

Prepared in cooperation with the City of Sioux Falls

Occurrence of Organic Wastewater Compounds in Drinking Water, Wastewater Effluent, and the Big Sioux River in or near Sioux Falls, South Dakota, 2001–2004

Scientific Investigations Report 2006–5118

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By Steven K. Sando, Edward T. Furlong, James L. Gray, and Michael T. Meyer

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Conversion Factors

Multiply	By	To obtain
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
foot (ft)	0.3048	meter (m)
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
mile (mi)	1.609	kilometer (km)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m ³ /s)
pounds per day (lb/d)	0.4536	kilograms per day (kg/d)
square mile (mi ²)	259.0	hectare (ha)
square mile (mi ²)	2.590	square kilometer (km ²)

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

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

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

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Loads of organic wastewater compounds were estimated by multiplying discharges at the times of sampling by constituent concentrations and by a conversion factor (0.0053919) to convert cubic feet per second and micrograms per liter to pounds per day.

Definition of Acronyms

AHTN	7-Acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene
AP	Alkylphenol
ASE	Accelerated solvent extraction
EDCs	Suspected endocrine-disrupting compounds
FDW	Finished drinking water
HHCB	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran
HIACs	Household, industrial, and minor agricultural use compounds
HLB	Hydrophilic-lipophilic-balance
HPCs	Human pharmaceutical compounds
HPLC/ESI-MS	High-performance liquid chromatography/electrospray ionization mass spectrometry
HVACs	Human and veterinary antibiotic compounds
LRL	Laboratory reporting level
MAHs	Major agricultural herbicides
NP	<i>para</i> -Nonylphenol
NP1EO	Nonylphenol monoethoxylate
NP2EO	Nonylphenol diethoxylate
NWQL	National Water Quality Laboratory
OGRL	Organic Geochemistry Research Laboratory
OP1EO	Octylphenol monoethoxylate
OP2EO	Octylphenol diethoxylate
OWCs	Organic wastewater compounds
PAHs	Polyaromatic hydrocarbons
QA/QC	Quality assurance/quality control
RPD	Relative percent difference
RSD	Relative standard deviation
SCs	Sterol compounds
SIM	Selected ion monitoring
SPE	Solid-phase extraction
SRL	Study reporting level
USGS	U.S. Geological Survey
WWE	Wastewater treatment plant effluent
WWTP	Wastewater treatment plant

Occurrence of Organic Wastewater Compounds in Drinking Water, Wastewater Effluent, and the Big Sioux River in or near Sioux Falls, South Dakota, 2001–2004

By Steven K. Sando, Edward T. Furlong, James L. Gray, and Michael T. Meyer

Abstract

The U.S. Geological Survey (USGS) in cooperation with the city of Sioux Falls conducted several rounds of sampling to determine the occurrence of organic wastewater compounds (OWCs) in the city of Sioux Falls drinking water and wastewater effluent, and the Big Sioux River in or near Sioux Falls during August 2001 through May 2004. Water samples were collected during both base-flow and storm-runoff conditions. Water samples were collected at 8 sites, which included 4 sites upstream from the wastewater treatment plant (WWTP) discharge, 2 sites downstream from the WWTP discharge, 1 finished drinking-water site, and 1 WWTP effluent (WWE) site.

A total of 125 different OWCs were analyzed for in this study using five different analytical methods. Analyses for OWCs were performed at USGS laboratories that are developing and/or refining small-concentration (less than 1 microgram per liter ($\mu\text{g/L}$)) analytical methods. The OWCs were classified into six compound classes: human pharmaceutical compounds (HPCs); human and veterinary antibiotic compounds (HVCs); major agricultural herbicides (MAHs); household, industrial, and minor agricultural compounds (HIACs); polyaromatic hydrocarbons (PAHs); and sterol compounds (SCs). Some of the compounds in the HPC, MAH, HIAC, and PAH classes are suspected of being endocrine-disrupting compounds (EDCs). Of the 125 different OWCs analyzed for in this study, 81 OWCs had one or more detections in environmental samples reported by the laboratories, and of those 81 OWCs, 63 had acceptable analytical method performance, were detected at concentrations greater than the study reporting levels, and were included in analyses and discussion related to occurrence of OWCs in drinking water, wastewater effluent, and the Big Sioux River.

OWCs in all compound classes were detected in water samples from sampling sites in the Sioux Falls area. For the five sampling periods when samples were collected from the Sioux Falls finished drinking water, only one OWC was detected at a concentration greater than the study reporting level (metolachlor; $0.0040 \mu\text{g/L}$).

During base-flow conditions, Big Sioux River sites upstream from the WWTP discharge had OWC contributions

that primarily were from nonpoint animal or crop agriculture sources or had OWC concentrations that were minimal. The influence of the WWTP discharge on OWCs at downstream river sites during base-flow conditions ranged from minimal influence to substantial influence depending on the sampling period. During runoff conditions, OWCs at sites upstream from the WWTP discharge probably were primarily contributed by nonpoint animal and/or crop agriculture sources and possibly by stormwater runoff from nearby roads. OWCs at sites downstream from the WWTP discharge probably were contributed by sources other than the WWTP effluent discharge, such as stormwater runoff from urban and/or agriculture areas and/or resuspension of OWCs adsorbed to sediment deposited in the Big Sioux River. OWC loads generally were substantially smaller for upstream sites than downstream sites during both base-flow and runoff conditions.

In general, HPCs and HVCs accounted for relatively small portions of the total OWC concentrations in water samples collected from all sampling sites. MAHs generally accounted for a relatively small part of the total OWC concentrations during base-flow conditions for all sites, and for a substantial part at the river sites during some but not all storm-runoff sampling periods. HIACs generally accounted for a substantial part of the total OWC concentrations in samples collected from the WWE site during all sampling periods. In samples collected from downstream sites, HIACs generally accounted for a substantial part of the total OWC concentration during base-flow conditions and during some but not all of the storm-runoff sampling periods. PAHs only were detected at Big Sioux River sites that might be substantially affected by storm-runoff from roads. PAHs were not detected during any base-flow sampling period and were detected during some but not all storm-runoff periods. SCs generally comprised a substantial part of the total detected OWC concentrations for WWE and Big Sioux River sites during both base-flow and storm-runoff conditions. Results indicate that the WWTP discharge substantially contributed to the occurrence of OWCs in the Big Sioux River during below-normal base-flow conditions.

There were no human-health concerns apparent in the results of this study. Occurrence of EDCs in aquatic systems is a very complex and sensitive issue. A complete assessment of potential effects of EDCs in the Big Sioux River in or near

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Sioux Falls based on the results of this study is not possible. However, EDC concentrations in the Big Sioux River generally were less than concentrations reported to have substantial endocrine-disrupting effects on aquatic organisms. The relatively large frequency of detection for atrazine might indicate a cause for concern with respect to endocrine-disruption effects for aquatic organisms.

Introduction

Many organic compounds used in or produced by household, industrial, and agricultural activities are soluble and resistant to wastewater treatment processes, and have been shown to occur in wastewater discharges to natural streams (Richardson and Bowron, 1985; Halling-Sorensen and others, 1998). Additionally, some of these organic wastewater compounds (OWCs) can persist in natural water systems (Barnes and others, 2002; Kolpin and others, 2002; Stackelberg and others, 2004) and potentially have long-term effects on stream biota; human exposure also might occur when those systems are used as water supplies. Some OWCs are hormonally active and have been shown to disrupt the endocrine systems of animals in laboratory studies (Jobling and others, 1996; Thorpe and others, 2001). Evidence also indicates that endocrine systems of some fish and other vertebrate animals in natural systems have been affected by OWCs (Sumpter and Johnson, 2005), although after a decade of intensive research in the laboratory and field, the mechanisms of endocrine modulation and the long-term, sublethal effects of low-level exposure to OWCs remain poorly understood. Thus, data documenting the concentrations and composition of OWC mixtures in the environment contribute to the understanding of the potential effect these chemicals might have in the environment.

Within the Big Sioux River drainage basin in eastern South Dakota (fig. 1), considerable agricultural activities occur; both crops and livestock are raised, and numerous concentrated animal feeding operations exist. Potential exists for OWCs associated with agricultural activities, including pesticides, antibiotics, and feed supplements from feeding operations, to be introduced into both surface and ground water in the basin. Additionally, wastewater discharges from some of the larger cities in South Dakota (including Watertown, Brookings, and Sioux Falls) and from several smaller cities are released directly into the Big Sioux River. These wastewater discharges also might contain OWCs.

The U.S. Geological Survey (USGS) in cooperation with the city of Sioux Falls conducted several rounds of sampling to determine the occurrence of OWCs in the city of Sioux Falls drinking water and wastewater effluent, and the Big Sioux River in or near Sioux Falls during August 2001 through May 2004. Water samples were collected from eight sites during both base-flow and runoff conditions. Bottom-sediment samples also were collected from three sites in September 2002.

The OWCs analyzed for in this study (table 7 in the Supplemental Information section at the back of this report) are classified into six compound classes: human pharmaceutical compounds (HPCs), which are commonly used prescription and non-prescription pharmaceutical drugs; human and veterinary antibiotic compounds (HVACs), which are prescription drugs used in the treatment of infectious diseases; major agricultural herbicides (MAHs), which include atrazine, metolachlor, and prometon; household, industrial, and minor agricultural compounds (HIACs), which are various generally synthetic organic compounds used for a variety of purposes including detergents, fire retardants, plasticizers, fragrances, solvents, preservatives, and disinfectants; polyaromatic hydrocarbons (PAHs), which are compounds often occurring in fossil fuels or produced by the combustion of fossil fuels; and sterol compounds (SCs), which are predominantly unsaturated solid alcohols of the steroid group naturally occurring in fatty tissues of plants and animals and present in animal fecal material. Some of the compounds in the HPC, MAH, HIAC, and PAH classes are suspected of being endocrine-disrupting compounds (EDCs).

Purpose and Scope

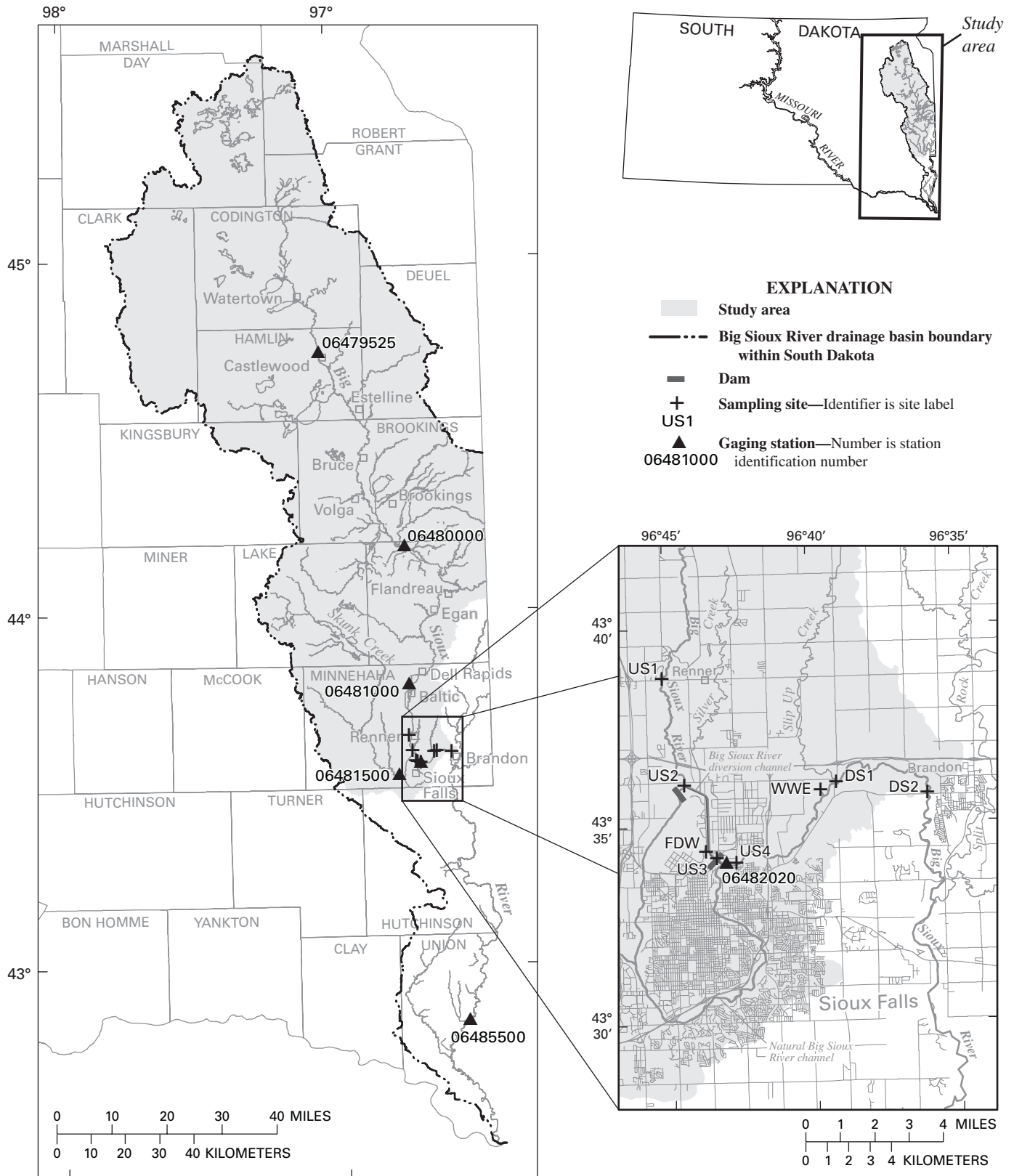
The purpose of this report is to describe the occurrence of OWCs in drinking water, wastewater effluent, and the Big Sioux River in or near Sioux Falls during 2001–2004. Specifically, this report describes the data-collection and analytical methods used in the study and the analytical results documenting the presence, concentrations, loads, and distributions of OWCs in this watershed.

Acknowledgments

The authors would like to recognize the valuable contributions to this study made by Lyle Johnson, Tim Stefanich, Kevin Smith, and Trent Lubbers of the city of Sioux Falls. Also, the authors thank the individuals involved in the field data collection for this study, including Dave Hernandez, Nate Stevens, Bryan Schaap, Mike Burr, Mark Freese, and Roy Bartholomay.

Description of Study Area

The Big Sioux River originates in northeastern South Dakota and flows to the south along the eastern edge of the State (fig. 1). The Big Sioux River drains an extended highland or plateau, the Coteau des Prairies, which is the largest single topographic feature in eastern South Dakota (Lawrence and Sando, 1989). The coteau is a 200-mi-long constructional remnant from glacial ice sheets that moved south along the eastern edge of South Dakota (Flint, 1971; Leap, 1988). The study area comprises about 5,120 mi² from a location near Brandon, South Dakota, upstream to the headwaters of the Big Sioux River



Base from U.S. Geological Survey digital data, 1:100,000, 1985
 Universal Traverse Mercator projection, zone 14

Figure 1. Location of study area.

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(fig. 1). Sampling sites were focused in or near Sioux Falls, South Dakota.

The climate in the study area is continental and is characterized by large seasonal and daily variations in temperature. The normal (1971–2000) mean daily July temperature at Sioux Falls is about 22.8°C, and the normal mean daily January temperature is about -10.0°C. Normal annual precipitation is about 25 in. (South Dakota State University, 2005). On average, about 81 percent of annual precipitation occurs as rainfall during the months of April through October.

Land use in the study area primarily is agricultural with corn, wheat, soybeans, miscellaneous small grains, and alfalfa as the major crops (Lawrence and Sando, 1989). Livestock raised in the basin primarily include dairy cattle, beef cattle, and hogs. The cities of Watertown, Brookings, and Sioux Falls are the major urban areas in the study area. Smaller cities in the study area that are close to the Big Sioux River channel include Castlewood, Estelline, Bruce, Volga, Flandreau, Egan, Dell Rapids, Baltic, and Renner (fig. 1).

Outwash deposits along the Big Sioux River and its tributaries underlie much of the Big Sioux River Basin (Lawrence and Sando, 1989). These outwash deposits include the various units of the Big Sioux aquifer, which is one of the more extensively developed aquifers in South Dakota. The outwash deposits consist of cross-bedded gravel, sand, and silt that range in thickness from a few feet to about 200 ft, and range in depth below land surface from about 1 to 100 ft (Lawrence and Sando, 1989). Many of the outwash deposits have areas where they are hydraulically connected with the Big Sioux River.

The Big Sioux River is a major tributary to the Missouri River in eastern South Dakota. The mean annual streamflow of the Big Sioux River for water years 1977–2004 is about 99 ft³/s for USGS gaging station 06479525 (located about 15 river miles downstream from the city of Watertown; contributing drainage area is about 780 mi²), about 434 ft³/s for USGS gaging station 06480000 (located about 20 river miles downstream from the city of Brookings; contributing drainage area is about 2,665 mi²), about 577 ft³/s for USGS gaging station 06481000 (located about 23 river miles upstream from the Sioux Falls city limits; contributing drainage area is about 3,250 mi²), about 732 ft³/s for USGS gaging station 06482020 (located in the city of Sioux Falls (shown as site US4 in fig. 1); contributing drainage area about 3,975 mi²), and about 1,935 ft³/s for USGS gaging station 06485500 (located about 55 river miles upstream from the confluence with the Missouri River near Sioux City, Iowa; contributing drainage area is about 7,345 mi²).

The Big Sioux River channel in the Sioux Falls area has been substantially modified from its natural condition primarily for flood control and water-level management. In 1961, the U.S. Army Corps of Engineers completed construction of a channelization, levee, and diversion dam project to reduce effects from flooding of the Big Sioux River and Skunk Creek on Sioux Falls. One of the major aspects of this project was the construction of a diversion dam and channel near the northern edge of Sioux Falls that allows the flow of the Big Sioux River to be routed either through the natural Big Sioux River channel

(which flows along the western and southern edges and through the center of Sioux Falls; fig. 1) or through the diversion channel (which bypasses most of Sioux Falls). A second low-head diversion dam is located on the diversion channel and functions to maintain the water level in the diversion channel to facilitate pump withdrawals from the Big Sioux River for the Sioux Falls drinking-water supply. Prior to 1990, the city of Sioux Falls relied entirely on ground water for its water supply. In late 1990, the city completed construction of an intake structure to withdraw and treat surface water from the Big Sioux River to provide drinking water. Since that time, the city has maintained a goal of obtaining at least 50 percent of its annual drinking-water supply directly from the Big Sioux River (Kevin Smith, Sioux Falls Public Works Department, written commun., May 2005).

During precipitation events, a substantial amount of the stormwater drainage from Sioux Falls flows into the natural Big Sioux River channel. Also, Skunk Creek, with a contributing drainage area of about 610 mi², enters the natural Big Sioux River channel in the southwest part of Sioux Falls.

Sioux Falls is the largest city in South Dakota with a population of about 124,000 (U.S. Census Bureau, 2005) and a land area of about 63 mi² (Kevin Smith, Sioux Falls Public Works Department, written commun., March 2005). Characteristics of the wastewater treatment plant (WWTP) for Sioux Falls are presented in table 1. The Sioux Falls WWTP discharges

Table 1. Selected characteristics of the Sioux Falls wastewater treatment plant.

Population served	123,975
Population density (people per square mile)	1,967.9
Design capacity (million gallons per day)	13.43
Number of permitted industries	20
General description of permitted industries	Farm, fire, and industrial equipment manufacturers, hospitals, electronics equipment manufacturer, metal fabricator, livestock sales, meat packing, fluid dairy and juices, bakery, prison, airport, cardboard box manufacturer, concrete products, truck wash
Preliminary treatment	Screening and grit removal
Primary treatment	Settling basin clarification
Secondary treatment	Trickling filtration, secondary clarification
Tertiary treatment	Aerated activated-sludge processing, sand gravity filtration, chlorine disinfection, sulfur dioxide to neutralize chlorine, post-treatment aeration
Primary sludge treatment	Anaerobic digestion

continuously to the Big Sioux River. During low-flow periods, the Sioux Falls WWTP effluent discharges can account for more than 50 percent of the Big Sioux River streamflow downstream from the effluent discharges. Wastewater effluent leaves the Sioux Falls WWTP in a concrete pipe about 0.2 mi in length that discharges directly to the Big Sioux River.

Methods of Study

Water samples were collected at eight sites to investigate the occurrence of OWCs in drinking water, wastewater effluent, and the Big Sioux River (fig.1; table 2) in or near Sioux Falls. The primary sampling objectives evolved during the course of sampling activities. Initially, a single round of sampling was conducted during August 2001 at three sites to determine whether detectable concentrations of OWCs were present in (1) raw water withdrawn from the Big Sioux River for treatment to supply drinking water, (2) finished drinking water in the drinking-water distribution system, and (3) the Big Sioux River downstream from the Sioux Falls urban area and the Sioux Falls wastewater effluent discharge.

After detectable concentrations of OWCs were found in the August 2001 Big Sioux River samples, four rounds of sampling were conducted during September 2002 through June 2003 (two during base-flow conditions and two during storm-runoff conditions) primarily to investigate the relative contribution of the Sioux Falls wastewater effluent discharge to the occurrence of OWCs in the Big Sioux River downstream from Sioux Falls. The results of these four rounds of sampling gener-

ally indicated that during below-normal base-flow periods, the primary source of OWCs in the Big Sioux River downstream from Sioux Falls probably was the Sioux Falls WWTP discharge. However, during storm-runoff conditions, loads of OWCs in the Big Sioux River downstream from Sioux Falls were substantially larger than what could only be accounted for by the Sioux Falls WWTP discharge. The network of sampling sites for the September 2002 through June 2003 sampling rounds was not adequate to confidently identify the possible sources of OWCs other than the Sioux Falls wastewater effluent discharge.

To better understand possible sources of OWCs in the Big Sioux River during storm-runoff conditions, two rounds of sampling were conducted during May 2004. Additional sampling sites were included in these sampling rounds.

Sampling Sites

A labeling scheme is used for the sampling sites consisting of a three-character identifier of the sample medium and the relation between the sampling site and the wastewater effluent (tables 2 and 3). The three-character identifiers are defined as follows:

- US1 = Big Sioux River near Renner; Big Sioux River sampling site farthest upstream from the Sioux Falls WWTP discharge; substantially upstream from any influences from the city of Sioux Falls and isolated from substantial road traffic;

Table 2. Sampling sites and streamflow-gaging stations.

[mi², square miles; e, estimated; --, not applicable]

Site label	Station identification	Station name	Drainage area (mi ²)	Contributing drainage area (mi ²)	Latitude (degrees, minutes, seconds)	Longitude (degrees, minutes, seconds)
--	06481000	Big Sioux River near Dell Rapids, SD	e4,330	e3,250	43° 47' 25"	096° 44' 42"
US1	433843096450500	Big Sioux River near Renner, SD	e4,365	e3,285	43° 38' 43"	096° 45' 05"
US2	433600096442400	Sioux Falls pump station intake from Big Sioux River at Sioux Falls, SD	e4,400	e3,320	43° 36' 00"	096° 44' 24"
FDW	433419096434200	Sioux Falls water treatment plant finished water at Sioux Falls, SD	--	--	--	--
US3	433408096432000	Big Sioux River diversion channel at North Drive at Sioux Falls, SD	e4,405	e3,325	43° 34' 08"	096° 43' 20"
US4	06482020	Big Sioux River at North Cliff Avenue, at Sioux Falls, SD	e5,065	e3,975	43° 34' 01"	096° 42' 39"
WWE	433531096394200	Sioux Falls wastewater treatment plant effluent	--	--	--	--
DS1	433559096390700	Big Sioux River downstream from Sioux Falls wastewater discharge	e5,110	e4,020	43° 35' 59"	096° 39' 07"
DS2	433541096355800	Big Sioux River at Brandon, SD	e5,120	e4,030	43° 35' 41"	096° 35' 58"
--	06485500	Big Sioux River at Akron, IA	e8,425	e7,345	43° 47' 25"	096° 44' 42"

Table 3. Intervening reach lengths between selected locations.

Starting location	Ending location	Intervening reach length (river miles)
USGS gaging station 06481000	Study sampling site US1	16.4
Study sampling site US1	Study sampling site US2	4.0
Study sampling site US2	Study sampling site US3	2.6
Study sampling site US3	Study sampling site US4 (USGS gaging station 06482020)	.6
Study sampling site US2	Study sampling site US4 (USGS gaging station 06482020) (through the natural Big Sioux River channel)	16.4
USGS gaging station 06481500	Study sampling site US4 (USGS gaging station 06482020) (through the natural Big Sioux River channel)	11.8
Study sampling site US4 (USGS gaging station 06482020)	Confluence of Sioux Falls wastewater treatment plant effluent and Big Sioux River	4.2
Confluence of Sioux Falls wastewater treatment plant effluent and Big Sioux River	Study sampling site DS1	.6
Study sampling site DS1	Study sampling site DS2	4.3

- US2 = Sioux Falls pump station intake from Big Sioux River at Sioux Falls; Big Sioux River sampling site second most upstream from the Sioux Falls WWTP discharge; intake for Sioux Falls drinking water where two low-head dams create a backwater pool on the Big Sioux River; located just downstream from where the Big Sioux River enters the Sioux Falls urban area; in an area of moderate-volume road traffic and downstream from a small amount of stormwater runoff from the Sioux Falls urban area;
- FDW = Sioux Falls water treatment plant finished water at Sioux Falls; city of Sioux Falls finished drinking water;
- US3 = Big Sioux River diversion channel at North Drive at Sioux Falls; Big Sioux River sampling site third most upstream from the Sioux Falls WWTP discharge; Big Sioux River diversion channel just upstream from confluence with natural Big Sioux River channel; in an area of moderate-volume road traffic and can be influenced to a small degree by stormwater runoff from the Sioux Falls urban area;
- US4 = Big Sioux River at North Cliff Avenue, at Sioux Falls; Big Sioux River sampling site closest upstream from the Sioux Falls WWTP discharge; just downstream from confluence of natural Big Sioux River channel and diversion channel; in an area of high volume road traffic and downstream from nearly all stormwater runoff from the Sioux Falls urban area; a short distance upstream from US4 is a meat packing plant that discharges an average of about 4 ft³/s of effluent to the Big Sioux River;
- WWE = Sioux Falls WWTP effluent;
- DS1 = Big Sioux River downstream from Sioux Falls WWTP discharge; Big Sioux River sampling site

closest downstream from the Sioux Falls WWTP discharge; and

- DS2 = Big Sioux River near Brandon; Big Sioux River sampling site farthest downstream from the Sioux Falls WWTP discharge.

Collection, Processing, and Analysis of Water and Bottom-Sediment Samples

Water samples were collected at sites in or near Sioux Falls during seven sampling periods: August 15–16, 2001, September 9–11, 2002, January 22–24, 2003, March 19–21, 2003, June 25–27, 2003, May 17–18, 2004, and May 30–31, 2004. Because the primary sampling objectives changed during the course of sampling activities, not all sampling sites were sampled during every sampling round. During all sampling periods, the Sioux Falls WWTP was continuously discharging to the Big Sioux River.

Variability in the flow of the Big Sioux River during the sampling periods (especially for the runoff sampling periods) complicates the ability to directly compare OWC loads and concentrations between sites for a given sampling period. Available resources did not allow conducting a Lagrangian scheme that samples a given pulse of water as it moves downstream. However, during a given sampling period, the timing of sample collection at each site was designed to generally provide reasonable representation of the streamflow conditions that were occurring in the Sioux Falls area during the sampling periods.

At Big Sioux River sampling sites (except US2 where Big Sioux River water is pumped from a backwater pool into the intake pipe of the Sioux Falls drinking-water treatment system), streamflow was measured using standard USGS procedures (Rantz and others, 1982a; Rantz and others 1982b). WWTP discharges at the time of sampling were determined from monitoring records provided by the city of Sioux Falls (Trent Lubbers,

Sioux Falls WWTP operator, written commun., 2005). For site US2, streamflow was estimated by analyzing the Big Sioux River flow at upstream and downstream sites. Other field-measured properties and constituents were determined using standard USGS procedures (U.S. Geological Survey, 1997–2004) (table 7).

Water-quality samples for analysis of OWCs were collected and processed using standard USGS techniques (U.S. Geological Survey, 1997–2004). Containers and sampling equipment contacting the sample water were constructed of fluorocarbon polymer, glass, aluminum, or stainless steel and were rigorously cleaned using standard USGS procedures. Ultra-clean two-person sampling procedures were used and sampling teams wore powderless nitrile gloves. Special requirements for collection of wastewater, pharmaceutical, and antibiotic compounds also were adhered to (U.S. Geological Survey, 1997–2004), including avoiding use of insect repellents, sunscreen, tobacco, caffeine, and pharmaceutical drugs by the sampling team.

Wastewater effluent samples were collected using a depth-integrated grab from the centroid of the effluent channel downstream from all treatment activities. Water samples for Big Sioux River sites (except US2) were collected using standard USGS width- and depth-integrating procedures, generally at 5 to 10 verticals across the sampling transect. For site US2, water samples were collected directly from a tap on the intake pipe of the Sioux Falls drinking-water treatment system. Following collection, samples were composited into a glass or fluorocarbon polymer compositing container that was immediately chilled and transported to a laboratory processing area. Samples were processed at the laboratory processing area within a few hours of sample collection. The composite samples were split, filtered (if required), decanted into final sample bottles, packaged with ice, and sent by 1-day shipping to the analytical laboratories. Where appropriate, filtration was performed by passing sample water through a pre-conditioned 0.7-micrometer (μm), nominal-pore-size, baked glass-fiber filter. In this report, constituents in filtered water samples are referred to as “dissolved,” which is operationally defined as that part of a water sample that passes through a 0.7- μm , nominal-pore-size, baked glass-fiber filter. Constituents in unfiltered water samples are referred to as “whole water.”

Bottom-sediment samples were collected from three sampling sites (US2, DS1, and DS2) during the September 2002 sampling period. Samples were collected following procedures described by Shelton and Capel (1994). All sampling equipment and containers contacting the bottom-sediment samples were constructed of stainless steel or glass, and were rigorously cleaned using standard USGS procedures. Ultra-clean two-person sampling procedures were used, and sampling teams wore powderless nitrile gloves. At each sampling site, 10 subsamples of fine-grained material were collected from the upper few centimeters of the stream bottom in depositional zones within about 300 ft of the water-sampling cross section. The subsamples were sieved through a 2-mm stainless-steel sieve into a compositing container and thoroughly homogenized. A

sample of the composited homogenate was placed into a glass sample container, placed on ice, and sent in for analysis.

A total of 125 different OWCs were analyzed for in this study using five different analytical methods. Analyses for OWCs were performed at USGS laboratories that are developing and/or refining small-concentration (less than 1 microgram per liter ($\mu\text{g/L}$)) analytical methods. The following five analytical methods were used:

Analytical method 1 (performed at USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado) determined 20 prescription and nonprescription HPCs and selected metabolites and 4 HVACs in filtered water samples (table 7; Cahill and others, 2004) by using hydrophilic-lipophilic-balance (HLB) solid-phase extraction (SPE) cartridges. Pharmaceuticals concentrated in sample extracts were separated, identified, and quantified by reversed-phase, high-performance liquid chromatography/electrospray ionization mass spectrometry (HPLC/ESI-MS) using selected ion monitoring (SIM) and operated in the positive ionization mode.

Analytical method 2 (performed at the USGS Organic Geochemistry Research Laboratory (OGRL) in Lawrence, Kansas) determined 43 human and veterinary antibiotic compounds in filtered water samples (table 7). Water samples were analyzed for compounds primarily in the *beta*-lactam, macrolide, quinoline, sulfonamide, and tetracycline classes of antibiotics. The *beta*-lactams, macrolides, quinolones, sulfonamides, and tetracyclines were analyzed separately using online SPE methods and HPLC/ESI-MS in positive-ion mode. Samples were extracted for the *beta*-lactams, macrolides, quinolones, and sulfonamides using Prospekt cartridges (Waters) and for the tetracyclines using a proprietary Glyphosate Prospekt cartridge (Spark-Holland). The antibiotics for each class were eluted and separated using liquid chromatography gradient. Individual antibiotic compounds were analyzed using SIM and were identified using retention times and the ratio(s) of a quantifying ion to one or two confirming ions. The antibiotic compounds were quantified using the ratio of the area of the base-peak ion of the analyte to the area of the base-peak ion of the internal standard. Prior to December 2003, samples were analyzed at OGRL using a single quadrupole HPLC mass spectrometer. After December 2003, samples were analyzed at OGRL using a triple quadrupole HPLC mass spectrometer that reduced the laboratory reporting levels (LRL) by a factor of about 10.

Analytical method 3 (performed at NWQL) determined 2 nonprescription HPCs, 3 MAHs, 50 HIACs, 10 PAHs, and 4 SCs in whole-water samples (table 7). Target compounds were extracted from water samples using continuous liquid-liquid extraction with methylene chloride at pH 2.0 (Lee and others, 2004). Extracts were separated and measured by gas chromatography/mass spectrometry using electron impact ionization and operated in the full-scan mode.

Analytical method 4 (performed at NWQL) determined 2 nonprescription HPCs, 2 MAHs, 43 HIACs, 10 PAHs, and 4 SCs in filtered samples (table 7). Target compounds were extracted from water samples by vacuum through disposable

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SPE cartridges that contain polystyrene-divinylbenzene resin. Sorbed compounds were eluted with dichloromethane-diethyl-ether. Compounds were measured by capillary-column gas chromatography/mass spectrometry. Other procedures of analytical method 4 were similar to method 3 but were performed on filtered samples (Zaugg and others, 2002).

Analytical method 5 (performed at NWQL) determined 3 MAHs, 44 HIACs, 10 PAHs, and 4 SCs in bottom sediment (table 7) using procedures described by Burkhardt and others (2005). Compound concentrations in solids samples were measured by placing a wet sediment sample in a stainless-steel cell and extracting it using an accelerated solvent extraction (ASE) system (Dionex ASE 200) with isopropyl alcohol/water. The compounds were then isolated from the ASE extracts using SPE cartridges (Waters, OASIS HLB polystyrenedivinylbenzene phase). The SPE cartridges were then dried, and a Florisil SPE cartridge was attached at the base to provide additional extract cleanup during elution with dichloromethane/diethyl ether. The volume of the extract was reduced under a gentle stream of nitrogen, and the methods compounds were analyzed by gas chromatography/mass spectrometry.

The determination of compounds of interest was a two-step process. First the compound was qualitatively identified followed by a quantitative determination of concentration. Strict criteria were used to assess both steps prior to reporting a compound and its concentration (Barnes and others, 2002; Kolpin and others, 2002; Lee and others, 2004). The first step of qualitative identification was the presence of the compound of interest within an expected chromatographic retention time. If present within the chromatographic window, compound mass spectrum and diagnostic ion abundance ratios were required to match that of the reference compound standard. After qualitative identification criteria were attained, analyte concentrations were calculated using a 5- to 8-point calibration curve (concentrations generally from 0.01 to 10.0 µg/L) using internal standard quantitation. The most abundant ion typically was used for quantitation, and, if possible, as many as two diagnostic fragment qualifier ions were used for ion abundance ratio confirmation. For method 2, calibration standards were processed throughout the extraction procedure, which generally corrects concentrations for methodological losses during extraction but not for matrix effects. Methods 1, 3, 4, and 5 did not extract calibration standards; thus, the reported compound concentrations determined using these methods were not corrected for method losses.

LRLs were determined for each analyte by a previously published procedure (U.S. Environmental Protection Agency, 1992) for methods 1, 3, 4, and 5. Selected analyte concentrations were flagged with an “e” to indicate estimated values. Several of the reasons that the concentration of a qualitatively identified compound was reported as an estimate include concentrations that fell outside the calibration range, concentrations for analytes with average recoveries less than 60 percent, analytes routinely detected in laboratory blanks, and constituents with reference standards prepared from technical mixtures (Barnes and others, 2002; Kolpin and others, 2002; and Lee and

others, 2004). Quality-assurance/quality-control (QA/QC) data were analyzed in detail, and for compounds that were determined to have acceptable QA/QC results, estimated values flagged with an “e” were considered to be reasonable estimates of actual concentrations and were included in analyses and discussions related to occurrence of OWCs.

In addition to the OWCs in table 7, samples also were analyzed for bromoform and four human hormone compounds (17-*beta*-estradiol, equilenin, estrone, and ethynyl estradiol). Bromoform is a volatile organic compound that typically occurs as a disinfection by-product and requires special sampling procedures (that were not used in this study) for accurate quantitation. Thus, analytical results for bromoform are not included in this report. NWQL has determined that the performance of the analytical methods for the four human hormone compounds have not yet been adequately verified to report the analytical results, given the particularly sensitive nature of the occurrence of these compounds in aquatic systems. Thus, analytical results for the four human hormone compounds are not included in this report.

Five OWCs—two HPCs (caffeine and cotinine) and three HVACs (erythromycin, sulfamethoxazole, and trimethoprim)—were determined by more than one analytical method. For each of these compounds, QA/QC results and LRLs were investigated, and the analytical method judged to provide the best performance was selected. Only the results for the selected method were included in analyses and discussion related to occurrence of OWCs in wastewater effluents and the Big Sioux River.

For the two May 2004 sampling periods, 2 HPCs, 2 MAHs, 43 HIACs, 10 PAHs, and 4 SCs were determined by analytical methods 3 and 4, on whole-water and filtered samples, respectively. QA/QC results and LRLs were investigated to assess performances of the two methods for each constituent. Analytical results also were investigated to determine whether whole-water concentrations were substantially larger than dissolved concentrations (that is, whether a substantial amount of the constituent was in the particulate phase), which could provide information concerning possible sources of OWCs. Only the results from one of the methods were included in summary analyses and discussion related to occurrence of OWCs in wastewater effluents and the Big Sioux River. Generally, selection of analytical method 3 results for inclusion in summary analyses and discussion was deemed preferable because it provides greater consistency than method 4 for comparison of the results of the May 2004 sampling periods with previous sampling periods. However, for several constituents, percent recoveries for laboratory reagent spikes and/or environmental matrix spikes were noticeably better (that is, closer to 100 percent) for analytical method 4 than for analytical method 3, and the analytical method 4 results were judged to provide the best method performance and were included in summary analyses and discussion. This might slightly affect the comparability of OWC concentrations between the May 2004 sampling periods and the previous sampling periods. Information on which constituents

were included in summary analyses and discussion for each sampling period is presented in table 7.

Calculation of Loads

Loads of OWCs were estimated to provide coarse information on sources and fate of OWCs in the Big Sioux River. Because non-Lagrangian sampling was conducted, no attempt was made to sample a specific pulse of water as it moved downstream. Thus, exact correspondence between water samples collected at different sampling sites would not be expected. A primary effect on comparison of loads between sites could be diurnal variability in the magnitude of WWTP effluent discharges and concentrations of OWCs in the wastewater effluent. The largest effect of this variability would occur when comparing concentrations and loads of OWCs for the WWTP effluent discharge with those for Big Sioux River sampling sites downstream from the WWTP effluent discharge for a given sampling period. Diurnal variability of the WWTP effluent discharge generally was about 10 ft³/s for most sampling periods. Typical daily operations of the Sioux Falls WWTP result in smaller and more variable discharges from about 2:00 a.m. to about 9:00 a.m., and larger and mostly stable discharges from about 9:00 a.m. to about 2:00 a.m. For sampling periods when the WWTP effluent discharge was sampled, sample collection at downstream Big Sioux River sampling sites generally was conducted such that the part of the sampled Big Sioux River discharge that was contributed by the WWTP effluent discharge was very similar to the WWTP effluent discharge at the time that the WWTP effluent discharge was sampled. However, no data were collected to evaluate diurnal variability in concentrations of OWCs in the WWTP effluent; the effect of this variability on comparison between concentrations and loads of OWCs for downstream Big Sioux River sampling sites and the WWTP effluent discharge is unknown.

Loads of OWCs were estimated by multiplying discharges at the times of sampling by constituent concentrations and by a conversion factor (0.0053919) to convert cubic feet per second and micrograms per liter to pounds per day. For constituents reported as less than the study reporting level (SRL) (defined in the Quality Assurance/Quality Control section), the concentrations were assumed to be zero in the load calculations. Load values are reported to two significant figures.

The load estimates presented in this report should be used with caution. Possible effects of non-Lagrangian sampling have been described. Also, most of the OWC concentrations were very small (often near the lower limits of analytical quantitation) and reported by the laboratories as estimated values. The multiplication of the concentrations by discharge, which can vary substantially from site to site and for some sampling periods was very large, might result in substantially increasing the effect of analytical error in the reported load estimates. However, although the error in the absolute values of the load estimates may be substantial, the load estimates probably provide

reasonably accurate estimates for relative comparison between sites and between sampling periods.

Quality Assurance/Quality Control

Analytical results for OWCs presented in this report require additional interpretive effort not typically necessary for other water-quality constituents that usually occur at larger concentrations. Many OWCs were analyzed for in this study and substantial differences exist in the capability to quantify low-level (part-per-billion and lower) concentrations of individual compounds. For the five analytical methods used in this study, method performance can vary substantially between methods, and between compounds within a given method because of the range of chemical classes and properties of the compounds included in any one method. Also, because several of these OWCs (including the plasticizers, surfactants, and caffeine) are widely used in common consumer and industrial products, the risk of sample contamination in either the laboratory or the field varies between compounds and may be an important issue in low-level analysis of some trace OWCs. These factors result in variable precision/accuracy among compounds and complicate presentation of OWC analytical results.

The long-term performance for a given compound in any of the analytical methods used in this study spans a continuum. Establishing specific QA/QC criteria to define an “acceptable performance” range within this continuum typically is done in analytical chemistry practice. However, such criteria are inherently arbitrary and can exclude detections that violate the specified criteria but for which qualitative identification are reliable. This can be the case for some compounds determined by the analytical methods used in this study, which rely on mass spectrometry. Thus, when a concentration is qualified by the laboratories as “estimated,” it serves as a categorical warning to pay particular attention to potential use of the numerical concentration, but not as a distinct boundary between “good” and “poor” data.

Given these complications, possible approaches for presentation of OWC analytical results that address the inherent complications include:

- Approach 1: reporting OWC analytical results in a manner that lessens the effect of precision/accuracy variability by focusing on presence/absence instead of quantification (for example, reporting frequency of detection instead of concentrations);
- Approach 2: selecting rigorous QA/QC criteria for screening analytical results and only presenting or discussing analytical results that are tightly controlled and have a very high probability of accurately representing “true” concentrations;
- Approach 3: selecting broader QA/QC criteria for screening analytical results, excluding from discussion compounds and concentration ranges that clearly are not accurately quantified, but presenting and discussing semiquantitative results for a larger set (than

Approach 2) of compounds and concentration ranges for which analytical results are determined to reasonably accurately represent “true” concentrations.

Selection of an appropriate approach for presenting OWC analytical results is subjective and dependent upon study objectives. Approaches 1 and 2 probably represent a more conservative presentation of OWC analytical results than Approach 3. However, these approaches truncate the data set, and potentially valuable information relevant to study objectives might be excluded from discussion. Approach 1 limits data presentation to simple qualitative categories of “presence/absence;” potentially useful semiquantitative information contained in the relative magnitudes of concentrations is excluded. Approach 2 might result in presentation of tightly controlled data for few compounds meeting rigorous QA/QC criteria, but useful semiquantitative information for many other compounds might be excluded. Approach 3 requires greater effort to define and report the selected QA/QC screening criteria but could provide additional valuable semiquantitative information on the occurrence of OWCs.

Approach 3 was selected for use in this report. Detailed information concerning QA/QC screening criteria is presented in this report to allow evaluation of levels of uncertainty associated with reported concentrations. Because some of the analytical methods for OWCs are relatively new or still in development, the QA/QC screening criteria used in this study were less amenable to stringent quantitative limits than those for well-established analytical methods; thus, screening criteria used in this study probably are broader than those for many water-quality studies. In general, individual concentrations presented in this report should be considered semiquantitative estimates (even though QA/QC results for many of the compounds would satisfy even very strict precision/accuracy criteria). Qualifying the data as semiquantitative does not undermine the suitability of the data for meeting important objectives of this study, which included investigation of the “relative” variability in OWC occurrence between different sites and between different sampling periods. Analytical results for OWCs that passed QA/QC screening criteria were determined to be appropriate for this purpose. Within this report, if a specific concentration for a specific compound is of particular interest to the reader, the QA/QC data presented in the report need to be reviewed in detail to better evaluate the uncertainty associated with the specific reported concentration.

Water Samples

QA/QC samples were collected to assess precision and accuracy of analytical results for water samples. For the water-sample results, QA/QC data were used to determine which compounds had acceptable method performance and to establish SRLs for individual OWCs. QA/QC included both laboratory and field activities.

Laboratory QA/QC procedures included processing and analyzing method-blank and reagent-spike samples, and adding

surrogate compounds to all laboratory QA/QC samples, field QA/QC samples, and environmental samples. Method-blank samples consist of analyte-free water that is processed and analyzed in the laboratory identically to environmental samples. Method-blank samples are used to evaluate possible introduction of method compounds or interferences in the laboratory setting. For compounds that were detected in laboratory method-blank samples, a screening level of five times the detected concentration was applied by the laboratories to reported detected concentrations in environmental samples associated with the method-blank samples with detections (that is, concentrations in environmental samples detected by the laboratories that were less than five times the detected concentration in the laboratory method-blank samples were reported as less than the LRL). Reagent-spike samples consist of a reagent water sample that is fortified with known concentrations of the method analytes. Reagent-spike samples are used to monitor the performance of a given analytical method (in the absence of environmental matrix influences) at the time the environmental samples were analyzed, and in aggregate to assess the long-term performance of the method over the course of the study. Surrogate compounds are similar in physical and chemical properties to one or more of the method analytes, and are added in known quantities to all QA/QC and environmental water samples prior to analysis. Surrogate compounds are used to assess the effects of specific environmental matrixes on the performance of a given analytical method and in some cases to assess the potential for errors during the processing of a specific environmental sample. At least one method-blank and reagent-spike sample typically are analyzed with each set of 10 to 15 environmental samples.

Field QA/QC samples included field equipment blanks, replicates, and matrix spikes. For this study, 4 to 6 field equipment-blank samples (depending on analytical method), 4 to 10 replicate samples, and 3 to 10 environmental matrix spikes were collected and analyzed for laboratory analytical constituents (table 7). This level of field QA/QC sampling represents about 50 percent of the environmental samples collected.

Field equipment-blank samples were collected at field sampling sites by passing analyte-free water through the collection and processing equipment used for environmental samples using procedures identical to those used to collect and process the environmental samples. A field equipment-blank sample with constituent concentrations equal to or less than the SRL for a given constituent indicates that the overall process of sample collection, processing, and laboratory analysis is free of significant contamination. Sporadic, infrequent detections at concentrations near the SRL probably represent random contamination or instrument calibration error that is not persistent in the process and that is not likely to cause significant positive bias in study results. Consistent detections in the field equipment-blank samples at concentrations that are substantially less than concentrations in environmental samples probably indicate routine contamination but do not substantially affect evaluation of the environmental data. None of the OWCs analyzed for in this study had consistent detections in field equipment-blank

samples. For OWCs that were sporadically detected in field equipment-blank samples, reported detected concentrations in environmental samples collected during the same sampling period as field equipment-blank samples with detections were at least five times greater than the field equipment-blank concentrations.

Field replicate samples were used to identify the level of precision (reproducibility) of analytical results at environmentally relevant concentrations. Field replicate samples were collected and processed immediately after each associated primary environmental sample was collected and processed, and procedures used for replicate samples were identical to those used for primary environmental samples. Field replicate samples are considered essentially identical in composition to the associated primary environmental samples. Precision of analytical results for field replicate samples is affected by numerous sources of variability potentially introduced by both field and laboratory processes, including sample collection, sample processing and handling, and laboratory preparation and analysis. Analyses of field replicate samples, therefore, can indicate the reproducibility of environmental data and provide information on the adequacy of procedures to produce consistent results.

Precision of analytical results for field replicate samples was determined by calculating the relative percent difference (RPD) for each primary/replicate sample pair as indicated in the following equation:

$$RPD = (d/\bar{x}) * 100, \quad (1)$$

where

- d = difference in concentration between the primary environmental sample and the field replicate sample for a given primary/replicate sample pair, and
- \bar{x} = mean concentration of the primary environmental sample and the field replicate sample for a given primary/replicate sample pair.

RPDs only were calculated for primary/replicate sample pairs in which a given compound was detected in both samples. Because many environmental OWC detections occur near the limit at which a compound can be qualitatively identified and quantified, a compound might be detected in a primary sample, but not the replicate, and vice versa. Thus, the number of primary/replicate sample pairs in which a given compound was detected in only one of the samples (but not both) was noted and also used to assess data quality and establish SRLs.

Generally, an RPD of 20 percent or less represents an acceptable level of precision, although for very small concentrations near the limit of analytical detectability, the percent differences can be substantially larger and still be considered reasonable due to the limits of resolution (Taylor, 1987). Most of the detected concentrations reported in this study are very small and near the limit of analytical detectability. Thus, a median RPD of 40 percent generally was used in this study to determine acceptability of results for field replicate samples. Three compounds (dissolved OP1EO, dissolved phenol, and whole-water pyrene) did not meet this criterion but were not

excluded from analyses and discussion. These compounds had only one primary/replicate sample pair in which the compound was detected, and the compound was detected in both the primary and replicate samples, but the RPDs exceeded 40 percent. All other QA/QC results for these compounds were examined in detail and judged to be acceptable. Because a single primary/replicate sample pair presents limited opportunity to evaluate analytical precision, and because the other QA/QC analyses for these compounds indicated acceptable analytical performance, it was determined that these compounds should not be excluded from analyses and discussion. RPDs for these three compounds ranged from 46 to 68 percent.

Environmental matrix spikes consist of replicate samples collected and processed identically to the primary environmental sample that were shipped to the laboratories where they were fortified with known concentrations of the method analytes. Concentrations of the method analytes in primary environmental samples and the environmental matrix spikes are determined, then the ambient concentrations in the primary sample are subtracted from the matrix-spike concentrations, and the resulting concentrations compared to the expected concentrations to calculate percent recoveries of analytes. Environmental matrix-spike samples are used to monitor the performance of a given analytical method for a specific environmental matrix.

Performance of the analytical methods for individual compounds was evaluated by calculating the relative standard deviation (RSD; expressed in percent) of the percent recoveries separately for laboratory reagent spikes, laboratory surrogates, and environmental matrix spikes. In the percent recovery calculations for the various spiked samples, any censored values reported as less than the LRL (for either the unspiked primary samples or the spiked samples) were arbitrarily assigned a value of zero. RSDs were computed from the standard deviations and the mean concentrations of percent recoveries for the spiked samples for a given compound. Expressing precision relative to a mean concentration standardizes comparison of precision among individual constituents. The RSD, in percent, is calculated using the following equation:

$$RSD = (S/\bar{X}) * 100, \quad (2)$$

where

- S = standard deviation of percent recoveries of spiked samples, and
- \bar{X} = mean of percent recoveries of spiked samples.

Analytical results for laboratory method blanks, laboratory reagent spikes, laboratory surrogates, field equipment blanks, field replicates, and environmental matrix spikes are summarized in tables 8–13, respectively, in the Supplemental Information section. QA/QC results were analyzed in a two-phase process that determined acceptability of analytical method performance for a given compound and then determined an SRL that represents the lower level of quantitation at which the compound could be consistently identified and reasonably accurately quantified. Acceptability of analytical method

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performance for a given compound was determined by analysis of percent recoveries for laboratory reagent spikes (table 9), laboratory surrogates (table 10), and environmental matrix spikes (table 13). Analytical method performance was considered to be acceptable when the median percent recoveries for laboratory reagent spikes, laboratory surrogates, and environmental matrix spikes were between 50 and 120 percent and when the RSDs of percent recovery for laboratory reagent spikes, laboratory surrogates, and environmental matrix spikes were less than 40 percent. Individual compounds that did not meet these method-performance acceptability criteria generally were excluded from analyses and discussion related to occurrence of OWCs in drinking water, wastewater effluent, and the Big Sioux River.

For several compounds, a single method-performance acceptability criterion was relaxed to allow inclusion of the compounds in analyses and discussion. Whole-water acetophenone, whole-water indole, and whole-water phenol had RSDs for percent recoveries for laboratory reagent-spike samples that slightly exceeded the acceptance criterion (less than 40 percent), ranging from 42 to 43 percent. Dissolved tri(2-butoxyethyl)phosphate had a median percent recovery for laboratory reagent-spike samples of 130 percent, which was outside of the acceptable range of 50–120 percent. Two compounds had median environmental matrix spike recoveries that exceeded the acceptable range (50–120 percent): whole-water 5-methyl benzotriazole (140 percent) and whole-water *beta*-sitosterol (160 percent). Three HPCs had median environmental matrix spike recoveries that were less than the acceptable range (50–120 percent): dissolved caffeine (analytical method 1; 33 percent), dissolved cotinine (analytical method 1; 41 percent), and dissolved dehydronifedipine (46 percent). One surrogate compound (dissolved fluoranthene-d10) had a median spike recovery of 123 percent, which slightly exceeded the acceptable range (50–120 percent). All other QA/QC data for these compounds (and in the case of the surrogate fluoranthene-d10, physically and chemically similar study target compounds) were acceptable, and the patterns of occurrence of the compounds in environmental samples were consistent with related compounds and intuitively reasonable. Although QA/QC acceptance criteria were relaxed for these constituents, the effect on the ability to make comparisons in results between sites and between sampling periods probably was small.

For compounds that had acceptable analytical method performance for laboratory reagent spikes and environmental matrix spikes, analytical results for laboratory method blanks (table 8), field equipment blanks (table 11), and field replicate samples (table 12) were evaluated to determine SRLs. SRLs were established to identify the lower levels of quantitation at which the compounds could be consistently identified by the analysts (determined by evaluating results for field replicate samples) and reasonably accurately quantified without being substantially influenced by routine contamination from either laboratory or field activities (determined by evaluating results for laboratory method blanks and field equipment blanks). For each compound meeting method performance criteria, the SRL

was established such that the compound was consistently detected in both samples of primary/replicate sample pairs, and the SRL generally was substantially larger than levels of contamination detected in laboratory method blanks and field equipment blanks.

There was a single detection of a compound that was not included in analyses and discussion. Isophorone was detected in a water sample collected from the Sioux Falls finished drinking water on March 19, 2003, at a very large concentration (36 µg/L). At the time of sample collection, renovation activities were being conducted at the Sioux Falls drinking-water treatment plant near the tap where the sample was collected. Isophorone is a solvent commonly found in paint, and it is likely that the detection of isophorone in the drinking-water sample occurred due to contamination of the tap from cleaning of painting equipment.

Information concerning compounds excluded from data analyses due to unacceptable method performance and the established SRLs for compounds with acceptable method performance are summarized in table 7. Of the 125 different OWCs analyzed for in this study, 81 OWCs had one or more detections in environmental water samples reported by the laboratories, and of those 81 OWCs, 63 had acceptable analytical method performance, were detected at concentrations greater than the SRLs, and were included in analyses and discussion related to occurrence of OWCs in drinking water, wastewater effluent, and the Big Sioux River.

Bottom-Sediment Samples

QA/QC data collected to assess precision and accuracy of analytical results for bottom-sediment samples were restricted to laboratory surrogates. No field QA/QC data were collected for bottom-sediment samples. Analytical results for laboratory surrogates indicated acceptable method performance for bottom-sediment analyses (table 10). Analytical results for bottom-sediment samples are presented exactly as reported by the analytical laboratories.

Occurrence of Organic Wastewater Compounds

This section of the report summarizes the occurrence of OWCs in drinking water, wastewater effluent, and the Big Sioux River in or near Sioux Falls. In addition to presenting analytical results of the OWCs, this section of the report includes results for field-measured properties and constituents. Wastewater discharges and streamflow conditions in the Big Sioux River at the time of sampling also are described.

Results for field-measured properties and constituents in water samples are given in table 14 in the Supplemental Information section. Laboratory analytical results for HPCs, HVACs, MAHs, HIACs, PAHs, and SCs in water samples are

given in tables 15–20 in the Supplemental Information section and are reported exactly as received from the laboratory. It should be noted that for some compounds, the established SRLs were larger than some of the detected concentrations reported by the laboratories. Thus, some of the reported detected concentrations in tables 15–20 were actually censored at the SRLs for the purposes of data analysis and summary. Detected concentrations greater than SRLs for compounds with acceptable QA/QC that were used in data analysis and summary related to occurrence of OWCs are noted in tables 15–20.

Summary calculations for OWCs, including total and median concentrations for compound classes, are rounded to two significant figures in this report. However, illustrations were created using unrounded raw values. Thus, there might be very small differences between values reported in text/tables and those shown in illustrations.

Streamflow Conditions and Field-Measured Properties and Constituents

Water samples were collected during base-flow and runoff conditions during summer, winter, and spring, 2001–2004. In this report, base flow is defined as flow in the stream that is not attributable to direct runoff from recent local precipitation or snowmelt. Base-flow and runoff conditions were determined by analysis of streamflow at USGS station 06482020 prior to sampling. Above-normal or below-normal flow at the time of sampling was determined by comparison to the long-term median flow (1977–2004) at USGS station 06482020 (<http://nwis.waterdata.usgs.gov>).

Streamflow conditions during sampling periods are shown in figure 2. The Sioux Falls WWTP discharged continuously to the Big Sioux River during all sampling periods. During August 15–16, 2001, above-normal flow/summer base-flow conditions existed for the Big Sioux River in the Sioux Falls area. No substantial precipitation had occurred for several days prior to sampling. Streamflow at long-term USGS gaging station 06482020 was about 250 percent of the long-term (water years 1977–2004) median mid-August streamflow (about 250 ft³/s), and the Sioux Falls WWTP effluent discharge accounted for about 4 percent of the streamflow of the Big Sioux River downstream. During September 9–11, 2002, below-normal flow/late-summer base-flow conditions existed for the Big Sioux River in the Sioux Falls area; streamflow at station 06482020 was about 35 percent of the long-term median early-September streamflow (about 200 ft³/s), and the Sioux Falls WWTP effluent discharge accounted for about 35 percent of the flow of the Big Sioux River downstream. During January 22–24, 2003, below-normal flow/winter base-flow conditions existed for the Big Sioux River in the Sioux Falls area; streamflow at station 06482020 was about 45 percent of the long-term median late-January streamflow (about 70 ft³/s), and the Sioux Falls WWTP effluent discharge accounted for about 55 percent of the flow of the Big Sioux River downstream. During March 19–21, 2003, near-normal flow/late-winter storm-runoff conditions resulting from precipitation that began on March 18 existed for the Big Sioux River in the Sioux

Falls area; streamflow at station 06482020 was about 100 percent of the long-term median late-March streamflow (about 750 ft³/s), and the Sioux Falls WWTP effluent discharge accounted for about 3 percent of the flow of the Big Sioux River downstream. During June 25–27, 2003, near-normal flow/early-summer storm-runoff conditions resulting from precipitation that began on June 24 existed for the Big Sioux River in the Sioux Falls area; streamflow at station 06482020 was about 125 percent of the long-term median late-June streamflow (about 840 ft³/s), and the Sioux Falls WWTP effluent discharge accounted for about 3 percent of the flow of the Big Sioux River downstream. During May 17–18, 2004, below-normal flow/spring storm-runoff conditions resulting from precipitation that began on May 16 existed for the Big Sioux River in the Sioux Falls area; due to an extended period of below-normal precipitation, streamflow at station 06482020 only reached a level of about 15 percent of the long-term median mid-May streamflow (about 1,000 ft³/s) during this runoff event, and the Sioux Falls WWTP effluent discharge accounted for about 15 percent of the flow of the Big Sioux River downstream. During May 30–31, 2004, above-normal flow/spring storm-runoff conditions resulting from intense precipitation that began on May 28 existed for the Big Sioux River in the Sioux Falls area; streamflow at station 06482020 was about 850 percent of the long-term median late-May streamflow (about 600 ft³/s) during this runoff event, and the Sioux Falls WWTP effluent discharge accounted for less than about 1 percent of the flow of the Big Sioux River downstream.

Results for field-measured properties and constituents in water samples are presented in table 14 and figure 3. Generally, results for field-measured properties and constituents are within typical ranges for the Big Sioux River Basin (East Dakota Water Development District, 2004).

Organic Wastewater Compounds in Water Samples

OWCs in all compound classes were detected in water samples from sampling sites in the Sioux Falls area (fig. 4, tables 21 and 22 in the Supplemental Information section). For the five sampling periods when samples were collected from the Sioux Falls finished drinking water (FDW), only one OWC was detected at a concentration greater than the SRL (metolachlor; 0.0040 µg/L). Due to the consistency in results for this site, analytical results for FDW generally are omitted from discussion in following sections.

Changes in sampling objectives during the course of sampling activities complicates presentation of results. Not all sampling sites were sampled during all sampling periods; thus, a simple and consistent format for presentation of results for the different sampling periods is not possible. For this reason, results for OWCs in water samples are presented in the following four sections: (1) occurrence of organic wastewater compounds by sampling period; (2) occurrence of organic wastewater compounds by sampling site; (3) occurrence of organic wastewater compounds by compound class; and (4) occurrence of endocrine disrupting compounds. The intent of the following

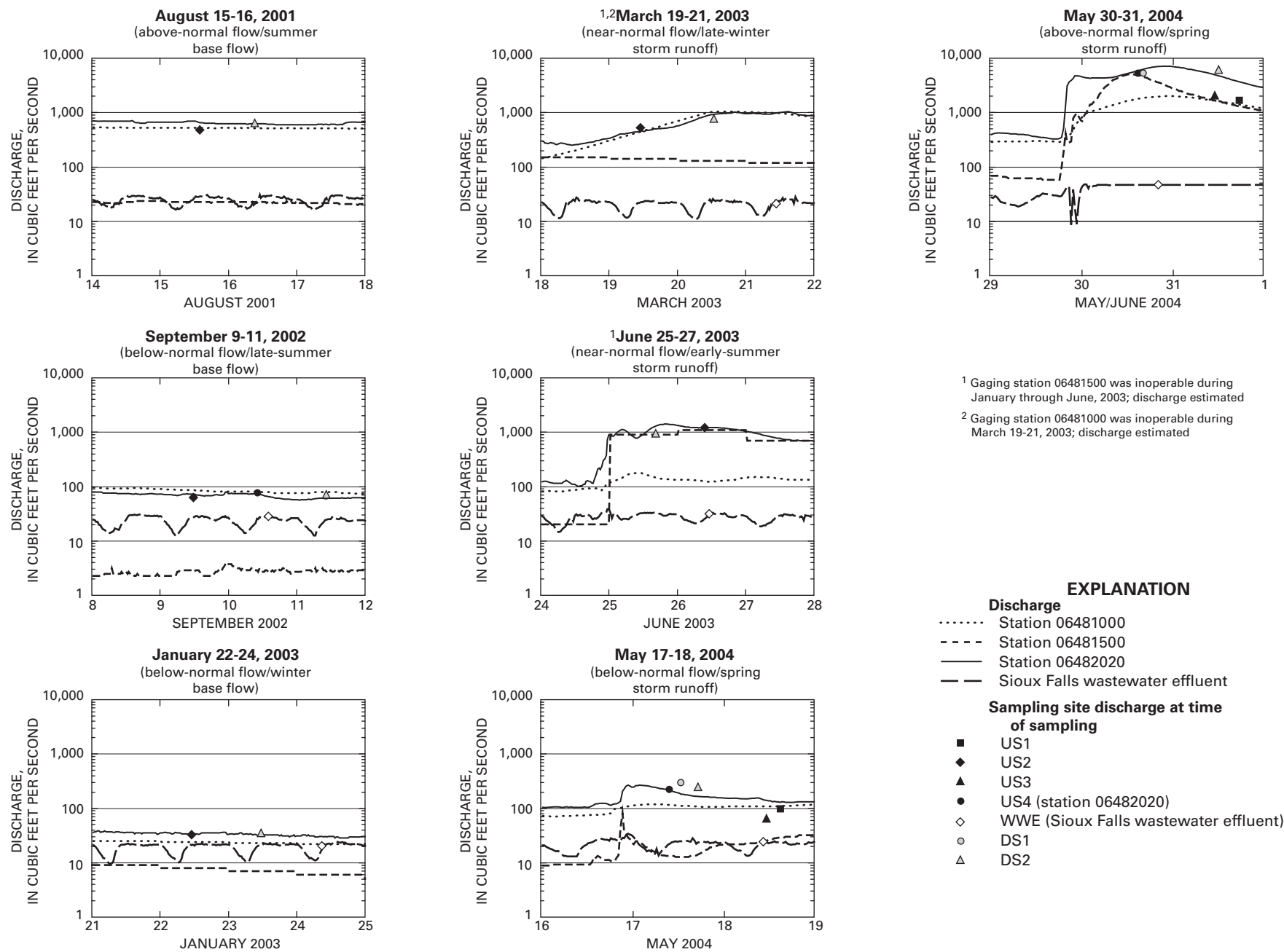


Figure 2. Flow conditions during sampling periods.

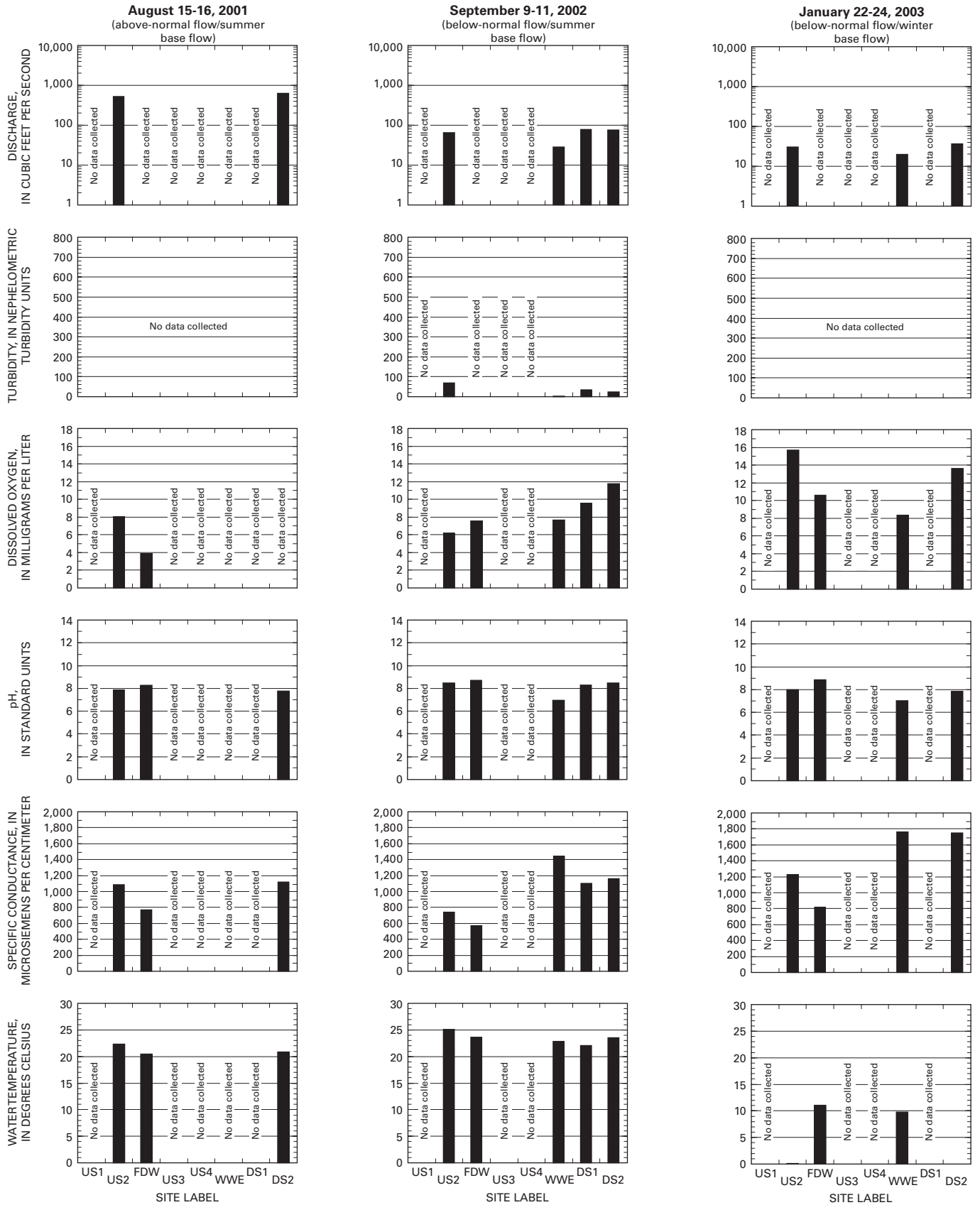


Figure 3. Results for field-measured properties and constituents.

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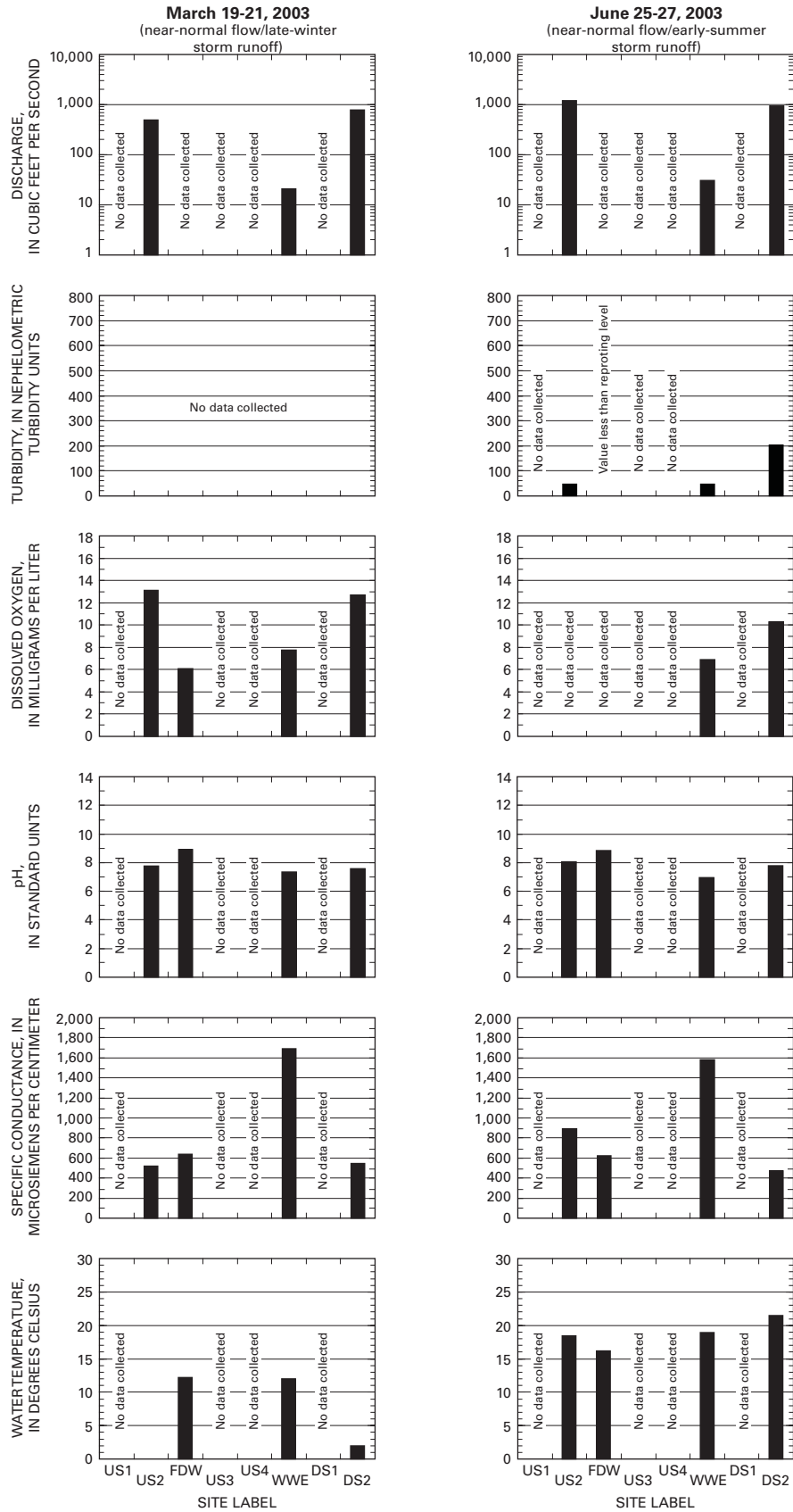


Figure 3. Results for field-measured properties and constituents.—Continued

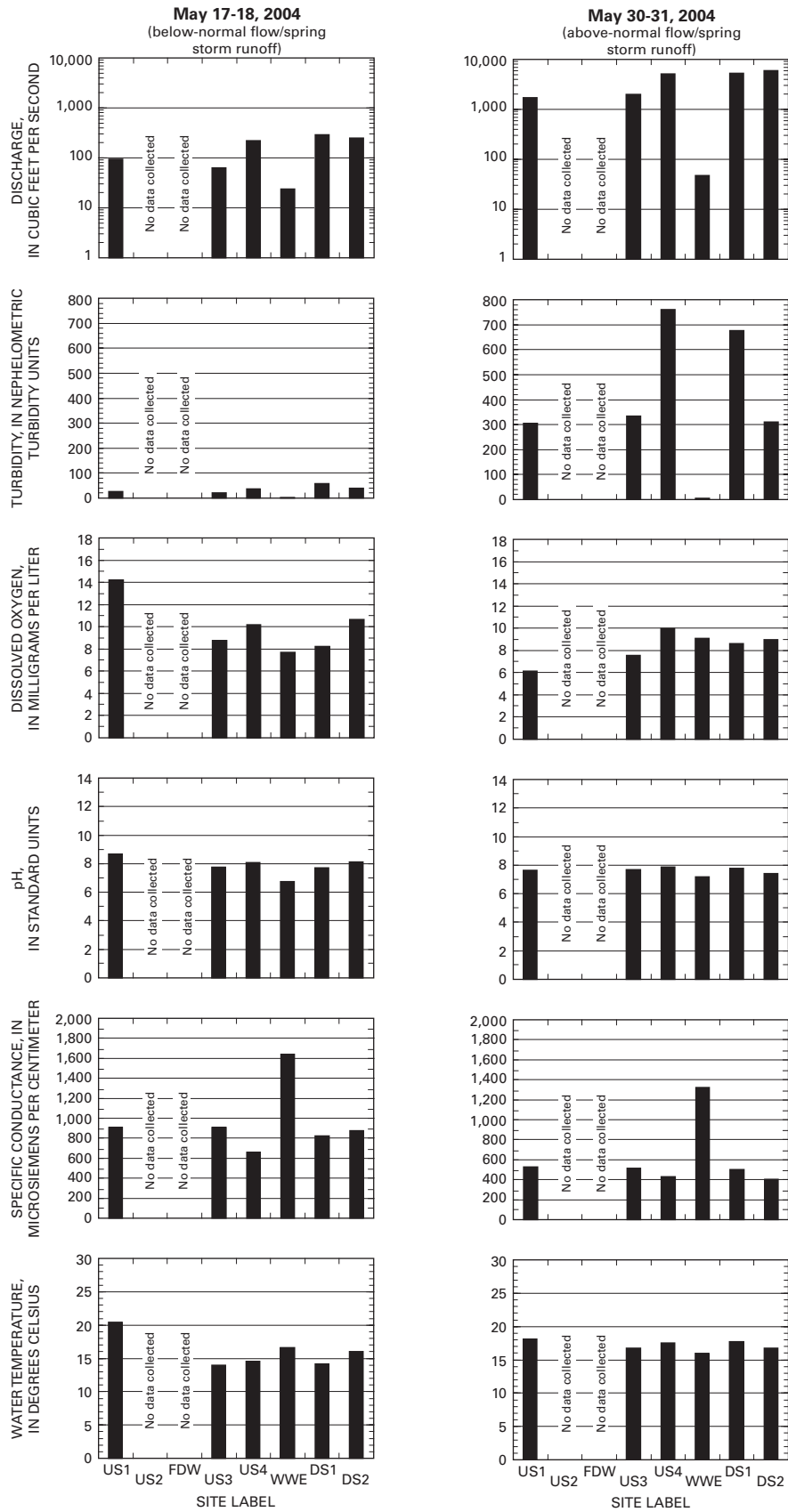


Figure 3. Results for field-measured properties and constituents.—Continued

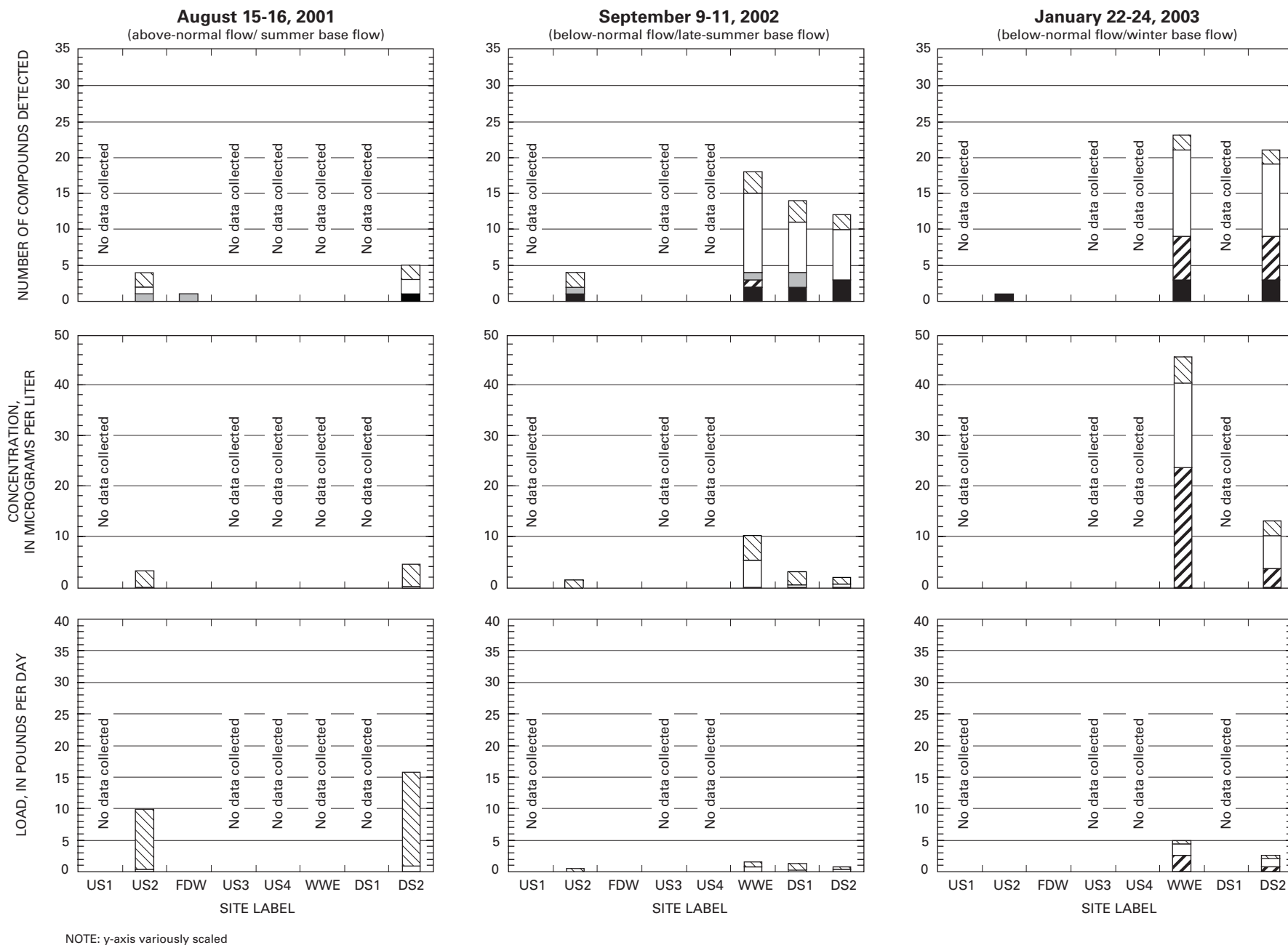


Figure 4. Results for organic wastewater compounds in water samples.

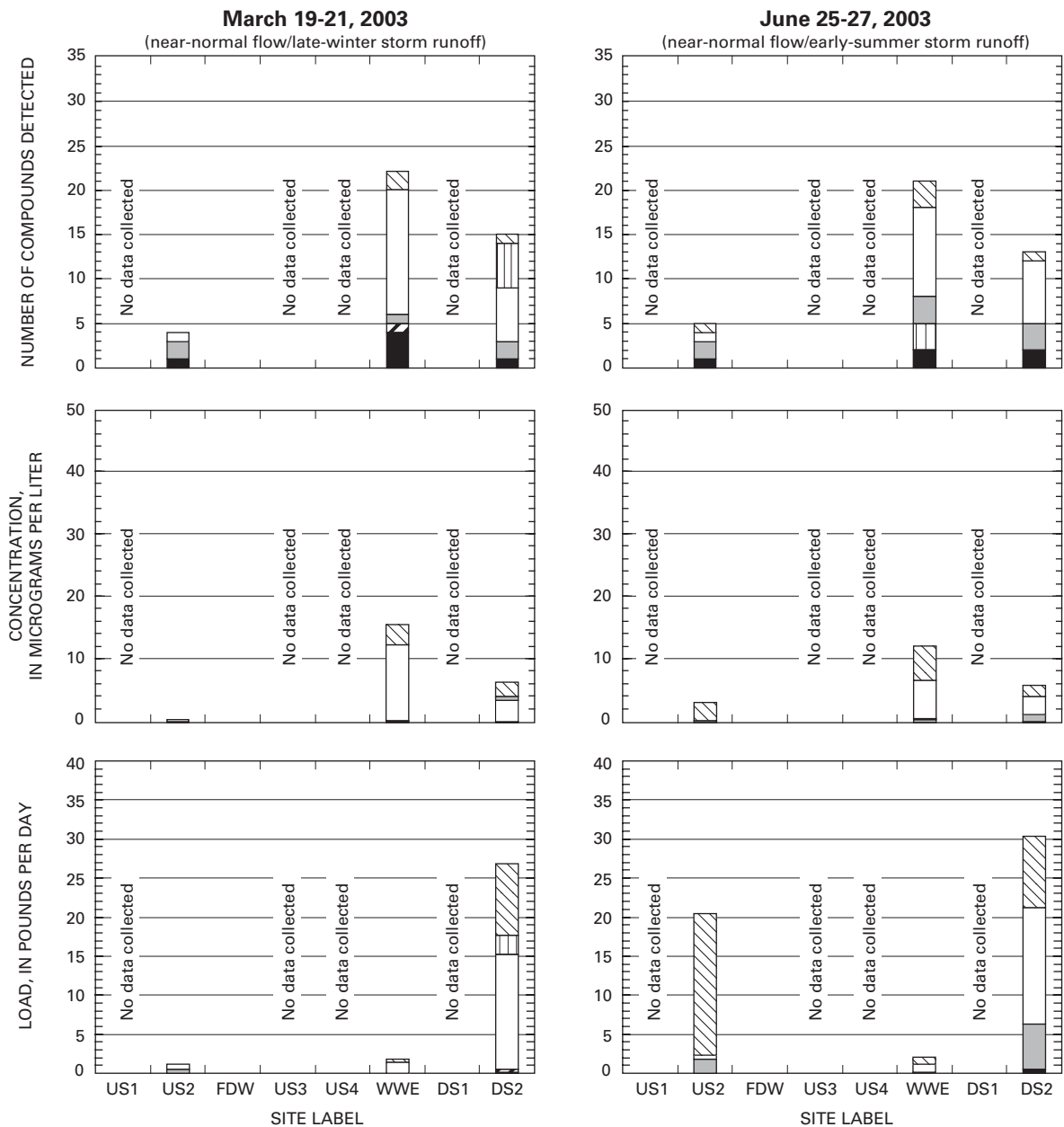


Figure 4. Results for organic wastewater compounds in water samples.—Continued

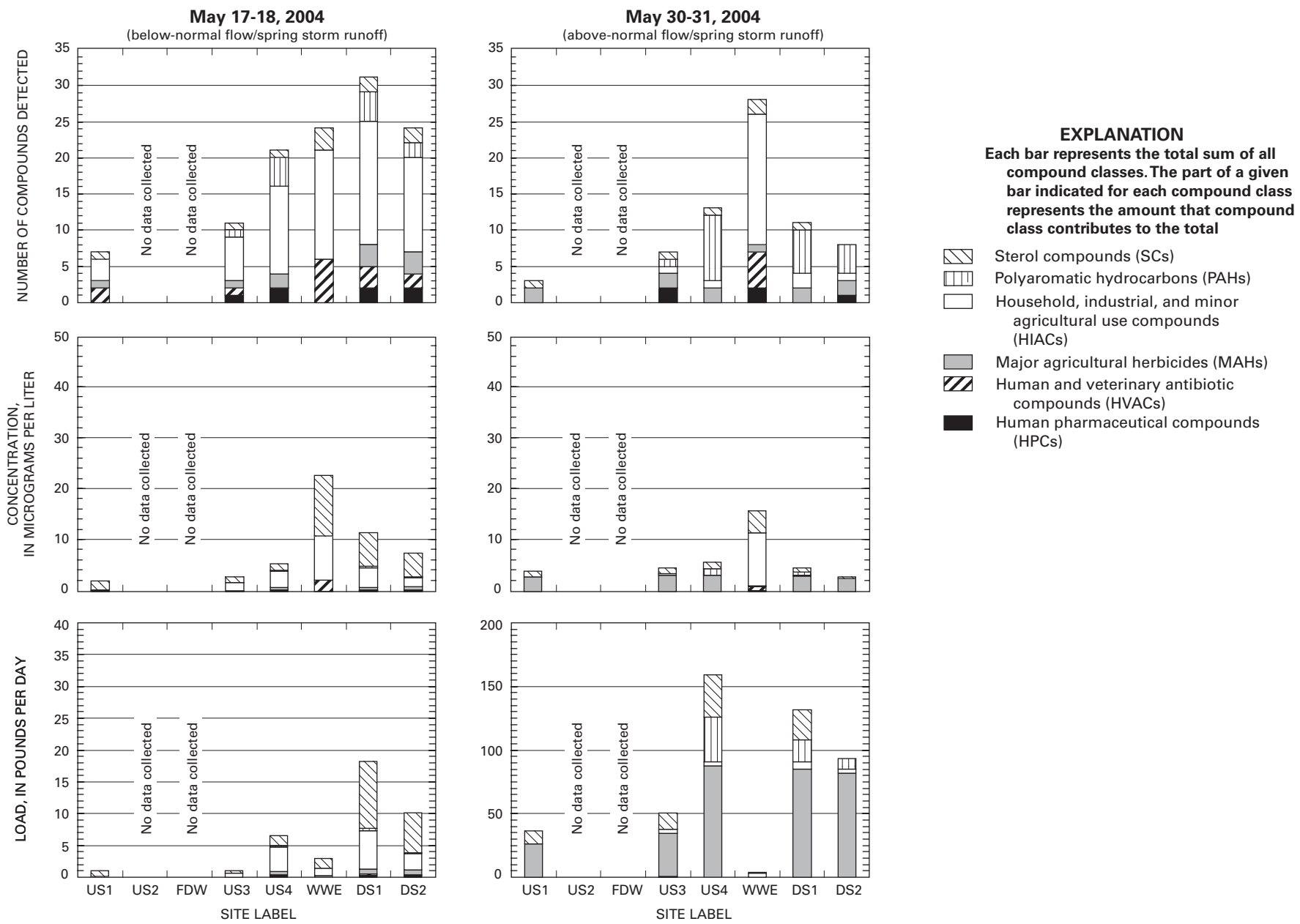


Figure 4. Results for organic wastewater compounds in water samples.—Continued

sections is to present the results thoroughly so that patterns in occurrence of OWCs are apparent despite the variability in data collection among sampling periods; thus, there is some redundancy in information presented in the different sections.

Occurrence of Organic Wastewater Compounds by Sampling Period

For the August 2001 sampling period (above-normal flow/summer base-flow conditions for the Big Sioux River in the Sioux Falls area), sites US2, FDW, and DS2 were sampled. Numbers of compounds detected, concentrations, and loads were smaller for the sampling site upstream from the WWTP effluent discharge (US2) than for the sampling site downstream (DS2) (fig. 4, tables 21 and 22). SCs accounted for nearly all of the total OWC concentration for both Big Sioux River sites. Concentrations and loads of SCs were larger at the downstream site, but the increase in SC load at the downstream site probably was larger than would have been contributed by the WWTP alone (assuming typical operations of the WWTP and comparison of typical WWTP effluent discharges to Big Sioux River flow during the sampling period). HIACs accounted for a small part of the total OWC concentration for site DS2 and might have been contributed by the WWTP discharge. OWC results for the August 2001 sampling period indicate that (1) OWCs for Big Sioux River sites probably were primarily contributed by nonpoint animal agriculture activities, and (2) OWC concentrations for the downstream Big Sioux River site (DS2) probably were not strongly influenced by contributions from the Sioux Falls WWTP.

For the September 2002 sampling period (below-normal flow/late-summer base-flow conditions for the Big Sioux River in the Sioux Falls area), sites US2, FDW, WWE, DS1, and DS2 were sampled. Numbers of OWCs detected, concentrations, and loads were larger for the WWTP effluent than for Big Sioux River sites, and were smaller for the upstream Big Sioux River sampling site (US2) than for downstream sampling sites (DS1 and DS2) (fig. 4, tables 21 and 22). Total OWC concentrations were composed primarily of SCs for Big Sioux River sampling sites, and HIACs and SCs for the WWTP effluent. Possible explanations for decreases in OWC loads moving downstream include (1) degradation of OWCs in the Big Sioux River; (2) adsorption of OWCs to particulate material and sedimentation from the water column; (3) diurnal variability in wastewater effluent discharges and concentrations of OWCs in the wastewater effluent combined with effects of non-Lagrangian sampling; and/or (4) dilution effects decreasing concentrations of individual OWCs below detectable concentrations. Although total OWC concentrations and loads for the Big Sioux River sites downstream from the WWTP effluent discharge (DS1 and DS2) were not substantially larger than for the upstream site (US2), the WWTP effluent discharge influenced OWC concentrations at the downstream sites, as evidenced by the occurrence of several individual OWCs, including 7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN) and several plasti-

cizers and fire retardants, only in samples collected from the WWTP effluent and Big Sioux River downstream sites. OWC results for the September 2002 sampling period indicate that (1) OWCs for the Big Sioux River site upstream from the WWTP effluent discharge were relatively small and probably were primarily contributed by nonpoint animal agriculture activities, and (2) OWCs for the downstream Big Sioux River sites (DS1 and DS2) were influenced by contributions from the Sioux Falls WWTP, but OWC concentrations and loads for site DS2 were not substantially larger than for site US2.

For the January 2003 sampling period (below-normal flow/winter base-flow conditions for the Big Sioux River in the Sioux Falls area), sites US2, FDW, WWE, and DS2 were sampled. Numbers of OWCs detected, concentrations, and loads were larger for the WWTP effluent than for Big Sioux River sites and were substantially smaller for the upstream Big Sioux River sampling site (US2) than for the downstream site (DS2) (fig. 4, tables 21 and 22). The total OWC concentration and load for site US2 were minimal. Total OWC concentrations were composed primarily of HVACs, HIACs, and SCs for the WWTP effluent and DS2 sites. Total OWC concentrations were large for the WWTP effluent (substantially larger than for site DS2). OWC results for the January 2003 sampling period indicate that (1) OWC concentrations at the Big Sioux River site upstream from the WWTP effluent discharge were minimal, and (2) OWCs for the downstream Big Sioux River site (DS2) probably were substantially influenced by contributions from the Sioux Falls WWTP.

For the March 2003 sampling period (near-normal flow/late-winter storm-runoff conditions for the Big Sioux River in the Sioux Falls area), sites US2, FDW, WWE, and DS2 were sampled. Numbers of OWCs detected and OWC concentrations were larger for the WWTP effluent than for Big Sioux River sites and were composed primarily of HIACs and SCs (fig. 4, tables 21 and 22). However, the OWC load for the WWTP effluent was substantially smaller than for the Big Sioux River site downstream from the WWTP effluent discharge (DS2). Numbers of OWCs detected, and OWC concentrations and loads for the upstream Big Sioux River sampling site (US2) were small and composed primarily of HIACs and MAHs. Numbers of OWCs detected, and OWC concentrations and loads for the downstream Big Sioux River sampling site (DS2) were relatively large and composed primarily of HIACs, SCs, and PAHs. These patterns indicate that there were substantial contributions of OWCs to the Big Sioux River in the Sioux Falls area from sources other than the WWTP effluent discharge. Possible sources of OWCs between sites US2 and DS2 other than the WWTP effluent discharge include stormwater runoff from urban and/or agricultural areas to the Big Sioux River and/or resuspension of OWCs adsorbed to sediment deposited in the Big Sioux River between sites US2 and DS2. OWC results for the March 2003 sampling period indicate that (1) OWC concentrations at the Big Sioux River sampling site upstream from the WWTP effluent discharge were small and probably were primarily contributed by nonpoint crop agriculture sources and possibly stormwater runoff from nearby roads,

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and (2) OWC concentrations at the Big Sioux River sampling site downstream from the WWTP probably were primarily contributed by OWC sources (probably a combination of urban stormwater runoff with OWCs derived from human activities and nonpoint animal agriculture sources) between sites US2 and DS2 other than the WWTP effluent discharge.

For the June 2003 sampling period (near-normal flow/early-summer storm-runoff conditions for the Big Sioux River in the Sioux Falls area), sites US2, FDW, WWE, and DS2 were sampled. Numbers of OWCs detected and OWC concentrations for the WWTP effluent were larger than for Big Sioux River sites and were composed primarily of HIACs and SCs (fig. 4, tables 21 and 22). However, the OWC load was substantially smaller for the WWTP effluent than for Big Sioux River sites both upstream (US2) and downstream (DS2) from the WWTP effluent discharge. OWCs detected for site US2 were composed primarily of SCs and MAHs. OWC load for site DS2 was relatively large and composed primarily of HIACs, SCs, and MAHs. The load of SCs decreased between sites US1 and DS2, which probably indicates deposition of SCs to sediments in the Big Sioux River between sites US1 and DS2. As is the case for the March 2003 sampling period, these patterns indicate that there were substantial contributions of OWCs to the Big Sioux River in the Sioux Falls area from sources other than the WWTP effluent discharge. OWC results for the June 2003 sampling period indicate that (1) OWC concentrations at the Big Sioux River sampling site upstream from the WWTP effluent discharge were fairly substantial and probably contributed by nonpoint animal and crop agriculture sources, and (2) OWC concentrations at the Big Sioux River sampling site downstream from the WWTP probably were contributed by OWC sources (probably a combination of urban runoff with OWCs derived from human activities and nonpoint animal agriculture sources) between sites US2 and DS2 other than the WWTP effluent discharge.

For the May 17–18, 2004, sampling period (below-normal flow/spring storm-runoff conditions for the Big Sioux River in the Sioux Falls area), sites US1, US3, US4, WWE, DS1, and DS2 were sampled. OWC concentrations for the WWTP effluent (WWE) were larger than for Big Sioux River sites and were composed primarily of HIACs and SCs (fig. 4, tables 21 and 22). However, the OWC load was substantially smaller for WWE than for the Big Sioux River sites US4, DS1, and DS2. Numbers of OWCs, and OWC concentrations and loads for sites US1 and US3 were smaller than for the other sampling sites, and were primarily composed of SCs for site US1, and HIACs and SCs for site US3. OWC concentrations and loads were substantially larger for site US4 than for sites US1 and US3, and primarily were composed of HIACs and SCs at site US4. OWC concentrations and loads for site DS1 were substantially larger than for site US4 and primarily were composed of SCs and HIACs. SCs account for most of the increase in OWC concentrations between sites US4 and DS1; HIAC loads generally were similar between sites US4 and DS1, but some individual HIACs detected for site DS1 corresponded with HIACs detected for WWE (table 22), indicating that the WWTP

effluent also contributed to HIACs for site DS1. The increase in load of SCs between sites US4 and DS1 might have been contributed by nonpoint animal agriculture sources or resuspension of sediment. OWC concentrations and loads for site DS2 were substantially smaller than for site DS1, and primarily were composed of SCs and HIACs. OWC results for the May 17–18, 2004, sampling period indicate that (1) OWC loads for Big Sioux River upstream sites US1 and US3 were relatively small and probably contributed by nonpoint animal agriculture sources and possibly storm runoff from nearby roads; (2) OWC loads for the Big Sioux River upstream site US4 were larger than loads for the WWTP effluent discharge and probably were contributed by a combination of urban stormwater runoff and nonpoint animal agriculture sources contributing to the Big Sioux River between sites US3 and US4; (3) OWC loads were larger for site DS1 than for either site US4 or the WWTP effluent discharge, and the increase in OWC load between sites US4 and DS1 probably was contributed by nonpoint animal agriculture and/or resuspension of sediment, with a relatively small contribution from the WWTP effluent; and (4) OWC loads were smaller for site DS2 than for site DS1.

For the May 30–31, 2004, sampling period (above-normal flow/spring storm-runoff conditions for the Big Sioux River in the Sioux Falls area), sites US1, US3, US4, WWE, DS1, and DS2 were sampled. Numbers of OWCs detected and OWC concentrations for the WWTP effluent were larger than for Big Sioux River sites and were composed primarily of HIACs and SCs (fig. 4, tables 21 and 22). However, the OWC load was substantially smaller for the WWTP effluent than for all Big Sioux River sampling sites. Numbers of OWCs, and OWC concentrations and loads for upstream sites US1 and US3 were smaller than for the other Big Sioux River sampling sites, and were primarily composed of MAHs and SCs. OWC concentrations and loads for upstream site US4 were larger than concentrations and loads for sites US1 and US3, and primarily were composed of MAHs, SCs, and PAHs. Loads for all of these compound classes increased between sites US3 and US4. Between sites US3 and US4, the increase in load for MAHs might have been contributed by nonpoint crop sources in the Skunk Creek Basin, the increase in loads for SCs might have been contributed by nonpoint animal agriculture sources in the Skunk Creek Basin and urban stormwater runoff, and the increase in load for PAHs might have been contributed by urban stormwater runoff. OWC concentrations and loads for downstream site DS1 were smaller than for site US4 and primarily were composed of MAHs, SCs, and PAHs. Although HIACs compose a relatively small part of the total OWC concentrations for site DS1, individual HIACs detected for site DS1 (table 22) showed little correspondence with those detected for the WWTP effluent and indicate that the WWTP effluent contributed very little to concentrations and loads of OWCs for site DS1. Between sites US4 and DS1, loads of SCs and PAHs decreased, loads of MAHs were similar, and loads of HIACs increased slightly. OWC concentrations and loads for site DS2 were substantially smaller than for site DS1, and primarily were composed of MAHs and PAHs. OWC results for the May 17–18, 2004, sampling period indicate that

(1) OWC loads for Big Sioux River upstream sites US1 and US3 were substantially smaller than for more downstream Big Sioux River sampling sites and probably were primarily contributed by nonpoint crop and animal agriculture sources; (2) OWC loads for the Big Sioux River upstream site US4 were larger than loads for the WWTP effluent discharge and probably were contributed by a combination of urban stormwater runoff contributing to the Big Sioux River downstream from sites US1 and US3 and nonpoint crop and animal agriculture sources contributing to the Big Sioux River both upstream and downstream from sites US1 and US3; (3) OWC loads for site DS1 were smaller than for site US4 and probably were contributed by sources upstream from site US4, with very little contribution from the WWTP effluent discharge; and (4) OWC loads were smaller for site DS2 than for site DS1.

Occurrence of Organic Wastewater Compounds by Sampling Site

Site US1 is the Big Sioux River sampling site farthest upstream from the Sioux Falls WWTP discharge and is substantially upstream from any influences from the city of Sioux Falls and also is isolated from substantial road traffic. Site US1 was sampled during two sampling periods: May 17–18, 2004 (below-normal flow/spring storm-runoff conditions) and May 30–31, 2004 (above-normal flow/spring storm-runoff conditions). During both of these sampling periods, SCs and MAHs accounted for most of the total OWC concentrations (fig. 4), and probably were primarily contributed by nonpoint animal and crop agriculture sources. Total OWC concentrations for site US1 ranged from about 2 to 4 $\mu\text{g/L}$. Total OWC loads and concentrations generally were smaller for site US1 than for more downstream Big Sioux River sites.

Site US2 is the Big Sioux River sampling site second most upstream from the Sioux Falls WWTP discharge. At site US2, Big Sioux River water is pumped from a backwater pool into the intake pipe of the Sioux Falls drinking-water treatment system, and water samples were collected directly from the intake pipe. Site US2 is located just downstream from where the Big Sioux River enters the Sioux Falls urban area. There is moderate-volume road traffic, and site US2 can be affected by local urban stormwater runoff. Site US2 was sampled during five sampling periods: August 2001 (above-normal flow/summer base-flow conditions), September 2002 (below-normal flow/late-summer base-flow conditions), January 2003 (below-normal flow/winter base-flow conditions), March 2003 (near-normal flow/late-winter storm-runoff conditions), and June 2003 (near-normal flow/early-summer storm-runoff conditions). During the base-flow sampling periods, SCs accounted for most of the total OWC concentrations (fig. 4) and probably were primarily contributed by nonpoint animal agriculture sources. During the storm-runoff sampling periods, HIACs, MAHs, and SCs accounted for most of the total OWC concentrations and probably were primarily contributed by local urban stormwater runoff and nonpoint source agriculture sources.

Total OWC concentrations for site US2 ranged from less than 0.01 to about 3.5 $\mu\text{g/L}$. Total OWC loads and concentrations generally were smaller for site US2 than more downstream Big Sioux River sites.

Site US3 is the Big Sioux River sampling site third most upstream from the Sioux Falls WWTP discharge. Site US3 is on the Big Sioux River diversion channel just upstream from the confluence with natural Big Sioux River channel and near the edge of the Sioux Falls urban area. Big Sioux River flow at site US3 consists primarily of flow past site US1 plus relatively small tributary inflow. There is moderate-volume road traffic, and site US3 can be affected by local urban stormwater runoff. Site US3 was sampled during two sampling periods: May 17–18, 2004 (below-normal flow/spring storm-runoff conditions) and May 30–31, 2004 (above-normal flow/spring storm-runoff conditions). During the May 17–18, 2004, sampling period, which was a relatively small runoff event following an extended dry period, HIACs and SCs accounted for most of the total OWC concentration (fig. 4) and probably were primarily contributed by local urban stormwater runoff and nonpoint animal agriculture sources. During the May 30–31, 2004, sampling period, which was a very large runoff event, MAHs and SCs accounted for most of the total OWC concentration and probably were primarily contributed by nonpoint crop and animal agriculture sources. Total OWC concentrations for site US3 ranged from about 3 to 5 $\mu\text{g/L}$. Total OWC loads and concentrations generally were smaller for site US3 than for more downstream Big Sioux River sites.

Site US4 is the Big Sioux River sampling site closest upstream from the Sioux Falls WWTP discharge. Site US4 is just downstream from the confluence of the natural Big Sioux River channel and the diversion channel. There is high-volume road traffic, and site US4 is downstream from nearly all potential urban stormwater runoff from Sioux Falls. Site US4 was sampled during two sampling periods: May 17–18, 2004, (below-normal flow/spring storm-runoff conditions) and May 30–31, 2004 (above-normal flow/spring storm-runoff conditions). During the May 17–18, 2004, sampling period, which was a relatively small runoff event following an extended dry period, HIACs and SCs accounted for most of the total OWC concentration (fig. 4) and probably were primarily contributed by urban stormwater runoff and nonpoint animal agriculture sources. During the May 30–31, 2004, sampling period, which was a very large runoff event, MAHs, PAHs, and SCs accounted for most of the total OWC concentration and probably were primarily contributed by nonpoint crop agriculture sources, urban stormwater runoff, and nonpoint animal agriculture sources. Total OWC concentrations for site US4 ranged from about 5 to 6 $\mu\text{g/L}$. Total OWC loads and concentrations were smaller for site US4 than for more downstream Big Sioux River sites during the May 17–18, 2004, sampling period but were larger for site US4 than for more downstream Big Sioux River sites during the May 30–31, 2004, sampling period.

Site WWE is the Sioux Falls WWTP effluent. Site WWE was sampled during six sampling periods: September 2002 (below-normal flow/late-summer base-flow conditions), Janu-

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ary 2003 (below-normal flow/winter base-flow conditions), March 2003 (near-normal flow/late-winter storm-runoff conditions), June 2003 (near-normal flow/early-summer storm-runoff conditions), May 17–18, 2004 (below-normal flow/spring storm-runoff conditions), and May 30–31, 2004 (above-normal flow/spring storm-runoff conditions). During these sampling periods, HIACs and SCs accounted for most of the total OWC concentrations (fig. 4). Total OWC concentrations for site WWE ranged from about 10 to 45 $\mu\text{g/L}$. Total OWC concentrations always were larger for site WWE than for Big Sioux River sites. Total OWC loads also were larger for site WWE than for all Big Sioux River sampling sites during base-flow sampling periods, but were smaller for site WWE than for Big Sioux River sites US4, DS1, and DS2 during storm-runoff sampling periods.

Site DS1 is the Big Sioux River sampling site closest downstream from the Sioux Falls WWTP discharge. Big Sioux River flow at site DS1 consists primarily of flow past site US4 plus the WWTP effluent discharge plus generally minor runoff contributed between sites US4 and DS1. Site DS1 was sampled during three sampling periods: September 2002 (below-normal flow/late-summer base-flow conditions), May 17–18, 2004 (below-normal flow/spring storm-runoff conditions), and May 30–31, 2004 (above-normal flow/spring storm-runoff conditions). During the base-flow sampling period (September 2002), SCs and HIACs accounted for most of the total OWC concentration (fig. 4) and probably were contributed by a combination of the Sioux Falls WWTP effluent discharge and nonpoint animal agriculture sources. Although the total OWC load during this sampling period was only slightly larger for site DS1 than for the upstream Big Sioux River site that was sampled (site US2), the contribution of the Sioux Falls WWTP effluent discharge to OWC concentrations at site DS1 is evidenced by occurrence of several individual OWCs, including AHTN and several plasticizers and fire retardants, only in samples collected from the WWTP effluent and Big Sioux River downstream sites (table 22). Relative proportions of OWC compound classes varied during storm-runoff conditions. During the May 17–18, 2004, sampling period (below-normal flow/spring storm-runoff conditions), SCs and HIACs accounted for most of the total OWC concentration and probably were contributed by nonpoint animal agriculture, urban stormwater runoff, and the Sioux Falls WWTP effluent discharge. Discernible contributions from the Sioux Falls WWTP effluent discharge to OWC concentrations for site DS1 are evidenced by occurrence of several individual OWCs, including AHTN, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), and benzophenone, only in samples collected from the WWTP effluent and Big Sioux River downstream sites. The total OWC load at site DS1 was larger than the combined loads of sites US4 and WWE; in addition to the contribution from the WWTP effluent, the increase in OWC load between sites US4 and DS1 probably was contributed by nonpoint animal agriculture sources and/or resuspension of sediment. During the May 30–31, 2004, sampling period (above-normal flow/spring storm-runoff conditions), MAHs, SCs, and PAHs accounted for

most of the total OWC concentration and probably were contributed by nonpoint crop and animal agriculture sources and urban stormwater runoff, with very little contribution from the WWTP effluent discharge. For all of the periods when site DS1 was sampled, total OWC concentrations ranged from about 3 to 12 $\mu\text{g/L}$. Contributions from the WWTP effluent discharge to OWC concentrations for site DS1 were discernible during base-flow and below-normal storm-runoff conditions but were very minor during above-normal runoff conditions. Total OWC loads and concentrations were larger for site DS1 than for site DS2 during all sampling periods when both sites were sampled.

Site DS2 is the Big Sioux River sampling site farthest downstream from the Sioux Falls WWTP discharge. Big Sioux River flow at site DS2 consists primarily of flow past site DS1 plus generally minor runoff contributed between sites DS1 and DS2. Site DS2 was sampled during seven sampling periods: August 2001 (above-normal flow/summer base-flow conditions), September 2002 (below-normal flow/late-summer base-flow conditions), January 2003 (below-normal flow/winter base-flow conditions), March 2003 (near-normal flow/late-winter storm-runoff conditions), June 2003 (near-normal flow/early-summer storm-runoff conditions), May 17–18, 2004 (below-normal flow/spring storm-runoff conditions), and May 30–31, 2004 (above-normal flow/spring storm-runoff conditions). Relative proportions of OWC compound classes varied during base-flow conditions. During the August 2001 sampling period (above-normal flow/base-flow conditions), SCs accounted for most of the total OWC concentration (fig. 4) and probably were primarily contributed by nonpoint animal agriculture sources. During the September 2002 sampling period (below-normal flow/base-flow conditions), HIACs and SCs accounted for most of the total OWC concentration and probably were contributed by a combination of the Sioux Falls WWTP effluent discharge and nonpoint animal agriculture sources. Although the total OWC load during this sampling period was only slightly larger for site DS2 than for the upstream Big Sioux River site that was sampled (site US2), the contribution of the WWTP effluent discharge to OWC concentrations at site DS2 is evidenced by occurrence of several individual OWCs, including AHTN and several plasticizers and fire retardants, only in samples collected from the WWTP effluent and Big Sioux River downstream sites (table 22). During the January 2003 sampling period (below-normal flow/base-flow conditions), HIACs, HVACs, and SCs accounted for most of the total OWC concentration and probably were contributed primarily by the WWTP effluent discharge. Relative proportions of OWC compound classes varied during storm-runoff conditions. During the March 2003 sampling period (near-normal flow/storm-runoff conditions), HIACs, SC, and PAHs accounted for most of the total OWC concentration and probably were primarily contributed by a combination of urban stormwater runoff and nonpoint animal agriculture sources. During the June 2003 sampling period (near-normal flow/storm-runoff conditions), HIACs, SCs, and MAHs accounted for most of the total OWC concentrations and probably were primarily contributed by a combination of urban

stormwater runoff and nonpoint agriculture sources. During the May 17–18, 2004, sampling period (below-normal flow/storm runoff), SCs and HIACs accounted for most of the total OWC concentration and probably were contributed by nonpoint animal agriculture, urban stormwater runoff, and the Sioux Falls WWTP effluent discharge. Discernible contributions from the Sioux Falls WWTP effluent discharge to OWC concentrations for site DS2 are evidenced by occurrence of individual OWCs, including AHTN and HHCB, only in samples collected from sites WWE, DS1, and DS2. During the May 30–31, 2004, sampling period (above-normal flow/storm runoff), MAHs and PAHs accounted for most of the total OWC concentration and probably were contributed by nonpoint crop agriculture sources and urban stormwater runoff, with very little contribution from the WWTP effluent discharge. For all of the periods when site DS2 was sampled, total OWC concentrations ranged from about 2 to 13 $\mu\text{g/L}$. Contributions from the WWTP effluent discharge to OWC concentrations for site DS2 were discernible during base-flow and below-normal storm-runoff conditions but were very minor during near- and above-normal runoff conditions. Total OWC loads and concentrations were smaller for site DS2 than for site DS1 during all sampling periods when both sites were sampled. Loads of all compound classes except MAHs decreased between sites DS1 and DS2 for all sampling period when both sites were sampled.

Occurrence of Organic Wastewater Compounds by Compound Class

HPCs were detected in samples collected from all sites in the Sioux Falls area except sites US1 and FDW (fig. 4, tables 21 and 22). Two different HPCs (caffeine and cotinine) were detected in samples collected from Big Sioux River sites upstream from the WWTP effluent discharge (sites US2, US3, and US4) with total detected concentrations for individual samples generally less than about 0.01 $\mu\text{g/L}$ and generally accounting for less than about 2 percent of the total OWC concentration for any sample. Five different HPCs (1,7-dimethylxanthine, caffeine, cotinine, dehydronifedipine, and salbutamol) were detected in samples collected from the Sioux Falls WWTP effluent with total detected concentrations for individual samples ranging from about 0.031 to 0.16 $\mu\text{g/L}$ and accounting for no more than about 1 percent of the total OWC concentration for any sample. Four different HPCs (1,7-dimethylxanthine, caffeine, cotinine, and salbutamol) were detected in samples collected from Big Sioux River sites downstream from the Sioux Falls WWTP effluent discharge with total detected concentrations for individual samples generally less than about 0.1 $\mu\text{g/L}$ and generally accounting for less than about 2 percent of the total OWC concentrations in samples. Generally, HPCs contributed very little to OWC concentrations at any of the sampling sites in the Sioux Falls area during any streamflow conditions.

HVACs were detected in samples collected from sites US1, US3, WWE, DS1, and DS2 (fig. 4, tables 21 and 22). Two

different HVACs (erythromycin- H_2O and sulfamethoxazole) were detected in the May 17–18, 2004, samples collected from Big Sioux River sites upstream from the WWTP effluent discharge (sites US1 and US3) with total detected concentrations for individual samples generally less than about 0.1 $\mu\text{g/L}$ and accounting for less than about 4 percent of the total OWC concentration. HVACs for upstream Big Sioux River sampling sites probably were contributed by nonpoint animal agriculture sources. Nine different HVACs were detected in WWE samples with total detected concentrations for individual samples ranging from about 0.050 to 24 $\mu\text{g/L}$. HVACs were detected in all WWE samples. HVACs generally accounted for less than 10 percent of the total OWC concentrations for individual WWE samples. However, the total HVAC concentration for the January 2003 WWE sample was very large (about 24 $\mu\text{g/L}$) and accounted for about 52 percent of the total OWC concentration for that sample. Seven different HVACs were detected in samples collected from downstream Big Sioux River sites (DS1 and DS2) with total detected concentrations for individual samples ranging from about 0.16 to 3.8 $\mu\text{g/L}$ and generally accounting for less than about 2 percent of the total OWC concentrations. HVACs were only detected in the January 2003 and May 17–18, 2004, samples for downstream Big Sioux River sites. The total HVAC concentration for the January 2003 sample for site DS2 was relatively large (about 3.8 $\mu\text{g/L}$) and accounted for about 28 percent of the total OWC concentration for that sample. HVACs for downstream Big Sioux River sites were primarily contributed by the WWTP effluent discharge for the January 2003 sampling period and possibly a combination of nonpoint animal agriculture sources and the WWTP effluent discharge for the May 17–18, 2004, sampling period. HVACs generally accounted for a relatively small part of the total OWC concentrations in water samples collected from all sampling sites except for the January 2003 and May 17–18, 2004, samples for site WWE and downstream Big Sioux River sites.

MAHs were detected in samples collected from all sites (fig. 4, tables 21 and 22). Two different MAHs (atrazine and metolachlor) were detected in samples collected from Big Sioux River sites upstream from the WWTP effluent discharge (sites US1, US2, US3, and US4) with total detected concentrations for individual samples ranging from about 0.013 to 3.2 $\mu\text{g/L}$. In all samples except those collected during the March 2003 and May 30–31, 2004, sampling periods, MAHs accounted for less than about 10 percent of the total OWC concentrations for upstream Big Sioux River sites. For samples collected during the March 2003 and May 30–31, 2004, sampling periods, MAHs accounted for about 41 to 72 percent of the total OWC concentrations for upstream Big Sioux River sites. MAHs for upstream Big Sioux River sites were primarily contributed by nonpoint crop agriculture sources. One MAH (metolachlor) was detected in a single sample (August 2001 sampling period) collected from site FDW at a very small concentration (0.0040 $\mu\text{g/L}$). Three different MAHs (atrazine, metolachlor, and prometon) were detected in WWE samples with total detected concentrations for individual samples ranging from about 0.030 to 0.26 $\mu\text{g/L}$ and accounting for less than about

2 percent of the total OWC concentration in any WWE sample. Three different MAHs (atrazine, metolachlor, and prometon) were detected in Big Sioux River sites downstream from the WWTP effluent discharge (sites DS1 and DS2) with total detected concentrations for individual samples ranging from 0.038 to 3.0 µg/L. In all samples except those collected during the June 2003 and May 30–31, 2004, sampling periods, MAHs accounted for less than about 10 percent of the total OWC concentrations for downstream Big Sioux River sites. For samples collected during the June 2003 and May 30–31, 2004, sampling periods, MAHs accounted for about 19 to 86 percent of the total OWC concentrations for downstream Big Sioux River sites. MAHs generally accounted for a relatively small part of the total OWC concentrations in samples collected from site WWE for all sampling periods and in samples collected from Big Sioux River sites during base-flow conditions. During some but not all of the storm-runoff sampling periods, MAHs accounted for a substantial part of the total OWC concentrations in samples collected from Big Sioux River sites.

HIACs were detected in samples collected from all sampling sites except FDW (fig. 4, tables 21 and 22). Thirteen different HIACs were detected in samples collected from Big Sioux River sites upstream from the WWTP effluent discharge (sites US1, US2, US3, and US4) with total detected concentrations for individual samples ranging from about 0.074 to 3.2 µg/L. HIACs generally accounted for less than 10 percent of the total OWC concentration in samples collected from upstream sites. However, HIACs accounted for 55 to 58 percent of the total OWC concentrations in samples collected from site US2 for the March 2003 sampling period, and from sites US3 and US4 for the May 17–18, 2004, sampling period. Greater proportions of HIACs for those samples probably were contributed by local stormwater runoff from roads. Individual HIACs that had the largest maximum concentrations for upstream sites include octylphenol diethoxylate (OP2EO; 0.20 µg/L), octylphenol monoethoxylate (OP1EO; 0.40 µg/L), *para*-nonylphenol (NP; 0.88 µg/L), and tri(2-butoxyethyl)phosphate (0.91 µg/L). Twenty-seven different HIACs were detected in samples collected from site WWE with total detected concentrations for individual samples ranging from about 5.5 to 17 µg/L. HIACs accounted for about 37 to 78 percent of the total OWC concentrations in WWE samples. Individual HIACs that had the largest maximum concentrations in samples collected from site WWE include AHTN (2.1 µg/L), nonylphenol diethoxylate (NP2EO; 6.2 µg/L), nonylphenol monoethoxylate (NP1EO; 1.7 µg/L), NP (1.9 µg/L), phenol (1.8 µg/L), triethyl citrate (1.1 µg/L), tri(2-butoxyethyl)phosphate (3.2 µg/L), and tri(2-chloroethyl)phosphate (2.9 µg/L). Twenty different HIACs were detected in samples collected from sites downstream from the WWTP effluent discharge (sites DS1 and DS2) with total detected concentrations for individual samples ranging from about 0.095 to 6.6 µg/L. HIACs generally accounted for about 20 to 55 percent of the total OWC concentrations in samples collected from downstream sites. However, HIACs accounted for less than about 5 percent of the total OWC concentrations in samples collected from down-

stream sites for the August 2001 and May 30–31, 2004, samples. Individual HIACs that had the largest maximum concentrations in samples collected from downstream sites include AHTN (0.56 µg/L), NP2EO (3.0 µg/L), NP1EO (0.82 µg/L), NP (1.2 µg/L), phenol (0.63 µg/L), and tri(2-butoxyethyl)phosphate (0.89 µg/L). In samples collected from upstream Big Sioux River sites, HIACs generally accounted for a relatively small part of the total OWC concentrations during base-flow conditions and for a substantial part during some but not all of the storm-runoff sampling periods. HIACs generally accounted for a substantial part of the total OWC concentrations in samples collected from site WWE during all sampling periods. In samples collected from downstream Big Sioux River sites, HIACs generally accounted for a substantial part of the total OWC concentration during base-flow conditions and during some but not all of the storm-runoff sampling periods.

PAHs were detected in samples collected from sites US3, US4, DS1, and DS2 (fig. 4, tables 21 and 22). Ten different PAHs were detected in samples collected from Big Sioux River sites upstream from the WWTP effluent discharge (sites US3 and US4) with total detected concentrations for individual samples ranging from about 0.019 to 1.3 µg/L. PAHs only were detected in water samples collected from upstream Big Sioux River sites for storm-runoff sampling periods, during which they accounted for about 0.7 to 17 percent of the total detected OWC concentrations. Individual PAHs that had the largest maximum concentrations for upstream sites include 1-methylnaphthalene (0.13 µg/L), 2-methylnaphthalene (0.11 µg/L), benzo[*a*]pyrene (0.13 µg/L), naphthalene (0.19 µg/L), and phenanthrene (0.11 µg/L). No PAHs were detected in samples collected from site WWE. Ten different PAHs were detected in samples collected from sites downstream from the WWTP effluent discharge (sites DS1 and DS2) with total detected concentrations for individual samples ranging from about 0.076 to 0.61 µg/L. PAHs only were detected in water samples collected from downstream Big Sioux River sites for storm-runoff sampling periods, during which they accounted for about 1.2 to 12 percent of the total detected OWC concentrations. Individual PAHs that had the largest maximum concentrations in samples collected from downstream sites include fluoranthene (0.17 µg/L), naphthalene (0.16 µg/L), phenanthrene (0.14 µg/L), and pyrene (0.12 µg/L). PAHs only were detected at Big Sioux River sites that might be substantially affected by storm-runoff from roads. PAHs were not detected during any base-flow sampling period and were detected during some but not all storm-runoff periods. Even during runoff periods, PAHs accounted for less than 20 percent of total OWC concentrations.

SCs were detected in samples collected from all sites except FDW (fig. 4, tables 21 and 22). Two different SCs (*beta*-sitosterol and cholesterol) were detected in samples collected from Big Sioux River sites upstream from the WWTP effluent discharge (sites US1, US2, US3, and US4), with total detected concentrations for individual samples ranging from about 1.1 to 3.3 µg/L and accounting for about 22 to 98 percent of the total detected OWC concentrations. The SC that had the largest maximum concentrations for upstream Big Sioux River sites was

cholesterol (2.8 µg/L). Three different SCs (3-*beta*-coprostanol, *beta*-sitosterol, and cholesterol) were detected in samples collected from site WWE, with total detected concentrations for individual samples ranging from about 3.1 to 12 µg/L and accounting for about 11 to 52 percent of the total detected OWC concentrations. The SC that had the largest maximum concentrations for site WWE was cholesterol (5.4 µg/L). Three different SCs (3-*beta*-coprostanol, *beta*-sitosterol, and cholesterol) were detected in samples collected at Big Sioux River sites downstream from the WWTP effluent discharge (sites DS1 and DS2), with total detected concentrations for individual samples ranging from about 0.82 to 6.7 µg/L and accounting for about 18 to 94 percent of the total detected OWC concentrations. The SC that had the largest maximum concentrations for downstream Big Sioux River sites was *beta*-sitosterol (3.7 µg/L). SCs generally comprised a substantial part of the total detected OWC concentrations for site WWE and Big Sioux River sites during both base-flow and storm-runoff conditions. Occurrence of the SC 3-*beta*-coprostanol is particularly relevant with respect to evaluating sources of OWCs because 3-*beta*-coprostanol is a major component of human feces, typically accounting for about 60 percent of the total fecal sterol content (Leeming and others, 1994). However, the relative amount of 3-*beta*-coprostanol that occurs in feces of most other animals (especially herbivores; Leeming and others, 1994) generally is much lower. Several factors affect the relative composition of 3-*beta*-coprostanol in WWTP effluents and receiving waters, including (1) variability in 3-*beta*-coprostanol concentrations in human feces between individuals (based largely on variable diet and composition of bacteria in the digestive tract); (2) variability in 3-*beta*-coprostanol removal between different WWTP processes; and (3) variability in environmental conditions that affect degradation of 3-*beta*-coprostanol in receiving waters (Bull and others, 2002). Because of these influencing factors, use of 3-*beta*-coprostanol indices to evaluate OWC sources between substantially different areas (with respect to WWTP technologies, human diet characteristics, and environmental characteristics of effluent receiving waters) should be used with caution. However, because the relative composition of 3-*beta*-coprostanol in Sioux Falls WWTP effluents and the environmental characteristics of the Big Sioux River in the Sioux Falls area might reasonably be expected to be somewhat stable, investigation of the relative composition of 3-*beta*-coprostanol in water samples collected from site WWE and Big Sioux River sites provides information on the relative contribution of the Sioux Falls WWTP effluent discharge to the occurrence of OWCs in the Big Sioux River. Statistical summaries of data related to the occurrence of whole-water 3-*beta*-coprostanol in water samples collected from site WWE and Big Sioux River sampling sites are presented in table 4. Whole-water 3-*beta*-coprostanol was detected in all samples collected from site WWE. Ratios of concentrations of 3-*beta*-coprostanol to cholesterol (which has been used to assess the relative contribution of human sewage to total wastewater contamination; Bull and others, 2002) in water samples collected from site WWE ranged from 46 to 77 percent. Whole-water 3-*beta*-coprostanol was not

detected in any samples collected from upstream Big Sioux River sites. Whole-water 3-*beta*-coprostanol was detected in two samples collected from downstream Big Sioux River sites and only during base-flow sampling periods. For the September 2002 sampling period (below-normal flow/late-summer base-flow conditions), when the Sioux Falls WWTP effluent discharge accounted for about 35 percent of the flow of the Big Sioux River, the ratio of concentrations of 3-*beta*-coprostanol to cholesterol was 77 percent for site WWE and 24 percent at site DS1, but 3-*beta*-coprostanol was not detected at site DS2. The occurrence of 3-*beta*-coprostanol at site DS1, but at a lower ratio to total SC concentration than for site WWE, probably indicates that human wastewater contributed to the OWC concentration at site DS1, but that 3-*beta*-coprostanol degraded or sedimented from the water column more quickly than cholesterol in the Big Sioux River, or was diluted relative to cholesterol by OWC sources other than the WWTP discharge. For the January 2003 sampling period (below-normal flow/winter base-flow conditions), when the Sioux Falls WWTP effluent discharge accounted for about 55 percent of the flow of the Big Sioux River, the ratio of concentrations of 3-*beta*-coprostanol to cholesterol was 46 percent for site WWE and 44 percent for site DS2. The similarity in ratios of concentrations of 3-*beta*-coprostanol to cholesterol for sites WWE and DS1 indicates that the WWTP discharge substantially contributed to the occurrence of OWCs in the Big Sioux River during below-normal base-flow conditions.

Occurrence of Endocrine-Disrupting Compounds

EDCs were detected in samples collected from all sampling sites except FDW (fig. 5, tables 21 and 22). Nine different EDCs (atrazine, which is an MAH; benzophenone, OP2EO, OP1EO, and NP, which are HIACs; and anthracene, benzo[*a*]pyrene, phenanthrene, and pyrene, which are PAHs) were detected in samples collected from Big Sioux River sites upstream from the WWTP effluent discharge (sites US1, US2, US3, and US4), with total detected concentrations for individual samples ranging from about 0.024 to 2.9 µg/L. EDCs in samples collected from upstream sites generally had larger concentrations and loads for runoff sampling periods than for base-flow sampling periods and probably were primarily contributed by nonpoint crop agriculture sources and urban stormwater runoff.

Twelve different EDCs (atrazine, which is an MAH; and AHTN, benzophenone, carbaryl, chlorpyrifos, diazinon, HHCb, NP2EO, NP1EO, NP, pentachlorophenol, and triclosan, which are HIACs) were detected in samples collected from site WWE, with total detected concentrations for individual samples ranging from about 2.3 to 9.5 µg/L. EDC concentrations in samples collected from site WWE were largest for the January 2003 and March 2003 sampling periods, exceeding about 9 µg/L.

Table 4. Statistical summaries of data related to occurrence of whole-water 3-*beta*-coprostanol in water samples collected from wastewater effluents and the Big Sioux River.

[WWTP, wastewater treatment plant; µg/L, micrograms per liter; --, no data]

Type of sampling sites	Frequency of detection (percent)		Number of samples	Number of detections	Statistical summary of 3- <i>beta</i> -coprostanol detected concentrations for all sampling periods (µg/L)			Statistical summary of the ratio of 3- <i>beta</i> -coprostanol to cholesterol concentration for samples with detections (percent)			
	Stable low-flow sampling periods	Stable high-flow and runoff sampling periods			Minimum	Median	Maximum	Minimum	Median	Maximum	Standard deviation
Big Sioux River sites upstream from WWTP effluent discharge	0	0	11	0	--	--	--	--	--	--	--
WWTP effluent	100	100	6	6	1.2	1.6	3.9	46	64	77	12
Big Sioux River sites downstream from WWTP effluent discharge	67	0	10	2	.26	.58	.89	24	34	44	15

Fourteen different EDCs (atrazine, which is an MAH; AHTN, benzophenone, diazinon, HHCB, NP2EO, NP1EO, NP, OP2EO, and OP1EO, which are HIACs; and anthracene, benzo[*a*]pyrene, phenanthrene, and pyrene, which are PAHs) were detected in samples collected from sites downstream from the WWTP effluent discharge (sites DS1 and DS2). Total detected EDC concentrations for individual samples ranged from about 0.048 to 4.5 µg/L.

During base-flow periods, EDCs in water samples collected from downstream sites primarily consisted of HIACs, and concentrations varied in association with concentrations in water samples collected from site WWE and the relation between the WWTP effluent discharges and the flow in the Big Sioux River. During September 2002, when the WWTP effluent discharge accounted for about 35 percent of the flow of the Big Sioux River, EDC concentrations in water samples collected from site WWE were relatively small, and EDC concentrations in water samples collected from downstream sites were very small. During January 2003, when the WWTP effluent discharge accounted for about 55 percent of the flow of the Big Sioux River, EDC concentrations were relatively large in water samples from site WWE and the downstream sites. During storm-runoff conditions, EDCs in water samples collected from downstream sites sometimes primarily consisted of HIACs (as was the case for the March 2003 and May 17–18, 2004, sampling periods) and sometimes primarily consisted of MAHs (as was the case for the June 2003 and May 30–31, 2004, sampling periods). However, the WWTP effluent discharge did not account for a substantial part of the EDC concentrations in water samples collected from downstream sites during any storm-runoff sampling periods. During the March 2003 and

May 17–18, 2004, sampling periods, EDC concentrations in water samples from downstream sites primarily consisted of HIACs and probably were primarily contributed by urban stormwater runoff. During the June 2003 and May 30–31, 2004, sampling periods, EDC concentrations in water samples from downstream sites primarily consisted of MAHs and probably primarily were contributed by nonpoint crop agriculture sources.

Organic Wastewater Compounds in Bottom Sediment

Bottom-sediment samples were collected from three sites (US2, DS1, and DS2) during the September 2002 sampling period (below-normal flow/late-summer base flow). The bottom-sediment samples were analyzed by analytical method 5 for 3 MAHs, 44 HIACs, 10 PAHs, and 4 SCs (table 7).

OWCs in the HIAC, PAH, and SC compound classes were detected in all bottom-sediment samples (fig. 6, tables 5 and 6). No MAH compounds were detected in any bottom-sediment samples. The OWCs detected in bottom sediment have varying degrees of hydrophobic properties, which results in those compounds having a tendency to partition to particulate phase and deposit in river sediments.

Twelve different OWCs, including 4 HIACs (3-methyl-1H-indole, indole, *para*-cresol, and phenol), 4 PAHs (2,6-dimethylnaphthalene, fluoranthene, phenanthrene, and pyrene), and 4 SCs (3-*beta*-coprostanol, *beta*-sitosterol, *beta*-stigmastanol, and cholesterol), were detected in bottom sediment collected from site US2. OWCs that occurred in bottom sediment collected from site US2 typically are associated with fecal

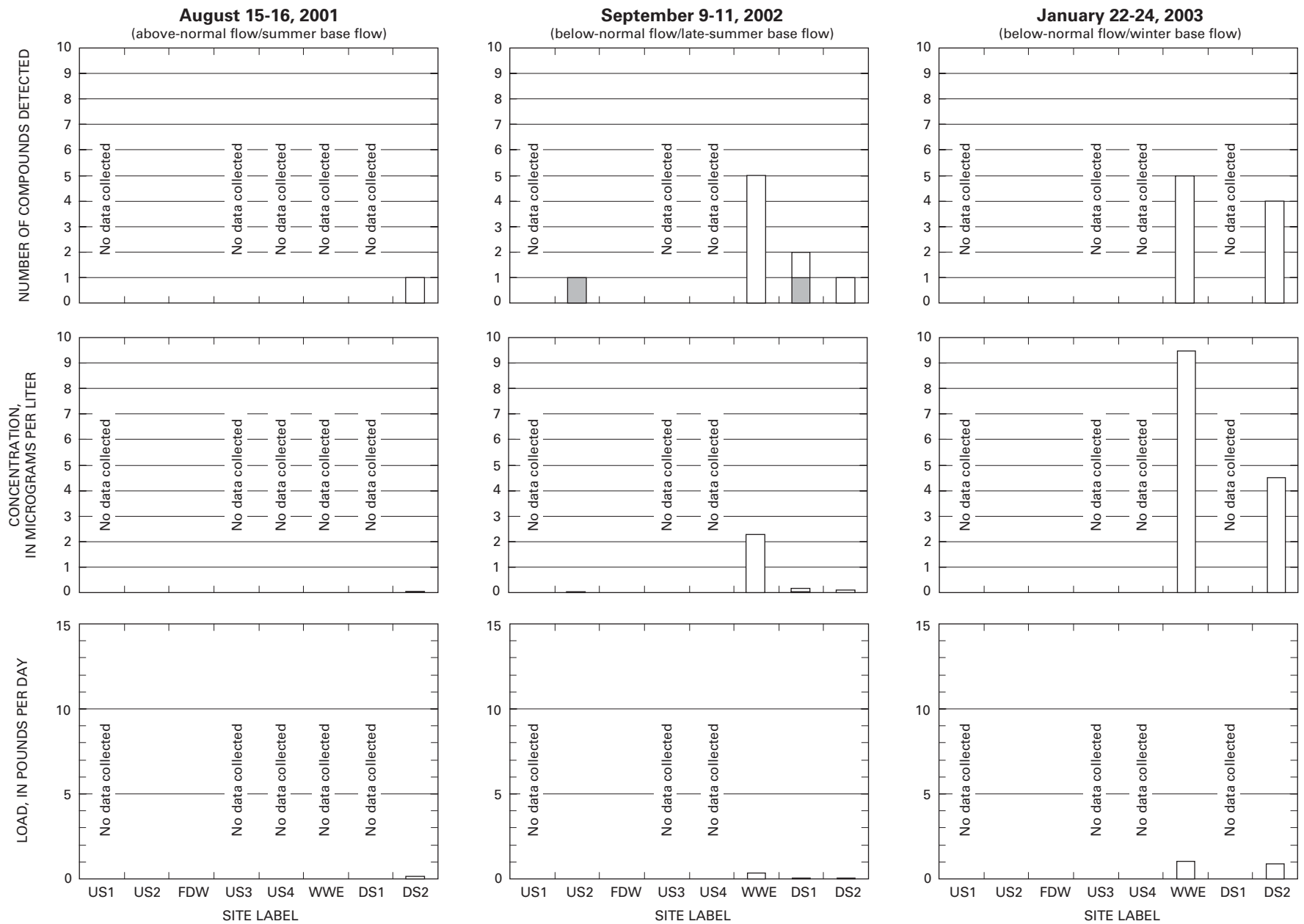


Figure 5. Results for endocrine-disrupting compounds.

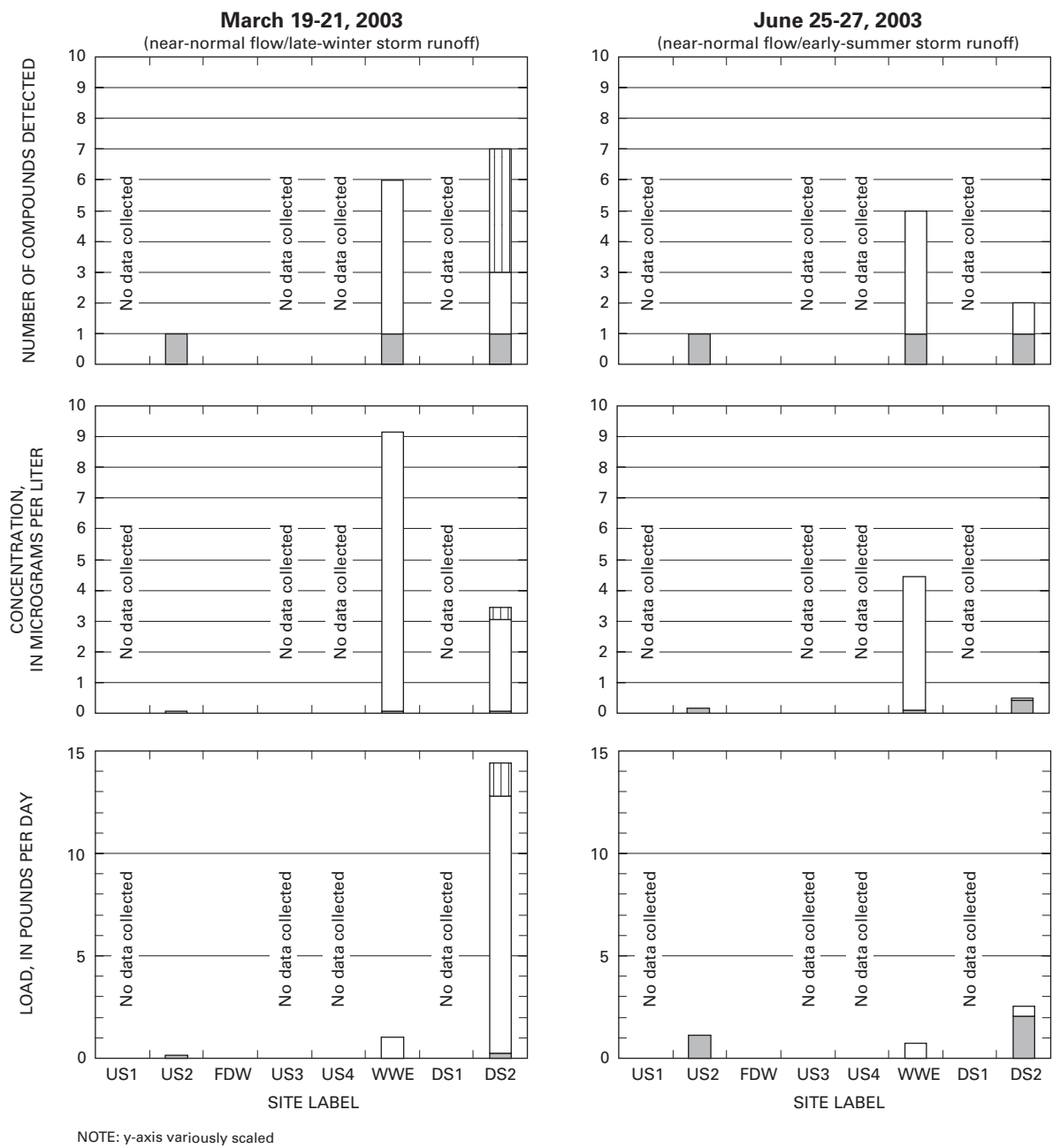
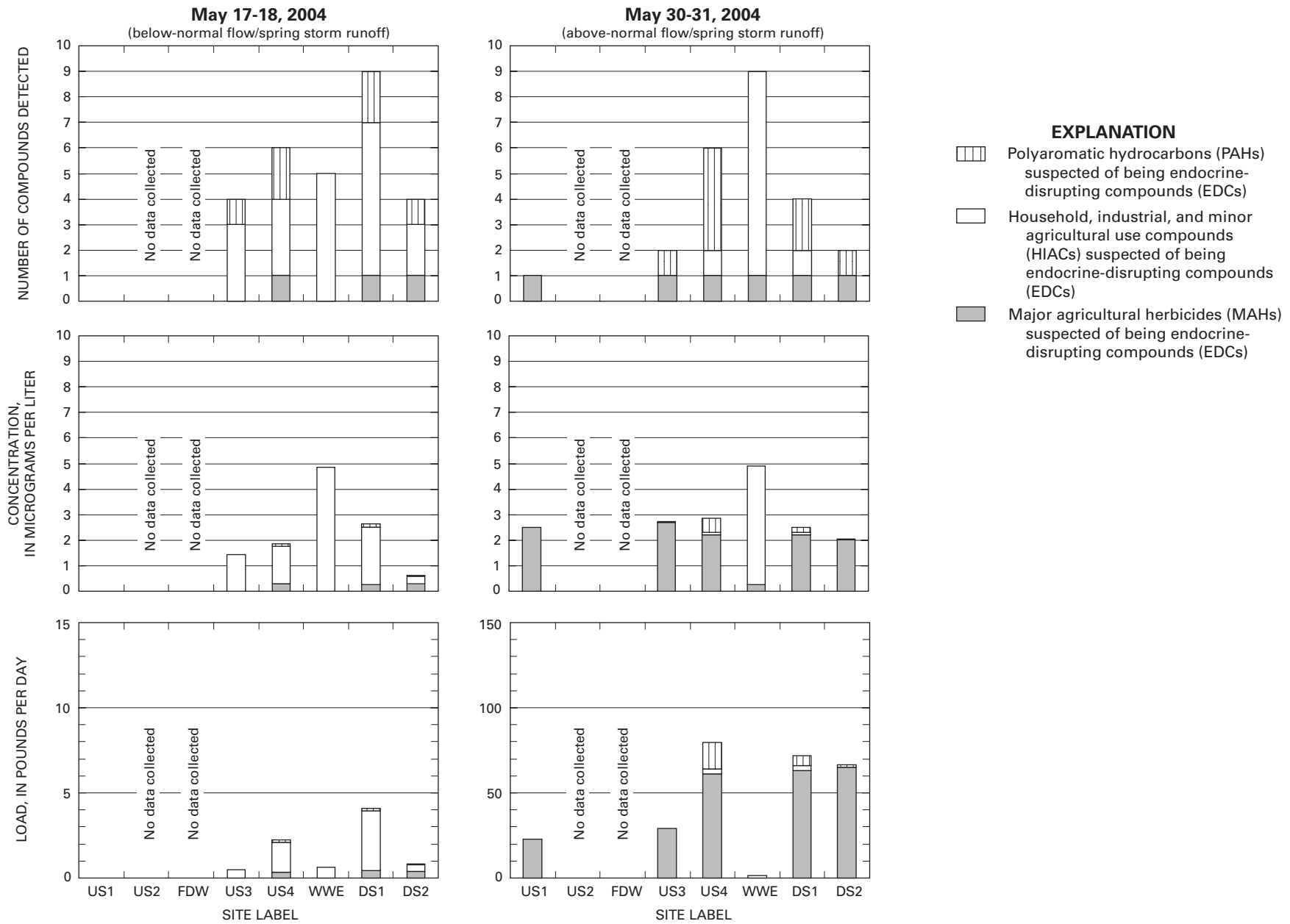


Figure 5. Results for endocrine-disrupting compounds.—Continued



NOTE: y-axis variously scaled

Figure 5. Results for endocrine-disrupting compounds.—Continued

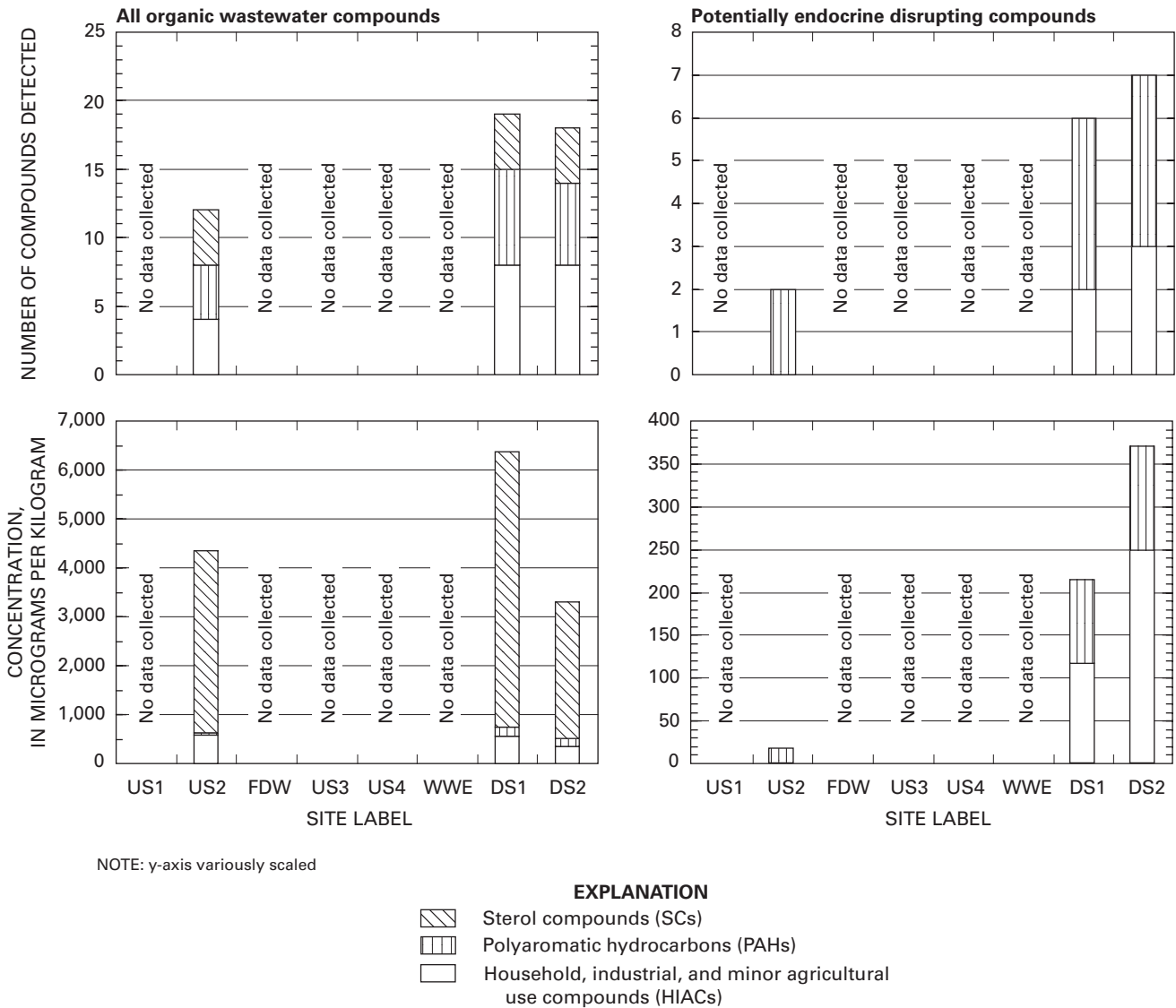


Figure 6. Results for organic wastewater compounds and suspected endocrine-disrupting compounds in bottom-sediment samples for the September 2002 sampling period.

material (3-methyl-1H-indole, indole, 3-*beta*-coprostanol, *beta*-sitosterol, *beta*-stigmasterol, and cholesterol) or with fuel combustion (2,6-dimethylnaphthalene, fluoranthene, phenanthrene, *para*-cresol, phenol, and pyrene). *Beta*-sitosterol and *beta*-stigmasterol are plant sterols and also can occur in natural waters and sediments through breakdown of native vegetation. Thus, the OWCs detected in bottom sediment collected from site US2 probably were contributed by upstream nonpoint animal agriculture sources, local runoff from roads, or (in the case of *beta*-sitosterol and *beta*-stigmasterol) breakdown of native vegetation.

Twenty different OWCs, including 9 HIACs (3-methyl-1H-indole, anthraquinone, *bis*(2-ethylhexyl) phthalate, bisphenol-A, indole, NP2EO, *para*-cresol, phenol, and triclosan), 7 PAHs (2,6-dimethylnaphthalene, anthracene, benzo[*a*]pyrene, fluoranthene, naphthalene, phenanthrene, and pyrene), and 4 SCs (3-*beta*-coprostanol, *beta*-sitosterol, *beta*-stigmasterol, and cholesterol), were detected in bottom

sediment collected from Big Sioux River sites downstream from the WWTP effluent discharge (sites DS1 and DS2). In addition to OWCs typically associated with animal fecal material (3-methyl-1H-indole, indole, 3-*beta*-coprostanol, *beta*-sitosterol, *beta*-stigmasterol, and cholesterol) or with fuel combustion (2,6-dimethylnaphthalene, anthracene, benzo[*a*]pyrene, fluoranthene, naphthalene, phenanthrene, *para* cresol, phenol, and pyrene), OWCs detected in bottom sediment collected from sites DS1 and DS2 also included some compounds typically associated with household or industrial wastewaters (anthraquinone, *bis*(2-ethylhexyl) phthalate, bisphenol-A, NP2EO, and triclosan). Thus, the OWCs detected in bottom sediment collected from sites DS1 and DS2 probably were contributed by a combination of upstream nonpoint animal agriculture sources, urban runoff, WWTP effluent discharges, or (in the case of *beta*-sitosterol and *beta*-stigmasterol) breakdown of native vegetation.

Table 5. Statistical summaries of analytical results for organic wastewater compounds in bottom-sediment samples.

[Units are micrograms per kilogram. --, no data collected or not detected]

	Station identification number and name (site label)		
	433600096442400 Sioux Falls pump station intake from Big Sioux River at Sioux Falls, SD (site US2, fig. 1)	433559096390700 Big Sioux River downstream from Sioux Falls wastewater discharge (site DS1, fig. 1)	433541096355800 Big Sioux River at Brandon, SD (site DS2, fig. 1)
Date of sample collection (month–day–year)	09–09–2002	09–10–2002	09–11–2002
Time of sample collection (24-hour)	1200	1030	1030
Human pharmaceutical compounds (HPCs)			
No compounds analyzed for	--	--	--
Human and veterinary antibiotic compounds (HVACs)			
No compounds analyzed for	--	--	--
Major agricultural herbicides (MAHs)			
Number of compounds detected	0	0	0
Minimum detected concentration	--	--	--
Median detected concentration	--	--	--
Maximum detected concentration	--	--	--
Total detected concentration	--	--	--
Household, industrial, and minor agricultural use compounds (HIACs)			
Number of compounds detected	4	8	8
Minimum detected concentration	42	4.6	1.9
Median detected concentration	50	58	26
Maximum detected concentration	430	240	180
Total detected concentration	570	560	340
Polyaromatic hydrocarbons (PAHs)			
Number of compounds detected	4	7	6
Minimum detected concentration	7.6	11	8.2
Median detected concentration	9.3	26	25
Maximum detected concentration	21	38	58
Total detected concentration	47	180	170
Sterol compounds (SCs)			
Number of compounds detected	4	4	4
Minimum detected concentration	190	410	190
Median detected concentration	960	1,300	700
Maximum detected concentration	1,600	2,600	1,200
Total detected concentration	3,700	5,600	2,800
All organic wastewater compounds (OWCs)			
Number of compounds detected	12	19	18
Minimum detected concentration	7.6	4.6	1.9
Median detected concentration	50	38	33
Maximum detected concentration	1,600	2,600	1,200
Total detected concentration	4,300	6,400	3,300

Table 5. Statistical summaries of analytical results for organic wastewater compounds in bottom-sediment samples.—Continued

[Units are micrograms per kilogram. --, no data collected or not detected]

	Station identification number and name (site label)		
	433600096442400 Sioux Falls pump station intake from Big Sioux River at Sioux Falls, SD (site US2, fig. 1)	433559096390700 Big Sioux River downstream from Sioux Falls wastewater discharge (site DS1, fig. 1)	433541096355800 Big Sioux River at Brandon, SD (site DS2, fig. 1)
Major agricultural herbicides (MAHs) that are suspected endocrine-disrupting compounds (EDCs)			
Number of compounds detected	0	0	0
Minimum detected concentration	--	--	--
Median detected concentration	--	--	--
Maximum detected concentration	--	--	--
Total detected concentration	--	--	--
Household, industrial, and minor agricultural use compounds (HIACs) that are suspected endocrine-disrupting compounds (EDCs)			
Number of compounds detected	0	2	3
Minimum detected concentration	--	6.3	2.9
Median detected concentration	--	58	65
Maximum detected concentration	--	110	180
Total detected concentration	--	120	250
Polyaromatic hydrocarbons (PAHs) that are suspected endocrine-disrupting compounds (EDCs)			
Number of compounds detected	2	4	4
Minimum detected concentration	7.6	11	14
Median detected concentration	8.4	24	25
Maximum detected concentration	9.3	38	58
Total detected concentration	17	97	120
All suspected endocrine-disrupting compounds (EDCs)			
Number of compounds detected	2	6	7
Minimum detected concentration	7.6	6.3	2.9
Median detected concentration	8.4	24	27
Maximum detected concentration	9.3	110	180
Total detected concentration	17	210	370

The ratios of concentrations of 3-*beta*-coprostanol to cholesterol in bottom sediment collected from sites US2, DS1, and DS2 were 12, 19, and 16 percent, respectively. The higher ratios for sites DS1 and DS2 probably indicate greater contributions from human sewage at those sites. The ratios in bottom sediment for sites DS1 and DS2 were smaller than ratios in water samples collected during base-flow conditions (table 4), which probably indicates degradation of 3-*beta*-coprostanol in bottom sediment over time and/or dilution of 3-*beta*-coprostanol in bottom sediment caused by deposition of organic material with smaller ratios originating from sources other than WWTP effluents.

Two EDCs (phenanthrene and pyrene, which are PAHs) were detected in bottom sediment collected from site US2. Seven EDCs (bisphenol-A, NP2EO, and triclosan, which are HIACs; and anthracene, benzo[*a*]pyrene, phenanthrene, and

pyrene, which are PAHs) were detected in bottom sediment collected from sites DS1 and DS2.

Relations Between Concentrations of Organic Wastewater Compounds in Dissolved and Whole-Water Fractions

For the May 17–18 and May 30–31, 2004, sampling periods, water samples were collected and analyzed for both dissolved and whole-water fractions of 2 nonprescription HPCs, 2 MAHs, 43 HIACs, 10 PAHs, and 4 SCs using analytical methods 3 and 4. Evaluation of whether these compounds were occurring in dissolved or particulate phase might provide information on possible sources of the compounds that occurred in the Big Sioux River and also provide information on the types

Table 6. Organic wastewater compounds detected in bottom-sediment samples.

[Bold text indicates suspected endocrine-disrupting compound (EDC). NP2EO, nonylphenol diethoxylate; --, no data collected]

	Station identification number and name (site label)		
	433600096442400 Sioux Falls pump station intake from Big Sioux River at Sioux Falls, SD (site US2, fig. 1)	433559096390700 Big Sioux River downstream from Sioux Falls wastewater discharge (site DS1, fig. 1)	433541096355800 Big Sioux River at Brandon, SD (site DS2, fig. 1)
Date of sample collection (month-day-year)	09-09-2002	09-10-2002	09-11-2002
Time of sample collection (24-hour)	1200	1030	1030
Number of compounds detected	12	19	18
Human pharmaceutical compounds (HPCs)			
No compounds analyzed for	--	--	--
Human and veterinary antibiotic compounds (HVACs)			
No compounds analyzed for	--	--	--
Major agricultural herbicides (MAHs)			
No compounds detected	--	--	--
Household, industrial, and minor agricultural-use compounds (HIACs)			
	3-Methyl-1H-indole (skatol)	3-Methyl-1H-indole (skatol)	3-Methyl-1H-indole (skatol)
	Indole	Anthraquinone	Anthraquinone
	<i>para</i> -Cresol	Bis(2-ethylhexyl) phthalate	Bisphenol-A
	Phenol	Indole	Indole
		NP2EO	NP2EO
		<i>para</i> -Cresol	<i>para</i> -Cresol
		Phenol	Phenol
		Triclosan	Triclosan
Polyaromatic hydrocarbons (PAHs)			
	2,6-Dimethylnaphthalene	2,6-Dimethylnaphthalene	Anthracene
	Fluoranthene	Anthracene	Benzo[<i>a</i>]pyrene
	Phenanthrene	Benzo[<i>a</i>]pyrene	Fluoranthene
	Pyrene	Fluoranthene	Naphthalene
		Naphthalene	Phenanthrene
		Phenanthrene	Pyrene
		Pyrene	
Sterol compounds (SCs)			
	3- <i>beta</i> -Coprostanol	3- <i>beta</i> -Coprostanol	3- <i>beta</i> -Coprostanol
	<i>beta</i> -Sitosterol	<i>beta</i> -Sitosterol	<i>beta</i> -Sitosterol
	<i>beta</i> -Stigmastanol	<i>beta</i> -Stigmastanol	<i>beta</i> -Stigmastanol
	Cholesterol	Cholesterol	Cholesterol

of hydrologic conditions that affect the occurrence of the compounds in the river. During storm-runoff conditions, the load of OWCs in the Big Sioux River downstream from the WWTP effluent discharge was substantially larger than the load contributed by the WWTP effluent discharge. An issue of interest was the relative contributions of either direct stormwater runoff or resuspension of bottom sediment to OWC concentrations in the Big Sioux River downstream from the WWTP effluent discharge.

For many compounds, differences in method performance between analytical methods 3 and 4 complicated comparison of dissolved and whole-water fractions. For most HPCs, MAHs, HIACs, and PAHs, analytical method 4 (performed on filtered water samples) had higher percent recoveries in laboratory reagent spike samples and environmental matrix spike samples than analytical method 3 (performed on unfiltered samples). However, percent recoveries for SCs were similar between analytical methods 3 and 4. Probably as a result of these patterns, dissolved concentrations of many HPCs, MAHs, and HIACs in environmental samples were larger than whole-water concentrations.

Analytical results for 3-*beta*-coprostanol and *beta*-sitosterol did not clearly indicate substantial differences between dissolved and whole-water fractions in water samples collected from Big Sioux River sites. Whole-water cholesterol concentrations generally were larger than dissolved concentrations, especially for the May 17–18, 2004, sampling period, which indicates that particulate material contributed to the whole-water concentrations.

Some PAHs (including fluoranthene, phenanthrene, and pyrene) generally had larger whole-water concentrations than dissolved concentrations, even though percent recoveries for analytical method 3 generally were lower than for analytical method 4, indicating that part of the whole-water concentration was contributed by particulate material. This general pattern was evident for samples from sites US3, US4, DS1, and DS2 during both the May 17–18 and May 30–31, 2004, sampling periods. PAHs generally are hydrophobic and tend to partition to particulate phase. The PAHs that generally had larger whole-water concentrations than dissolved concentrations also were detected in bottom sediment (collected during the September 2002 sampling period) at sites US1, DS1, and DS2 (fig. 6, tables 5 and 6). Hydrologic conditions that might result in resuspension of sediment from the river bottom also are the same types of conditions that could mobilize terrestrial particulate material and contribute it to the river in stormwater runoff, making it difficult to conclusively determine sources of the particulate fraction of OWCs in the Big Sioux River during runoff sampling periods. The data collected in this study are not adequate to conclusively determine the extent to which resuspension of bottom material might have contributed to OWC concentrations in the Big Sioux River during storm-runoff sampling periods. However, the load of OWCs for the May 17–18, 2004, sampling period (below-normal flow/spring storm-runoff conditions following extended below-normal stream-flow) was substantially larger at site DS1 than at site US4. The

increase in load between sites US4 and DS1 primarily was due to individual HIACs, PAHs, and SCs that also were detected in bottom-sediment samples collected during the September 2002 sampling period. These patterns might indicate that part of the increase in OWC load at site DS1 was contributed by resuspension of bottom sediment during the May 17–18, 2004, sampling period. For the May 30–31, 2004, sampling period (above-normal flow/spring storm-runoff conditions) the load of OWCs at site DS1 was less than at site US4, and loads of PAHs and SCs decreased between sites US4 and DS1. These patterns might indicate that the load of OWCs in the Big Sioux River downstream from site US4 primarily was contributed by urban runoff and nonpoint agricultural sources upstream from site US4.

Implications of Occurrence

Several previous USGS studies have reported concentrations of OWCs in natural waters and WWTP effluents in the United States. Kolpin and others (2002) reported OWCs in water samples collected from a network of 139 streams across 30 States during 1999–2000. Glassmeyer and others (2005) reported OWCs in water samples collected from WWTP effluents and natural receiving waters for 10 municipalities across the United States. Lee and others (2004) reported OWCs in water samples collected from 65 sites (wastewater, surface water, ground water, and drinking water) in Minnesota. Kolpin and others (2004) reported OWC concentrations in water samples collected from stream sites both upstream and downstream from WWTP effluent discharges of 10 cities in Iowa. Detected concentrations of individual OWCs found in water samples collected from the Big Sioux River in or near Sioux Falls described in this report generally were within ranges of concentrations reported in these previous studies. Maximum concentrations of detected OWCs found in water samples collected from the Big Sioux River in or near Sioux Falls generally were substantially less than maxima reported by Kolpin and others (2002), Lee and others (2004), and Glassmeyer and others (2005), and generally were similar to maxima reported by Kolpin and others (2004). It should be noted that the maximum concentrations reported by Lee and others (2004) and Glassmeyer and others (2005) included results for WWTP effluents. A notable exception to these patterns is that some HVACs (including ciprofloxacin, erythromycin-H₂O, sulfamethoxazole, tetracycline, and trimethoprim) were detected in water samples collected from the Big Sioux River in or near Sioux Falls at concentrations generally larger than the median concentrations reported by Kolpin and others (2004) and approaching or exceeding maxima reported by Kolpin and others (2004), Lee and others (2004), and Glassmeyer and others (2005), even when concentrations in WWTP effluents were included.

There were no human-health concerns apparent in the results of this study. Only one OWC (metolachlor) was detected in the Sioux Falls finished drinking water at an extremely small concentration. Also, water-contact recreation in the Big Sioux

River near Sioux Falls is very limited. Thus, concerns related to the occurrence of OWCs from the Big Sioux River near Sioux Falls focus primarily on effects on aquatic ecology; perhaps of primary concern would be potential endocrine-disrupting effects on aquatic organisms.

Occurrence of EDCs in aquatic systems is a very complex and sensitive issue. A complete assessment of potential effects of EDCs in the Big Sioux River in or near Sioux Falls based on the results of this study is not possible for several reasons. Sex hormones, which are the most potent EDCs, commonly are present in WWTP effluent at concentrations sufficient to cause endocrine disruption; however, sex hormones were not reported for this study. Also, a relatively small number of water-quality samples were collected from the Big Sioux River Basin during this study. WWTP effluent discharges vary with time, and concentrations of EDCs in wastewaters vary seasonally and inter-annually (Rodgers-Gray and others, 2000; Sheahan and others, 2002). Thus, it is very difficult to accurately quantify inputs of EDCs to the Big Sioux River Basin by determining EDC concentrations in a relatively small number of samples. Also, mixtures of individual EDCs, like those that typically were found in samples collected from the Big Sioux River, generally are believed to have the potential to act additively, but mixture effects are poorly understood (Sumpter and Johnson, 2005). Further, relatively few of the many organic compounds that might be present in WWTP effluents have been evaluated for potential endocrine-disrupting effects (Sumpter and Johnson, 2005). For the EDCs that were determined in this study, total concentrations in water samples collected from the Big Sioux River downstream from WWTP effluents rarely exceeded 2 µg/L. It has been determined that some EDCs can have endocrine-disrupting effects at very low concentrations (near or less than 1 µg/L), and some mechanisms of endocrine disruption make it very difficult to define no-effect levels (Welshons and others, 2003). However, for the EDCs determined in this study, concentrations that result in observable endocrine-disruption effects generally have been reported to be much larger than those observed in the Big Sioux River (Sumpter and Johnson, 2005).

Although this study cannot provide a definitive assessment of EDC effects in the Big Sioux River, a brief synopsis of research on the occurrence of EDCs in aquatic environments provides a context for the EDC results and illustrates the complexity of the issue of EDCs in aquatic environments. Effects of endocrine disruptors in aquatic environments often are investigated by documenting atypical sexual characteristics in individual organisms (for example, occurrence of female biomarkers in male fish), but very few studies have conclusively documented that these effects actually result in either reduced reproductive potential of the individuals or negative effects on reproductive success at the population level (Sumpter and Jobling, 1995; Gies and others, 2001). Thus, few studies of EDCs conclusively indicate negative reproductive effects in aquatic ecosystems. However, in some studies skewed sex ratios and abnormal gonadal histology indicate that individual- and population-level

effects on reproductive success are possible (Desbrow and others, 1998).

Potential EDCs detected in the Big Sioux River probably were derived from three general types of sources: (1) WWTP discharges (AHTN, benzophenone, HHCb, NP2EO, NP1EO, and NP were detected in the Big Sioux River and probably were attributable to WWTP discharges); (2) urban runoff (anthracene, benzo[*a*]pyrene, diazinon, OP2EO, OP1EO, phenanthrene, and pyrene were detected in the Big Sioux River and probably were attributable to urban runoff); and (3) nonpoint source crop agriculture (atrazine was detected in the upper Big Sioux River Basin and primarily is attributable to nonpoint agricultural crop sources). Research has been conducted on EDCs from these types of sources. Sex hormones, alkylphenols (APs), and AP ethoxylates generally have been implicated as the primary causative agents in WWTP effluents that result in estrogenic effects in aquatic organisms (Jobling and Sumpter, 1993; Desbrow and others, 1998; Gies and others, 2001; Harris and others, 2001; and Jobling and Tyler, 2003). Sex hormones (primarily the natural and synthetic estrogens 17β estradiol and ethynyl estradiol) generally are regarded as the most potent EDCs, can produce significant atypical sexual characteristics in fish at concentrations less than 0.025 µg/L (Sumpter and Johnson, 2005), and in some studies have been implicated as the primary compounds contributing to feminization of male fish (Huggett and others, 2003) as a result of exposure to WWTP effluents. Sex hormones commonly are found in WWTP effluent discharges (Jobling and Tyler, 2003), so it is possible that they occur in the Big Sioux River downstream from the Sioux Falls WWTP.

AP ethoxylates and their shorter chain metabolites are complex nonionic surfactants. Of the various APs and AP ethoxylates, certain isomers of nonylphenol and octylphenol appear to have the largest endocrine-disrupting activities and have shown substantial estrogenic activity at concentrations in the range of about 8 to 10 µg/L (Jobling and others, 1996; Harris and others, 2001). APs and AP ethoxylates detected in the Big Sioux River at concentrations greater than the SRL include NP2EO, NP1EO, NP, OP2EO, and OP1EO. The largest combined concentration for these compounds in any water sample collected from the Big Sioux River was about 3.8 µg/L, which is less than the reported endocrine-disruption substantial-effect level of even the most potent individual AP (Sumpter and Johnson, 2005).

Other WWTP-sourced EDCs in the Big Sioux River have shown endocrine-disrupting effects in various laboratory studies but generally are not implicated as major causative agents of endocrine disruption in aquatic organisms in field studies. The other WWTP-sourced EDCs detected in the Big Sioux River that have shown endocrine-disrupting effects include AHTN (Richard and others, 2002; Richard and others, 2004), benzophenone (Schlumpf and others, 2001), and HHCb (Richard and others, 2002; Richard and others, 2004). Generally, these compounds have much less potent endocrine-disrupting effects than either sex hormones or APs and AP ethoxylates, with substantial-effect levels based on laboratory studies

generally exceeding 50 µg/L (Richard and others, 2004; Sumpter and Johnson, 2005). The maximum concentration found in any water sample collected from the Big Sioux River for any of these compounds was about 0.56 µg/L (AHTN was detected at this concentration in a water sample collected from site DS2).

Some researchers have concluded that EDCs are present in most, if not all, treated sewage effluents (Jobling and Tyler, 2003). In some settings, endocrine-disruption effects on aquatic organisms have occurred where WWTP effluent discharges accounted for between 25 and 50 percent of the flow of receiving waters for relatively short periods of time (about 1 month) and as little as 10 percent of the flow of receiving waters for longer periods (about 4 months) (Harries and others, 1999; Rodgers-Gray and others, 2000). Assuming an average discharge from the Sioux Falls WWTP of 22 ft³/s (which was about the average discharge during the study sampling periods) and comparing this level of effluent discharge to the observed flow of the Big Sioux River during water years 1977–2004, an effluent discharge of 22 ft³/s would have accounted for about 50 percent of the flow of the Big Sioux River about 8 percent of the time, about 25 percent of the flow of the Big Sioux River about 25 percent of the time, and about 10 percent of the flow of the Big Sioux River about 45 percent of the time. Based on these observations, it is possible that the Sioux Falls WWTP effluent discharges might during some periods produce endocrine-disrupting effects on aquatic organisms. However, it should be noted that concentrations and loads of EDCs decreased substantially between sites DS1 and DS2, so potential endocrine-disrupting effects of the Sioux Falls WWTP effluent discharges probably would be restricted to a relatively short reach of the Big Sioux River. Also, results of other studies demonstrating endocrine-disrupting effects of WWTP effluent discharges on aquatic organisms do not necessarily have direct application to the Big Sioux River because (1) wastewater treatment technologies and types of raw sewage inputs to different WWTPs vary substantially and result in large variability in EDC concentrations in different WWTP effluents; and (2) EDC effects on aquatic organisms are species dependent (Sumpter and Johnson, 2005), and species present in the Big Sioux River may differ from species in other studies.

The EDCs anthracene, benzo[*a*]pyrene, diazinon, OP2EO, OP1EO, phenanthrene, and pyrene were detected in the Big Sioux River and probably were attributable to urban runoff. Anthracene, benzo[*a*]pyrene, phenanthrene, and pyrene are PAHs that occur as a result of incomplete combustion of fossil fuels or petroleum products that are used in road materials. Laboratory studies have implicated these compounds as EDCs (Chaloupka and others, 1993; Cooke and others, 1994; Keith, 1998) but at much higher concentrations than were detected in samples collected from the Big Sioux River. The maximum total concentration of these PAH EDCs in any individual Big Sioux River sample was about 0.55 µg/L. OP2EO and OP1EO are alkylphenol ethoxylates with typical uses as surfactants in detergents and a large variety of other products. The maximum total concentration of OP2EO and OP1EO in any individual Big

Sioux River sample was about 0.64 µg/L. The most potent individual APs have been reported to have substantial endocrine-disruption effects at about 8 to 10 µg/L (Sumpter and Johnson, 2005).

Atrazine is a herbicide contributed to the Big Sioux River primarily from nonpoint crop agriculture activities and has been implicated in both field and laboratory studies as having endocrine-disrupting effects on aquatic organisms (Hayes and others, 2003; Spano and others, 2004). Atrazine exposure has been reported to result in reproductive abnormalities in frogs at concentrations as small as 0.1 µg/L (Hayes and others, 2003), but reported effect levels for fish generally are substantially larger. Spano and others (2004) reported gonadal abnormalities in fish exposed to atrazine at a concentration of 100 µg/L. Brin-golf and others (2004) reported lower egg production in fathead minnows exposed to atrazine at a concentration of 0.5 µg/L; however, the results were not found to be statistically significant. Atrazine was detected in about 67 percent of samples collected from Big Sioux River sites at concentrations ranging from 0.02 to 2.7 µg/L (median of 0.29 µg/L). Based on the lack of definitive research establishing endocrine-disruptive effect levels for atrazine and the relatively small number of samples collected during this study, it is not possible to assess whether atrazine concentrations detected in Big Sioux River samples might have the potential for endocrine disruption of aquatic organisms. However, the relatively large frequency of detection for atrazine might indicate a cause for concern.

Summary and Conclusions

The U.S. Geological Survey (USGS) in cooperation with the city of Sioux Falls conducted several rounds of sampling to determine the occurrence of organic wastewater compounds (OWCs) in the city of Sioux Falls drinking water and wastewater effluent, and the Big Sioux River in or near Sioux Falls during August 2001 through May 2004. Water samples were collected during both base-flow and storm-runoff conditions. Water samples were collected at 8 sites, which included 4 sites upstream from the wastewater treatment plant (WWTP) discharge, 2 sites downstream from the WWTP discharge, 1 finished drinking-water site, and 1 WWTP effluent site (WWE). Not all sampling sites were sampled during every sampling round. Bottom-sediment samples were collected from three sampling sites during one of the sampling periods when water samples were collected.

A total of 125 different OWCs were analyzed for in this study using five different analytical methods. Analyses for OWCs were performed at USGS laboratories that are developing and/or refining small-concentration (less than 1 microgram per liter (µg/L)) analytical methods. The OWCs were classified into six compound classes: human pharmaceutical compounds (HPCs); human and veterinary antibiotic compounds (HVACs); major agricultural herbicides (MAHs); household, industrial, and minor agricultural compounds (HIACs); polyaromatic

hydrocarbons (PAHs); and sterol compounds (SCs). Some of the compounds in the HPC, MAH, HIAC, and PAH classes are suspected of being endocrine-disrupting compounds (EDCs). Of the 125 different OWCs analyzed for in this study, 81 OWCs had one or more detections in environmental samples reported by the laboratories, and of those 81 OWCs, 63 had acceptable analytical method performance, were detected at concentrations greater than the study reporting levels, and were included in analyses and discussion related to occurrence of OWCs in drinking water, wastewater effluent, and the Big Sioux River.

OWCs in all compound classes were detected in water samples from sampling sites in the Sioux Falls area. For the five sampling periods when samples were collected from the Sioux Falls finished drinking water, only one OWC was detected at a concentration greater than the study reporting level (metolachlor; 0.0040 µg/L).

During base-flow conditions, Big Sioux River sites upstream from the WWTP discharge had OWC contributions that primarily were from nonpoint animal or crop agriculture sources or had OWC concentrations that were minimal. The influence of the WWTP discharge on OWCs at downstream river sites during base-flow conditions ranged from small influence to substantial influence depending on the sampling period. During runoff conditions, OWCs at sites upstream from the WWTP discharge probably were primarily contributed by nonpoint animal and/or crop agriculture sources and possibly by stormwater runoff from nearby roads. OWCs at sites downstream from the WWTP discharge probably were contributed by sources other than the WWTP effluent discharge, such as stormwater runoff from urban and/or agriculture areas and/or resuspension of OWCs adsorbed to sediment deposited in the Big Sioux River. OWC loads generally were substantially smaller for upstream sites than downstream sites during both base-flow and runoff conditions.

Total OWC concentrations ranged from about 2 to 4 µg/L at the site farthest upstream from the WWTP discharge, from 0.01 to about 3.5 µg/L at the second most upstream site, from 3 to 5 µg/L at the third most upstream site, and from about 5 to 6 µg/L for the site closest upstream from the WWTP discharge. Total OWC loads and concentrations generally were smaller for the upstream sites than for the downstream sites. Total OWC concentrations for site WWE ranged from about 10 to 45 µg/L and always were larger than for Big Sioux River sites. Total OWC loads also were larger for site WWE than for all Big Sioux River sampling sites during base-flow sampling periods but were smaller for site WWE than for one upstream site and both downstream sites during storm-runoff sampling periods. Total OWC concentrations ranged from about 3 to 12 µg/L at the site closest downstream from the WWTP discharge and from about 2 to 13 µg/L at the farthest downstream site. Discernible concentrations from the WWTP effluent discharge to OWC concentrations at the downstream sites are evidenced by occurrence of several individual OWCs only in samples collected from site WWE and the downstream sites. Total loads and concentrations were smaller at the farthest downstream site than at the closest site downstream from the WWTP effluent.

HPCs were detected in samples collected from all Big Sioux River sites (except the site farthest upstream) and from site WWE. Generally HPCs contributed very little to OWC concentrations at any of the sampling sites during any streamflow conditions. HVACs probably were contributed by nonpoint animal agriculture sources for sites upstream from the WWTP effluent and by the WWTP effluent discharge and possibly from nonpoint animal agriculture sources for downstream sites. HVACs generally accounted for a relatively small part of the total OWC concentrations in water samples collected from all sampling sites, with the exception of two sampling periods for site WWE and the downstream sites. MAHs generally accounted for a relatively small part of the total OWC concentrations in samples collected from the WWTP effluent for all sampling periods and in samples collected from the Big Sioux River sites during base-flow conditions. During some but not all of the storm-runoff sampling periods, MAHs accounted for a substantial part of the total OWC concentrations at the river sites. In samples from the upstream sites, HIACs generally accounted for a relatively small part of the total OWC concentrations during base-flow conditions and for a substantial part during some but not all of the storm-runoff sampling periods. HIACs generally accounted for a substantial part of the total OWC concentrations in samples collected from site WWE during all sampling periods. In samples collected from downstream sites, HIACs generally accounted for a substantial part of the total OWC concentration during base-flow conditions and during some but not all of the storm-runoff sampling periods. PAHs only were detected at Big Sioux River sites that might be substantially affected by storm-runoff from roads. PAHs were not detected during any base-flow sampling period and were detected during some but not all storm-runoff periods. Even during runoff periods, PAHs accounted for less than 20 percent of total OWC concentrations. SCs generally comprised a substantial part of the total detected OWC concentrations for site WWE and Big Sioux River sites during both base-flow and storm-runoff conditions. The occurrence of the SC *3-beta-coprostanol* in samples from site WWE and downstream sites is particularly relevant with respect to evaluating sources of OWCs because *3-beta-coprostanol* is a major component of human feces. Results indicate that the WWTP discharge substantially contributed to the occurrence of OWCs in the Big Sioux River during below-normal base-flow conditions.

EDCs were detected in samples collected from all sampling sites except the finished drinking water. EDCs in samples collected from upstream sites generally had larger concentrations and loads during runoff sampling periods than during base-flow periods and probably were primarily contributed by nonpoint crop agriculture sources. During base-flow periods, EDCs in water samples collected from downstream sites primarily consisted of HIACs, and concentrations varied in association with concentrations in water samples collected from site WWE and the relation between the WWTP effluent discharges and the flow in the Big Sioux River. During storm-runoff conditions, EDCs in water samples collected from downstream sites sometimes primarily consisted of HIACs, which

probably were primarily contributed by urban stormwater runoff, and sometimes primarily consisted of MAHs, which probably primarily were contributed by nonpoint crop agriculture sources.

Bottom-sediment samples were collected from one upstream sampling site and two downstream sampling sites during a base-flow sampling period. The bottom-sediment samples were analyzed for 3 MAHs, 44 HIACs, 10 PAHs, and 4 SCs. OWCs in the HIAC, PAH, and SC compound classes were detected in all bottom-sediment samples, but no MAH compounds were detected in any bottom-sediment samples. The OWCs detected in bottom sediment collected from the upstream site probably were contributed by upstream nonpoint animal agriculture sources, local runoff from roads, or the breakdown of native vegetation. The OWCs detected in bottom sediment collected from the downstream sites probably were contributed by a combination of upstream nonpoint animal agriculture sources, urban runoff, WWTP effluent discharges, or breakdown of native vegetation.

There were no human-health concerns apparent in the results of this study. Occurrence of EDCs in aquatic systems is a very complex and sensitive issue. A complete assessment of potential effects of EDCs in the Big Sioux River in or near Sioux Falls based on the results of this study is not possible. However, EDC concentrations in the Big Sioux River generally were less than concentrations reported to have substantial endocrine-disrupting effects on aquatic organisms. The relatively large frequency of detection for atrazine might indicate a cause for concern with respect to endocrine-disruption effects for aquatic organisms.

References

- Barnes, K.K., Meyer, M.T., Thurman, M.T., Furlong, E.T., Zaugg, S.D., and Barber, L.B., 2002, Water-quality data for pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: U.S. Geological Survey Open-File Report 02–94, accessed July 7, 2006, at <http://toxics.usgs.gov/pubs/OFR-02-94/>
- Bringolf, R.B., Belden, J.B., and Summerfelt, R.C., 2004, Effects of atrazine on fathead minnow in a short-term reproductive assay: *Environmental Toxicology and Chemistry*, v. 23, p. 1019–1023.
- Bull, I.D., Lockheart, M.J., Elhmmali, M.M., Roberts, D.J., and Evershed, R.P., 2002, The origin of faeces by means of biomarker detection: *Environment International*, v. 27, p. 647–654.
- Burkhardt, M.R., ReVello, R.C., Smith, S.G., and Zaugg, S.D., 2005, Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for industrial and anthropogenic waste-indicator compounds in sediment: *Analytica Chimica Acta*, v. 534, p. 89–100.
- Cahill, J.D., Furlong, E.T., Burkhardt, M.R., Kolpin, Dana, and Anderson, L.G., 2004, Determination of pharmaceutical compounds in surface- and ground-water samples by solid-phase extraction and high-performance liquid chromatography/electrospray ionization mass spectrometry: *Journal of Chromatography A*, v. 1041, nos. 1–2, p. 171–180.
- Chaloupka, K.L., Harper, N.R., Krishnan, V., Santostefano, M., Rodriguez, L.V., and Safe, S.H., 1993, Synergistic activity of polynuclear aromatic hydrocarbon mixtures as aryl hydrocarbon (Ah) receptor agonists: *Chemico-Biological Interactions*, v. 89, p. 141–158.
- Cook, J.W., Dodds, E.C., Hewett, C.L., and Lawson, W., 1994, The estrogenic activity of some condensed-ring compounds in relation to their other biological activities: *Proceedings of the Royal Society of London*, v. 114, p. 272–286.
- Desbrow, C., Routledge, E.J., Brighty, G.C., Sumpter, J.P., and Waldock, M., 1998, Identification of estrogenic chemicals in STW effluent—1. Chemical fractionation and in vitro biological screening: *Environmental Science & Technology*, v. 32, p. 1549–1558.
- East Dakota Water Development District, 2004, Central Big Sioux River Watershed Assessment draft final report and TMDL: Pierre, South Dakota, South Dakota Department of Environment and Natural Resources, 230 p.
- Flint, R.F., 1971, *Glacial and Quaternary geology*: New York, John Wiley and Sons, 892 p.
- Gies, Andreas; Gottschalk, Christa; Greiner, Petra; Heger, Wolfgang; Kolossa, Marike; Rechenberg, Bettina; Robkamp, Elke; Schroeter-Kermani, Christa; Steinhäuser, Klaus; and Throl, Christine, 2001, Chemicals in the environment which interfere with the endocrine systems of humans and wildlife—pollution, effects, control strategies: Report by the German Federal Environmental Agency (UBA), 53 p., accessed August 5, 2005, at <http://www.umweltdaten.de/download/chempol2.pdf>
- Glassmeyer, S.T., Furlong, E.T., Kolpin, D.W., Cahill, J.D., Zaugg, S.D., Werner, S.L., Meyer, M.T., and Kryak, D.D., 2005, Transport of chemical and microbial compounds from known wastewater discharges—potential for use as indicators of human fecal contamination: *Environmental Science & Technology*, v. 39, no. 14, p. 5157–5169.
- Halling-Sorensen, B., Nielsen, S.N., Lanzky, P.F., Ingerslev, F., Lutzhoft, H.C.H., and Jorgensen, S.E., 1998, Occurrence, fate, and effects of pharmaceutical substances in the environment—a review: *Chemosphere*, v. 36, no. 2, p. 357–394.
- Harries, J.E.; Janbakhsh, Afsaneh; Jobling, Susan; Matthiessen, Peter; Sumpter, J.P.; and Tyler, C.R., 1999, Estrogenic potency of effluent from two sewage treatment works in the United Kingdom: *Environmental Toxicology and Chemistry*, v. 18, p. 932–937.
- Harris, C.A., Santos, E.M., Janbakhsh, A., Pottinger, T.G., Tyler, C.R., and Sumpter, J.P., 2001, Nonylphenol affects gonadotropin levels in the pituitary gland and plasma of female rainbow trout: *Environmental Science & Technology*, v. 35, p. 2909–2916.

- Hayes, Tyrone; Haston, Kelly; Tsui, Mable; Hoang, Anhthu; Haeffele, Cathryn; and Vonk, Aaron; 2003, Atrazine-induced hermaphroditism at 0.1 ppb in American leopard frogs (*Rana pipiens*)—laboratory and field evidence: *Environmental Health Perspectives*, v. 111, p. 568–575.
- Huggett, D.B.; Foran, C.M.; Brooks, B.W.; Weston, Jim; Peterson, Bethany; Marsh, D.E.; La Point, T.W.; and Schlenk, Daniel, 2003, Comparison of in vitro and in vivo bioassays for estrogenicity in effluent from North American municipal wastewater facilities: *Toxicological Sciences*, v. 72, p. 77–83.
- Jobling, Susan; Sheahan, David; Osborne, J.A.; Matthiessen, Peter; and Sumpter, J.P., 1996, Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals: *Environmental Toxicology and Chemistry*, v. 15, no. 2, p. 194–202.
- Jobling, Susan, and Sumpter, J.P., 1993, Detergent components in sewage effluent are weakly estrogenic to fish—an in vitro study using rainbow trout (*Oncorhynchus mykiss*) hepatocytes: *Aquatic Toxicology*, v. 27, p. 361–372.
- Jobling, Susan, and Tyler, C.R., 2003, Endocrine disruption in wild freshwater fish: *Pure and Applied Chemistry*, v. 75, p. 2219–2234.
- Keith, L.W., 1998, Environmental endocrine disruptors: *Pure and Applied Chemistry*, v. 70, p. 2319–2326.
- Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., and Buxton, H.T., 2002, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000—a national reconnaissance: *Environmental Science & Technology*, v. 36, no. 6, p. 1202–1211.
- Kolpin, D.W., Skopec, Mary, Meyer, M.T., Furlong, E.T., and Zaugg, S.D., 2004, Urban contribution of pharmaceutical and other organic wastewater contaminants to streams during differing flow conditions: *Science of the Total Environment*, v. 328, p. 119–130.
- Lawrence, S.J., and Sando, S.K., 1989, Quality of water from surficial-outwash aquifers in the Big Sioux River Basin, eastern South Dakota: U.S. Geological Survey Water-Resources Investigations Report 89–4170, 81 p.
- Leap, D.I., 1988, Geology and hydrology of Day County, South Dakota: *South Dakota Geological Survey Bulletin* 24, 113 p.
- Lee, K.E., Barber, L.B., Furlong, E.T., Cahill, J.D., Kolpin, D.W., Meyer, M.T., and Zaugg, S.D., 2004, Presence and distribution of organic wastewater compounds in wastewater, surface, ground, and drinking waters, Minnesota, 2000–02: U.S. Geological Survey Scientific Investigations Report 2004–5138, 47 p.
- Leeming, R.L., Ball, A., Ashbolt, N.J., and Nichols, P.D., 1994, Distinguishing between human and animal sources of faecal pollution: *Australian Journal of Chemistry*, v. 61, p. 434–435.
- Rantz, S.E., and others, 1982a, Measurement and computation of streamflow—volume 1. Measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, p. 1–285.
- Rantz, S.E., and others, 1982b, Measurement and computation of streamflow—volume 2. Computation of discharge: U.S. Geological Survey Water-Supply Paper 2175, p. 285–631.
- Richard, H.M.; Schreurs, M.; Legler, Juliette; Artola-Garicano, Elsa; Sinnige, T.L.; Lanser, P.H.; Seinen, Willem; and van der Burg, Bart, 2004, In vitro and in vivo antiestrogenic effects of polycyclic musks in zebrafish: *Environmental Science & Technology*, v. 38, no. 38, p. 997–1002.
- Richard, H.M., Schreurs, M., Quaedackers, M.E., Seinen, Willem, and van der Burg, Bart, 2002, Transcriptional activation of estrogen receptor ER α and ER β by polycyclic musks is cell type dependent: *Toxicology and Applied Pharmacology*, v. 183, no. 1, p. 1–9.
- Richardson, M.L., and Bowron, J.M., 1985, The fate of pharmaceutical chemicals in the aquatic environment: *Journal of Pharmacy and Pharmacology*, v. 37, p. 1–12.
- Rodgers-Gray, T.P.; Jobling, Susan; Morris, Steven; Kelly, Carole; Kirby, Sonia; Janbakhsh, Afsaneh; Harries, J.E.; Waldock, M.J.; Sumpter, J.P.; and Tyler, C.R., 2000, Long-term temporal changes in the estrogenic composition of treated sewage effluent and its biological effects on fish: *Environmental Science & Technology*, v. 34, no. 8, p. 1521–1528.
- Schlumpf, Margret; Cotton, Beata; Conscience, Marianne; Haller, Vreni; Steinmann, Beate; and Lichtensteiger, Walter, 2001, In vitro and in vivo estrogenicity of UV screens: *Environmental Health Perspectives*, v. 109, p. 239–244.
- Sheahan, D.A.; Brighty, G.C.; Daniel, Mic; Jobling, Susan; Harries, J.E.; Hurst, M.R.; Kennedy, Joe; Kirby, S.J.; Morris, Steven; Routledge, E.J.; Sumpter, J.P.; and Waldock, M.J., 2002, Reduction in the estrogenic activity of a treated sewage effluent discharge to an English river as a result of a decrease in the concentration of industrially derived surfactants: *Environmental Toxicology and Chemistry*, v. 21, no. 3, p. 515–519.
- Shelton, L.R., and Capel, P.D., 1994, Guidelines for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94–458, 20 p.
- South Dakota State University, 2005, South Dakota climate and weather—precipitation normals (1971–2000): Data available on Web, accessed April 7, 2005, at <http://climate.sdstate.edu/data/pptnormals.shtml>
- Spano, Laura; Tyler, C.R.; van Aerle, Ronny; Devos, Pierre; Mandiki, S.N.M.; Silvestre, Frederic; Thome, J.P.; and Kestemont, Patrick, 2004, Effects of atrazine on sex steroid dynamics, plasma vitellogenin concentration and gonad development in adult goldfish (*Carassius auratus*): *Aquatic Toxicology*, v. 66, p. 369–379.
- Sumpter, J.P., and Jobling, Susan, 1995, Vitellogenesis as a biomarker for estrogenic contamination of the aquatic environment: *Environmental Health Perspectives*, v. 103, p. 173–187.

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- Sumpter, J.P., and Johnson, A.C., 2005, Lessons from endocrine disruption and their application to other issues concerning trace organics in the aquatic environment: *Environmental Science & Technology*, v. 39, no. 12, p. 4321–4332.
- Stackelberg, P.E., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Henderson, A.K., and Reissman, D.B., 2004, Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant: *Science of the Total Environment*, v. 329, nos. 1–3, p. 99–113.
- Taylor, J.K., 1987, *Quality assurance of chemical measurements*: Chelsea, Mich., Lewis Publishers, 328 p.
- Thorpe, K.L., Hutchinson, T.H., Hetheridge, M.J., Scholze, Martin, Sumpter, J.P., and Tyler, C.R., 2001, Assessing the biological potency of binary mixtures of environmental estrogens using vitellogenin induction in juvenile rainbow trout (*Oncorhynchus mykiss*): *Environmental Science & Technology*, v. 35, no. 35, p. 2476–2481.
- U.S. Census Bureau, 2005, American factfinder: Information available on Web, accessed July 28, 2005, at http://factfinder.census.gov/home/saff/main.html?_lang=en
- U.S. Environmental Protection Agency, 1992, Guidelines establishing test procedures for the analysis of pollutants (Appendix B to part 136, Definition and procedure for the determination of the method detection limit): U.S. Code of Federal Regulations, Title 40, revised as of July 1, 1992.
- U.S. Geological Survey, 1997–2004, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, 2 v., variously paged, available on Web at <http://pubs.water.usgs.gov/twri9A> (chapters were originally published from 1997–1999; updates and revisions are ongoing and are summarized at <http://water.usgs.gov/owq/FieldManual/mastererrata.html>).
- Welshons, W.V., Thayer, K.A., Judy, B.M., Tayler, J.A., Curran, E.M., and vom Saal, F.S., 2003, Large effects from small exposures—mechanisms for endocrine disrupting chemicals with estrogenic activity: *Environmental Health Perspectives*, v. 111, p. 994–1006.
- Zaugg, S.D., Smith, S.G., Schroeder, M.P., Barber, L.B., and Burkhardt, M.R., 2002, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of wastewater compounds by polystyrene-divinylbenzene solid-phase extraction and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01–4186, 37 p.

Supplemental Information
