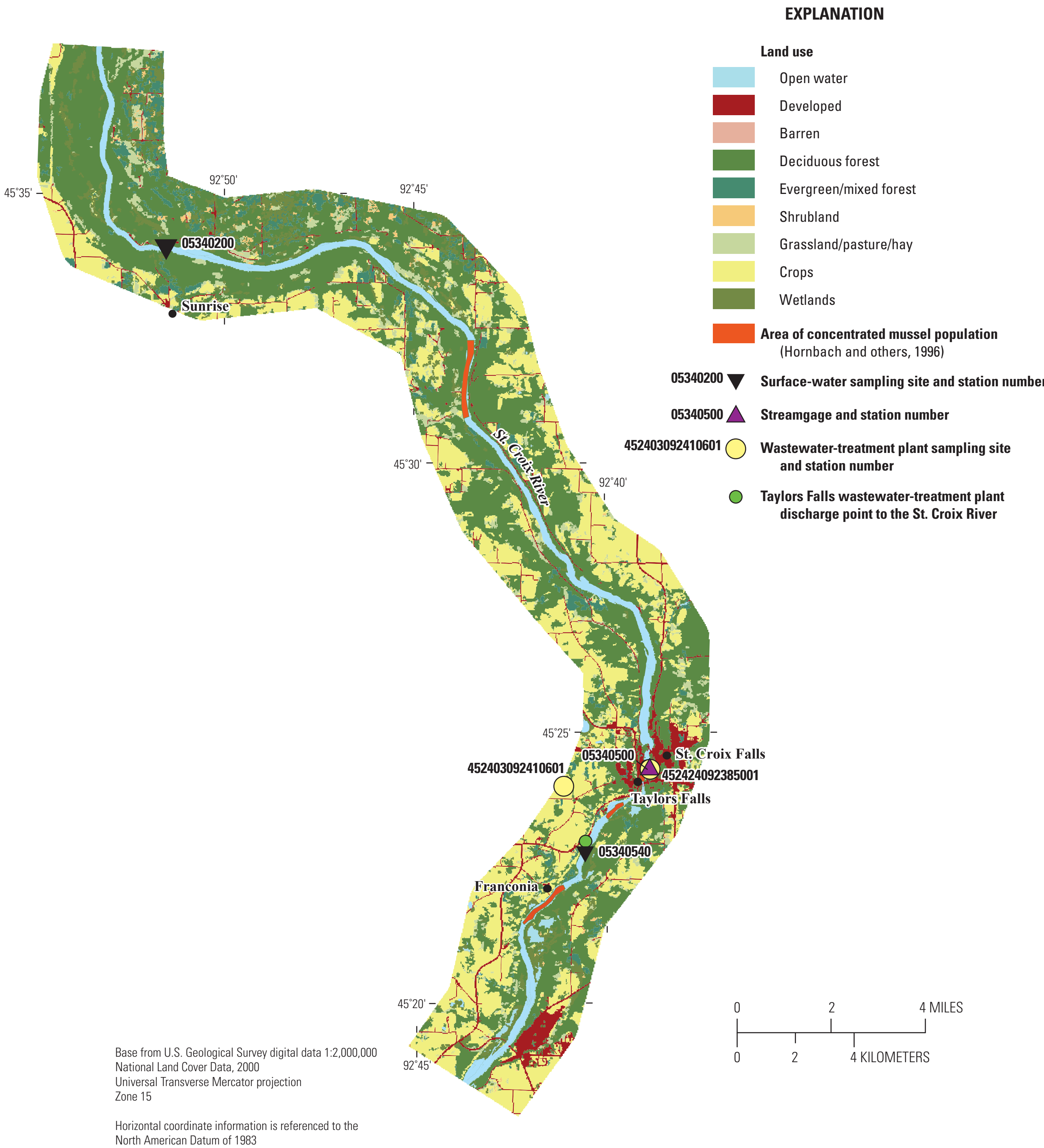

Figure 2. Sampling sites and areas of concentrated mussel population along the St. Croix River, Minnesota and Wisconsin, during 2007–08.

are known to have high mussel species diversity and density, and large numbers of the endangered winged mapleleaf, especially downstream from the dam at St. Croix Falls (Hornbach and others, 1996).

To address concerns about wastewater indicator compounds (major ions, nutrients, pharmaceuticals, and other OWCs) affecting aquatic health in the St. Croix National Scenic Riverway, the U.S. Geological Survey (USGS) in cooperation with the NPS conducted a study to determine the occurrence of these compounds in wastewater effluent, surface water, and bed sediment at selected sites in the St. Croix River Basin. Knowledge of the occurrence of wastewater indicator compounds in the WWTP effluent is important because the detected compounds provide information about the potential aquatic species exposure in the Riverway. The water and bed-sediment samples collected from the river upstream from the WWTPs provide information about the occurrence of wastewater indicator compounds that are present upstream from discharges of wastewater effluent from WWTPs. The water and bed-sediment samples collected from the river downstream from the WWTPs provide information about exposure after degradation and dilution processes have occurred.

The purpose of this report is to describe the occurrence of wastewater indicator compounds in wastewater effluent, surface water, and bed sediment at selected sites in the St. Croix River Basin and to describe implications for water resources and aquatic biota on the basis of the data collected for this study. Samples of treated wastewater effluent from two WWTPs, located in St. Croix Falls, Wisc. (SCF-WWTP) and Taylors Falls, Minn. (TF-WWTP), were collected from May 2007 to October 2008. During this same period, water and bed-sediment samples from the St. Croix River below Sunrise River near Sunrise, Minn., upstream from the two WWTPs (hereafter referred to as the Sunrise site), and from the St. Croix River above Rock Island near Franconia, Minn., downstream from the WWTPs (hereafter referred to as the Franconia site), also were collected. Water samples were analyzed for physical properties, major ions, nutrients, pharmaceuticals, and other OWCs. Bed-sediment samples were analyzed for pharmaceuticals and other OWCs.

Study Methods

Four sites were selected for sampling (figs. 1 and 2; table 1); WWTP effluent was sampled at two sites and water and bed sediment were sampled at the other two sites. Samples of WWTP effluent were collected at the TF-WWTP (station 452403092410601) and SCF-WWTP (station 452424092385001). These WWTPs discharge wastewater effluent into the St. Croix River upstream from mussel populations. Water and bed-sediment samples were collected from a site upstream from the two WWTPs and located downstream from the confluence of the Sunrise River and the St. Croix River (Sunrise site; station 05340200), and from a site downstream from the WWTPs at Franconia, Minn. (Franconia site; station 05340500). Mussel populations occur throughout the study area, and concentrated areas of mussels occur near the two sampled river sites (fig. 2).

Table 1. Sites sampled in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, during 2007–08 and areas of concentrated mussel population.

[Sites were sampled between May 17, 2007, and October 9, 2008. USGS, U.S. Geological Survey; WWTP, wastewater-treatment plant]

USGS station identification number	Site name	Abbreviated site name used in report
452403092410601	Taylors Falls WWTP at Taylors Falls, Minn.	TF-WWTP
452424092385001	St. Croix Falls WWTP at St. Croix Falls, Wisc.	SCF-WWTP
05340200	St. Croix River below Sunrise River near Sunrise, Minn.	Sunrise site
05340540	St. Croix River above Rock Island near Franconia, Minn.	Franconia site

Water and bed-sediment samples were collected twice a year for 2 years during different seasons and streamflow conditions; sampling coincided with the discharge of wastewater effluent from TF-WWTP in the spring and fall. It was expected that WWTP effluent would constitute a greater percentage of streamflow during fall base-flow conditions than during other times of the year, and therefore, constituents would be more concentrated in stream water during the fall.

Site Descriptions

Information on the TF-WWTP was provided by personnel from the treatment plant. The TF-WWTP serves 1,051 people (in 2009) and receives its wastewater almost entirely from domestic sources. The WWTP discharges twice a year (May and October) for 8 days at a time. During this period, the WWTP discharges 1.125 million gallons per day (Mgal/d) of effluent, for a total of 9 million gallons per discharge period using a treatment schematic of a three-cell pond system.

The TF-WWTP design consists of two primary ponds, each of which are 6.5 acres, and a secondary 7-acre polishing pond. Wastewater enters the WWTP from three lift stations and goes through a screening device to remove large solids, which are collected, dewatered, and sent to a solid waste disposal site. The wastewater then is pumped into the primary ponds where most of the remaining solid matter settles. During the spring, summer, and fall months, typically only one primary pond is filled at a time to allow the other pond to sit for 180 days or until the pond is filled to maximum capacity at a 6-foot depth; in winter, both primary ponds are filled simultaneously to prevent freezing.

During the 180-day period in the primary ponds at the TF-WWTP, biological, chemical, and physical processes aid in nutrient and organic matter removal. The water then moves to the polishing pond (fig. 3*A*), where additional exposure to sun, wind, microorganisms, and algae further reduces 5-day biochemical oxygen demand, fecal coliform, and nutrients to allowable discharge limits. No settlement occurs in this pond so the residence time is reduced to only a couple of days compared to 180 days for the primary ponds. Once the water is within the allowable discharge limits, it is discharged into the St. Croix River over 8-day periods (fig. 3*B*).

Information on the SCF-WWTP was provided by personnel at the treatment plant. The SCF-WWTP serves 2,033 people (during the sampling period in 2009) and receives its influent from domestic (86 percent) and industrial (14 percent) sources; the industrial inflow is primarily from a medical center (about 89 percent) and a mill (6 percent). The SCF-WWTP discharges continuously and has a peak-inflow capacity of 0.657 Mgal/d, or a mean inflow of 0.398 Mgal/d, and a design effluent quality of 30 milligrams per liter (mg/L) for 5-day biochemical oxygen demand and 30 mg/L for suspended solids. The daily discharge varies at SCF-WWTP, and the effluent discharges on the days of sampling, measured by the SCF-WWTP, were 0.194, 0.175, 0.210, and 0.200 Mgal/d on May 7, 2007; September 17, 2007; May 16, 2008; and October 9, 2008, respectively.

The SCF-WWTP uses a design typical of smaller WWTPs and has more processing steps than the TF-WWTP. The influent first passes through a screening channel and a grit chamber to remove large particles and sand from the wastewater. From there, the wastewater moves into a primary clarifier (fig. 4*A*), where suspended solids (sludge) begin to settle out, and then passes through two stages of trickling filters, where wastewater is biologically treated by microorganisms. The water then is split into two final clarifiers, and the remaining solids settle out. Chlorine gas in water solution is added to disinfect the water, and the effluent is discharged into the St. Croix River (fig. 4*B*).

At the SCF-WWTP, the sludge that settled out in the clarifiers is pumped to the primary digester where it is heated and mixed in the absence of oxygen (anaerobic digestion) to reduce the volume and odors. A byproduct of this process is methane gas, which is burned off, and the sludge is then transferred to the secondary digester. The supernatant then is returned back into the primary clarifier, and the remaining solids and liquids are disposed of on land.

The upstream surface-water and bed-sediment sampling site on the St. Croix River near Sunrise, Minn., is located in

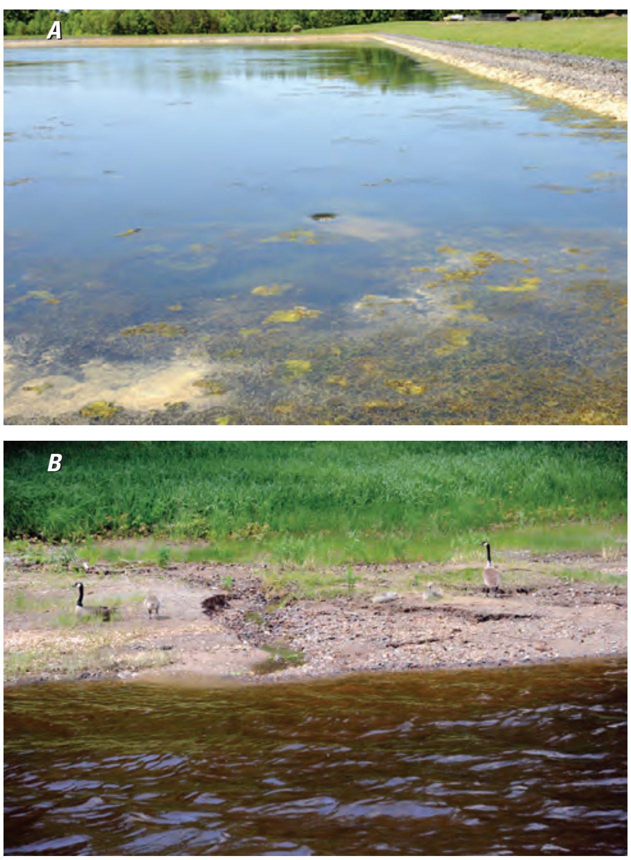

Figure 3. Photographs showing *A*, polishing pond for Taylors Falls wastewater-treatment plant and *B*, outflow from the treatment plant to the St. Croix River.

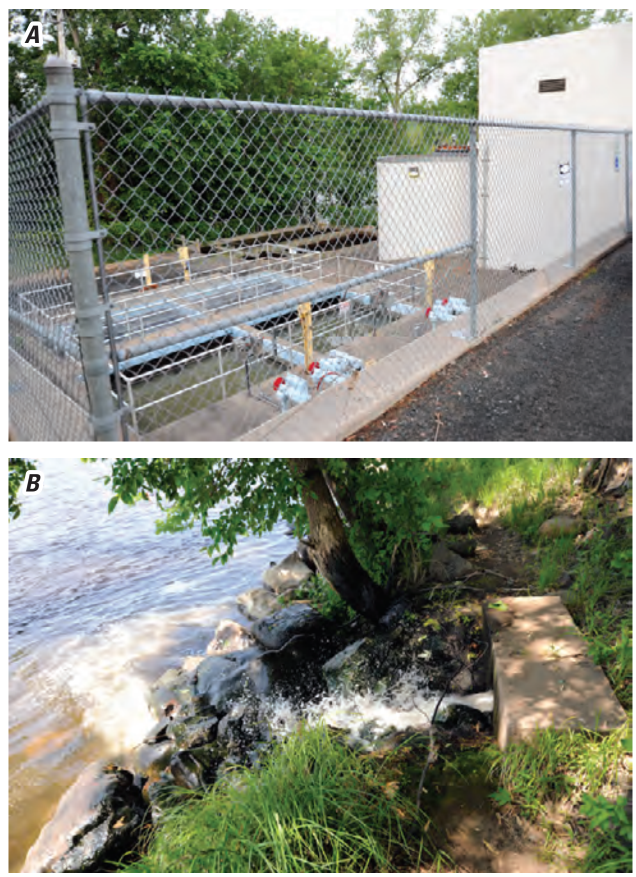

Figure 4. Photographs showing *A*, St. Croix Falls wastewater-treatment plant clarifiers and *B*, outflow from the treatment plant to the St. Croix River.

Wild River State Park. This site was selected because of its location away from large population centers and upstream WWTPs. The site was selected to serve as a reference location from which concentrations at the downstream Franconia site could be compared. The entire reach of the St. Croix River between Sunrise and Franconia contains mussels; however, a concentrated population of mussels is present downstream from the confluence with the Sunrise River. The Sunrise site is located just downstream from the St. Croix River's confluence with the Sunrise River. Other WWTPs discharge to tributary streams upstream from the Sunrise site including the North Branch WWTP, which discharges (continuous design flow of about 0.8 Mgal/d) to the North Branch of the Sunrise River approximately 9 miles upstream from the sampling location (fig. 1).

The downstream surface-water and bed-sediment sampling site on the St. Croix River near Franconia, Minn., is located downstream from both WWTP discharge locations (fig. 5) and downstream from the hydroelectric dam at St. Croix Falls. The Franconia site was selected because of its location near mussel populations that include the federally endangered Higgins eye pearly mussel and winged mapleleaf species.

Figure 5. St. Croix River above Rock Island near Franconia, Minn. (station 05340540) looking upstream. Photograph by Donald S. Hansen, U.S. Geological Survey.

Sample Collection Methods

All four sites were sampled twice a year in 2007 and 2008 with the exception of the TF-WWTP, which was sampled once in 2007 and twice in 2008 (table 2). Physical properties of specific conductance, water temperature, pH, and dissolved oxygen were measured during each river sampling event using a submersible multi-parameter sonde to assess the basic water-quality differences between sampling locations. The sonde was calibrated before each sampling event in accordance with U.S. Geological Survey (variously dated) and manufacturer's specifications to ensure accurate measurements. Water samples were collected from the St. Croix River using integrated width-and-depth sampling techniques (Edwards and Glysson, 1988; U.S. Geological Survey, variously dated), and WWTP effluent samples were collected directly from the effluent outflows. Water samples were collected using USGS procedures for low-level contaminants (U.S. Geological Survey, variously dated).

To avoid contamination, personnel collecting and analyzing samples avoided use of personal-care items such as insect repellent, sunscreen, cologne, aftershave, and perfume. Personnel also did not consume caffeinated or tobacco products before or during collection or processing of samples. Nitrile, powderless, disposable gloves were worn during sample collection. All samples were collected with inert materials such as Teflon®, glass, or stainless steel. All collection and processing equipment was cleaned between samples with a succession of native water, soapy tap water, tap water, deionized water, methanol, and organic-free water rinses. Following collection, samples were chilled and processed within 1 to 2 hours before they were shipped for analyses.

Each sample was filtered by using a baked (oven baked at 450 degrees Celsius (°C) for 2 hours) 0.7-micron glass fiber filter with the exception of samples for total analyses of selected nutrients (total ammonia plus organic nitrogen and total phosphorus), which were not filtered. The pumping system was a peristaltic pump with Teflon® tubing. The filter support was made of stainless steel with a 5.6-inch (in.) (142-millimeter) diameter. Approximately 100 milliliters (mL) of the sample water was filtered prior to actual sample filtration to flush the filtration system. Once the system was flushed, water was filtered into labeled, baked amber glass sample bottles and refrigerated prior to shipping to the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., for analyses.

Bed-sediment samples were collected according to USGS procedures (U.S. Geological Survey, variously dated). Samples were collected with stainless-steel sampling equipment from the top 8 inches (in.; 20 centimeters) of bed sediment at five depositional areas at each sampling location and were composited to yield a representative sample of site conditions. If a sample contained large amounts of vegetation or was disturbed, the sample was discarded and a new sample was collected. Fine-grained sediments were collected from the top 5.9 in. (15 centimeters) of bed sediment where most benthic organisms reside. Samples from at least five areas at each location were collected and composited to yield a sample representing average site conditions. The samples were transferred to glass containers and shipped to the NWQL for analyses.

Table 2. List of constituents analyzed in samples from four sites in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, during 2007–08.

[USGS, U.S. Geological Survey; WWTP, wastewater-treatment plant]

USGS station identification number	Date	Major Ions	Nutrients	Organic wastewater compounds in water	Organic wastewater compounds in bed sediment	Pharmaceuticals in water	Pharmaceuticals in bed sediment
Taylors Falls WWTP at Taylors Falls, Minn. (TF-WWTP)							
452403092410601	05/17/2007	No	Yes	Yes	No	Yes	No
452403092410601	05/15/2008	No	Yes	Yes	No	Yes	No
452403092410601	10/09/2008	No	Yes	Yes	No	Yes	No
St. Croix Falls WWTP at St. Croix Falls, Wisc. (SCF-WWTP)							
452424092385001	05/17/2007	No	Yes	Yes	No	Yes	No
452424092385001	09/17/2007	No	Yes	Yes	No	Yes	No
452424092385001	05/16/2008	No	Yes	Yes	No	Yes	No
452424092385001	10/09/2008	No	Yes	Yes	No	Yes	No
St. Croix River below Sunrise River near Sunrise, Minn. (Sunrise site)							
05340200	05/25/2007	No	Yes	Yes	Yes	Yes	Yes[1,6]
05340200	09/12/2007	No	Yes	Yes	Yes	Yes	Yes[1,6]
05340200	05/15/2008	Yes	Yes	Yes[2,3]	Yes	Yes	Yes[1,3,6]
05340200	10/09/2008	No	Yes[4]	Yes[4]	Yes	Yes[4]	Yes
St. Croix River above Rock Island near Franconia, Minn. (Franconia site)							
05340540	05/17/2007	No	Yes[5]	Yes[5]	Yes[4]	Yes[4,5]	Yes[1,3,6]
05340540	09/12/2007	No	Yes	Yes	Yes	Yes[3]	Yes[3]
05340540	05/16/2008	Yes	Yes	Yes[4]	Yes	Yes[3]	Yes[1,3,6]
05340540	10/09/2008	No	Yes	Yes[3]	Yes	Yes[3]	Yes

[1] Laboratory replicate sample prepared.

[2] Sample broken in laboratory.

[3] Spike sample collected.

[4] Field replicate sample collected.

[5] Field blank sample collected.

[6] Laboratory replicate sample.

Laboratory Analysis

Water samples from the St. Croix River near Sunrise and Franconia (stations 05340200 and 05340540, respectively) were analyzed for 95 compounds including 10 major ions, 6 nutrients, 58 OWCs, and 16 pharmaceuticals; 3 OWC surrogates and 2 pharmaceutical surrogates also were analyzed for quality assurance. Effluent samples from TF-WWTP and SCF-WWTP were analyzed for the same compounds as the surface-water samples with the exception of major ions. Bed-sediment samples were analyzed for 87 compounds (52 OWCs and 30 pharmaceuticals); 2 OWC surrogates and 2 pharmaceutical surrogates also were included in the analysis (*appendix 1*).

Water samples were analyzed at the NWQL using standard analytical techniques for major ions and nutrients as described in Fishman and Friedman (1989), Patton and Truitt (1992), Fishman (1993), U.S. Environmental Protection Agency (1993), and Fishman and others (1994). Samples analyzed for dissolved major-ion and nutrient concentrations were filtered using 0.45-micron pore-size encapsulated filters. Nutrient samples were preserved and maintained at 4°C until analyzed at the NWQL. Samples analyzed to determine total nutrient concentrations were not filtered.

OWCs are a broad suite of organic compounds that are indicators of industrial, domestic, and agricultural wastewaters and were selected for this study on the basis of usage, toxicity, potential estrogenic activity, and persistence in the environment (Barnes and others, 2002; Kolpin and others, 2002). Plastic components, fire retardants, caffeine, triclosan, and synthetic musk compounds were included in the analysis because of their frequent detection downstream from WWTPs, making these compounds good indicators of WWTP effluent (Glassmeyer and others, 2005; Lee and others, 2008). The USGS analysis for OWCs in water samples includes synthetic musks, sterols, fragrances, detergent metabolites, antimicrobial compounds, plastic components, fire retardants, pesticides (Zaugg and others, 2002), and eight endocrine active compounds (EACs) known to affect the endocrine system of fish: 4-*n*-octylphenol, 4-nonylphenol, 4-nonylphenol diethoxylate, 4-*tert*-octylphenol diethoxylate, 4-*tert*-octylphenol monoethoxylate, 4-*tert*-octylphenol, acetyl hexamethyl tetrahydronaphthalene (AHTN), and hexahydrohexamethyl cyclopentabenzopyran (HHCB). Pharmaceuticals analyzed include over-the-counter pharmaceuticals, such as acetaminophen, and prescription pharmaceuticals, such as carbamazepine and codeine.

Water samples collected for the analyses of OWCs were analyzed at the NWQL in accordance to a method described by Zaugg and others (2002). Water samples were first filtered in the field using a glass-fiber filter with a 0.7-micron nominal pore diameter to remove suspended particulate matter. The water samples then were sent to the NWQL on ice by overnight carrier where they were extracted within 48 hours using disposable, polypropylene solid-phase extraction (SPE) cartridges that contain a polystyrene-divinylbenzene phase, and the cartridges were subsequently dried. After drying, the sample bottles were rinsed thoroughly with a mixture of 0.5 fluid ounce (fl. oz; 15 mL) dichloromethane and diethyl ether at a ratio of 4:1. The dichloromethane–diethyl ether rinsate also was used to elute sorbed compounds from the corresponding SPE cartridges. The extract then was evaporated to a final volume of 0.01 fl. oz (0.4 mL), and transferred to an austosampler vial that contains a 400-microliter glass insert. The concentrated extracts were determined by capillary-column gas chromatography/mass spectrometry for the OWCs listed in *appendix 1*.

Water samples were analyzed for pharmaceuticals using a method described in Furlong and others (2008). The method uses a chemically modified styrene-divinylbenzene resin-based SPE cartridge for analyte isolation and concentration. For analyte detection and quantification, an instrumental method was developed that used a high-performance liquid chromatography/mass spectrometry system to separate the pharmaceuticals of interest from each other and co-extracted material. Immediately following separation, the pharmaceuticals were ionized by electrospray ionization operated in the positive mode; the positive ions produced were detected, identified, and quantified using a quadrupole mass spectrometer.

Bed-sediment samples were analyzed at the NWQL using a method developed by Burkhardt and others (2006) for OWCs and using an additional custom method for pharmaceuticals. Sediment and soil samples were extracted using a pressurized water/isopropyl alcohol extraction. Compounds were isolated by SPE, and sorbed compounds were eluted with methylene chloride (80 percent) and diethyl ether (20 percent) and then determined by capillary-column gas chromatography/mass spectrometry. For the analysis of pharmaceuticals in bed sediment, a method described by Kinney and others (2006) was used for extraction and quantification of a suite of pharmaceuticals. The method of Schultz and Furlong (2008) was applied to extracts prepared using the method of Kinney and others (2006), as described in Schultz and others (2010). 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 identification and quantification of human-use pharmaceuticals, the instrument analysis method of Kinney and others (2006) was used. Antidepressants were identified and quantified with liquid chromatography and electrospray ionization tandem mass spectrometry (Schultz and Furlong, 2008; Schultz and others, 2010). Detection limits for this method range from 0.0010–0.0021 nanograms per gram (ng/g) for individual antidepressants in sediment extracts.

The analytical methods for OWCs in water and bed sediment are defined as information-rich methods because compound identifications are determined by mass spectrometry; consequently, results are not censored at the minimum reporting level (MRL) (Childress and others, 1999). The MRL is the smallest measured concentration of a constituent that may be reliably reported by using a given analytical method (Timme, 1995). The intention is to produce as much information as possible for complex samples, but for which it is difficult to consistently report concentrations near the method detection limit (MDL). The MDL is the minimum concentration that can be measured and reported with a 99-percent confidence that the concentration is greater than zero (U.S. Environmental Protection Agency, 2002). The MRLs are set higher than the calculated MDLs as a precaution to reduce the risk of reporting false positives (Zaugg and others, 2006). Reporting compound concentrations as estimated because their concentrations are less than the MRL does not decrease confidence in qualitative identification of a compound. However, there is more uncertainty for concentrations reported near or less than the MDL (Zaugg and others, 2006). In this report, concentrations with an “E” remark code were considered as detections and reported as the estimated value.

Quality Assurance and Quality Control

The USGS National Field Manual (U.S. Geological Survey, variously dated) was used to guide water and bed-sediment data collection. A quality-assurance plan for this study was established to evaluate field sampling and laboratory techniques for water and bed sediment, to assess possible sources of contamination, and to ensure that collected samples were representative of streamflow conditions. All field personnel were familiar with study design and sampling protocols before sampling and sample processing to ensure sample integrity. Laboratory quality-control samples were used to validate analytical data, and field quality-control samples were obtained to validate collection and processing methods.

Laboratory quality-control samples for water analyses included laboratory blanks, reagent spikes, and surrogates. Details of USGS quality-control specifications can be found in Maloney (2005). Some concentrations of compounds for analyses at the NWQL were reported as estimated (coded with an "E") for one of following reasons: unacceptably low-biased recovery (less than 60 percent) or highly variable method performance (greater than 25-percent relative standard deviation), unstable instrument response, or reference standards prepared from technical mixtures. Nine additional compounds (coded with an "e") in *appendix 1* had variable performance during the initial method validation. The concentration of compounds was reported as estimated if the spike recovery or expected continuing calibration verification concentrations for each set of samples were not within control limits (Zaugg and others, 2002). Estimated values that are less than the MRL can present challenges in data interpretation. For example, there is a lack of assurance that the environmental sample concentrations are greater than potential field and laboratory blank concentrations. In order to address these challenges, extensive quality-assurance data are presented.

Blank Samples

Field and laboratory blank samples were analyzed to ensure that environmental samples were not contaminated during collection and processing and to assess potential contamination. Laboratory blank samples were analyzed with each sample sent to the NWQL during the study. Field blank samples were prepared at a sampling site where corresponding environmental samples were collected.

For this study, one field blank water sample was collected at the Franconia site. The field blank sample was analyzed for nutrients, pharmaceuticals, and other OWCs and was processed using high-performance liquid-chromatography-grade organic-free water from the same equipment used for collection of the environmental and replicate samples. Nine compounds were detected in the field blank water sample (table 3). Three of the nine detected compounds were nutrients. Most concentrations of compounds in the field blank water sample were less than the concentrations measured in environmental samples, with the exception of acetaminophen, *N,N*-diethyl-*meta*-toluamide (DEET), and triphenyl phosphate.

Thirty compounds were detected in the laboratory blank water samples (table 4). Compounds were detected in the laboratory blank water samples at concentrations less than method reporting levels. Twenty-three compounds were detected in the laboratory blank bed-sediment samples; however, most of these compounds were detected at concentrations less than those measured in environmental samples, and only six compounds (benzo[*a*]pyrene, cholesterol, fluoranthene,

Table 3. Concentrations of constituents in the field blank water sample collected at the St. Croix River above Rock Island near Franconia, Minn. (station 05340540), and average of detected concentrations in environmental samples collected in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

[mg/L, milligrams per liter; µg/L, micrograms per liter; DEET, *N,N*-diethyl-*meta*-toluamide; HHCB, hexahydrohexamethyl cyclopentabenzopyran; ND, compound was not detected]

Constituent	Concentration in blank sample	Detection range for environmental samples (surface water and wastewater)	Average concentration in surface-water environmental samples	Average concentration in wastewater effluent	Number of environmental samples for surface water (wastewater effluent)	Number of environmental samples with detections for surface water (wastewater effluent)
Dissolved ammonia, in mg/L	0.023	0.013–14.8	0.024	3.94	8(7)	2(7)
Total ammonia plus organic nitrogen, in mg/L	.054	0.446–20.6	.658	7.15	8(7)	8(7)
Dissolved orthophosphate, in mg/L	.003	0.005–6.93	.018	3.79	8(7)	8(7)
4-*tert*-Octylphenol monoethoxylate, in µg/L	.033	0.530–2.19	ND	1.21	8(7)	0(3)
Acetaminophen, in µg/L	.015	0.007–0.014	.011	ND	8(7)	2(0)
DEET, in µg/L	.017	0.014–2.79	.061	.930	8(7)	7(6)
HHCB, in µg/L	.012	0.038–2.16	ND	.689	8(7)	0(6)
Triethyl citrate, in µg/L	.008	0.019–0.564	ND	.249	8(7)	0(4)
Triphenyl phosphate, in µg/L	.009	0.007–0.113	.010	.058	8(7)	2(4)

Table 4. Concentrations of compounds detected in laboratory blank water samples and the corresponding environmental data associated with the blank samples, St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

[Only compounds detected in environmental samples are shown.]

Constituent	Number of blank samples	Number of blank samples with detections	Blank concentration range	Environmental concentration range	Number of environmental samples with detections	Number of blank samples with corresponding environmental sample detections
Surface water and wastewater effluent samples						
Dissolved ammonia[1]	15	11	0.001–0.008	0.013–14.8	9	7
Dissolved nitrite plus nitrate[1]	15	15	0.005–0.013	0.071–22.5	15	15
Dissolved nitrite[1]	15	5	0.000–0.001	0.003–0.567	15	5
Total ammonia plus organic nitrogen[1]	15	9	0.003–0.020	0.400–21.0	15	9
Dissolved orthophosphate[1]	15	15	0.000–0.003	0.005–6.93	15	15
Total phosphorous[1]	8	8	0.023–0.025	0.031–6.87	8	8
1-Methylnaphthalene[2]	14	4	0.002	0.005–0.031	6	2
2-Methylnaphthalene[2]	14	9	0.002–0.005	0.009–0.061	5	3
3-*beta*-Coprostanol[2]	14	3	0.130	0.135–4.74	5	2
4-Nonylphenol[2]	14	13	0.053–0.190	0.574–18.2	6	6
4-Nonylphenol diethoxylate[2]	14	4	0.132–0.444	0.545–46.7	4	1
4-*tert*-Octylphenol[2]	14	10	0.004–0.011	0.410–2.48	3	2
4-*tert*-Octylphenol diethoxylate[2]	14	2	0.044	0.770–1.38	3	0
4-*tert*-Octylphenol monoethoxylate[2]	14	4	0.008–0.048	0.530–2.19	3	1
Benzophenone[2]	14	9	0.002–0.011	0.026–0.220	6	4
beta-Stigmastanol[2]	14	3	0.262	0.354–1.18	3	1
Caffeine[2]	14	6	0.003–0.007	0.042–2.60	6	2
Camphor[2]	14	3	0.002–0.003	0.011–0.085	9	2
Carbaryl[2]	14	4	0.001–0.004	0.113	1	0
Cholesterol[2]	14	4	0.044–0.302	0.522–3.60	5	3
Cotinine[2]	14	3	0.003–0.004	0.064–0.092	3	1
d-Limonene[2]	14	4	0.003–0.011	0.047–0.117	2	1
Methyl salicylate[2]	14	5	0.001–0.005	0.154	1	0
Naphthalene[2]	14	13	0.006–0.009	0.024–0.074	2	2
p-Cresol[2]	14	6	0.006–0.008	0.160–2.23	3	1
Phenanthrene[2]	14	11	0.001–0.003	0.022	2	2
Phenol[2]	14	13	0.021–0.061	0.266–0.717	2	2
Triphenol phosphate[2]	14	3	0.005	0.007–0.113	6	1
Tris(2-butoxyethyl) phosphate[2]	14	1	0.015	0.062–217	9	1
Diphenhydramine[2]	15	9	0.000–0.001	0.002–0.010	2	2
Bed-sediment samples						
2,6-Dimethylnaphthalene[3]	8	2	0.560	1.03–9.87	3	0
3-*beta*-Coprostanol[3]	8	2	38.1	97.2	1	0
Anthracene[3]	8	2	0.715	5.25–49.9	4	1
Benzo[*a*]pyrene[3]	8	4	1.66–1.78	3.33–89.5	5	3
Benzophenone[3]	8	2	2.87	6.81	1	0
Cholesterol[3]	8	2	76.9	176–993	8	2
Flouranthene[3]	8	6	1.71–5.03	7.24–293	5	4
Indole[3]	8	2	2.62	12.4–198	7	1
p-Cresol[3]	8	6	2.59–7.82	11.7–32.4	3	1
Phenanthrene[3]	8	6	1.30–4.84	9.52–161	4	3
Phenol[3]	8	8	7.73–40.2	24.9–126	4	4
Pyrene[3]	8	6	0.813–3.58	6.16–218	5	4

[1] Concentration in milligrams per liter.

[2] Concentration in micrograms per liter.

[3] Concentration in micrograms per kilogram.

phenol, phenanthrene, and pyrene) had environmental sample concentrations that were less than 10 times the corresponding laboratory blank concentration.

Replicate Samples

Replicate samples are used to evaluate the variability introduced during field processing. Field replicate samples are split from the environmental sample, so the environmental sample concentrations should vary little, if any, from their corresponding replicate sample concentrations. 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:

$$RPD = \left| \frac{(ENV - REP)}{Average(ENV + REP)} \right| * 100 \qquad (1)$$

where *ENV* represents the environmental sample concentration and *REP* is the corresponding replicate sample concentration. Replicate samples were split in the field for nutrients and pharmaceutical analyses in water and for OWC analyses in water and bed sediment. Bed-sediment samples were split in the laboratory for pharmaceutical analyses of replicates. Tables 2 and 5 show the environmental and replicate samples collected for each sampling date, and table 6 shows the concentration of the environmental and replicate samples along with the RPD for the compound. At the Sunrise site, four replicate samples were collected including one field replicate sample analyzed for nutrients, OWCs, and pharmaceuticals in water, and three laboratory replicate samples analyzed for pharmaceuticals in bed sediment (two samples were analyzed in 2007 and one in 2008). At the Franconia site, five replicate samples were collected including one field replicate for OWC analyses in water, one field replicate for pharmaceutical analyses in water, one field replicate for OWCs in bed sediment, and two laboratory replicate samples for pharmaceutical analyses in bed sediment (one sample was analyzed in 2007 and one in 2008). Samples collected from the WWTP effluents were not replicated.

In samples from the Sunrise site, environmental and replicate pairs were analyzed for 80 compounds including nutrients, OWCs, and pharmaceuticals in water samples (table 5). At this site, 100 percent of the compounds detected in the environmental sample were correspondingly detected in the replicate sample. The RPDs ranged from 1–46 percent for the 11 compounds that were detected in both the environmental and replicate samples (table 6). The RPDs were less than 15 percent for all constituents except tributyl phosphate (RPD: 29 percent) and tris(2-chloroethyl) phosphate (RPD: 46 percent). Although the RPDs for tributyl phosphate and tris(2-chloroethyl) phosphate were relatively larger than RPDs for other compounds, the concentrations in the environmental and replicate samples were similar in absolute value (table 6). This is particularly important at low concentrations and near the minimum reporting level.

In samples from the Franconia site, environmental and replicate pairs were analyzed for 74 compounds in water samples (table 5). Nutrient analyses were not replicated in samples from the Franconia site. Detection frequencies were equal in 96 percent of the compound pairs analyzed. Concentrations for more than 90 percent of the compounds were reported as less than the MRL for the environmental samples and the paired replicate samples. Two compounds (acetaminophen and isophorone) were detected in the environmental and paired replicate samples at this site. The RPDs for these two compounds were 55 and 106 percent, respectively. In three cases, a compound was not consistently detected in the environmental and paired replicate sample (caffeine, DEET and tris(2-butoxyethyl) phosphate); that is, the compound was detected in the environmental or replicate sample but not in both.

Table 5. Detections of constituents analyzed in environmental and replicate surface-water and bed-sediment samples from sites in the St. Croix National Scenic Riverway, Minnesota, 2007–08.

[ENV, environmental sample; REP, replicate sample]

Total number of ENV and REP constituent pairs reported by laboratory	Number of constituents not detected in ENV and REP pairs[1]	Number of constituents detected in ENV and REP pairs	Number of constituents detected in ENV or REP but not in both	Detection consistency between ENV and REP samples (percent)
Surface-water samples from St. Croix River below Sunrise River near Sunrise, Minn. (Sunrise site; station 05340200)[2]				
80	69	11	0	100
Surface-water samples from St. Croix River above Rock Island near Franconia, Minn. (Franconia site; station 05340540)[3]				
76	71	2	3	96
Bed-sediment samples from St. Croix River below Sunrise River near Sunrise, Minn. (Sunrise site; station 05340200)				
96	84	8	4	96
Bed-sediment samples from St. Croix River above Rock Island near Franconia, Minn. (Franconia site; station 05340540)				
119	99	15	5	96

[1] Concentrations too low to quantify constituent concentration (reported as less than values).

[2] ENV and REP pairs reported for 80 constituents including nutrients; analyses for pentachlorophenol, fluoxetine, and ranitidine not replicated.

[3] ENV and REP pairs reported for 74 constituents; cotinine and caffeine reported twice (two methods for analysis), and analysis for pentachlorophenol was not replicated.

Table 6. Concentrations and relative percent difference for constituents detected in both environmental and replicate water and bed-sediment samples from sites in the St. Croix National Scenic Riverway, Minnesota, 2007–08.

[ENV, environmental sample; REP, replicate sample; RPD, relative percent difference; DEET, *N,N*-diethyl-*meta*-toluamide]

Constituent	ENV concentration	REP concentration	Absolute RPD (percent)
Surface-water samples from St. Croix River below Sunrise River near Sunrise, Minn. (Sunrise site; station 05340200), in milligrams per liter unless otherwise noted			
Dissolved ammonia	0.013	0.012	8
Dissolved nitrate plus nitrite	.095	.106	11
Dissolved nitrite	.003	.003	0
Total ammonia plus organic nitrogen	.725	.795	9
Dissolved orthophosphate	.008	.008	0
Total phosphorus	.070	.069	1
DEET, in µg/L	.033	.036	9
Tributyl phosphate, in µg/L	.015	.020	29
Tris(2-chloroethyl) phosphate, in µg/L	.040	.025	46
Surface-water samples from St. Croix River above Rock Island near Franconia, Minn. (Franconia site; station 05340540), in micrograms per liter			
Acetaminophen	0.007	0.004	55
Isophorone	.055	.017	106
Bed-sediment samples from St. Croix River below Sunrise River near Sunrise, Minnesota (Sunrise site; station 05340200), in micrograms per kilogram			
Acetaminophen[1]	503	400	23
Carbamazepine[1]	2.40	3.23	29
Carbamazepine[1,2]	.920	1.27	32
Citalopram[1,3]	.072; .068	.033; .095	80; 35
Diphenhydramine[1]	.354	.251	33
Miconazole[1]	.339	.308	9
Sertraline[1]	.009	.023	67
Bed-sediment samples from St. Croix River above Rock Island near Franconia, Minn. (Franconia site; station 05340540), in micrograms per kilogram			
9,10-Anthraquinone	18.7	10.5	56
Benzo[*a*]pyrene	89.5	16.0	139
beta-Sitosterol	944	1,070	13
beta-Stigmastanol	210	312	39
Cholesterol	309	360	15
Fluoranthene	293	31.2	162
Indole	72.9	54.4	29
Phenol	24.9	24.8	0
Pyrene	218	28.1	154
Acetaminophen[1]	552	422	27
Carbamazepine[1]	.563	.619	9
Carbamazepine[1,2]	.201	.301	40
Diphenhydramine[1]	.088	.150	52
Miconazole[1]	.269	.183	38
Sertraline[1]	.076	.034	76

[1] Replicate concentrations from laboratory split (pharmaceutical compounds).

[2] Carbamazepine analyzed twice in bed-sediment samples using two different methods.

[3] Citalopram was detected in environmental sample and replicate sample on two separate dates (5–25–2007 and 9–12–2007).

At the Sunrise site, pharmaceuticals in bed sediment were analyzed three times for 32 compounds, giving a total of 96 replicate pairs. Detection frequencies were equal in 96 percent of compound pairs analyzed. RPDs for the seven compounds that were detected in the environmental and paired replicate samples ranged from 9 to 80 percent (table 6).

For bed-sediment sample replicates at the Franconia site, 55 OWCs were analyzed once and 32 pharmaceutical compounds were analyzed twice, giving a total of 119 replicate pairs. Detection frequencies were equal in 96 percent of replicate pairs analyzed. The RPDs for the 15 compounds that were detected in the environmental and paired replicate samples ranged from 0 to 162 percent (table 6).

Differences between reported environmental sample and replicate sample concentrations may have been due to sample splitting inconsistencies, complex water or sediment matrices, or laboratory contamination (blank contamination, table 4). A possible explanation of large RPDs in bed-sediment samples is that analysis for OWCs in bed-sediment is complicated by the complex composition of bed sediments that creates interference during analyses. In addition, small differences in sample splitting techniques can result in large differences in concentration, especially when dealing with concentrations in the microgram-per-kilogram range.

Spiked Samples

Sample spikes were used to determine the recovery of OWCs and pharmaceuticals in solution. A known (theoretical) concentration of a compound was added to the environmental sample, and the percent recovery (PR) was determined using the following equation:

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

When an environmental concentration was coded with a less than (<) remark code and the measured spiked environmental concentration was coded as estimated or was without a remark code, PRs were computed in two ways to determine the range. The low end of this range was computed using the MDL (one-half of the MRL) as the environmental compound concentration in equation 2, and the upper end of the range was computed using zero as the environmental compound concentration. In the reported data, if the environmental and spiked concentrations were coded with less than remark codes, the compound was considered to be not recovered.

Spiked samples were prepared for OWC and pharmaceutical analyses in water and bed-sediment samples. One spiked sample was prepared for analysis of OWCs, and three spiked samples were prepared for analyses of pharmaceuticals in water samples collected at the Franconia site. One spiked sample was prepared for analyses of pharmaceuticals in bed sediments collected from the Sunrise site, and three spiked samples were prepared for pharmaceutical analyses of bed sediments at the Franconia site. No spiked samples were prepared at the WWTP sites or for OWCs in bed sediment at either of the river sites.

The PRs for all OWCs in the spiked water sample collected at the Franconia site were on average 77 percent plus or minus 25-percent standard deviation. The OWCs 3-*tert*-butyl-4-hydroxyanisole, *d*-limonene, and tetrachloroethene had the lowest percent recoveries (less than 40 percent) among all OWCs measured (table 7). The PRs for pharmaceuticals in three spiked water samples collected from the Franconia site were on average 65 percent plus or minus 35-percent standard deviation (table 7) among all pharmaceuticals measured. Diltiazem, diphenhydramine, sulfamethoxazole, and thibendazole had the lowest average recoveries (less than 12 percent) among all pharmaceuticals measured. The PRs for pharmaceuticals in the four bed-sediment spiked samples were low (averaged 39 percent plus or minus 66-percent standard deviation) among all pharmaceuticals measured with the exception of acetaminophen, which had an average percent recovery of 407.5 percent.

Surrogate Samples

Surrogate samples are fortified with compounds that are similar to the analytes but do not interfere with the analyses of the analytes. The PR of the fortified compounds is indicative of how well the analytical method quantifies the analytes because the compounds are similar in structure. Surrogate samples are used to potentially explain large variances in analyte concentrations between sites. For example, if the recovery of a compound surrogate similar to the analyte is low, then the method recovery for the analyte was most likely low, and the actual analyte concentration is most likely greater than the reported value. If the recovery of a compound surrogate similar to the analyte is large, then the method recovery for the analyte is most likely large, and the reported value is most likely accurate. Surrogates have a range of acceptable values, so a small recovery of one surrogate may be similar to a large recovery of a different surrogate.

Nine surrogate compounds were added to the environmental samples: five to water samples (wastewater effluent and surface water) and four to bed-sediment samples. The water surrogates were caffeine-^{13}C, carbamazepine-d_{10}, decafluorobiphenyl, ethyl nicotinate-d_4, and fluoranthene-d_{10}. The four bed-sediment surrogates were carbamazepine-d_{10}, decafluorobiphenyl, ethyl nicotinate-d_4, and fluoranthene-d_{10}.

In general, the PRs for the surrogate compounds from bed sediment were much smaller than the recoveries from the water samples, and the sites had comparable recoveries for all compounds in water samples with the exception of relatively lower PRs for carbamazepine-d_{10} at SCF-WWTP (table 8). Decafluorobiphenyl had the lowest PRs in bed-sediment samples among surrogates for both the Sunrise and Franconia sites.

Table 7. Percent recoveries for compounds in water and bed-sediment spiked samples from sites in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

[Values for spiked compounds reported as percent recoveries. NA, not analyzed; --, not applicable; ND, not detected]

Constituent	Spiked water samples		Spiked bed-sediment sample	
	Mean	Standard deviation	Mean	Standard deviation
Organic wastewater compounds				
1,4-Dichlorobenzene	60.0	1.8	NA	NA
1-Methylnaphthalene	75.6	--	NA	NA
2,6-Dimethylnaphthalene	56.3	5.3	NA	NA
2-Methylnaphthalene	67.6	--	NA	NA
3-*beta*-Coprostanol	59.4	22.1	NA	NA
3-Methyl-1H-indole (skatol)	87.5	1.8	NA	NA
3-*tert*-Butyl-4-hydroxyanisole (BHA)	18.8	15.9	NA	NA
4-Cumylphenol	89.4	4.4	NA	NA
4-*n*-Octylphenol	60.0	7.1	NA	NA
4-Nonylphenol (NP)	73.4	11.0	NA	NA
4-Nonylphenol diethoxylate (NP2EO)	67.3	13.6	NA	NA
4-Nonylphenol monoethoxylate (NP1EO)	NA	NA	NA	NA
4-*tert*-Octylphenol	65.6	30.9	NA	NA
4-*tert*-Octylphenol diethoxylate (OP2EO)	58.1	29.6	NA	NA
4-*tert*-Octylphenol monoethoxylate (OP1EO)	65.4	27.2	NA	NA
5-Methyl-1H-benzotriazole	59.4	11.0	NA	NA
9,10-Anthraquinone	95.0	7.1	NA	NA
Acetophenone	88.8	17.7	NA	NA
Acetyl hexamethyl tetrahydronaphthalene (AHTN) (tonalide)	86.9	22.1	NA	NA
Anthracene	82.5	1.8	NA	NA
Atrazine	NA	NA	NA	NA
Benzo[*a*]pyrene	82.5	3.5	NA	NA
Benzophenone	101.3	5.3	NA	NA
beta-Sitosterol	43.8	44.2	NA	NA
beta-Stigmastanol	65.6	22.1	NA	NA
Bromacil	98.4	11.0	NA	NA
Camphor	97.6	--	NA	NA
Carbaryl	60.0	44.2	NA	NA
Carbazole	98.8	1.8	NA	NA
Chlorpyrifos	75.0	5.3	NA	NA
Cholesterol	68.8	22.1	NA	NA
Diazinon	112.5	3.5	NA	NA
d-Limonene	35.6	6.2	NA	NA
Fluoranthene	96.3	1.8	NA	NA
Hexahydrohexamethyl cyclopentabenzopyran (HHCB) (galaxolide)	84.4	22.1	NA	NA
Indole	81.3	3.5	NA	NA
Isoborneol	83.1	8.0	NA	NA
Isophorone	93.3	.7	NA	NA
Isopropylbenzene (cumene)	43.8	8.8	NA	NA
Isoquinoline	71.3	17.7	NA	NA

Table 7. Percent recoveries for compounds in water and bed-sediment spiked samples from sites in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.—Continued

[Values for spiked compounds reported as percent recoveries. NA, not analyzed; --, not applicable; ND, not detected]

Constituent	Spiked water samples		Spiked bed-sediment sample	
	Mean	Standard deviation	Mean	Standard deviation
Organic wastewater compounds—Continued				
Menthol	80.0	17.7	NA	NA
Metalaxyl	113.8	5.3	NA	NA
Methyl salicylate	83.1	4.4	NA	NA
Metolachlor	111.3	3.5	NA	NA
Naphthalene	82.5	1.8	NA	NA
N,N-diethyl-*meta*-toluamide (DEET)	105.0	--	NA	NA
p-Cresol (4-Methylphenol)	76.9	8.0	NA	NA
Pentachlorophenol	ND	ND	NA	NA
Phenanthrene	88.8	1.8	NA	NA
Phenol	57.5	61.9	NA	NA
Prometon	96.3	8.8	NA	NA
Pyrene	96.3	1.8	NA	NA
Tetrachloroethylene	13.8	5.3	NA	NA
Tributyl phosphate	97.5	8.8	NA	NA
Triclosan	80.0	8.8	NA	NA
Triethyl citrate (ethyl citrate)	85.0	17.7	NA	NA
Triphenyl phosphate	79.8	--	NA	NA
Tris(2-butoxyethyl) phosphate	76.3	35.4	NA	NA
Tris(2-chloroethyl) phosphate	99.4	4.4	NA	NA
Tris(dichloroisopropyl) phosphate	102.5	5.3	NA	NA
Pharmaceuticals				
1,7-Dimethylxanthine	77.2	20.4	36.4	19.3
Acetaminophen	65.4	22.2	407.5	136.5
Azithromycin	NA	NA	ND	ND
Albuterol	114.4	27.8	32.5	25.0
Bupropion	NA	NA	4.2	6.3
Caffeine	89.1	28.8	80.1	53.7
Carbamazepine	84.9	8.8	44.2	41.9
Cimetidine	NA	NA	18.3	--
Citalopram	NA	NA	.9	1.2
Codeine	85.4	17.6	44.9	12.3
Cotinine	90.5	5.8	48.2	17.6
Dehydronifedipine	102.5	7.7	51.5	50.1
Diltiazem	23.2	18.0	29.8	16.5
Diphenhydramine	20.8	14.8	20.2	10.6
Duloxetine	NA	NA	.2	--
Erythromycin	NA	NA	36.5	17.1
Fluoxetine	NA	NA	22.0	10.6

Table 7. Percent recoveries for compounds in water and bed-sediment spiked samples from sites in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.—Continued

[Values for spiked compounds reported as percent recoveries. NA, not analyzed; --, not applicable; ND, not detected]

Constituent	Spiked water samples		Spiked bed-sediment sample	
	Mean	Standard deviation	Mean	Standard deviation
Pharmaceuticals—Continued				
Fluvoxamine	NA	NA	2.5	1.6
Miconazole	NA	NA	24.2	8.3
Norfluoxetine	NA	NA	3.3	1.5
Norsertraline	NA	NA	1.8	.6
Paroxetine	NA	NA	2.0	--
Paroxetine metabolite	NA	NA	ND	ND
Ranitidine	NA	NA	ND	ND
Sertraline	NA	NA	1.6	--
Sulfamethoxazole	21.5	9.8	24.7	24.9
Thiabendazole	11.6	11.4	21.4	10.7
Trimethoprim	53.3	11.1	39.6	11.8
Venalafaxine	NA	NA	1.5	--
Warfarin	63.7	9.3	28.6	40.0

Table 8. Percent recoveries for surrogate compounds in water and bed-sediment samples from sites in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

[Values for surrogate compounds reported as percent recoveries. WWTP, wastewater-treatment plant; Std Dev, standard deviation; NA, surrogate sample not analyzed]

Compound	Taylors Falls WWTP at Taylors Falls, Minn. (TF-WWTP) (452403092410601)		St. Croix Falls WWTP at St. Croix Falls, Wisc. (SCF-WWTP) (452424092385001)		St. Croix River below Sunrise River near Sunrise, Minn. (Sunrise site) (05340200)		St. Croix River above Rock Island near Franconia, Minn. (Franconia site) (05340540)	
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
Surrogate compounds in surface-water samples								
Caffeine-^{13}C	97	15	91	11	98	7	92	8
Carbamazepine-d_{10}	53	5	26	4	77	16	89	14
Decafluorobiphenyl	54	2	53	8	55	6	62	10
Ethyl nicotinate-d_4	67	6	52	7	74	6	77	2
Fluoranthene-d_{10}	95	8	86	10	93	10	90	8
Surrogate compounds in bed-sediment samples								
Carbamazepine-d_{10}	NA	NA	NA	NA	62	30	58	23
Decafluorobiphenyl	NA	NA	NA	NA	21	8	29	10
Ethyl nicotinate-d_4	NA	NA	NA	NA	36	31	40	33
Fluoranthene-d_{10}	NA	NA	NA	NA	89	16	82	23

Hydrologic Characteristics

Streamflow data from the St. Croix River near St. Croix Falls, Wisc. (station 05340500; fig. 1) were used to characterize hydrologic conditions during the 2007–08 sampling period. Figure 6 shows the daily mean streamflow for the study period and the long-term daily mean statistics (25th, 50th, and 75th percentiles) for the period of record (1902–2008) (*http://waterdata.usgs.gov/mn/nwis/sw*).

In 2007, streamflow at the site for the sampling dates was equal to or less than the 25th-percentile long-term daily mean flow during most of the year. During 2008, streamflow during the sampling dates was greater than or equal to the 75th-percentile long-term daily mean flow. During 2008, daily mean flows greater than the long-term streamflows occurred, but for short durations—May and June 2008.

Other than these brief periods of high streamflow, most days during the 2007–08 sampling period had flow less than the long-term daily mean flow. The percentage of days that had flows greater than the 75th-percentile long-term daily mean flow during the sampling period (729 days) was 16 percent (115 days had greater flow), and the percentage of days that had flows greater than the 50th-percentile long-term daily mean was 38 percent (280 days had greater flows). The sampling period was drier than the long-term daily mean flow of the site.

Streamflow can affect compound concentrations through transport of compounds from surface runoff and through dilution during runoff events. Samples were collected during higher flows in 2008 than in 2007. However, correlations between high streamflow in 2008 and compound concentrations were not evident in this study.

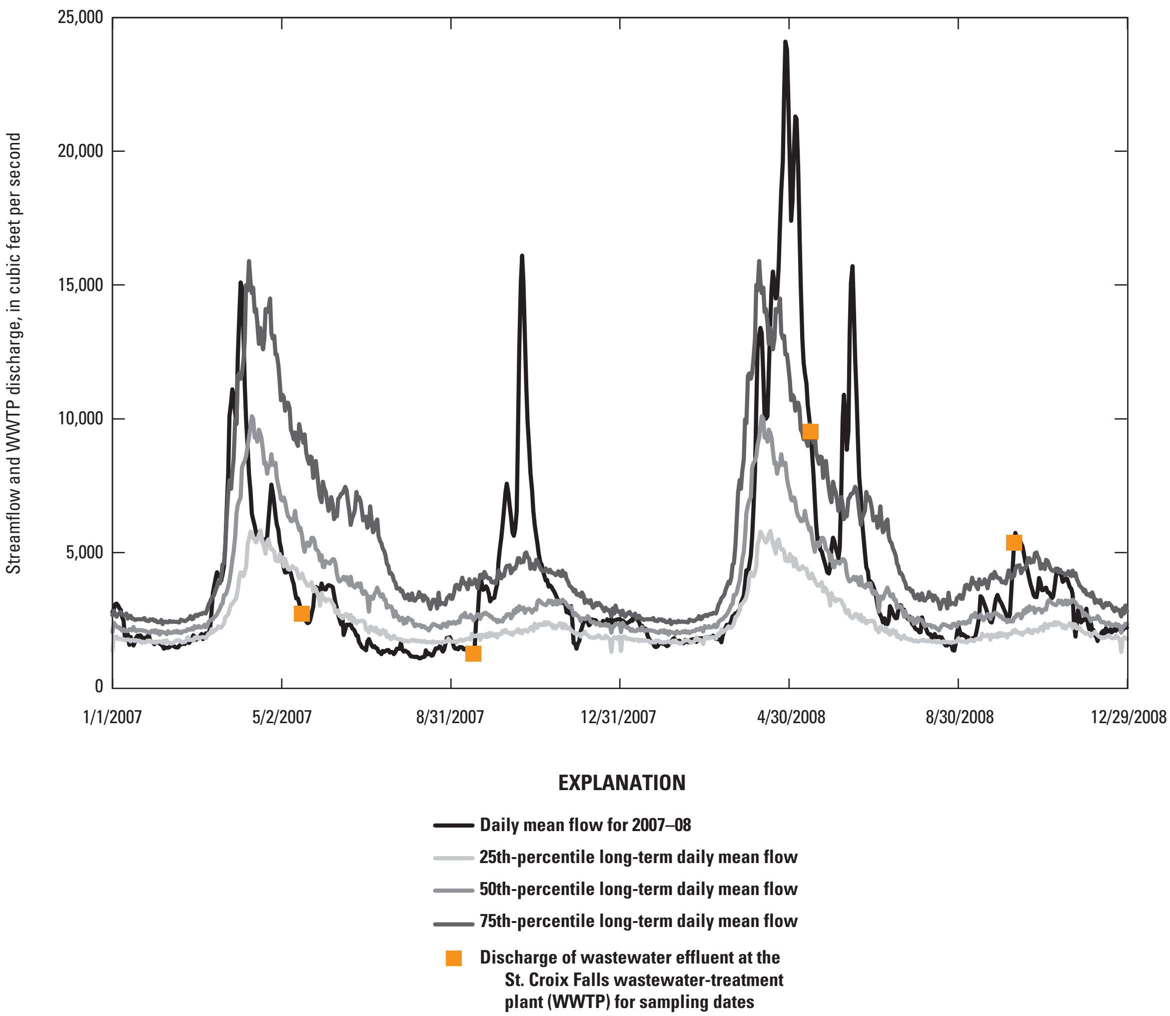

Figure 6. Streamflow during 2007 and 2008 and long-term (1902–2008) streamflow percentiles in the St. Croix River near St. Croix Falls, Wisc. (station 05340500) and wastewater-treatment plant (WWTP) discharge of wastewater effluent for sampling dates.

Occurrence of Wastewater Indicator Compounds in Water Samples

The occurrence of wastewater indicator compounds in water samples (surface water or wastewater effluent) and other compounds collected from four sites in the St. Croix National Scenic Riverway are described in this section. The compounds analyzed in water samples (major ions (surface-water samples only), nutrients, OWCs, and pharmaceuticals (*appendix 1*) are described separately. Mean concentrations presented in this section were calculated by determining the mean of the detected concentrations. Water-quality results for samples analyzed at the NWQL for this study can be accessed at *http://waterdata.usgs.gov/mn/nwis/qw*.

Major Ions

Major-ion occurrence and concentrations between the Sunrise and Franconia sites closely corresponded (*appendix 2*; table 9). Although calcium, magnesium, sodium, sulfate, chloride, and iron concentrations were greater at the Sunrise site than at the Franconia site (fluoride was not detected at either site), the largest percent difference in concentration between the two sites was 13 percent (chloride). All concentrations varied by less than 0.6 mg/L between the two sites.

Nutrients

Nutrient concentrations were greater in effluent samples from the SCF-WWTP than in effluent samples from the TF-WWTP (*appendix 3*; table 9; figs. 7 and 8). Nutrient concentrations and distributions differed between wastewater effluent samples and surface-water samples. Wastewater effluent samples were dominated by different nutrients, had a wider distribution of nutrient occurrence, and had greater concentrations than did the surface-water samples from the two river sites.

At the Franconia and Sunrise sites, nutrients were detected in surface-water samples for all sampling dates with the exception of ammonia, which was only detected at both sites for the fall 2008 sample. Differences in nutrient concentrations between the two sites were small. Means of the detected dissolved ammonia and total ammonia plus organic nitrogen concentrations for all sampling dates (table 9) were greater at the downstream site (Franconia), whereas nitrite, nitrate plus nitrite, and total phosphorus concentrations were greater at the upstream site (Sunrise). Orthophosphate had the same mean concentration at both sites.

Organic Wastewater Compounds and Pharmaceuticals

A variety of OWCs and pharmaceuticals were detected in the wastewater effluent from both WWTPs and in surface-water samples from the river sites (*appendixes 4* and *5*). The number of total detections and the types of compounds detected varied among the four sites and varied temporally at each site.

Wastewater effluent samples from both WWTPs had more detections than did the surface-water samples from the river sites (fig. 9; table 9). The types of OWCs detected in the effluent from both WWTPs included plant and animal sterols, surfactants, fragrances, flavors, fire retardants, antimicrobial compounds, and mosquito repellants. Although many of the compounds were detected in samples from both WWTPs, the two WWTPs had unique chemical compositions. Effluent samples from the SCF-WWTP contained more OWCs and pharmaceuticals than did the effluent samples from the TF-WWTP. In total, 38 OWCs and 7 pharmaceuticals were detected in the SCF-WWTP effluent, whereas 20 OWCs and 3 pharmaceuticals were detected in the TF-WWTP effluent (fig. 9). The most frequently detected pharmaceuticals in effluent samples from both WWTPs were 1,7-dimethylxanthine (caffeine metabolite), caffeine (stimulant), and carbamazepine (anti-seizure). Sulfamethoxazole (antibiotic) and cotinine (nicotine metabolite) also were frequently detected in effluent samples from SCF-WWTP.

Compound concentrations also varied among sites and time periods at each site. The compounds with the greatest mean of detected concentrations among the four sites were 3-*beta*-coprostanol, 4-nonylphenol, 4-nonylphenol diethoxylate, cholesterol, and tris(2-butoxyethyl) phosphate (table 9). DEET, isophorone, tributyl phosphate, tris(2-choroethyl) phosphate, and caffeine were detected in samples from all four sites—effluent samples from TF-WWTP and SCF-WWTP and surface-water samples from the Sunrise and Franconia sites (fig. 10; table 9).

Concentrations of wastewater indicator compounds were greater in the effluent from the SCF-WWTP than in effluent from the TF-WWTP for all but four compounds—*beta*-stigmastanol, *d*-limonene, isophorone, and tris(2-chloroethyl) phosphate (table 9). In the effluent from the TF-WWTP, only four compounds during the study had concentrations greater than 1 microgram per liter (µg/L)—*beta*-sitosterol, *beta*-stigmastanol, caffeine, and cholesterol—all of which occurred in the May 2008 sample (*appendix 4*). In samples of effluent from the SCF-WWTP, 13 compounds had concentrations greater than 1 µg/L—3-*beta*-coprostanol, 4-nonylphenol, 4-nonylphenol diethoxylate, 4-*tert*-octylphenol,

Table 9. Summary of mean detected concentrations of major ions, nutrients, organic wastewater compounds, and pharmaceuticals at the four sites in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

[Concentrations reported in micrograms per liter for water samples unless otherwise noted; bed-sediment sample values reported as recoverable solids with the dry weight in micrograms per kilogram; if more than one detection for site, detected concentrations were averaged; if only one detection for site, that concentration was used; number of times compound detected shown in parenthesis; replicate concentrations used for concentration averages for all analyses except pharmaceuticals in bed sediment, because these were laboratory replicates rather than field replicates; replicate samples were not included in the overall number of detections. WWTP, wastewater-treatment plant; NA, not analyzed; ND, not detected]

Detected constituent	Taylors Falls WWTP at Taylors Falls, Minn. (TF-WWTP) (452403092410601)	St. Croix Falls WWTP at St. Croix Falls, Wisc. (SCF-WWTP) (452424092385001)	St. Croix River below Sunrise River near Sunrise, Minn. (Sunrise site) (05340200)	St. Croix River above Rock Island near Franconia, Minn. (Franconia site) (05340540)
Detected major ions in water samples				
Calcium[1]	NA	NA	14.9	14.5
Magnesium[1]	NA	NA	4.84	4.81
Sodium[1]	NA	NA	3.56	3.29
Potassium[1]	NA	NA	1.28	1.32
Sulfate[1]	NA	NA	3.54	3.41
Chloride[1]	NA	NA	4.85	4.26
Silica[1]	NA	NA	6.08	6.26
Iron	NA	NA	357	354
Manganese	NA	NA	15.74	18.5
Detected nutrients in water samples				
Dissolved nitrite[1,2]	0.133 (3)	0.409 (4)	0.005 (4)	0.003 (4)
Dissolved nitrate plus nitrite[1,2]	.865 (3)	17.6 (4)	.135 (4)	.119 (4)
Dissolved ammonia[1,2,3]	.136 (3)	7.74 (4)	.013 (1)	.034 (1)
Total ammonia plus organic nitrogen[1,2]	1.68 (3)	12.7 (4)	.668 (4)	.680 (4)
Dissolved orthophosphate[1,2,3]	2.37 (3)	5.21 (4)	.007 (4)	.007 (4)
Total phosphorus[1,2]	2.38 (3)	5.63 (4)	.052 (4)	.043 (4)
Detected organic wastewater compounds in water samples[4]				
1,4-Dichlorobenzene[2,3]	0.018 (1)	0.335 (3)	ND	0.020 (1)
1-Methylnaphthalene[2,3]	ND	.014 (3)	ND	.015 (3)
2,6-Dimethylnaphthalene[3]	ND	.011 (1)	ND	.007 (1)
2-Methylnaphthalene[2,3]	ND	.019 (3)	ND	.035 (2)
3-*beta*-Coprostanol[2,3]	.417 (2)	3.32 (3)	ND	ND
3-Methyl-1H-indole[3]	.009 (1)	ND	ND	ND
4-Cumylphenol[3]	ND	.008 (1)	ND	ND
4-Nonylphenol[2,3,5]	.799 (2)	13.6 (3)	0.574 (1)	ND
4-Nonylphenol diethoxylate[2,3,5]	.545 (1)	25.2 (3)	ND	ND
4-*tert*-Octylphenol[2,3]	ND	1.18 (3)	ND	ND
4-*tert*-Octylphenol diethoxylate[2,3]	ND	1.08 (2)	ND	ND
4-*tert*-Octylphenol monoethoxylate[2,3]	ND	1.21 (3)	ND	ND
5-Methyl-1H-benzotriazole[2,3]	ND	.841 (3)	ND	ND
Acetyl hexamethyl tetrahydronaphthalene (AHTN)[2,3]	.012 (2)	.223 (3)	ND	ND
Benzophenone[2,3]	.038 (3)	.174 (3)	ND	ND
beta-Sitosterol[2,3]	.808 (2)	1.19 (3)	ND	ND
beta-Stigmastanol[2,3]	.767 (2)	.567 (1)	ND	ND
Camphor[2,3]	ND	.050 (3)	.012 (2)	.014 (3)
Carbaryl[3]	ND	.113 (1)	ND	ND

Table 9. Summary of mean detected concentrations of major ions, nutrients, organic wastewater compounds, and pharmaceuticals at the four sites in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.—Continued

[Concentrations reported in micrograms per liter for water samples unless otherwise noted; bed-sediment sample values reported as recoverable solids with the dry weight in micrograms per kilogram; if more than one detection for site, detected concentrations were averaged; if only one detection for site, that concentration was used; number of times compound detected shown in parenthesis; replicate concentrations used for concentration averages for all analyses except pharmaceuticals in bed sediment, because these were laboratory replicates rather than field replicates; replicate samples were not included in the overall number of detections. WWTP, wastewater-treatment plant; NA, not analyzed; ND, not detected]

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Detected organic wastewater compounds in water samples[4]—Continued				
Cholesterol[2,3]	0.806 (2)	2.99 (3)	ND	ND
d-Limonene[3]	.117 (1)	.047 (1)	ND	ND
Hexahydrohexamethyl cyclopentabenzo-pyran (HHCB)[2,3]	.048 (2)	1.33 (4)	ND	ND
Isophorone[2,3]	.032 (3)	.019 (3)	.010 (1)	.023 (4)
Menthol[2]	ND	.329 (2)	ND	ND
Methyl salicylate[3]	ND	.154 (1)	ND	ND
Metolachlor[3]	ND	ND	.008 (1)	ND
Naphthalene[3]	ND	.024 (1)	ND	.074 (1)
N,N-diethyl-*meta*-toluamide (DEET)[2,3]	.283 (3)	1.58 (3)	.029 (3)	.093 (4)
p-Cresol[2,3]	ND	1.17 (3)	ND	ND
Pentachlorophenol[3]	ND	.075 (1)	ND	ND
Phenanthrene[2,3]	ND	.022 (2)	ND	ND
Phenol[2]	ND	.492 (2)	ND	ND
Tribromomethane (bromoform)[3]	ND	.014 (1)	ND	ND
Tributyl phosphate[2,3]	.049 (2)	.329 (3)	.015 (1)	.023 (1)
Triclosan[2]	ND	1.41 (3)	ND	ND
Triethyl citrate[2,3]	.019 (1)	.479 (3)	ND	ND
Triphenyl phosphate[2,3]	.011 (1)	.105 (3)	ND	.010 (2)
Tris(2-butoxyethyl) phosphate[2,3]	.496 (2)	112 (4)	ND	.073 (3)
Tris(2-chloroethyl) phosphate[2,3]	.305 (3)	.256 (3)	.040 (1)	.018 (2)
Tris(dichloroisopropyl) phosphate[2,3]	.088 (2)	.443 (3)	ND	ND
Detected pharmaceuticals in water samples[6]				
1,7-Dimethylxanthine[2]	0.190 (1)	0.210 (4)	ND	ND
Acetaminophen[2,3]	ND	ND	0.014 (1)	0.007 (1)
Caffeine[2,3]	.499 (3)	2.43 (3)	.034 (1)	.012 (1)
Carbamazepine[2]	.049 (2)	.116 (4)	ND	ND
Cotinine[2]	ND	.076 (3)	ND	ND
Diphenhydramine[3]	ND	.010 (1)	ND	.002 (1)
Sulfamethoxazole[2,3]	ND	.429 (4)	ND	ND
Trimethoprim	ND	.056 (1)	ND	ND
Detected organic wastewater compounds in bed-sediment samples[7]				
2,6-Dimethylnaphthalene[2,3]	NA	NA	8.11 (2)	1.03 (1)
3-*beta*-Coprostanol[3]	NA	NA	97.2 (1)	ND
3-Methyl-1H-indole[2,3]	NA	NA	5.96 (3)	5.45 (1)
4-Cumylphenol[2,3]	NA	NA	ND	15.0 (2)
4-*n*-Octylphenol[3]	NA	NA	ND	2.64 (1)

Table 9. Summary of mean detected concentrations of major ions, nutrients, organic wastewater compounds, and pharmaceuticals at the four sites in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.—Continued

[Concentrations reported in micrograms per liter for water samples unless otherwise noted; bed-sediment sample values reported as recoverable solids with the dry weight in micrograms per kilogram; if more than one detection for site, detected concentrations were averaged; if only one detection for site, that concentration was used; number of times compound detected shown in parenthesis; replicate concentrations used for concentration averages for all analyses except pharmaceuticals in bed sediment, because these were laboratory replicates rather than field replicates; replicate samples were not included in the overall number of detections. WWTP, wastewater-treatment plant; NA, not analyzed; ND, not detected]

Detected constituent	Taylors Falls WWTP at Taylors Falls, Minn. (TF-WWTP) (452403092410601)	St. Croix Falls WWTP at St. Croix Falls, Wisc. (SCF-WWTP) (452424092385001)	St. Croix River below Sunrise River near Sunrise, Minn. (Sunrise site) (05340200)	St. Croix River above Rock Island near Franconia, Minn. (Franconia site) (05340540)
Detected organic wastewater compounds in bed-sediment samples[7]—Continued				
9,10-Anthraquinone[2,3]	NA	NA	5.91 (1)	10.6 (3)
Anthracene[2,3]	NA	NA	5.81 (1)	22.1 (3)
Benzo[*a*]pyrene[2,3]	NA	NA	16.5 (2)	45.8 (3)
Benzophenone[3]	NA	NA	ND	6.81 (1)
beta-Sitosterol[2,3]	NA	NA	1,690 (4)	850 (3)
beta-Stigmastanol[2,3]	NA	NA	506 (3)	233 (3)
Carbazole[3]	NA	NA	8.24 (1)	11.3 (1)
Cholesterol[2,3]	NA	NA	688 (4)	286 (4)
Fluoranthene[2,3]	NA	NA	38.7 (2)	134 (3)
Indole[2,3]	NA	NA	117 (3)	57.7 (4)
p-Cresol[3]	NA	NA	27.1 (2)	11.7 (1)
Phenanthrene[2,3]	NA	NA	30.9 (1)	71.6 (3)
Phenol[2,3]	NA	NA	86.6 (2)	25.5 (2)
Pyrene[2,3]	NA	NA	31.2 (2)	104 (3)
Tributyl phosphate[3]	NA	NA	ND	12.2 (1)
Triclosan[3]	NA	NA	8.91 (1)	14.0 (1)
Tris(2-butoxyethyl) phosphate[3]	NA	NA	7.28 (1)	35.9 (1)
Detected pharmaceuticals in bed-sediment samples[7]				
Acetaminophen	NA	NA	503 (1)	552 (1)
Carbamazepine[8]	NA	NA	2.40; .920 (1)	.563; .201 (1)
Cimetidine	NA	NA	.116 (1)	ND
Citalopram[2]	NA	NA	.070 (2)	.047 (1)
Diphenhydramine	NA	NA	.354 (1)	.088 (1)
Miconazole[2]	NA	NA	.339 (1)	.276 (2)
Sertraline	NA	NA	.009 (1)	.076 (1)
Venalafaxine	NA	NA	.231 (1)	.129 (1)
Warfarin	NA	NA	ND	.050 (1)

[1]Measured in milligrams per liter.

[2]Detected values averaged for compound (at least one site with more than one detection).

[3]Estimated value (at least one site with one or more estimated values).

[4]Taylors Falls WWTP sampled three times; St. Croix Falls WWTP sampled four times; Sunrise site sampled three times; Franconia site sampled four times.

[5]Sum of all isomers.

[6]Taylors Falls WWTP sampled three times; St. Croix Falls sampled four times; Sunrise site sampled four times; Franconia site sampled four times.

[7]Sunrise site sampled four times; Franconia site sampled four times.

[8]Carbamazepine analyzed two times in bed sediment using two different methods.

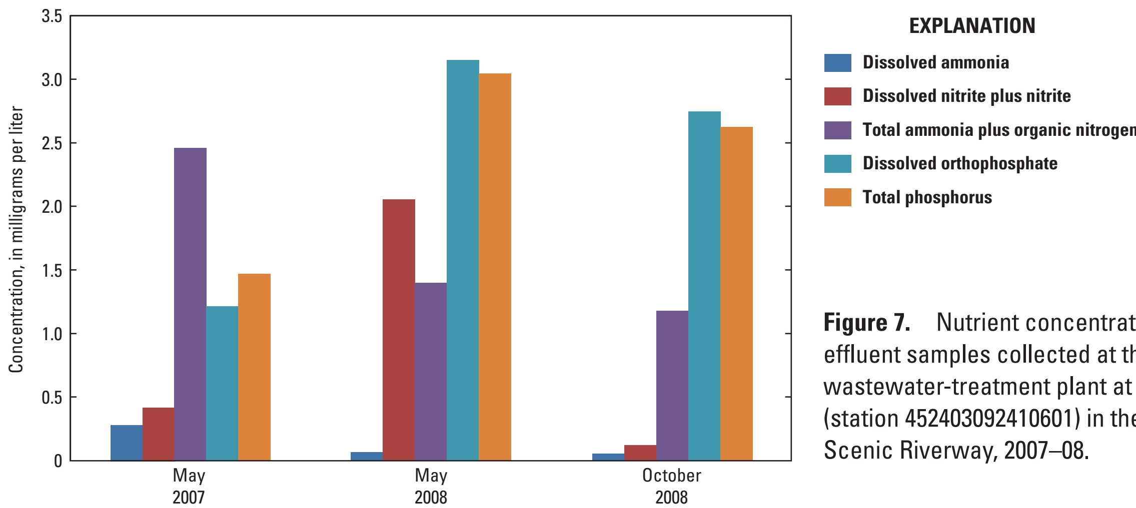

Figure 7. Nutrient concentrations in wastewater effluent samples collected at the Taylors Falls wastewater-treatment plant at Taylors Falls, Minn. (station 452403092410601) in the St. Croix National Scenic Riverway, 2007–08.

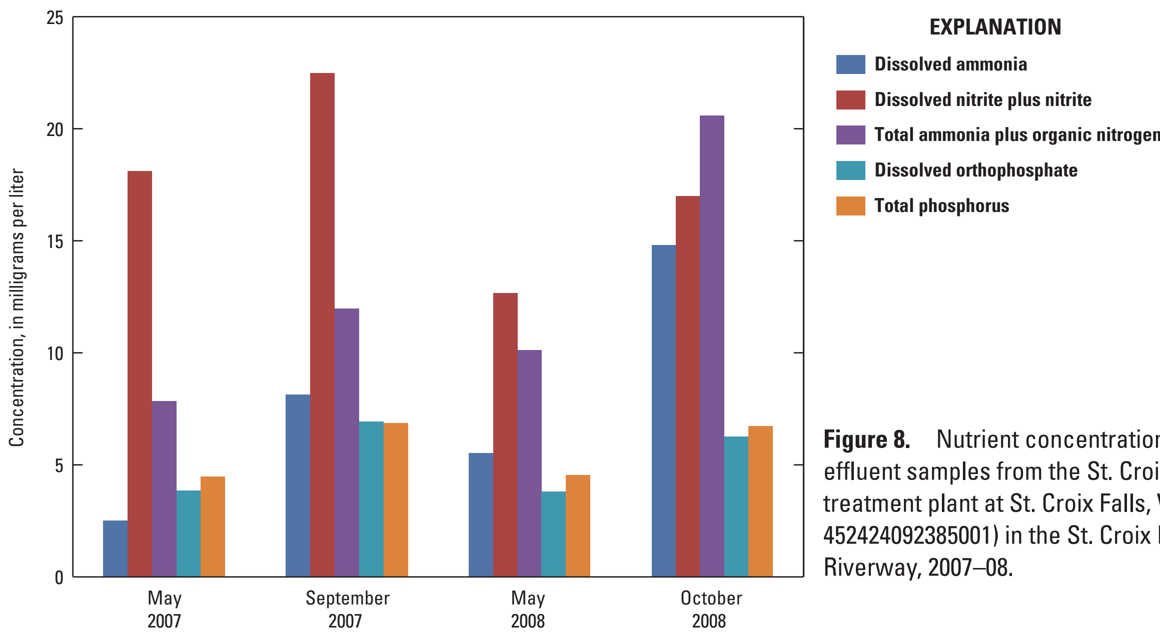

Figure 8. Nutrient concentrations in wastewater effluent samples from the St. Croix Falls wastewater-treatment plant at St. Croix Falls, Wisc. (station 452424092385001) in the St. Croix National Scenic Riverway, 2007–08.

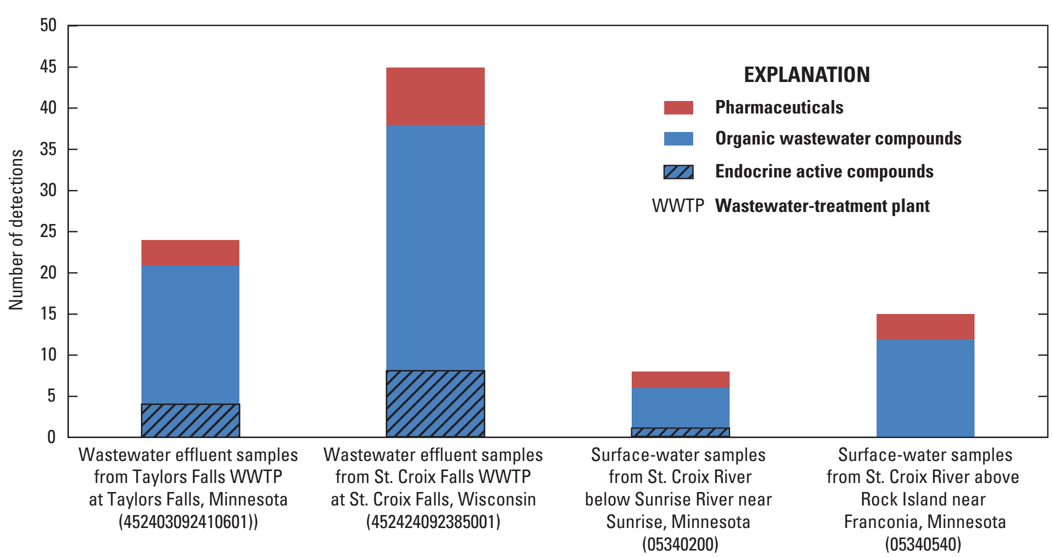

Figure 9. Overall number of detections of classes of wastewater indicator compounds in water samples at four sites in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

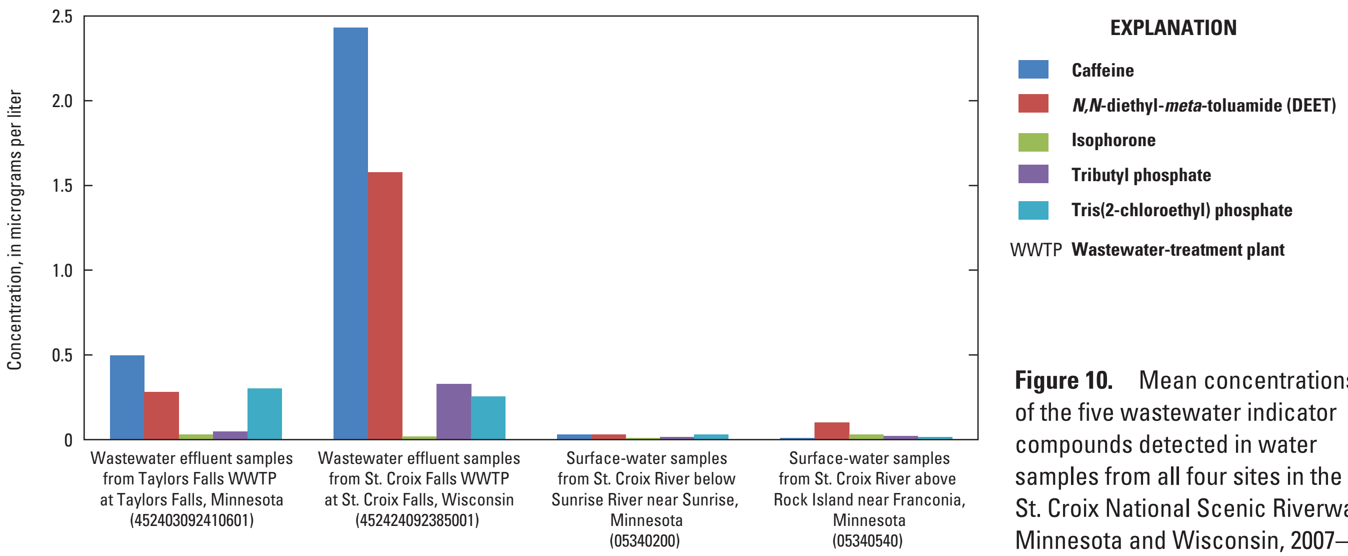

Figure 10. Mean concentrations of the five wastewater indicator compounds detected in water samples from all four sites in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

4-*tert*-octylphenol diethoxylate, *beta*-sitosterol, caffeine, cholesterol, DEET, HHCB, *p*-cresol, triclosan, and tris(2-butoxyethyl) phosphate (*appendix 4*).

The flame retardant tris(2-butoxyethyl) phosphate had the greatest concentration of any compound at any site in the effluent from the SCF-WWTP. The concentrations of tris(2-butoxyethyl) phosphate were about 200 percent greater in the 2008 effluent samples when compared to the concentration in the effluent samples collected from the same WWTP in 2007. In 2007, the concentrations were 28.7 and 0.39 µg/L for the spring and fall samples, respectively, and in 2008, the concentrations were 217 and 200 µg/L for the spring and fall samples, respectively. For comparison, in Lee and others (2008), the concentrations of tris(2-butoxyethyl) phosphate were 2.62 µg/L in the effluent from the WWTP in Hutchinson, Minn., 0.30 µg/L in the effluent from the WWTP in Hinckley, Minn., and was not detected in the effluent from the WWTP in Marshall, Minn.

Other organophosphate fire retardants such as tributyl phosphate, triphenyl phosphate, tris(2-choroethyl) phosphate, and tris(dichloroisopropyl) phosphate were detected in WWTP samples. Of those, only tris(dichloroisopropyl) phosphate was not detected in surface-water samples from the Franconia site. Only tributyl phosphate and tris(2-choroethyl) phosphate were detected in surface-water samples from the Sunrise site. These organophosphate compounds are used as flame retardants, plasticizers, antifoaming agents, and additives in lubricants and hydraulic fluids. These compounds have a variety of uses and have been detected in indoor environments and wastewater effluent, yet little is known about their potential toxicity (Marklund and others, 2005).

Concentrations and occurrence of chemicals varied among sampling periods in the wastewater effluent from the TF-WWTP. The site was not sampled during the fall of 2007 (fig. 11). With the exception of AHTN, the concentrations for all compounds analyzed were greater in the sample collected in May 2008 than in the sample collected in May 2007 highlighting the temporal variability in compound occurrence (*appendix 4*).

In contrast to the TF-WWTP effluent samples, compound concentrations in the SCF-WWTP effluent samples generally were greater in the May 2007 sample than in the May 2008 sample (fig. 12). Of the OWCs shown in figure 12, only HHCB was detected in the sample collected in September 2007, and only 6 compounds were detected on this date compared to a total of 45 OWCs and pharmaceuticals that were detected in the effluent from the SCF-WWTP over the duration of this study (*appendix 4*).

The 10 most frequently detected compounds in the surface-water samples (fig. 13) included a variety of compounds with different uses. DEET was the most frequently detected compound among all surface-water samples. Eight compounds (1,4-dichlorobenzene, 1-methylnaphthalene, 2,6-dimethylnapthalene, 2-methylnaphthalene, naphthalene, triphenyl phosphate, tris(2-butoxyethyl) phosphate, and diphenhydramine) were detected in the effluent samples from the TF-WWTP or the SCF-WWTP and in surface-water samples from the Franconia site but not in surface-water samples from the Sunrise site potentially indicating that the WWTP effluent from both WWTPs are potential sources of these compounds to the St. Croix River near Franconia. Seven compounds (camphor, DEET, isophorone, tributyl phosphate, tris(2-chloroethyl) phosphate, acetaminophen, and caffeine) were detected at both surface-water sites indicating that there is a source of these chemicals to the Franconia site that is located upstream from the two treatment plants sampled.

More OWCs and pharmaceuticals were detected in surface-water samples collected from the Franconia site than in samples collected from the Sunrise site (fig. 9). The detection of nine compounds at the Franconia site and at the Sunrise site indicates an upstream source of these chemicals to the Sunrise site. Although the overall trend was that compound concentrations in water samples collected from the Franconia site were greater (table 9), a few compounds had greater concentrations in water samples collected from the Sunrise site. Concentrations of five compounds—4-nonylphenol, metolachlor, and tris(2-choroethyl) phosphate, acetaminophen, and caffeine—in

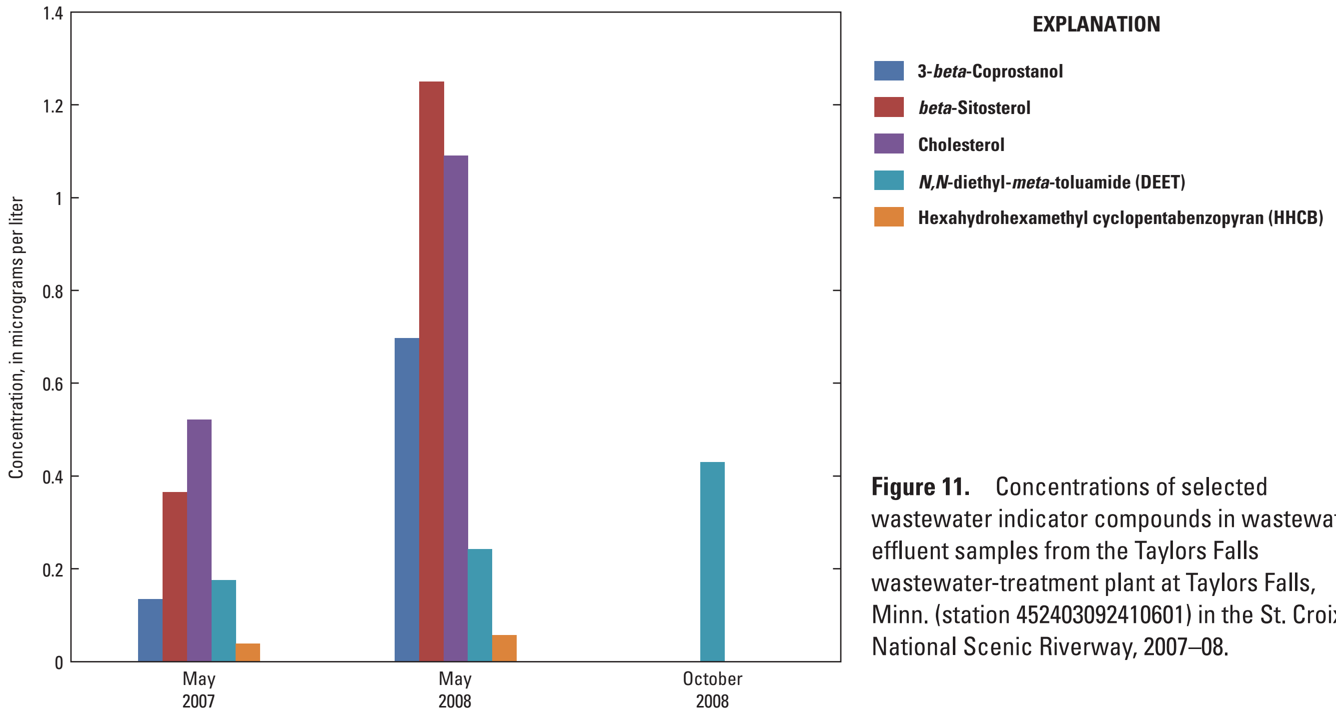

Figure 11. Concentrations of selected wastewater indicator compounds in wastewater effluent samples from the Taylors Falls wastewater-treatment plant at Taylors Falls, Minn. (station 452403092410601) in the St. Croix National Scenic Riverway, 2007–08.

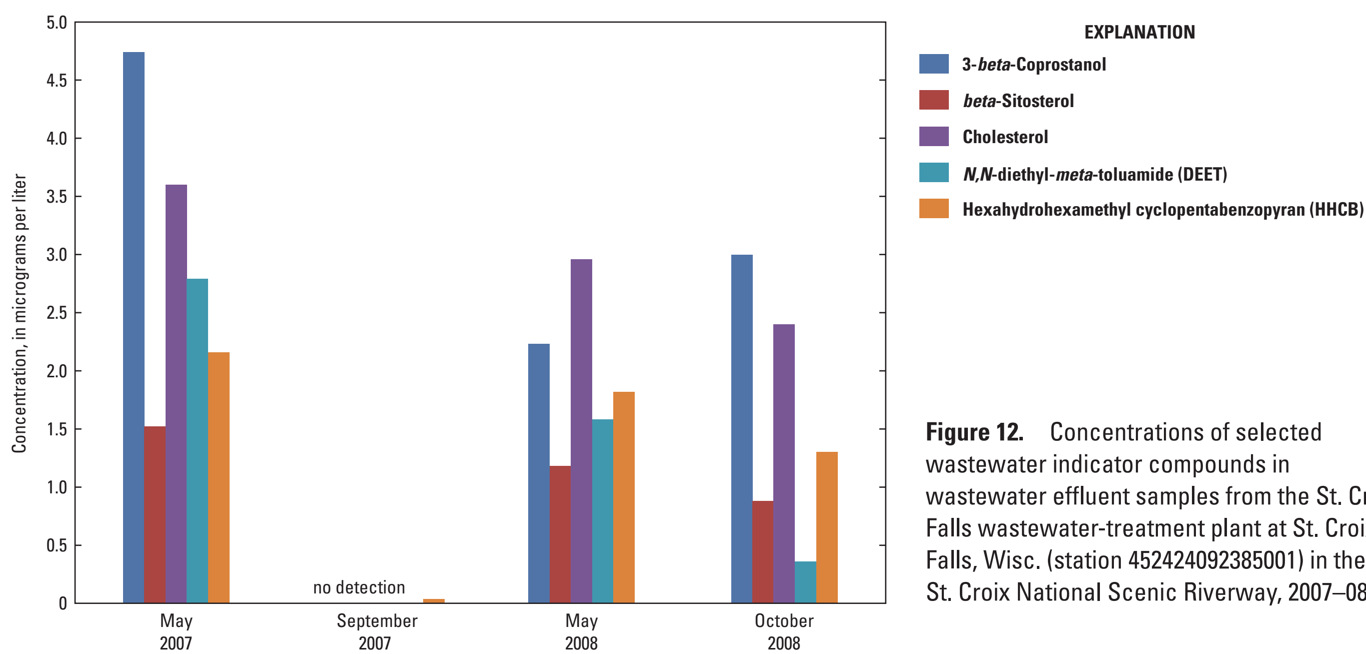

Figure 12. Concentrations of selected wastewater indicator compounds in wastewater effluent samples from the St. Croix Falls wastewater-treatment plant at St. Croix Falls, Wisc. (station 452424092385001) in the St. Croix National Scenic Riverway, 2007–08.

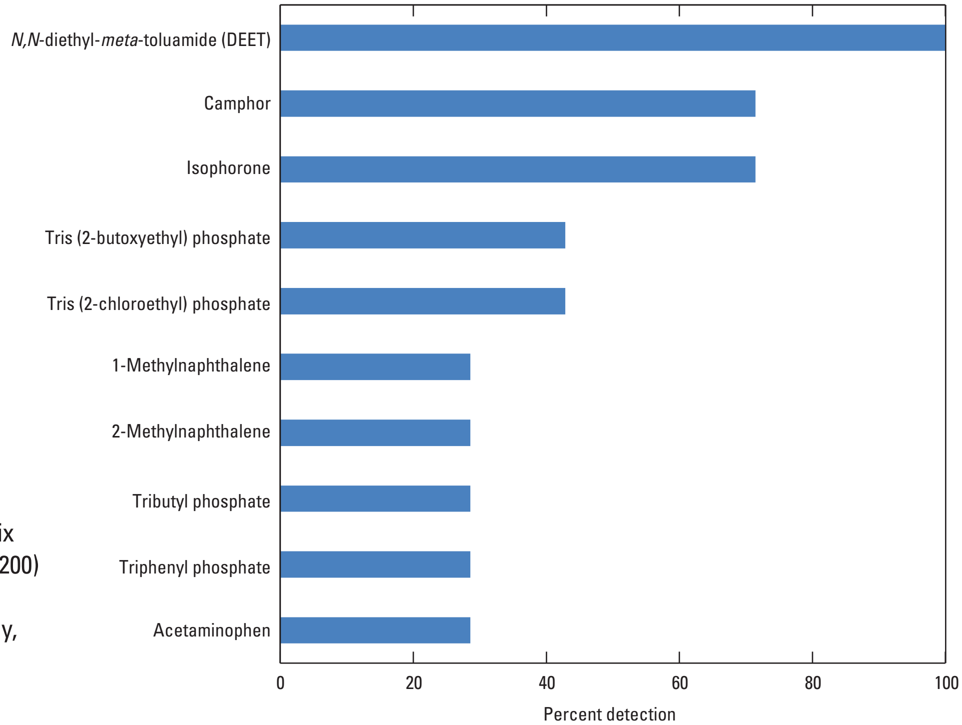

Figure 13. Most frequently detected wastewater indicator compounds in surface-water samples from the St. Croix River near Sunrise, Minn. (station 05340200) and Franconia, Minn. (station 05340540) in the St. Croix National Scenic Riverway, 2007–08.

the water samples from the Sunrise site were greater than concentrations in the water samples from the Franconia site.

Endocrine Active Chemicals

Eight EACs were included in analysis of OWCs in water samples: 4-nonylphenol, 4-nonylphenol diethoxylate, 4-*n*-octylphenol, 4-*tert*-octylphenol, 4-*tert*-octylphenol monoethoxylate, 4-*tert*-octylphenol diethoxylate, AHTN, and HHCB. EACs affect characteristics in fish such as production of vitellogenin in male fish, changes in nest holding ability, and changes in gonadal tissues (Barber and others, 2007; Bistodeau and others, 2006; Schoenfuss and others, 2007; Lee and others, 2010). More EACs were detected in the effluent samples from the SCF-WWTP (7 detected) than from the TF-WWTP (4 detected) (fig. 14; table 9; *appendix 4*).

The EACs with the greatest concentrations were 4-nonylphenol and 4-nonylphenol diethoxylate. These two compounds, in addition to tris(2-butoxyethyl) phosphate, had the greatest concentrations of all detected OWCs and pharmaceuticals at the SCF-WWTP (table 9). In the May 2007 effluent sample from the SCF-WWTP, the concentration of 4-nonylphenol was 18.2 µg/L and the concentration of 4-nonylphenol diethoxylate was 46.7 µg/L. These concentrations were greater than the concentrations measured in effluent from 25 WWTPs in Minnesota during a 2009 study, for which nonylphenol concentrations ranged from 0.1 to 10 µg/L with an average of 0.74 µg/L, and nonylphenol diethoxylate concentrations ranged from 0.14 to 3.4 µg/L with an average of 0.98 µg/L (Lee and others, 2011). The EAC with the greatest concentration in the effluent from the TF-WWTP was 4-nonylphenol, which had a concentration of 0.915 µg/L in the May 2007 sample. This concentration is in the range of concentrations measured in effluent from 25 WWTPs in Minnesota (Lee and others, 2011).

Only one EAC, 4-nonylphenol, was detected in surface-water samples collected from the Sunrise site, and EACs were not detected in the surface-water samples collected from the Franconia site. The 4-nonylphenol concentration in the surface-water sample from the Sunrise site was 0.574 µg/L in the May 2007 sample. For comparison, nonylphenol concentrations in samples collected in 2009 from 24 Minnesota stream sites located downstream from wastewater discharges ranged from 0.1 to 0.29 µg/L with an average concentration of 0.17 µg/L (Lee and others, 2011).

Occurrence of Wastewater Indicator Compounds in Bed-Sediment Samples

The occurrence of wastewater indicator compounds in bed-sediment samples collected from two sites in the St. Croix National Scenic Riverway is described in this section. For the bed-sediment samples, OWC data are presented in *appendix 6*, and pharmaceutical data are presented in *appendix 7*.

Bed-sediment samples collected from the Franconia site had more occurrences of OWCs and pharmaceuticals than did the bed-sediment samples collected from the Sunrise site

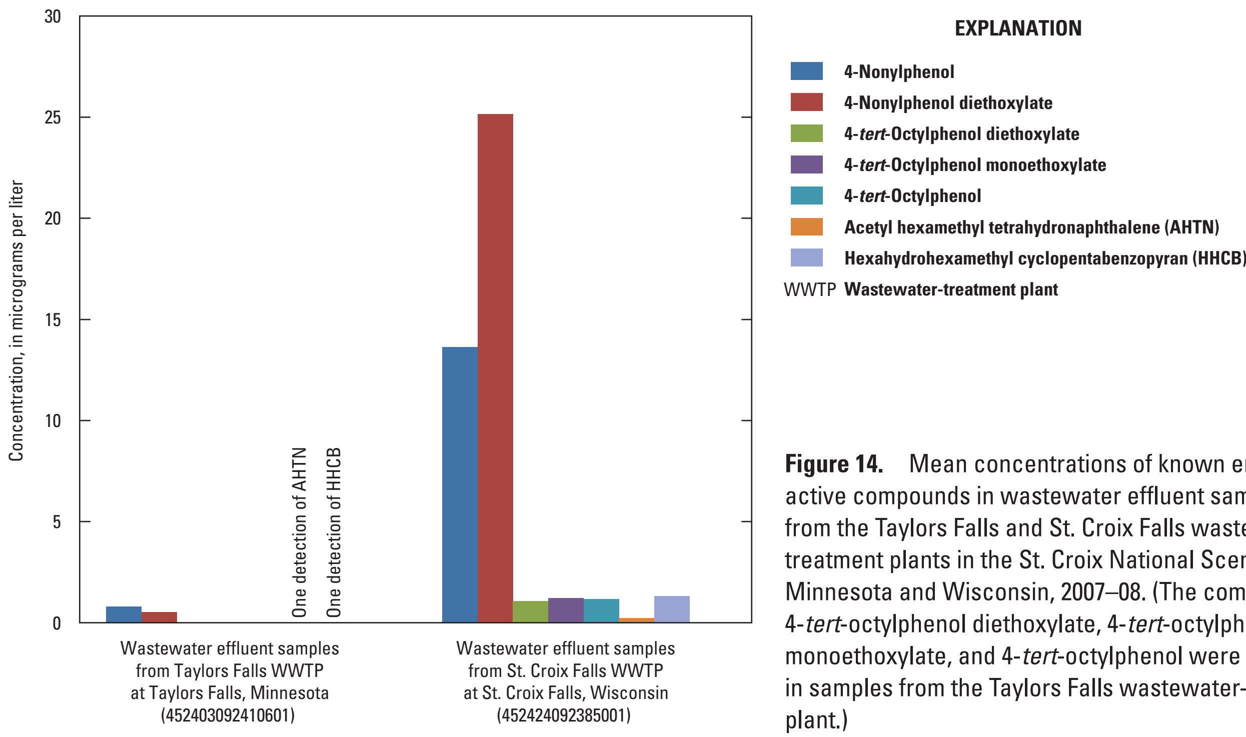

Figure 14. Mean concentrations of known endocrine active compounds in wastewater effluent samples from the Taylors Falls and St. Croix Falls wastewater-treatment plants in the St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08. (The compounds 4-*tert*-octylphenol diethoxylate, 4-*tert*-octylphenol monoethoxylate, and 4-*tert*-octylphenol were not detected in samples from the Taylors Falls wastewater-treatment plant.)

(fig. 15). The types of OWCs did vary between the sites and the sampling periods, but in general sterols (cholesterol, *beta*-sitosterol, and *beta*-stigmastanol) and polycyclic aromatic hydrocarbons (PAHs; anthracene, benzo[*a*]pryene, fluoranthene, phenanthrene, and pyrene) were the most frequently detected compounds among all sampling periods at both sites (fig. 16). Pharmaceuticals were less frequently detected in bed sediments than OWCs. Most pharmaceuticals were detected once at each site with the exception of citalopram and miconazole, which were detected twice each at an individual site. Nine pharmaceuticals were detected among the samples collected at both sites (table 9; *appendix 1*). No EACs were detected in the bed-sediment samples collected from the Sunrise site, whereas one EAC, 4-*n*-octylphenol, was detected in the bed-sediment samples collected from the Franconia site (fig. 15; *appendix 6*).

The number of compounds detected (OWCs and pharmaceuticals) in the bed-sediment samples was greater than the number of compounds detected in the surface-water samples. For example, 21 OWCs and 8 pharmaceuticals were detected in the bed sediment at the Franconia site, whereas only 12 OWCs and 3 pharmaceuticals were detected in the surface-water samples from the same site. Frequently detected compounds differed between the WWTP effluent and the surface-water samples from the Franconia and Sunrise sites. This indicates that some of these compounds may have the potential to accumulate in sediments, resulting in long-term storage and potential redistribution in aquatic systems, and that the compounds present in the bed sediment may be different than the compounds detected in the water column.

The OWC and pharmaceutical concentrations in bed-sediment samples varied between the river sites with some compounds having a higher concentration in the bed sediments collected from the Sunrise site and others having a higher concentration in bed sediments from the Franconia site. These data should be interpreted with caution because of the accuracy and precision of the method used to quantify compound concentrations in the parts-per-trillion range in complex sediment matrices. In the bed-sediment samples from the Sunrise site, 9 OWCs (2,6-dimethylnaphthalene, 3-*beta*-coprostanol, 3-methyl-1H-indole, *beta*-sitosterol, *beta*-stigmastanol, cholesterol, indole, *p*-cresol, and phenol) and 6 pharmaceuticals (carbomazepine, cimetidine, citalopram, diphenhydramine, miconazole, and venalafaxine) had concentrations greater than in the bed-sediment samples from the Franconia site. In the bed-sediment samples from the Franconia site, 13 OWCs (4-cumylphenol, 4-*n*-octylphenol, 9,10-anthraquinone, anthracene, benzo[*a*]pyrene, benzophenone, carbazole, flouranthene, phenanthrene, pyrene, tributyl phosphate, triclosan, and tris(2-butoxyethyl) phosphate) and 3 pharmaceuticals (acetaminophen, sertraline, and warfarin) had concentrations greater than in bed-sediment samples from the Sunrise site. The compound tris(2-butoxyethyl) phosphate, which was found at large concentrations in the wastewater effluent samples from SCF-WWTP, was detected in the bed-sediment samples from both river sites with a larger concentration detected at the Franconia site.

The Sunrise site was selected because of its distance from major population centers and because of the lack of substantial wastewater effluent discharges from WWTPs. The number of

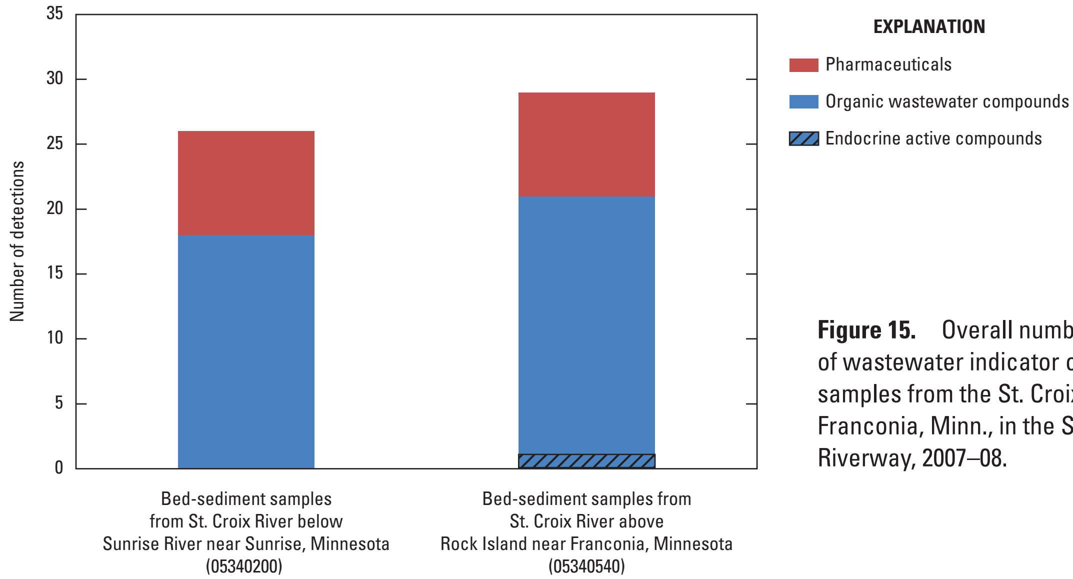

Figure 15. Overall number of detections of classes of wastewater indicator compounds in bed-sediment samples from the St. Croix River near Sunrise and Franconia, Minn., in the St. Croix National Scenic Riverway, 2007–08.

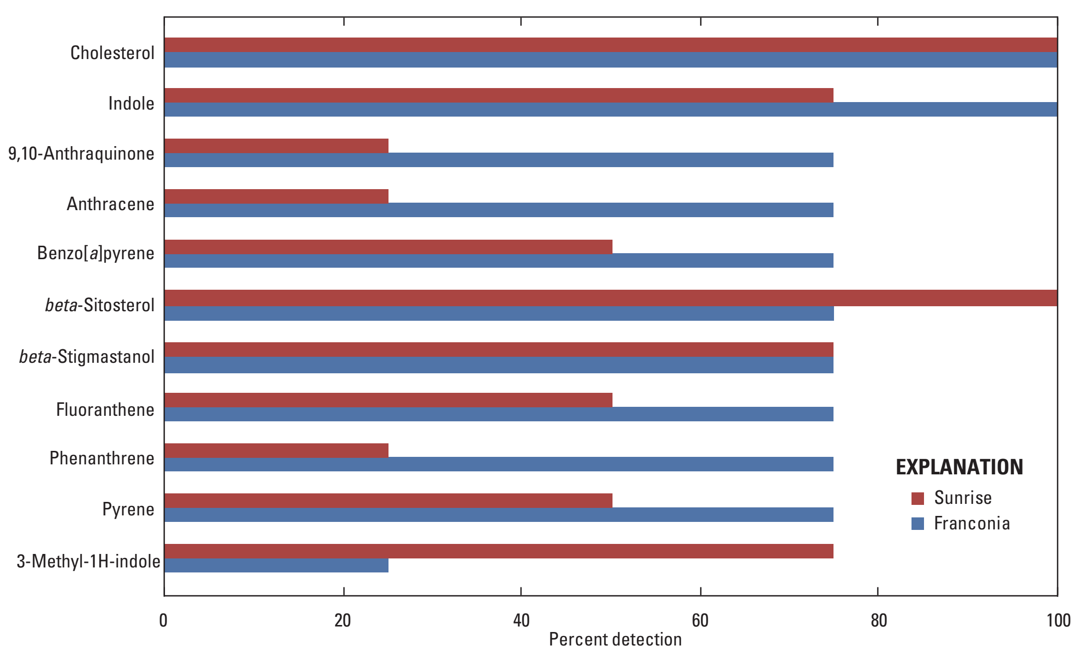

Figure 16. Most frequently detected wastewater indicator compounds in the bed-sediment samples from the St. Croix River near Sunrise (station 05340200) and Franconia (station 05340540), Minn., in the St. Croix National Scenic Riverway, 2007–08.

compounds detected and compound concentrations for some compounds were greater at the Sunrise site than at the Franconia site potentially due to contributions of OWCs and pharmaceuticals from other sources upstream from the sampling location on the St. Croix River and from the tributaries of the St. Croix River. These contributions may be from agricultural runoff, industrial discharges, atmospheric deposition, PAHs from road runoff, landfills, and other WWTPs that discharge to the St. Croix River and its tributaries. These results indicate that further investigation into the occurrence and source of these compounds in the St. Croix River Basin may be warranted.

Implications for Water Resources and Aquatic Biota

Organic wastewater contaminants and pharmaceuticals were detected in water and bed-sediment samples collected in the St. Croix River National Scenic Riverway. These contaminants were found at a site directly downstream from the effluent discharge of two wastewater treatment plants and at an upstream location not directly downstream from effluent discharge. The presence of the compounds in the bed sediment indicates their potential to accumulate in sediments, resulting in long-term storage and potential redistribution in aquatic systems. The compounds present in the bed sediment were different than the compounds detected in the water column. Results from this study indicate that the contaminants originate from wastewater effluent and other unknown upstream sources.

The results of this study indicate that aquatic organisms in the St. Croix River near Sunrise and Franconia, Minn., are exposed to a variety of organic contaminants associated with wastewater, such as pharmaceuticals, EACs, PAHs, and organophosphate fire retardants, although detected concentrations generally were small, on average less than 1 μg/L in water and less than 10 micrograms per kilogram in sediment. Each sampling event yielded different concentrations and combinations of compounds. The presence of OWCs and pharmaceuticals in both surface water and bed sediment indicates that multiple pathways of exposure to a variety of compounds exist for aquatic organisms, and the data indicate that exposures are temporally and spatially variable. Multiple interacting factors control whether these compounds occur in the aquatic environment including the sources and natural conditions that affect instream processing and degradation. These results also indicate that OWCs and pharmaceuticals in water and bed sediments increase downstream from discharge of wastewater effluent to the St. Croix River; however, the presence of OWCs and pharmaceuticals in surface water and bed sediment at the Sunrise site indicates that there are sources upstream from the Taylors Falls-St. Croix Falls area.

OWCs and pharmaceuticals may have the potential to accumulate in biota. Accumulation of compounds like mercury, polychlorinated biphenyls, and polybrominated diphenyl ethers (PBDEs) was recently found in plasma and feathers of bald eagle populations along the St. Croix River during a recent NPS study (Route and Key, 2009). The PBDE compounds are widely used as flame retardants. Although the USGS analytical methods used in this study do not include PBDEs, the methods do include other flame retardants, one of which, tris(2-butoxyethyl) phosphate, occurred at relatively high concentrations in the SCF-WWTP effluent; however, the bioaccumulation potential of this compound and the others in this study is not well known.

Although concentrations generally were low for OWCs and pharmaceuticals in water, the combined effects of numerous organic contaminants on aquatic organisms, including mussels, are largely unknown. 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 organisms.

Summary

The U.S. Geological Survey and the National Park Service cooperated on a study to determine the occurrence of wastewater indicator compounds including nutrients, organic wastewater compounds (OWCs), such as plasticizers, surfactant metabolites, antimicrobials, fragrances, and fire retardants, and pharmaceuticals that are associated with wastewater-treatment plant (WWTP) effluent in the St. Croix National Scenic Riverway in Minnesota and Wisconsin. Information regarding site descriptions, sample collection, laboratory analysis, and surface-water and bed-sediment chemistry are presented in this report. Samples of treated wastewater effluents from two WWTPs, located in St. Croix Falls, Wisc. (SCF-WWTP) and Taylors Falls, Minn. (TF-WWTP), were collected from May 2007 to October 2008. During this same period, surface-water and bed-sediment samples from the St. Croix River below Sunrise River near Sunrise, Minn., upstream from the two WWTPs (Sunrise site), and from the St. Croix River above Rock Island near Franconia, Minn., downstream from the WWTPs (Franconia site), also were collected. Wastewater effluent and surface-water samples were collected twice a year for 2 years and analyzed for nutrients; OWCs, including nine endocrine active compounds (EACs; compounds known to affect the endocrine systems of fish); and pharmaceuticals. Major ions were analyzed once in surface-water samples from each river site. Bed-sediment samples were collected from the two river sites twice each year and analyzed for OWCs and pharmaceuticals.

Major-ion and nutrient concentrations in surface-water samples were similar between the two river sites. Nutrient concentrations in wastewater effluent samples from the SCF-WWTP were greater than in effluent samples from the TF-WWTP. The wastewater effluent samples from the two WWTPs were dominated by different nutrients, had a wider distribution of nutrient occurrence, and had greater concentrations than did the surface-water samples from the two river sites.

The number of OWCs detected and OWC and pharmaceutical concentrations varied among sites and among sampling periods. Of the four sites sampled, the wastewater effluent samples from the SCF-WWTP consistently had the most detections of compounds and greatest concentrations of those compounds. More compounds were detected in SCF-WWTP (38 OWCs and 7 pharmaceuticals) than in TF-WWTP (20 OWCs and 3 pharmaceuticals). Effluent samples had greater numbers of compounds detected than surface water sites. More OWCs and pharmaceuticals were detected in surface-water samples collected from the Franconia site (12 OWCs and 3 pharmaceuticals) than in samples collected from the Sunrise site (7 OWCs and 2 pharmaceuticals). Concentrations also varied among sites. For example, concentrations of phosphate flame retardants were greater in effluent from SCF-WWTP than from TF-WWTP, with the concentration of tris(2-butoxyethyl) phosphate greater than 200 micrograms per liter (μg/L) in the 2008 spring and fall sampling. The concentrations of tris(2-butoxyethyl) phosphate were about 200 percent greater in the 2008 effluent samples from the SCF-WWTP than in the effluent samples collected from the same WWTP in 2007.

Four EACs were detected in the effluent from the TF-WWTP. Detections at the SCF-WWTP included eight EACs, and two of those compounds, 4-nonylphenol and 4-nonylphenol diethoxylate, were detected at relatively high concentrations, with the highest concentrations of 18.2 μg/L and 46.7 μg/L respectively, in the May 2007 samples. Four EACs—4-nonylphenol, 4-nonylphenol diethoxylate, acetyl hexamethyl tetrahydronaphthalene (AHTN) and hexahydrohexamethyl cyclopentabenzopyran (HHCB)—were detected in effluent samples from both WWTPs. Only one EAC, 4-nonylphenol, was detected in surface-water samples collected from the Sunrise site, and EACs were not detected in the surface-water samples collected from the Franconia site.

Bed-sediment samples collected from the Franconia site had more occurrences of both OWCs and pharmaceuticals than did the bed-sediment samples collected from the Sunrise site. In the bed-sediment samples collected from the Sunrise site, 18 OWCs and 8 pharmaceuticals were detected. In bed-sediment samples collected from the Franconia site, 21 OWCs and 8 pharmaceuticals were detected. No EACs were detected in the bed-sediment samples collected from the Sunrise site, whereas one EAC, 4-*n*-octylphenol, was detected in the bed-sediment samples collected from the Franconia site. The compound tris(2-butoxyethyl) phosphate, which was found at high concentrations in the effluent from SCF-WWTP, was detected in the bed-sediment samples from both sites, with a higher concentration detected at the Franconia site. At both the Franconia and Sunrise sites, more OWCs and pharmaceuticals were detected in bed-sediment samples than in surface-water samples, indicating that these compounds may accumulate in bed sediment.

Although more compounds were detected in bed-sediment samples at the Franconia site than at the Sunrise site, more compounds were detected at the Sunrise site than were expected. The Sunrise site was selected because of its distance from major population centers and because of the lack of substantial discharges from WWTPs. The Sunrise site was expected to have only a few compounds detected at low concentrations. The occurrence of wastewater indicator compounds at the Sunrise site indicates that the St. Croix River is receiving OWCs and pharmaceuticals from an upstream source, and because the Sunrise site was sampled downstream from the confluence of the Sunrise River and the St. Croix River, it is possible that the Sunrise River and other tributaries are contributing these compounds to the St. Croix River. These contributions could be from various pathways such as agricultural runoff, industrial discharges, atmospheric deposition, polycyclic aromatic hydrocarbons from road runoff, landfills, and other WWTPs that discharge to St. Croix River and its tributaries. These results indicate that further investigation into the occurrence and source of these compounds in the St. Croix River Basin may be warranted.

The results of this study indicate that aquatic organisms in the St. Croix River near Sunrise and Franconia, Minn., are exposed to a variety of organic contaminants associated with wastewater, such as pharmaceuticals, EACs, polycyclic aromatic hydrocarbons, and organophosphate fire retardants. Each sampling event yielded different concentrations and combinations of compounds. The presence of wastewater indicator compounds in surface water and bed sediment indicates that multiple pathways of exposure to a variety of compounds exist for aquatic organisms. The results of this study also indicate that OWCs in water and bed sediments increase downstream from wastewater discharges to the St. Croix; however, the presence of OWCs in surface water and bed sediment at the Sunrise site indicates that potential sources of compounds, such as WWTPs or other sources, are upstream from the Taylors Falls-St. Croix Falls area. Aquatic organisms, including mussels, are being exposed to a wide variety of compounds at varying concentrations, and the data indicate that exposures are temporally and spatially variable. Although the results from this study provide information useful for characterizing organic contaminants, a combined multidisciplinary approach is necessary to continue to better understand the potential effects these compounds may have on aquatic organisms.

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Appendixes 1–7

Appendix 1. Physical Properties and Constituents Analyzed for in Water or Bed-Sediment Samples, St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

[MRL, minimum reporting level; EDP, endocrine-disrupting potential; K_{ow}, octanol-water partition coefficient; CASRN, Chemical Abstracts Services Registry Number; µS/cm, microsiemens per centimeter at 25 degrees Celsius (˚C); mg/L, milligrams per liter; µg/L, micrograms per liter; S, suspected; K, known; E or e, remark code estimated concentration reported; F, fungicide; H, herbicide; I, insecticide; GUP, general-use pesticide; FR, flame retardant; WW, wastewater; manuf., manufacturing; CP, combustion product; PAH, polycyclic aromatic hydrocarbon; SSRI, selective serotonin reuptake inhibitor; UV, ultraviolet; %, percent; >, greater than; --, no data or not applicable]

Property/constituent name	Abbreviation	MRL[1]	EDP[2]	Log K_{ow}[3]	CASRN[4]	Possible compound uses or sources[5]
Physical properties in water						
Specific conductance (µS/cm)	SC	--	--	--	--	Field measurement.
Dissolved oxygen (mg/L)	DO	--	--	--	--	Field measurement.
pH	pH	--	--	--	--	Field measurement.
Water temperature (°C)	TEMP	--	--	--	--	Field measurement.
Major ions (mg/L) in water						
Calcium	Ca	0.04	--	--	7440–70–2	Mineral.
Magnesium	Mg	.02	--	--	7439–95–4	Mineral.
Potassium	K	.02	--	--	7440–09–7	Mineral.
Sodium	Na	.12	--	--	7440–23–5	Mineral.
Chloride	Cl	.12	--	--	16887–00–6	Mineral.
Fluoride	F	.12	--	--	16984–48–8	Mineral.
Silica	Si	.018	--	--	7631–86–9	Mineral.
Sulfate	SO4	.18	--	--	14808–79–8	Mineral.
Iron	Fe	8.0	--	--	7439–89–6	Mineral.
Manganese	Mn	.4	--	--	7439–96–5	Mineral.
Nutrients (mg/L) in water						
Dissolved ammonia	NH_3	0.02	--	--	7664–41–7	Nutrient.
Nitrite plus nitrate	NO_2+NO_3	.04	--	--	--	Nutrient.
Nitrogen, nitrite	NO_2	.002	--	--	14797–65–0	Nutrient.
Total ammonia plus organic nitrogen	NH_3+N, unf	.1	--	--	17778–88–0	Nutrient
Dissolved orthophosphate	ORTHOP	.008	--	--	14265–44–2	Nutrient.
Total phosphorus, unfiltered	TP, unf	.008	--	--	7723–14–0	Nutrient.
Organic wastewater compounds (µg/L) in water and bed sediment						
1,4-Dichlorobenzene	1,4DCB	0.5E	S	3.28	106–46–7	Moth repellent, fumigant, deodorant.
1-Methylnaphthalene	--	.5E	--	3.72	90–12–0	2–5% of gasoline, diesel fuel, or crude oil.
2,6-Dimethylnaphthalene	--	.5E	--	4.26	581–42–0	Percent in diesel/kerosene (trace in gasoline).
2-Methylnaphthalene	--	.5E	--	3.72	91–57–6	2–5% of gasoline, diesel fuel, or crude oil.
3-*beta*-Coprostanol	COP	2e	--	8.82	360–68–9	Carnivore fecal indicator.
3-Methyl-1H-indole (skatol)	--	1e	--	2.60	83–34–1	Fragrance, stench in feces, and coal tar.
3-*tert*-Butyl-4-hydroxyanisole	BHA	5E	S	3.50	25013–16–5	Antioxidant.
4-Cumylphenol	--	1.0	S	4.12	599–64–4	Surfactant metabolite.
4-*n*-Octylphenol	NOP	1.0	K	5.50	1806–26–4	Surfactant metabolite.
4-Nonylphenol	NP	5E	K	5.92	84852–15–3	Surfactant metabolite.
4-Nonylphenol monoethoxylate[6]	NP1EO	2E	K	5.58	--	Surfactant metabolite.
4-Nonylphenol diethoxylate	NP2EO	5E	K	--	--	Surfactant metabolite.
4-*tert*-Octylphenol	TOP	1.0	K	5.28	140–66–9	Surfactant metabolite.
4-*tert*-Octylphenol diethoxylate	OP2EO	1E	K	--	--	Surfactant metabolite.
4-*tert*-Octylphenol monoethoxylate	OP1EO	1E	K	--	--	Surfactant metabolite.
5-Methyl-1H-benzotriazole[8]	5,MBNZ	2e	--	1.71	136–85–6	Antioxidant in antifreeze and deicers.
9,10-Anthraquinone	--	.5	--	3.34	84–65–1	Manuf. dye/textiles, seed treatment, bird repellent.
Acetophenone	--	.5	--	1.67	98–86–2	Fragrance and flavor.
Acetyl-hexamethyl-tetrahydronaphthalene (tonalide)	AHTN	.5	K	6.35	21145–77–7	Musk fragrance.
Anthracene	--	--	--	4.35	120–12–7	CP, component of tar, diesel, or crude oil.
Atrazine[6]	--	1e	K	2.82	1912–24–9	Selective triazine herbicide.

Appendix 1. Physical Properties and Constituents Analyzed for in Water or Bed-Sediment Samples, St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.—Continued

[MRL, minimum reporting level; EDP, endocrine-disrupting potential; K_{ow}, octanol-water partition coefficient; CASRN, Chemical Abstracts Services Registry Number; µS/cm, microsiemens per centimeter at 25 degrees Celsius (˚C); mg/L, milligrams per liter; µg/L, micrograms per liter; S, suspected; K, known; E or e, remark code estimated concentration reported; F, fungicide; H, herbicide; I, insecticide; GUP, general-use pesticide; FR, flame retardant; WW, wastewater; manuf., manufacturing; CP, combustion product; PAH, polycyclic aromatic hydrocarbon; SSRI, selective serotonin reuptake inhibitor; UV, ultraviolet; %, percent; >, greater than; --, no data or not applicable]

Property/constituent name	Abbreviation	MRL[1]	EDP[2]	Log K_{ow}[3]	CASRN[4]	Possible compound uses or sources[5]
Organic wastewater compounds (µg/L) in water and bed sediment—Continued						
Benzo[*a*]pyrene	--	.5	S	6.11	50–32–8	CP, regulated PAH.
Benzophenone	--	.5	S	3.15	119–61–9	Fixative for perfumes and soaps.
beta-Sitosterol	--	2E	--	9.65	83–46–5	Plant sterol.
beta-Stigmastanol	--	2e	--	9.73	19466–47–8	Herbivore fecal indicator (digestion of sitosterol).
Bromacil	--	.5	--	1.68	314–40–9	H (GUP), >80% noncrop usage on grass/brush.
Camphor	--	.5	--	3.04	76–22–2	Flavor, odorant, ointments.
Carbaryl[8]	--	.5E	S	2.35	63–25–2	I, crop and garden uses, low persistence.
Carbazole	--	.5	--	3.23	86–74–8	I, manuf. dyes, explosives, and lubricants.
Chlorpyrifos	--	.5	S	4.66	2921–88–2	I, historically for domestic pest and termite control.
Cholesterol	CHO	2e	--	8.74	57–88–5	Often a fecal indicator, also a plant sterol.
Diazinon	--	.5	S	3.86	333–41–5	I, > 40% nonagricultural usage, ants, flies.
d-Limonene	--	.5E	--	4.83	5989–27–5	F, antimicrobial, antiviral, fragrance in aerosols.
Fluoranthene	--	.5	--	4.93	206–44–0	CP, in coal tar, asphalt (traces in gasoline or diesel fuel).
Hexahydrohexamethyl-cyclopenta-benzo-pyran (galaxolide)	HHCB	.5e	K	6.26	1222–05–5	Musk fragrance.
Indole	--	.5	--	2.05	120–72–9	Pesticide inert ingredient, fragrance in coffee.
Isoborneol	--	.5	--	2.85	124–76–5	Fragrance in perfumery, in disinfectants.
Isophorone	--	.5	--	2.62	78–59–1	Solvent for lacquer, plastic, oil, silicon, resin.
Isopropylbenzene (cumene)	--	.5E	--	3.45	98–82–8	Manuf. phenol/acetone, fuels and paint thinner.
Isoquinoline	--	.5	--	2.14	119–65–3	Flavors and fragrances.
Menthol	--	.5	--	3.38	89–78–1	Cigarettes, cough drops, liniment, mouthwash.
Metalaxyl[8]	--	.5	--	1.70	57837–19–1	H, F (GUP), mildew, blight, pathogens, golf/turf.
Methyl salicylate[8]	--	.5	--	2.60	119–36–8	Liniment, food, beverage, UV-absorbing lotion.
Metolachlor	--	.5	--	3.24	51218–45–2	H (GUP), indicator of agricultural drainage.
Naphthalene	--	.5E	--	3.17	91–20–3	Fumigant, moth repellent, component (10%) of gasoline.
N,N-diethyl-*meta*-toluamide	DEET	.5	--	2.26	134–62–3	I, urban uses, mosquito repellent.
p-Cresol (4-Methylphenol)[8]	MP	1.0	--	2.06	106–44–5	Disinfectant.
Pentachlorophenol[7]	--	2.0E	S	4.74	87–86–5	H, F, wood preservative, termite control.
Phenanthrene	--	.5	--	4.35	85–01–8	CP, manuf. explosives, in tar, diesel fuel, or crude oil.
Phenol	--	.5	--	1.51	108–95–2	Disinfectant, manuf. several products, leachate.
Prometon	--	.5	--	3.57	1610–18–0	H (non-crop only), applied prior to blacktop.
Pyrene	--	.5	--	4.93	129–00–0	CP , In coal tar, asphalt (traces in gasoline or diesel fuel).
Tetrachloroethene[8]	PCE	.5E	--	2.97	127–18–4	Solvent, degreaser, veterinary anthelmintic.
Tributyl phosphate	--	.5	--	3.82	126–73–8	Antifoaming agent, flame retardant.
Triclosan	TRIC	1.0	S	4.66	3380–34–5	Disinfectant, antimicrobial.
Triethyl citrate (ethyl citrate)[8]	--	.5	--	.33	77–93–0	Cosmetics, pharmaceuticals.
Triphenyl phosphate	--	.5	--	4.70	115–86–6	Flame retardant, plasticizer, resin, wax, finish, roofing paper.
Tris(2-butoxyethyl) phosphate	--	.5e	--	3.00	78–51–3	Flame retardant.
Tris(2-chloroethyl) phosphate	--	.5	S	1.63	115–96–8	Plasticizer, flame retardant.
Tris(dichloroisopropyl) phosphate	--	.5	S	3.65	13674–87–8	Flame retardant.
Caffeine-^{13}C (percent)	--	--	--	--	--	Surrogate standard.
Decafluorobiphenyl (percent)	--	--	--	--	--	Surrogate standard.
Fluoranthene-d_{10} (percent)	--	--	--	--	--	Surrogate standard.

Appendix 1. Physical Properties and Constituents Analyzed for in Water or Bed-Sediment Samples, St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.—Continued

[MRL, minimum reporting level; EDP, endocrine-disrupting potential; K_{ow}, octanol-water partition coefficient; CASRN, Chemical Abstracts Services Registry Number; µS/cm, microsiemens per centimeter at 25 degrees Celsius (°C); mg/L, milligrams per liter; µg/L, micrograms per liter; S, suspected; K, known; E or e, remark code estimated concentration reported; F, fungicide; H, herbicide; I, insecticide; GUP, general-use pesticide; FR, flame retardant; WW, wastewater; manuf., manufacturing; CP, combustion product; PAH, polycyclic aromatic hydrocarbon; SSRI, selective serotonin reuptake inhibitor; UV, ultraviolet; %, percent; >, greater than; --, no data or not applicable]

Property/constituent name	Abbreviation	MRL[1]	EDP[2]	Log K_{ow}[3]	CASRN[4]	Possible compound uses or sources[5]
Human-health pharmaceutical compounds (µg/L) in water and bed sediment						
1,7-Dimethylxanthine	--	--	--	-0.39	611–59–6	Precursor is a stimulant.
Acetaminophen	--	--	--	.27	103–90–2	Analgesic.
Albuterol	--	--	--	.64	18559–94–9	Bronchodilator.
Caffeine[9,10]	CAFF	0.5	--	.16	58–08–2	Beverages, diuretic, very mobile/biodegradable.
Carbamazepine[9]	--	--	--	2.25	298–46–4	Antiepileptic.
Codeine	--		--	1.28	76–57–3	Opiate agonist.
Cotinine[9,10]	--	1E	--	.34	486–56–6	Primary nicotine metabolite.
Dehydronifedipine	--	--	--	--	67035–22–7	Precursor is an antiangial.
Diltiazem	--	--	--	2.79	42399–41–7	Antihypertensive.
Diphendydramine	--	--	--	3.11	58–73–1	Antipruritic.
Fluoxetine	--	--	--	4.65	54910–89–3	SSRI antidepressant.
Ranitidine	--	--	--	.29	66357–35–5	H_2-receptor antagonist, antihistimine.
Sulfamethoxazole	--	--	--	.48	723–46–6	Antibiotic.
Thiabendazole	--	--	--	2.00	148–79–8	Anthelmintic, fungicide.
Trimethoprim	--	--	--	.73	738–70–5	Antibiotic.
Warfarin	--	--	--	2.23	81–81–2	Anticoagulant, rodenticide.
Carbamazepine-d_{10} (percent)	--	--	--	--	--	Surrogate standard.
Ethyl nicotinate-d_4 (percent)	--	--	--	--	--	Surrogate standard.
Additional pharmaceuticals analyzed in bed sediment						
Azithromycin[6]	--	--	--	3.24	83905–01–5	Antibiotic.
Bupropion[6]	--	--	--	--	34841–39–9	Antidepressant.
Cimetidine[6]	--	--	--	.57	51481–61–9	H_2-receptor antagonist.
Citalopram[6]	--	--	--	3.74	59729–33–8	Antidepressant.
Duloxetine[6]	--	--	--	--	116539–59–4	Antidepressant.
Erythromycin[6]	EES	--	--	3.06	114–07–8	Macrolide antibiotic.
Fluvoxamine[6]	--	--	--		54739–18–3	
Miconazole[6]	--	--	--	6.25	22916–47–8	SSRI antidepressant.
Norfluoxetine[6]	--	--	--	--	--	Imidazole antifungal agent, film developer.
Norsertraline[6]	--	--	--	--	91797–58–9	Fluoxetine metabolite.
Paroxetine[6]	--	--	--	3.95	61869–08–7	Sertraline metabolite.
Paroxetine metabolite[6]	--	--	--	--	--	SSRI antidepressant.
Sertraline[6]	--	--	--	5.29	79617–96–2	SSRI antidepressant.
Venalafaxine[6]	--	--	--	3.28	93413–69–5	Antidepressant.

[1]Chemicals with and "E" following the number indicate a compound with low recovery, unstable instrument response, or reference standard prepared from a technical mixture for water analyses (Zaugg and others, 2006). Chemicals with an "e" following the number are estimated if the spike recovery or expected continuing calibration verification concentrations for each set of samples are not within control limits (Zaugg and others, 2006).

[2]Endocrine disrupting potential (EDP) from the following sources: Kime, 1998; Tremblay and Van der Kraak, 1998; EC-BKH, 2000; Nishihara and others, 2000; Global Water Research Coalition, 2003; Versonnen and others, 2003; Institute of Environmental Health, 2005; Korner and others, 2005; and Schreurs and others, 2004.

[3]Log K_{ow} is the octanol-water partition coefficient and is a measure of the equilibrium concentration of a compound between octanol and water. A high value indicates a compound that will preferentially partition into soil organic matter rather than water. It was calculated using the U.S. Environmental Protection Agency's exposure assessment tools and models (EPI-suite software, WSKOWWINTM version 1.40; U.S. Environmental Protection Agency, 2005).

[4]This report contains Chemical Abstracts Services Registry Numbers (CASRN)®, which is a Registered Trademark of the American Chemical Society. A CASRN is a numeric identifier that can contain up to nine digits, divided by dashes into three parts. For example, 58–08–2 is the CASRN for caffeine. The online database provides a source for the latest registry number information: *http://www.cas.org/index.html.* Chemical Abstracts Services recommends the verification of the CASRNs through CAS Client Services℠.

Appendix 1. Physical Properties and Constituents Analyzed for in Water or Bed-Sediment Samples, St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.—Continued

[MRL, minimum reporting level; EDP, endocrine-disrupting potential; K_{ow}, octanol-water partition coefficient; CASRN, Chemical Abstracts Services Registry Number; µS/cm, microsiemens per centimeter at 25 degrees Celsius (˚C); mg/L, milligrams per liter; µg/L, micrograms per liter; S, suspected; K, known; E or e, remark code estimated concentration reported; F, fungicide; H, herbicide; I, insecticide; GUP, general-use pesticide; FR, flame retardant; WW, wastewater; manuf., manufacturing; CP, combustion product; PAH, polycyclic aromatic hydrocarbon; SSRI, selective serotonin reuptake inhibitor; UV, ultraviolet; %, percent; >, greater than; --, no data or not applicable]

[5]Sources are Kime, 1998; Tremblay and Van der Kraak, 1998; EC-BKH, 2000; Nishihara and others, 2000; Zaugg and others, 2002; Versonnen and others, 2003; Barber and others, 2003; Global Water Research Coalition, 2003; Institute of Environmental Health, 2005; Furlong and others, 2008; Korner and others, 2005; Terasaki and others, 2005.

[6]Analyzed in only bed-sediment samples; if not otherwise noted, compound was analyzed in both bed-sediment and water samples.

[7]Analyzed in wastewater effluent samples but not in surface-water samples; if not otherwise noted, compound was analyzed in both bed-sediment and all water samples.

[8]Analyzed in water samples only; if not otherwise noted, compound was analyzed in both bed-sediment and water samples; pentachlorophenol only analyzed once at St. Croix Falls wastewater-treatment plant.

[9]Analyzed using two methods.

[10]Analyzed using methods for organic wastewater chemicals and pharmaceuticals, but categorized as a pharmaceutical in this report.

Appendix 2. Dissolved Concentrations of Major Ions in Surface-Water Samples Analyzed at the U.S. Geological Survey National Water Quality Laboratory, St. Croix National Scenic Riverway, Minnesota, 2008.

The Excel spreadsheet appendix_2.xls contains concentration data for major ions analyzed in surface-water samples during 2008. This Excel file can be accessed at *http://pubs.usgs.gov/sir/2011/5208/downloads/appendix_2.xlsx*.

Appendix 3. Concentrations of Nutrients in Water Samples Analyzed at the U.S. Geological Survey National Water Quality Laboratory, St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

The Excel spreadsheet appendix_3.xls contains concentration data for nutrients analyzed in surface-water samples and wastewater effluent during 2007–08. This Excel file can be accessed at *http://pubs.usgs.gov/sir/2011/5208/downloads/appendix_3.xlsx*.

Appendix 4. Concentrations of Organic Wastewater Compounds in Water Samples Analyzed at the U.S. Geological Survey National Water Quality Laboratory, St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

The Excel spreadsheet appendix_4.xls contains concentration data for organic wastewater compounds analyzed in surface-water samples and wastewater effluent during 2007–08. This Excel file can be accessed at *http://pubs.usgs.gov/sir/2011/5208/downloads/appendix_4.xlsx*.

Appendix 5. Concentrations of Pharmaceuticals in Water Samples Analyzed at the U.S. Geological Survey National Water Quality Laboratory, St. Croix National Scenic Riverway, Minnesota and Wisconsin, 2007–08.

The Excel spreadsheet appendix_5.xls contains concentration data for pharmaceuticals analyzed in surface-water samples and wastewater effluent during 2007–08. This Excel file can be accessed at *http://pubs.usgs.gov/sir/2011/5208/downloads/appendix_5.xlsx*.

Appendix 6. Concentrations of Organic Wastewater Compounds Analyzed in Bed-Sediment Samples at the U.S. Geological Survey National Water Quality Laboratory, St. Croix National Scenic Riverway, Minnesota, 2007–08.

The Excel spreadsheet appendix_6.xls contains concentration data for organic wastewater compounds analyzed in bed-sediment samples during 2007–08. This Excel file can be accessed at *http://pubs.usgs.gov/sir/2011/5208/downloads/appendix_6.xlsx*.

Appendix 7. Concentrations of Pharmaceuticals Analyzed in Bed-Sediment Samples at the U.S. Geological Survey National Water Quality Laboratory, St. Croix National Scenic Riverway, Minnesota, 2007–08.

The Excel spreadsheet appendix_7.xls contains concentration data for pharmaceuticals analyzed in bed-sediment samples during 2007–08. This Excel file can be accessed at *http://pubs.usgs.gov/sir/2011/5208/downloads/appendix_7.xlsx*.

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Back cover. Top left: Polishing pond for Taylors Falls wastewater-treatment plant. Top right: St. Croix Falls wastewater-treatment plant clarifiers. Bottom right: Outflow from the treatment plant to the St. Croix River. Bottom left: Outflow from the treatment plant to the St. Croix River.

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