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Occurrence of Organic Wastewater Compounds in Wastewater Effluent and the Big Sioux River in the Upper Big Sioux River Basin, South Dakota, 2003–2004

Scientific Investigations Report 2005–5249

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

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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)
yard (yd)	0.9144	meter (m)

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

$$°C = (°F - 32) / 1.8$$

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

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

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	Alkylphenols
DEET	N,N-diethyl-*meta*-toluamide
EDCs	Endocrine-disrupting compounds
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
MCX	Cation exchange cartridge
NP	*para*-Nonylphenol
NP1EO	Nonylphenol monoethoxylate
NP2EO	Nonylphenol diethoxylate
NWQL	U.S. Geological Survey National Water Quality Laboratory
OGRL	U.S. Geological Survey 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
TMDL	Total Maximum Daily Load
USGS	U.S. Geological Survey
WWTP	Wastewater treatment plant

Occurrence of Organic Wastewater Compounds in Wastewater Effluent and the Big Sioux River in the Upper Big Sioux River Basin, South Dakota, 2003–2004

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

Abstract

The U.S. Geological Survey (USGS) in cooperation with the East Dakota Water Development District conducted a reconnaissance study to determine the occurrence of organic wastewater compounds (OWCs) in wastewater effluent and the Big Sioux River at or near the cities of Watertown, Volga, and Brookings in the upper Big Sioux River Basin during August 2003 through June 2004. For each city, samples were collected from the wastewater treatment plant (WWTP) effluent and from Big Sioux River sites upstream and downstream from where the wastewater effluent discharges to the Big Sioux River. For Watertown and Brookings, samples were collected during a low-flow period (August 2003) and a runoff period (June 2004). For Volga, samples were collected during two low-flow periods (August 2003 and October 2003) and a runoff period (June 2004).

A total of 125 different OWCs were analyzed for and 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). Of the 125 different OWCs, 45 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 wastewater effluents and the Big Sioux River.

OWCs in all six compound classes were detected in water samples from sampling sites in the Watertown area. The Watertown WWTP discharged continuously to the Big Sioux River during both the low-flow August 2003 and runoff June 2004 sampling periods. Total OWC concentrations for Big Sioux River sites upstream from the Watertown WWTP discharge generally were small, less than 6 micrograms per liter (μg/L) for both sampling periods. SCs accounted for nearly all of the total OWC concentrations for upstream Big Sioux River sites for the low-flow August 2003 sampling period, and MAHs accounted for nearly all of the total OWC concentrations for the runoff June 2004 sampling period. Total OWC concentrations for samples collected from the Watertown wastewater effluent were relatively large for both sampling periods (estimated concentrations ranged from 20 to 41 μg/L), and primarily consisted of HIACs, SCs, and HVACs. Total OWC concentrations for Big Sioux River sites downstream from the Watertown WWTP discharge were relatively large for the low-flow August 2003 sampling period (estimated concentrations ranged from 6.9 to 19 μg/L) and smaller for the runoff June 2004 sampling period (estimated concentrations ranged from 3.3 to 6.5 μg/L), a pattern that probably reflects a greater fraction of the total flow of the Big Sioux River being derived from WWTP discharge during the low-flow sampling period. Major OWC classes contributing to total OWC concentrations for Big Sioux River sites downstream from the Watertown WWTP were HIACs, SCs, and HVACs. Total OWC concentrations decreased substantially between the two downstream Big Sioux River sites. Although confident conclusions could not be made primarily due to possible effects of non-Lagrangian sampling, OWC results for the Watertown area might indicate that (1) OWCs for upstream Big Sioux River sites probably were primarily contributed by nonpoint agricultural sources, with livestock agriculture accounting for most of the total OWC concentration for the low-flow August 2003 sampling period, and crop agriculture accounting for most of the total OWC concentration for the runoff June 2004 sampling period; (2) OWCs for downstream Big Sioux River sites were substantially influenced by contributions from the Watertown WWTP during both the low-flow and runoff sampling periods; and (3) contributions of OWCs that might be derived from nonpoint livestock agricultural sources increased in proportion for the most downstream site for both the low-flow and runoff sampling periods. Suspected endocrine-disrupting compounds (EDCs) were detected in all Big Sioux River samples in the Watertown area. For both the low-flow and runoff sampling periods, the numbers of EDCs detected, and EDC concentrations and loads generally were larger for downstream Big Sioux River sites than for upstream Big Sioux River sites. Combined EDC concentrations for downstream Big Sioux River sites consisted mostly of HIACs for the low-flow sampling period and both HIACs and MAHs for the runoff sampling period.

OWCs in all compound classes except PAHs were detected in samples from sites in the Volga area. The Volga WWTP was not discharging to the Big Sioux River during the low-flow August 2003 and runoff June 2004 sampling periods, but was discharging continuously to the Big Sioux River during the low-flow October 2003 sampling period. For the low-flow August 2003 sampling period, the upstream Big Sioux River site had larger total OWC concentrations and loads than downstream Big Sioux River sites, and SCs accounted for most of the total OWC concentration for all Big Sioux River sites. For the low-flow October 2003 sampling period, when the Volga WWTP was discharging to the Big Sioux River, total OWC concentrations and loads were larger for the downstream Big Sioux River site than for the upstream site, and the increase in load corresponded well with the load contributed by the Volga wastewater effluent discharge, especially for HIACs. HIACs and SCs accounted for most of the total OWC concentrations for Big Sioux River sites for the October 2003 sampling period. For the June 2004 runoff sampling period, the upstream Big Sioux River site had smaller total OWC concentrations and loads than downstream Big Sioux River sites, and MAHs accounted for most of the total OWC concentrations for all Big Sioux River sites. Although confident conclusions could not be made due to possible effects of non-Lagrangian sampling, the data might indicate that (1) for the low-flow August 2003 sampling period, nonpoint livestock agricultural and/or human wastewater sources might have been the primary contributors to occurrence of OWCs at Big Sioux River sampling sites; (2) for the low-flow October 2003 sampling period, nonpoint livestock sources and upstream human wastewater sources primarily contributed to occurrence of OWCs at Big Sioux River sampling sites; (3) for the runoff June 2004 sampling period, nonpoint crop agricultural sources primarily contributed to occurrence of OWCs at Big Sioux River sampling sites; (4) for the low-flow August 2003 and runoff June 2004 sampling periods, seepage of water from the Volga WWTP had little effect on downstream OWC concentrations; and (5) for the low-flow October 2003 sampling period, the Volga wastewater effluent discharge contributed to downstream OWC concentrations. EDCs were detected in all samples collected from sampling sites in the Volga area. For all sampling periods, total EDC concentrations generally were similar between upstream and downstream Big Sioux River sites and consisted of HIACs and MAHs. HIACs accounted for most of the total EDC concentrations for the low-flow August 2003 and October 2003 sampling periods, and MAHs accounted for most of the total EDC concentrations for the runoff June 2004 sampling period for all Big Sioux River sites.

OWCs in all compound classes except PAHs were detected in water samples from sampling sites in the Brookings area. The Brookings WWTP discharged continuously to the Big Sioux River during all sampling periods. For the low-flow August 2003 sampling period, the upstream site had slightly smaller total OWC concentrations and loads compared to the downstream Big Sioux River sites. SCs and HIACs accounted for most of the total OWC concentration in all Big Sioux River sampling sites, but the proportion of SCs increased at the most downstream site. For the runoff June 2004 sampling period, the upstream site generally had smaller total OWC concentrations and loads than downstream Big Sioux River sites. MAHs accounted for most of the total OWC concentration for all Big Sioux River sites, but the proportion of SCs increased at the most downstream site. Although confident conclusions could not be made due to possible effects of non-Lagrangian sampling, the data might indicate that (1) for the low-flow August 2003 sampling period, nonpoint livestock agricultural sources probably primarily contributed to occurrence of OWCs at all Big Sioux River sampling sites, and the Brookings WWTP wastewater effluent discharge contributed but did not have a substantial effect on concentrations at downstream sites; and (2) for the runoff June 2004 sampling period, nonpoint crop agricultural sources primarily contributed to occurrence of OWCs at all Big Sioux River sites, contributions of OWCs that might be derived from nonpoint livestock agricultural sources increased in proportion to other sources for the most downstream site, and the Brookings WWTP wastewater effluent discharge probably did not substantially contribute to total OWC concentrations at downstream sampling sites. EDCs were detected in all samples collected from sampling sites in the Brookings area. Total EDC concentrations for the upstream site consisted entirely of MAHs. Total EDC concentrations for downstream sites consisted of MAHs and HIACs. HIACs accounted for most of the total EDC concentrations for the low-flow August 2003 sampling period, and MAHs accounted for most of the total EDC concentrations for the runoff June 2004 sampling period for downstream Big Sioux River sites.

The city of Watertown is located near the upstream part of the Big Sioux River Basin, where the mean annual flow of the Big Sioux River is less than 100 cubic feet per second (ft^3/s). Watertown WWTP discharges can account for a substantial part of the flow in the Big Sioux River, especially during low-flow periods. Effects of the Watertown WWTP wastewater effluent discharges on the occurrence of OWCs in the Big Sioux River downstream were apparent during both the low-flow and runoff sampling periods. For Volga and Brookings, which are farther downstream and where the mean annual flow of the Big Sioux River exceeds 400 ft^3/s, wastewater effluent discharges from the Volga and Brookings WWTPs probably influenced the occurrence of OWCs in the Big Sioux River, but probably did not substantially contribute to total OWC concentrations, especially during the runoff sampling period.

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 and potentially have long-term effects on stream biota; human exposure also might occur when those systems are used as water supplies (Barnes and others, 2002; Kolpin and others, 2002; Stackelberg and others, 2004). 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) along with discharges from several smaller cities are released directly into the Big Sioux River. These wastewater discharges also might contain OWCs.

The upper Big Sioux River Basin has been a focus for Total Maximum Daily Load (TMDL) activities, and a large-scale assessment currently is underway. Reaches of the upper Big Sioux River are listed in the South Dakota 303(d) Water List (South Dakota Department of Environment and Natural Resources, 2004) as being impaired for dissolved oxygen, fecal coliform, nitrate, and total suspended solids. Most of these impairments are directly influenced by contributions of either human and/or animal wastes. Although OWCs are not directly related to TMDL impairments in the upper Big Sioux River Basin, it is possible that information on the occurrence of emerging contaminants will provide useful information in tracking sources of TMDL contaminants. Also, information on the occurrence of OWCs in the upper Big Sioux River Basin can provide valuable information of the ecosystem health of the upper Big Sioux River.

The U.S. Geological Survey (USGS), in cooperation with the East Dakota Water Development District, conducted a reconnaissance study to determine the occurrence of OWCs in wastewater effluent and the Big Sioux River in the upper Big Sioux River Basin during August 2003 through June 2004. Samples were collected during summer/fall low-flow conditions in 2003 and after a rainfall event in the early summer of 2004 to evaluate flow conditions on the occurrence of OWCs.

The purpose of this report is to describe the occurrence of OWCs in wastewater effluent and the Big Sioux River near the cities of Watertown, Volga, and Brookings during 2003–2004. Specifically, this report describes the data-collection and analytical methods used in the study, and the analytical results documenting the presence, concentrations, and distributions of these environmentally significant OWCs in the upper Big Sioux River Basin.

The OWCs analyzed for in this study (table 10 in the Supplemental Information section at the end of the report) are classified into the following six compound classes: (1) human pharmaceutical compounds (HPCs), which are commonly used prescription and non-prescription pharmaceutical drugs; (2) human and veterinary antibiotic compounds (HVACs), which are prescription drugs used in the treatment of infectious diseases; (3) major agricultural herbicides (MAHs), which include atrazine, metolachlor, and prometon; (4) 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; (5) polyaromatic hydrocarbons (PAHs), which are compounds often occurring in fossil fuels or produced by the combustion of fossil fuels; and (6) 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).

Description of Study Area

The Big Sioux River Basin originates in northeastern South Dakota and extends southerly along the eastern edge of the State (fig. 1). The Big Sioux River drains an extended highland or plateau, the Coteau des Prairie, 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 3,900 mi^2 in the upper part of the basin, from the headwaters of the Big Sioux River downstream to an area south of Brookings (fig. 1).

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 is about 70.5°F, and the normal mean daily January temperature is about -10.6°F (South Dakota State University, 2005a). Normal annual precipitation (1971–2000) is about 22.5 in. (South Dakota State University, 2005b). On average, about 80 percent of annual precipitation occurs as rainfall during the months of April through October.

Land use in the study area is primarily 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 and Brookings are the major

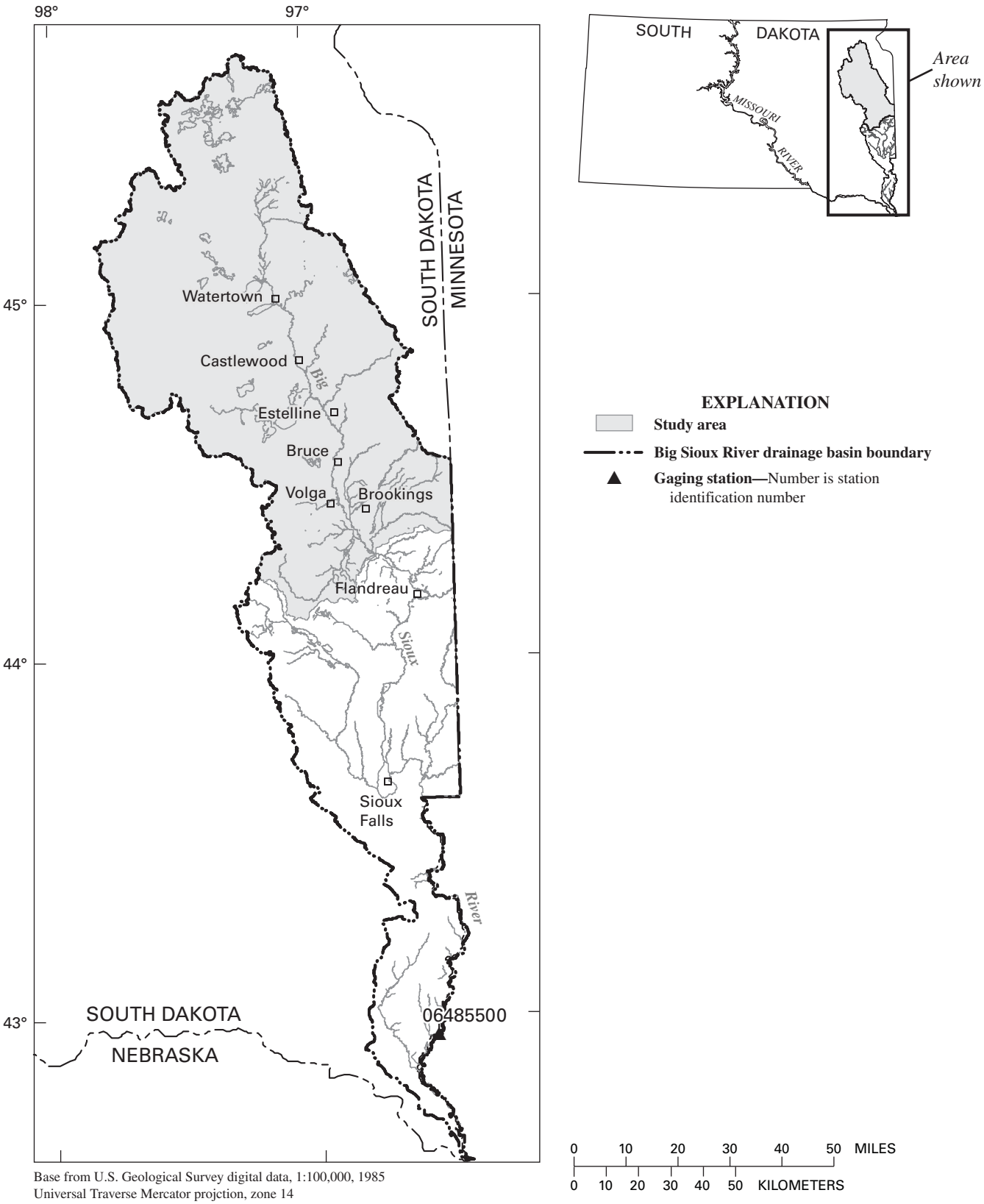

Figure 1. Location of study area.

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, and Volga (fig. 1). Occurrence of OWCs in wastewater effluent and the Big Sioux River near the cities of Watertown, Volga, and Brookings were investigated in this study.

The Big Sioux River is a major tributary to the Missouri River in eastern South Dakota and is a major water source for many cities in eastern South Dakota, including Sioux Falls, the largest city in South Dakota. The mean annual flow of the Big Sioux River for water years 1977–2004 is about 99 ft^3/s for USGS gaging station 06479525 (located about 15 river miles downstream from the city of Watertown (fig. 2); contributing drainage area is about 780 mi^2), about 434 ft^3/s for USGS gaging station 06480000 (located about 20 river miles downstream from the city of Brookings (fig. 2); contributing drainage area is about 2,815 mi^2), and about 1,940 ft^3/s for USGS gaging station 06485500 (located about 55 river miles upstream from the confluence with the Missouri River near Sioux City, Iowa (fig. 1); contributing drainage area is about 7,345 mi^2) (data from U.S. Geological Survey, 2005; drainage areas revised from previously reported values; Ryan F. Thompson, U.S. Geological Survey, written commun., 2005).

Outwash deposits along the Big Sioux River and its tributaries underlie much of the upper 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 range in thickness from a few feet to 200 ft and consist of cross-bedded gravel, sand, and silt, 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.

Watertown and Brookings are the two largest cities in the upper Big Sioux River Basin, with populations in 2000 of 20,237 and 18,504, respectively (U.S. Census Bureau, 2005). Volga is a smaller farming community with a population of 1,435. Characteristics of the wastewater treatment plants (WWTPs) for Watertown, Volga, and Brookings are presented in table 1. The WWTPs at Watertown and Brookings discharge continuously to the Big Sioux River. During low-flow periods, the wastewater discharges for Watertown can account for more than 75 percent of the Big Sioux River streamflow for several miles downstream, and the wastewater discharges for Brookings can account for more than 25 percent of the Big Sioux River streamflow for several miles downstream. Wastewater effluent leaves the Watertown WWTP in a concrete pipe about 0.5 mi in length that discharges to a natural channel about 50 yd upstream from the confluence of the channel with the Big Sioux River. Wastewater effluent leaves the Brookings WWTP in a concrete pipe about 1.4 mi in length that discharges to a natural channel about 100 yd upstream from the confluence of the channel with the Big Sioux River. The Volga WWTP discharges intermittently to the Big Sioux River. Part of the treatment process of the Volga WWTP involves holding the wastewater in lagoons and a large wetland area for substantial periods of time during which the wastewater undergoes natural biological processing. When discharges from the Volga WWTP occur, the wastewater effluent is discharged directly into an intermittent surface-water channel and then travels about 0.25 mi to the confluence with the Big Sioux River. Prior to the first sampling period for this study (August 2003), the Volga WWTP had last discharged to the Big Sioux River during April 1–30, 2003. The Volga WWTP also discharged continuously during October 1–31, 2003. The lagoons and the wetland area are located immediately adjacent to the Big Sioux River channel. The smallest distance between the lagoons and the Big Sioux River channel is about 300 ft, and the smallest distance between the wetland area and the Big Sioux River channel is about 620 ft. Monitoring wells located between the lagoons/wetland area and the Big Sioux River channel have indicated substantial seepage of water from the lagoons and wetland area into shallow ground water (Steven Meyer, Volga WWTP operator, oral commun., 2005). Any contaminated shallow ground water might discharge to the Big Sioux River at times.

Methods of Study

Water samples were collected at 12 sites to investigate the occurrence of OWCs in wastewater effluent and the Big Sioux River (fig. 2; table 2) at or near the cities of Watertown, Volga, and Brookings. For each city, samples were collected from the WWTP effluent, and from the Big Sioux River at sites upstream and downstream from where the wastewater effluent enters the Big Sioux River.

Sampling Sites

A labeling scheme is used for the sampling sites consisting of a 2-character identifier of the city, and a 3-character identifier of the relation between the sampling site and the wastewater effluent. Values of the 2-character identifier of the city are defined as follows:

WT = Watertown;

VL = Volga; and

BK = Brookings.

Values of the 3-character identifier of the relation between the sampling site and the wastewater effluent are defined as follows:

US1 = Big Sioux River site farthest upstream from the wastewater discharge point (that is, where the wastewater effluent enters the Big Sioux River) of the given city;

US2 = Big Sioux River site closest upstream from the wastewater discharge point;

WWE = wastewater effluent site of the given city;

DS1 = Big Sioux River site closest downstream from the wastewater discharge point of the given city; and

DS2 = Big Sioux River site farthest downstream from the wastewater discharge point of the given city.

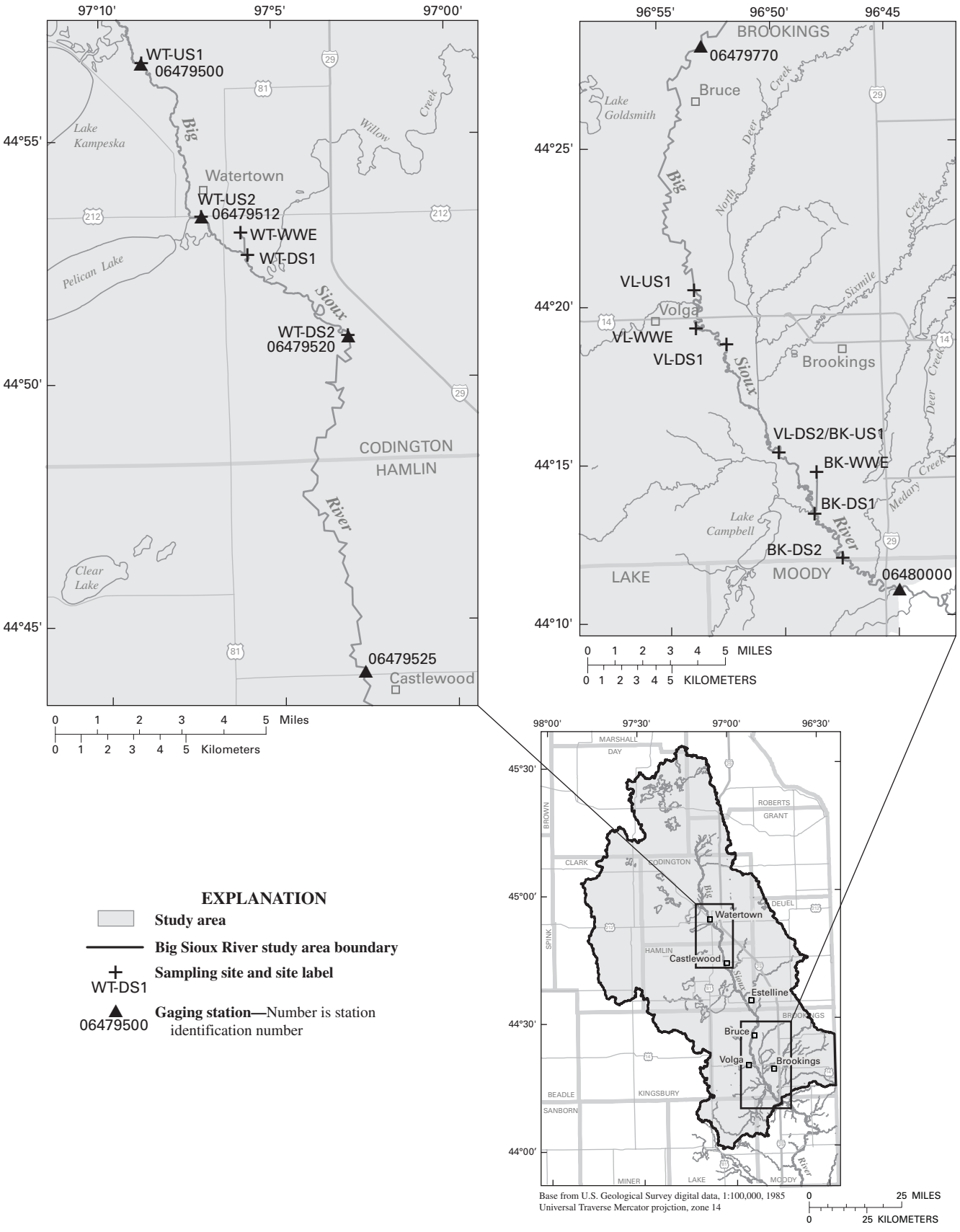

Figure 2. Location of sampling sites and gaging stations in study area.

Table 1. Selected characteristics of the Watertown, Volga, and Brookings wastewater treatment plants.

[--, no data]

	Watertown wastewater treatment plant	Volga wastewater treatment plant	Brookings wastewater treatment plant
Population	20,237	1,435	18,504
Population density (people per square mile)	1,331.4	1,863.6	1,549.7
Design capacity (million gallons per day)	4	--	3
Number of permitted industries	12	2	5
General description of permitted industries	Primarily metal finishers, one rubber manufacturer	Dairy-products manufacturer, soybean processor	Primarily metal finishers, one non-pharmaceutical medicinal products manufacturer, one electronics manufacturer
Preliminary treatment	Screening and grit removal	Screening and grit removal	Screening and grit removal
Primary treatment	Settling basin clarification	Cell aeration	Settling basin clarification
Secondary treatment	Trickling filtration; aerated activated-sludge processing; secondary clarification	Lagoon holding and natural processing	Rotating-biological-contacter processing; aerated activated-sludge processing; secondary clarification; sand gravity filtration
Tertiary treatment	Ultraviolet light disinfection; post-treatment aeration	Wetland holding and natural processing	Chlorine disinfection; post-treatment aeration; addition of sulfur dioxide to neutralize chlorine
Primary sludge treatment	Anaerobic digestion	Anaerobic digestion	Anaerobic digestion

For the Watertown area, there were two sampling sites on the Big Sioux River upstream from the wastewater discharge point—the Big Sioux River site farthest upstream from the wastewater discharge point is designated WT-US1, and the Big Sioux River site closest upstream from the wastewater discharge point is designated WT-US2. The Big Sioux River site farthest downstream from the Volga wastewater discharge point was co-located with the site upstream from the Brookings wastewater discharge point. This site is designated VL-DS2/BK-US1. Information on intervening reach lengths for the sampling sites is presented in table 3.

Collection, Processing, and Analysis of Water Samples

Samples were collected at sites in or near Watertown, Volga, and Brookings during August 18–22, 2003, and June 15–18, 2004. During these periods, the Watertown and Brookings WWTPs were continuously discharging to the Big Sioux River, but the Volga WWTP was not discharging. The Volga WWTP continuously discharged to the Big Sioux River during October 1–31, 2003. During this period, the maximum wastewater effluent discharge was about 0.7 ft^3/s, and the average discharge was about 0.6 ft^3/s (Steven Meyer, Volga WWTP operator, oral commun., 2005). To assess effects of the Volga WWTP discharges on the Big Sioux River, samples were collected at sites VL-US1, VL-WWE, and VL-DS1 during October 21–22, 2003. The wastewater effluent discharge at the time of sampling was estimated to be 0.6 ft^3/s.

Samples generally were collected in upstream-to-downstream order, especially for the Big Sioux River sampling sites. Available resources did not allow conducting a Lagrangian scheme that samples a given pulse of water as it moves downstream. However, the timing of sample collection probably provided a reasonable representation of consistent flow conditions at sites upstream and downstream from the WWTP effluent discharges during the sampling periods to assess the effects of the discharges on water quality.

Table 2. Sampling sites and streamflow-gaging stations.

[mi^2, square miles; e, estimated; --, not applicable]

Sampling site number	Station identification number	Station name	Site label (figs. 1 and 2)	Drainage area[1] (mi^2)	Contributing drainage area[1] (mi^2)	Latitude	Longitude
Sampling sites at or near Watertown, South Dakota							
1	06479500	Big Sioux River at Watertown, SD	WT-US1	e1,010	e230	445633	0970845
2	06479512	Big Sioux River at Broadway, at Watertown, SD	WT-US2	e1,280	e595	445322	0970707
3	445301097055900	Watertown wastewater effluent at Watertown, SD	WT-WWE	--	--	445301	0970559
4	445234097054800	Big Sioux River below wastewater effluent at Watertown, SD	WT-DS1	e1,285	e600	445234	0970548
5	06479520	Big Sioux River below Watertown, SD	WT-DS2	e1,400	e760	445032	0970257
--	06479525	Big Sioux River near Castlewood, SD	--	e1,500	e780	444354	0970239
Sampling sites at or near Volga, South Dakota							
--	06479770	Big Sioux River near Bruce, SD	--	e2,800	e1,740	442804	0965314
6	442023096533600	Big Sioux River near Volga, SD	VL-US1	e2,915	e1,860	442023	0965336
7	441913096533400	Volga wastewater wetland near Volga, SD	VL-WWE	--	--	441913	0965334
8	441841096521400	Big Sioux River below wastewater wetland, near Volga, SD	VL-DS1	e3,020	e1,940	441841	0965214
9	441422096491200	Big Sioux River above wastewater effluent, near Brookings, SD	VL-DS2/ BK-US1	e3,235	e2,155	441421	0964912
Sampling sites at or near Brookings, South Dakota							
9	441422096491200	Big Sioux River above wastewater effluent, near Brookings, SD	VL-DS2/ BK-US1	e3,235	e2,155	441421	0964912
10	441434096482500	Brookings wastewater effluent near Brookings, SD	BK-WWE	--	--	441434	0964825
11	441316096483300	Big Sioux River below wastewater effluent, near Brookings, SD	BK-DS1	e3,495	e2,415	441316	0964833
12	441151096472200	Big Sioux River above Medary Creek, at Medary, SD	BK-DS2	e3,525	e2,445	441151	0964722
--	06480000	Big Sioux River near Brookings, SD	--	e3,900	e2,815	441048	0964455
--	06481000	Big Sioux River near Dell Rapids, SD	--	e4,480	e3,400	434725	0964442
--	06485500	Big Sioux River at Akron, IA	--	e8,425	e7,345	425014	0963341

[1]Drainage areas revised from previously reported values (Ryan F. Thompson, U.S. Geological Survey, written commun., 2005).

Table 3. Intervening reach lengths between selected locations.

[e, estimated; --, not applicable]

Starting location	Ending location	Intervening reach length, in river miles	For Big Sioux River sampling sites, distance from starting location to confluence of wastewater effluent channel with Big Sioux River for specified city
Study site WT-US1 (USGS gaging station 06479500)	Study site WT-US2 (USGS gaging station 06479512)	5.2	6.8 river miles upstream from WT-WWE confluence
Study site WT-US2 (USGS gaging station 06479512)	Confluence of Watertown wastewater effluent channel and Big Sioux River	1.5	1.5 river miles upstream from WT-WWE confluence
Study site WT-WWE	Confluence of Watertown wastewater effluent channel and Big Sioux River	e.5	--
Confluence of Watertown wastewater effluent channel and Big Sioux River	Study site WT-DS1	.10	--
Study site WT-DS1	Study site WT-DS2 (USGS gaging station 06479520)	4.7	0.10 river miles downstream from WT-WWE confluence
Study site WT-DS2 (USGS gaging station 06479520)	USGS gaging station 06479525	14	4.8 river miles downstream from WT-WWE confluence
USGS gaging station 06479525	USGS gaging station 06479770	e36	--
USGS gaging station 06479770	Study site VL-US1	e15	--
Study site VL-US1	Study site VL-DS1	5.2	3.4 river miles upstream from VL-WWE confluence
Study site VL-WWE	Confluence of Volga wastewater effluent channel and Big Sioux River	.24	--
Confluence of Volga wastewater effluent channel and Big Sioux River	Study site VL-DS1	1.9	--
Study site VL-DS1	Study site VL-DS2/BK-US1	7.4	1.8 river miles downstream from VL-WWE confluence
Study site VL-DS2/BK-US1	Study site BK-DS1	5.1	9.3 river miles downstream from VL-WWE confluence; 4.85 river miles upstream from BK-WWE confluence
Study site BK-WWE	Confluence of Brookings wastewater effluent channel and Big Sioux River	e1.4	--
Confluence of Brookings wastewater effluent channel and Big Sioux River	Study site BK-DS1	.22	--
Study site BK-DS1	Study site BK-DS2	4.2	0.22 river miles downstream from BK-WWE confluence
Study site BK-DS2	USGS gaging station 06480000	4.7	4.4 river miles downstream from BK-WWE confluence
USGS gaging station 06480000	USGS gaging station 06485500	e200	--

At each Big Sioux River sampling site, streamflow was determined using standard USGS procedures (Rantz and others, 1982a, 1982b). WWTP wastewater effluent discharges at the time of sampling were determined from monitoring records provided by the WWTPs (Craig Mitchell, Watertown WWTP operator, written commun., 2005; Gary Englund, Brookings WWTP operator, written commun., 2005; Steven Meyer, Volga WWTP operator, oral commun., 2005). Other field-measured properties and constituents (table 10) were determined using standard USGS procedures (U.S. Geological Survey, 1997–2004). Depth-integrated grab samples were collected near the centroid of flow for analysis of auxiliary constituents, including nitrite plus nitrate nitrogen, total coliform bacteria, and fecal coliform bacteria (table 10) using standard USGS procedures (U.S. Geological Survey, 1997–2004).

Water-quality samples for analysis of OWCs were collected and processed using standard USGS techniques (U.S. Geological Survey, 1997–2004) (table 10). 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 ("Clean hands/Dirty hands"), and sampling teams wore powderless nitrile gloves. Special requirements, including avoiding use of insect repellents, sunscreen, tobacco, caffeine, and pharmaceutical drugs by the sampling team, also were adhered to for collection of wastewater, pharmaceutical, and antibiotic compounds (U.S. Geological Survey, 1997–2004).

Wastewater effluent samples were collected using a depth-integrated grab from the centroid of the effluent channel downstream from all treatment activities. Water samples from the Big Sioux River were collected using standard USGS width- and depth-integrating procedures, generally at 5 to 10 verticals across the sampling transect. 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 one-day shipping to the analytical laboratories. Where appropriate, filtration was performed by passing sample water through a pre-conditioned 0.7-millimeter (mm) 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-mm nominal-pore size baked glass-fiber filter. Constituents in unfiltered water samples are referred to as "whole-water."

Analyses for nitrite-plus-nitrate nitrogen were performed at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, by colorimetry (Fishman, 1993). Analyses for total and fecal coliform bacteria were performed at the South Dakota State Public Health Laboratory by most-probable-number method and membrane filter method, respectively (American Public Health Association, 1998).

Concentrations of a total of 125 different OWCs were determined by laboratories using three different analytical methods, and the analytical results were analyzed to describe the occurrence of OWCs in wastewater effluent and the Big Sioux River (table 10). 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 following three analytical methods were used:

Analytical method 1 (performed at NWQL) determined concentrations of 20 prescription and nonprescription HPCs and selected metabolites and 4 HVACs in filtered water samples (table 10; 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, analyzed for 38 HVACs in filtered water samples (table 10). Target compounds were extracted from water samples using tandem SPE that included an Oasis HLB cartridge followed by a mixed mode HLB cation exchange cartridge (MCX) (Meyer and others, 2000; Lee and others, 2004). Extracts were separated and measured by HPLC/ESI-MS using SIM. Prior to December 2003, samples were analyzed at OGRL using a single quadrapole HPLC mass spectrometer. After December 2003, samples were analyzed at OGRL using a triple quadrapole HPLC mass spectrometer that reduced the laboratory reporting levels (LRLs) by a factor of about 10.

Analytical method 3 (performed at NWQL) determined 2 nonprescription HPCs, 3 MAHs, 48 HIACs, 11 PAHs, and 4 SCs in whole-water samples (table 10). 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.

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 analytical method 2, calibration standards were processed throughout the extraction procedure, which generally corrects concentrations for methodological losses during extraction, but not for matrix effects. Analytical methods 1 and 3 do 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 analytical methods 1 and 3). 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 qualified 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; 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 discussed above, 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, including 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.

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, temporal correspondence between water samples collected at different sampling sites would not be expected. Thus, comparison of loads between sites could be affected primarily by diurnal variability in wastewater effluent discharges and concentrations of OWCs in the wastewater effluent. 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; discussed 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. Most of the concentrations of OWCs 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 samples was very large, might result in substantially increasing the effect of analytical error in the reported load estimates. However, while there might be substantial error in the absolute values of the load estimates, the load estimates probably provide reasonably accurate estimates for relative comparison between sites and between sampling periods.

Quality Assurance/Quality Control

QA/QC samples were collected to assess precision and accuracy of collected data. QA/QC data were used to determine which compounds had acceptable method performance and to establish SRLs for individual OWCs, as described later in this section. QA/QC included both laboratory and field activities.

Laboratory QA/QC included method-blank, reagent-spike, and surrogate samples. Method-blank samples consist of analyte-free water that is processed and analyzed in the laboratory identically to environmental samples. 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 at the time the environmental samples were analyzed. Surrogate compounds are compounds that are similar in physical and chemical properties to the method analytes, and which are added to all QC and environmental water samples prior to analysis. Surrogate compounds are used to monitor the accuracy of a given analytical method for a specific environmental matrix. At least one method-blank sample and one reagent-spike sample typically are analyzed with each set of 10 to 15 environmental samples. Surrogates are added to and analyzed for every environmental sample and every QC sample.

Field QA/QC samples included field equipment blanks and replicates. For this study, three field equipment-blank samples and three replicate samples were collected and analyzed for the laboratory analytical constituents listed in table 10. This

level of field QA/QC sampling represents about 22 percent of the environmental samples collected and probably is not adequate to fully evaluate the OWC data quality. As a result, field equipment blanks, replicates, and environmental matrix spikes that were collected during other data-collection activities in the Big Sioux River Basin also were analyzed to evaluate OWC data quality. These other field QA/QC samples were collected during 2002–2004 as part of an investigation of the occurrence of OWCs in wastewater effluent and the Big Sioux River in the vicinity of Sioux Falls, South Dakota (fig. 1). The samples were collected using identical equipment and methods as were used in the upper Big Sioux River Basin study, and the matrices sampled probably were very similar. Thus, the QA/QC data collected in the vicinity of Sioux Falls probably provide OWC data-quality information that is representative of the data-collection efforts of the upper Big Sioux River Basin study. QA/QC activities for the Sioux Falls study included 5 to 6 field equipment blanks (depending on analytical method), 6 to 10 field replicates (depending on analytical method), and 3 to 10 environmental matrix spikes (depending on analytical method).

Field equipment-blank samples were collected at field sampling sites by passing ultra-pure 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 which is not likely to cause significant positive bias in study results. Also, 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 study results.

Field replicate samples were used to identify the level of precision (reproducibility) of analytical results. 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 primary environmental samples they are associated with. Precision of analytical results for field replicate samples potentially is affected by numerous sources of variability 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 were only calculated for primary/replicate sample pairs in which a given compound was detected in both samples. 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, an RPD of about 40 percent generally was used in this study to determine acceptability of results for field replicate samples.

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 analyzed to determine 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 of laboratory reagent spikes, laboratory surrogates, and environmental matrix spikes. RSDs were calculated separately for laboratory reagent spikes, laboratory surrogates, and environmental matrix spikes. 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 according to 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.

In the percent recovery calculations for the various spiked samples, any censored values reported as less than the SRL (for either the unspiked primary samples or the spiked samples) were arbitrarily assigned a value of zero.

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 generally represents the lower level of quantitation at which the compound could be consistently identified and reasonably accurately quantified. Acceptability of method performance for a given compound was determined by analysis of percent recoveries for laboratory reagent spikes, laboratory surrogates, and environmental matrix spikes. Method performance was determined to be acceptable when the median percent recoveries for laboratory reagent spikes, laboratory surrogates, and environmental matrix spikes were between 30 to 120 percent, and the percent recovery RSDs 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 wastewater effluent and the Big Sioux River. The compounds 5-methyl-1H-benzotriazole and *beta*-sitosterol had median percent recoveries for environmental matrix spikes of 140 and 160 percent, respectively, which exceeded the method-performance acceptability criterion of 120 percent. However, because these compounds had relatively small percent recovery RSDs for environmental matrix spikes (about 20 percent) and all other QA/QC results were acceptable, method performance for these compounds was determined to be acceptable.

For compounds that had acceptable method performance for laboratory reagent spikes and environmental matrix spikes, analytical results for laboratory method blanks, field equipment blanks, and field replicate samples were analyzed to determine SRLs. SRLs were established to identify the lower levels of quantitation at which the compounds could be consistently identified by the analysts and reasonably accurately quantified without being substantially influenced by routine contamination resulting from either laboratory or field activities. For each compound, the SRL was established such that the compound was consistently detected in both samples of primary/replicate sample pairs with acceptable variability (median RPD generally less than 40 percent); the SRL generally was substantially larger than levels of contamination detected in laboratory method blanks and field equipment blanks. Generally, compounds that were determined to have acceptable QA/QC had median RPDs for field replicate samples less than 40 percent. The compounds acetophenone and nonylphenol monoethoxylate (NP1EO) had median RPDs of 50 and 44 percent, respectively. However, because all other QA/QC results for these compounds were acceptable, they were included in analyses and discussion related to occurrence of OWCs in wastewater effluent and the Big Sioux River.

Analytical results for laboratory method blanks, laboratory reagent spikes, laboratory surrogate samples, field equipment blanks, field replicate samples, and environmental matrix spikes are summarized in tables 11–16, respectively, in the Supplemental Information section. Information concerning compounds excluded from data analysis due to unacceptable method performance, and the established SRLs for compounds with acceptable method performance are summarized in table 10. Of the 125 different OWCs analyzed for in this study, 73 OWCs had one or more detections in environmental samples reported by the laboratories, and of those 73 OWCs, 45 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 wastewater effluents and the Big Sioux River.

Occurrence of Organic Wastewater Compounds

This section of the report summarizes the occurrence of OWCs in wastewater effluent and the Big Sioux River in the vicinity of three cities—Watertown, Volga, and Brookings. In addition to presenting analytical results of OWCs, results for field measured properties and constituents and auxiliary constituents are included. Wastewater discharges and flow conditions in the Big Sioux River at the time of sampling also are described.

Results for field measured properties and constituents and auxiliary constituents are given in table 17 in the Supplemental Information section. Laboratory analytical results for HPCs, HVACs, MAHs, HIACs, PAHs, and SCs are given in tables 18–23, respectively, 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 18–23 were censored at the SRLs for the purposes of data analysis and summary.

Summary calculations for OWCs, including total and median concentrations for compound classes, are rounded to two significant figures. 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.

Watertown Area Results

Sites in the Watertown area were sampled during August 18–20, 2003, when low-flow conditions prevailed and during June 15–16, 2004, when runoff conditions prevailed. Flow conditions during sampling periods are shown in figure 3. During August 18–20, 2003, streamflow at long-term USGS gaging station 06479525, located about 14 river miles downstream from sampling site WT-DS2, was about 18 percent of the long-term (1976–2004) median mid-August flow. During June 15–16, 2004, streamflow at station 06479525 was about 110 percent of the long-term median mid-June flow. The Watertown WWTP discharged continuously to the Big Sioux River during both sampling periods. During the August 2003 sampling period, the Watertown WWTP discharge accounted for about 50 to 95 percent of the flow of the Big Sioux River from the confluence of the WWTP discharge to about 5 mi downstream. During the June 2004 sampling period, the Watertown WWTP discharge accounted for about 10 to 50 percent of the flow of the Big Sioux River from the confluence of the WWTP discharge to about 5 mi downstream.

Field-Measured Properties and Constituents and Auxiliary Constituents

Results for field-measured properties and constituents and auxiliary constituents in samples from sites in the Watertown area are presented in table 17 and figure 4. Generally, results for field-measured properties and constituents and auxiliary constituents for the Watertown area are within typical ranges for the upper Big Sioux River Basin (East Dakota Water Development District, 2004).

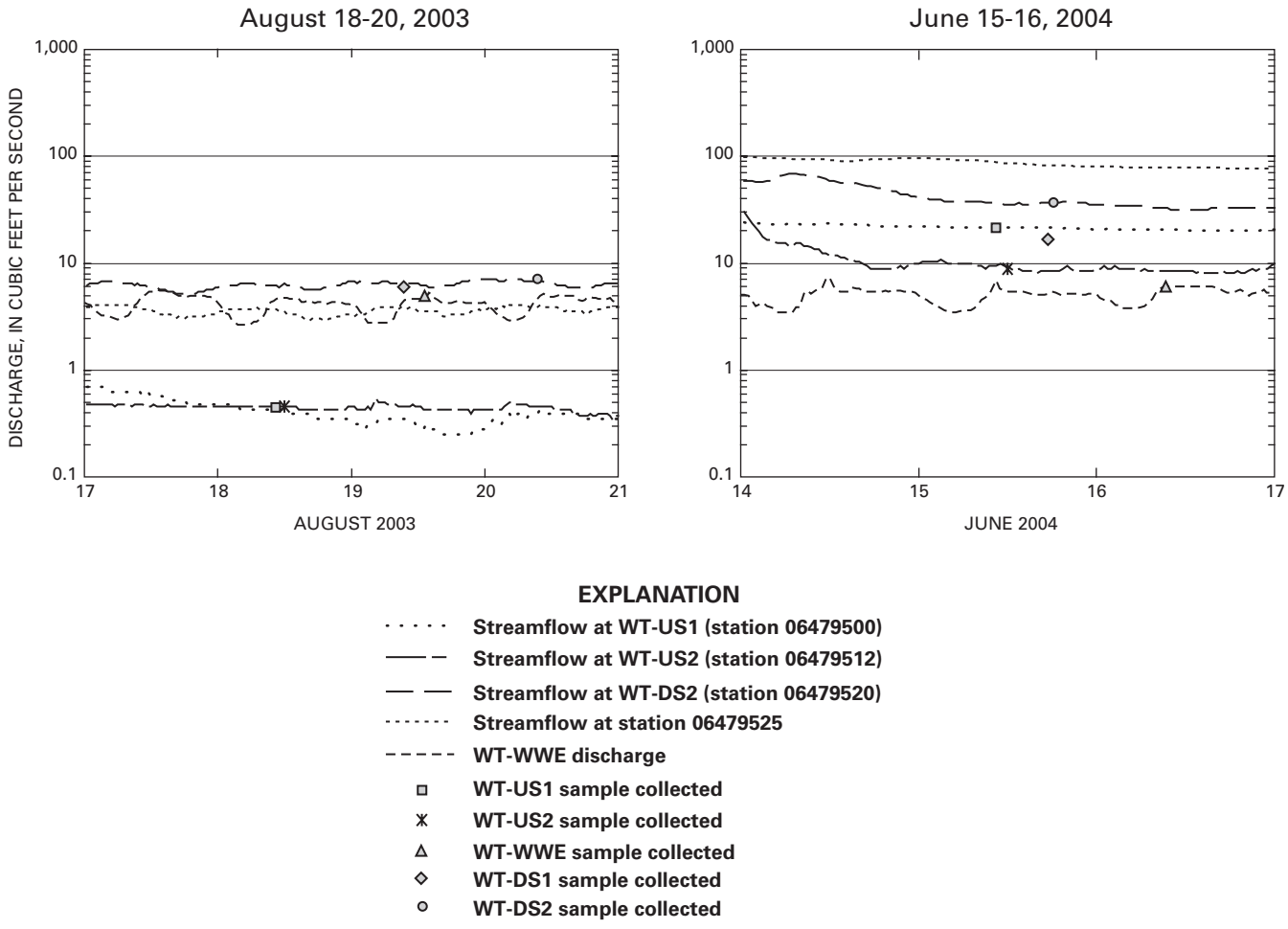

Figure 3. Flow conditions during sampling periods for sites in the Watertown area.

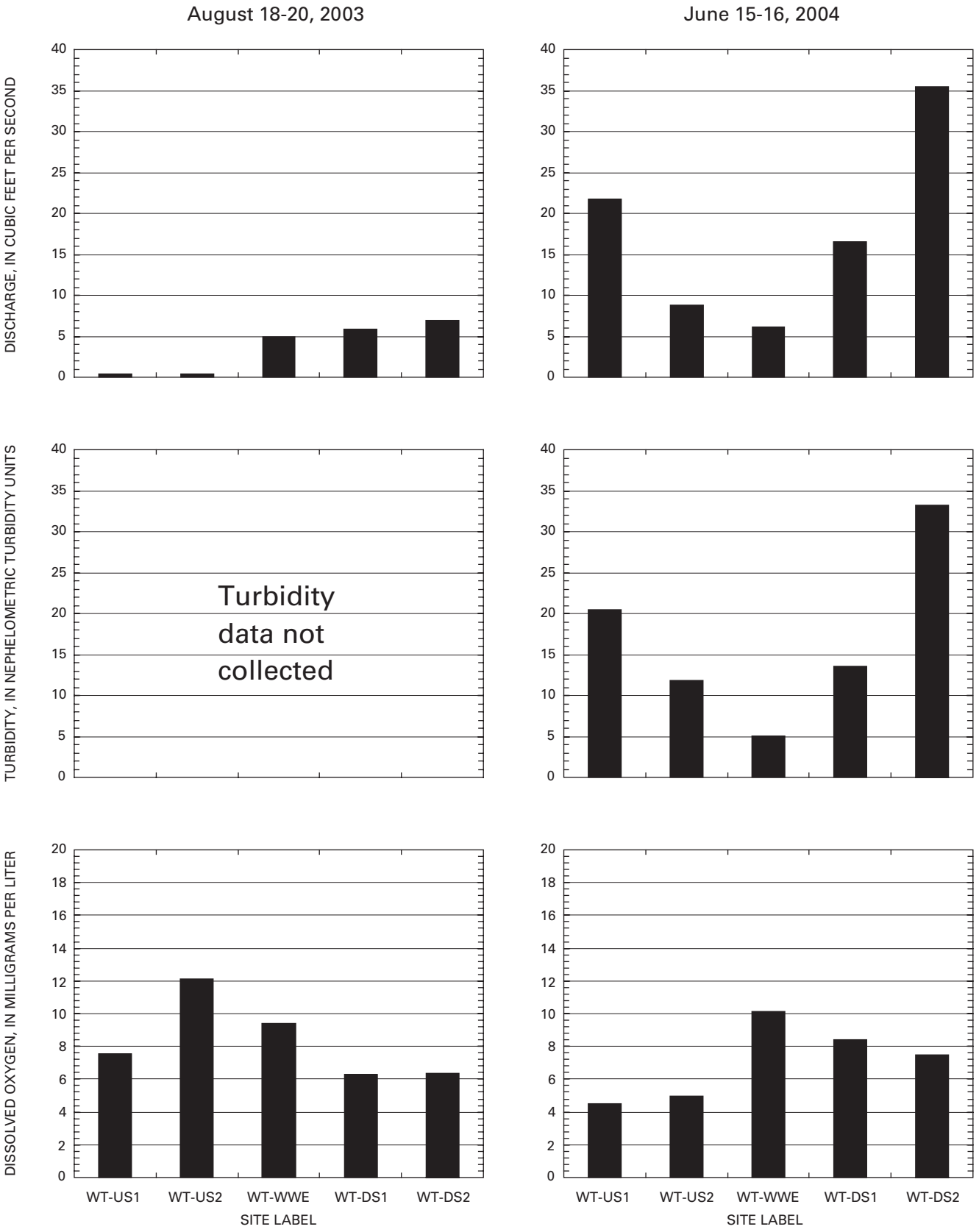

Figure 4. Results for selected field-measured properties and constituents and auxiliary constituents in wastewater effluent and the Big Sioux River in the Watertown area.

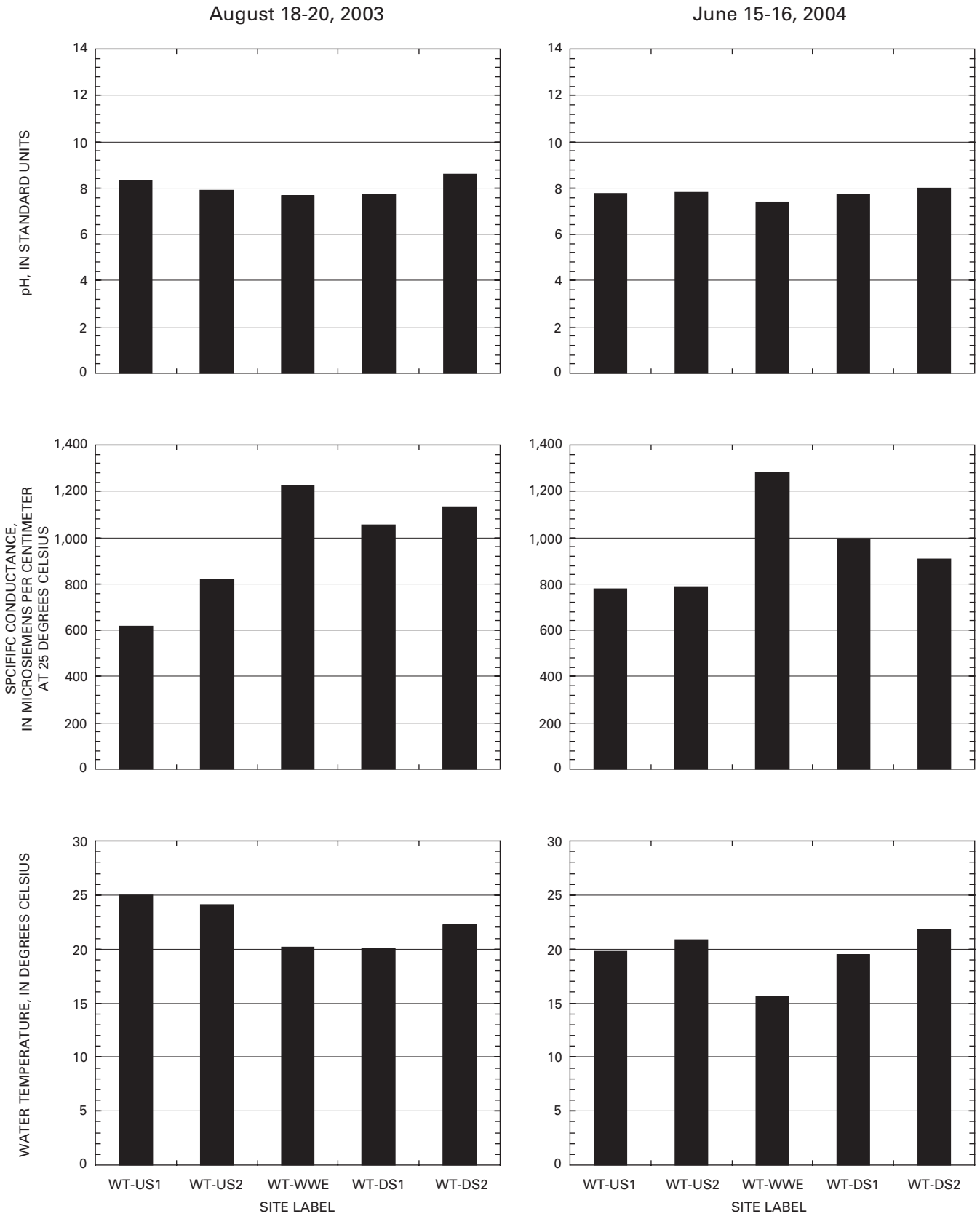

Figure 4. Results for selected field-measured properties and constituents and auxiliary constituents in wastewater effluent and the Big Sioux River in the Watertown area.—Continued

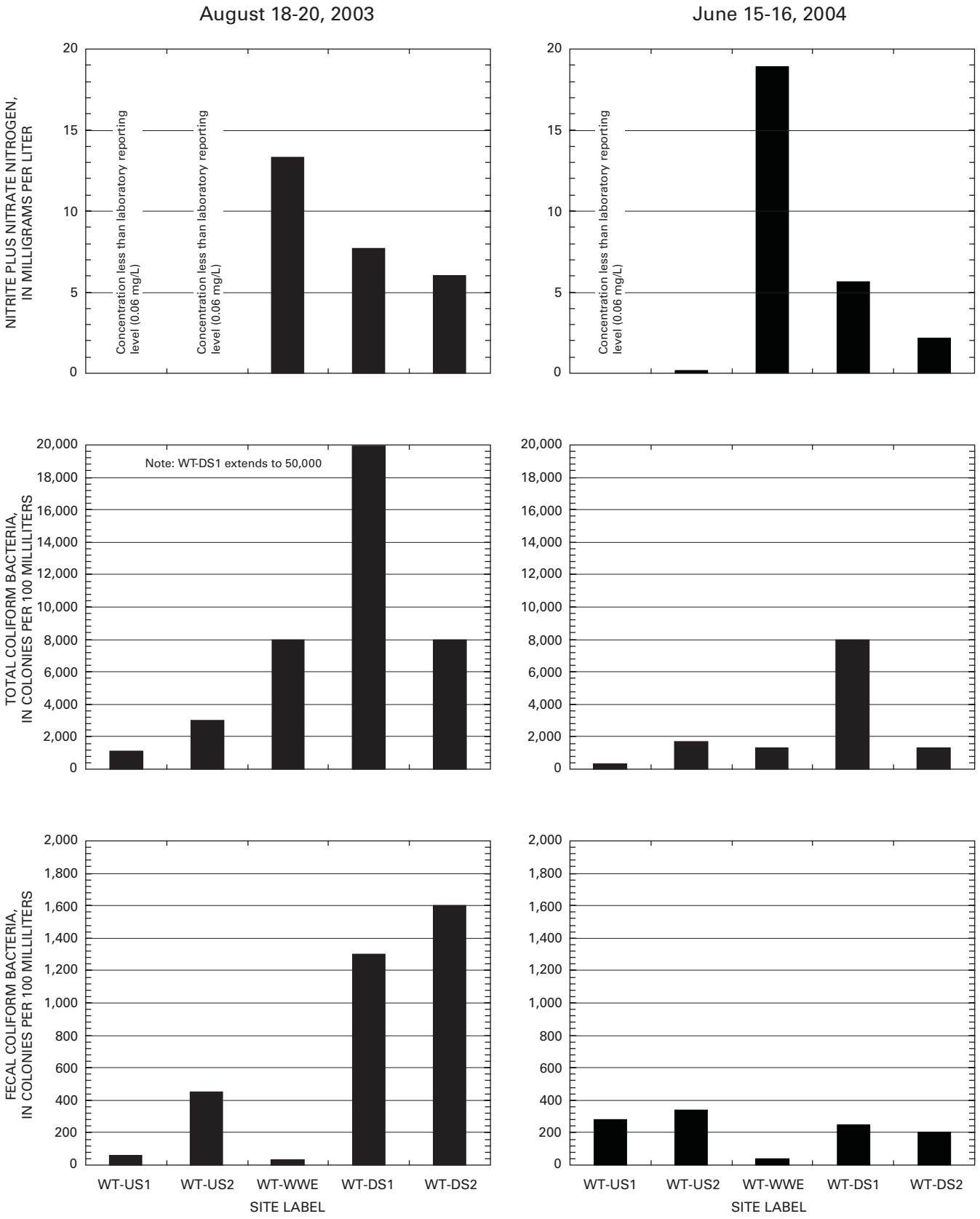

Figure 4. Results for selected field-measured properties and constituents and auxiliary constituents in wastewater effluent and the Big Sioux River in the Watertown area.—Continued

Organic Wastewater Constituents

OWCs in all compound classes were detected in water samples from sampling sites in the Watertown area (fig. 5, tables 4 and 5). Total OWC concentrations for upstream Big Sioux River sites generally were small, about 6 µg/L for August 2003 and about 0.2 µg/L for June 2004.

SCs accounted for nearly all of the total OWC concentration for upstream Big Sioux River sites (WT-US1 and WT-US2) for August 2003, and MAHs accounted for nearly all of the total OWC concentrations for June 2004. Total OWC concentrations for WT-WWE were relatively large for both August 2003 and June 2004 (about 41 and 20 µg/L, respectively). Major OWC classes contributing to total OWC concentrations for WT-WWE included HIACs, SCs, and HVACs. HIACs accounted for about 78 and 32 percent, SCs accounted for about 13 and 20 percent, and HVACs accounted for about 10 and 45 percent of the total OWC concentrations for the August 2003 and June 2004 WT-WWE samples, respectively. Total OWC concentrations for WT-DS1 were relatively large for August 2003 (about 19 µg/L) and smaller for June 2004 (about 6.5 µg/L). Major OWC classes contributing to total OWC concentrations for WT-DS1 were HIACs, SCs, and HVACs. HIACS accounted for about 74 and 46 percent, SCs accounted for about 19 and 28 percent, and HVACs accounted for 6 and 23 percent of total OWC concentrations for August 2003 and June 2004, respectively. Total OWC concentrations were smaller for WT-DS2 (about 6.9 and 3.3 µg/L for August 2003 and June 2004, respectively) than for WT-WWE and WT-DS1. In a larger scale but similarly designed study, Glassmeyer and others (2005) reported similar decreases in total OWC concentrations moving in a downstream direction from WWTP effluent discharges. Major OWC classes contributing to total OWC concentrations for WT-DS2 were SCs, HIACs, and HVACs. SCs accounted for about 70 and 45 percent, HIACS accounted for 17 and 29, and HVACs accounted for 12 and 18 percent of total OWC concentrations for August 2003 and June 2004, respectively. For both August 2003 and June 2004, concentrations and loads of HIACs were smaller for WT-DS2 than for WT-DS1, and SCs accounted for a larger proportion of the total OWC concentration and load for WT-DS2 than for WT-DS1. This might be due to (1) contribution of SCs from nonpoint livestock agricultural and/or human wastewater sources between WT-DS1 and WT-DS2; (2) degradation of HIACs in the Big Sioux River; (3) adsorption of HIACs to particulate material and sedimentation from the water column; (4) diurnal variability in wastewater effluent discharges and concentrations of OWCs in the wastewater effluent combined with effects of non-Lagrangian sampling; and (5) dilution effects decreasing concentrations of individual HIACs below detectable concentrations. Although confident conclusions cannot be made primarily due to possible effects of non-Lagrangian sampling, OWC results for the Watertown area might indicate that (1) OWCs for upstream Big Sioux River sites probably were contributed by nonpoint agricultural sources, with nonpoint livestock agricultural accounting for most of the total OWC concentration for the August 2003 (low-flow) sampling period, and crop agriculture accounting for most of the total OWC concentration for the June 2004 (runoff) sampling period; (2) OWCs for downstream Big Sioux River sites were strongly influenced by contributions from the Watertown WWTP during both the August 2003 (low-flow) and June 2004 (runoff) sampling periods; and (3) contributions of OWCs from nonpoint livestock agricultural and/or human wastewater sources (other than the Watertown WWTP wastewater effluent discharge) accounted for a larger proportion of OWCs for WT-DS2 than for WT-DS1 for both the August 2003 (low-flow) and June 2004 (runoff) sampling periods.

HPCs were detected in samples collected from all sites in the Watertown area (fig. 5, tables 4 and 5). One HPC (cotinine) was detected in samples collected from the upstream sites WT-US1 and WT-US2 at estimated concentrations less than 0.01 µg/L and accounted for about 0.1 percent of the total OWC concentrations. Three HPCs (cotinine, dehydronifedipine, and salbumatol) were detected in samples collected from WT-WWE with combined estimated concentrations less than 0.1 µg/L and accounted for no more than about 0.3 percent of the total OWC concentration for any sample. Four HPCs were detected in samples collected from the downstream sites WT-DS1 and WT-DS2 with total estimated concentrations less than 0.15 µg/L, which accounted for no more than about 1 percent of the total OWC concentration for any sample.

HVACs were not detected in any samples collected from upstream sites WT-US1 and WT-US2, but HVACs were detected in samples collected from WT-WWE and downstream sites WT-DS1 and WT-DS2 (fig. 5, tables 4 and 5). Ten HVACs were detected in samples from WT-WWE. Erythromycin, erythromycin-H_2O, and sulfamethoxazole had the largest concentrations (maxima of 1.3, 5.7, and 1.2 µg/L, respectively). Total HVAC concentrations were about 4 and 9 µg/L, which accounted for about 10 and 45 percent of the total OWC for the August 2003 and June 2004 samples, respectively. Eight HVACs were detected in samples from WT-DS1 and WT-DS2 with total estimated HVAC concentrations ranging from 0.59 to 1.5 µg/L. Erythromycin-H_2O and sulfamethoxazole had the largest concentrations (maxima of 0.56 and 0.85 µg/L, respectively, at WT-DS1). For the WT-DS1 samples, total estimated HVAC concentrations were 1.1 and 1.5 µg/L, which accounted for about 6 and 23 percent of the total OWC concentration for the August 2003 and June 2004 samples, respectively. For the WT-DS2 samples, total HVAC concentrations were 0.83 and 0.59 µg/L, and accounted for about 12 and 18 percent of the total OWC concentration for the August 2003 and June 2004 samples, respectively. The increase in numbers of HVACs detected and total HVAC concentrations for the June 2004 sample relative to the August 2003 sample might be related to changes in the analytical method that substantially reduced the LRLs for HVACs.

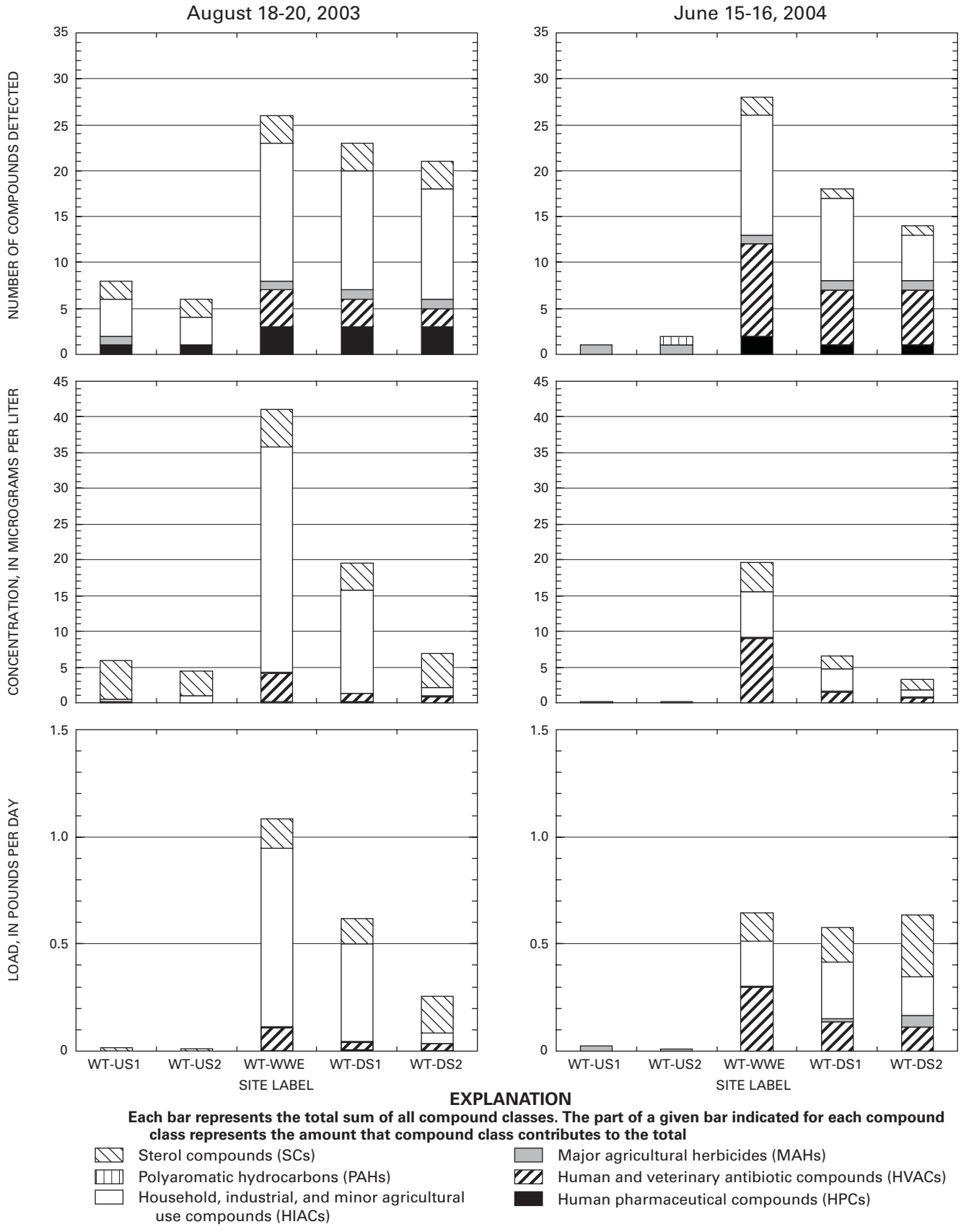

Figure 5. Summary of results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Watertown area.

Table 4. Statistical summaries of analytical results and load results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Watertown area.

[µg/L, micrograms per liter; lb/d, pounds per day; e, estimated]

	Station identification number and name (site label)									
	06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)		445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)		06479520 Big Sioux River below Watertown, SD (WT-DS2)	
Date of sample collection	08-18-2003	06-15-2004	08-18-2003	06-15-2004	08-19-2003	06-16-2004	08-19-2003	06-15-2004	08-20-2003	06-15-2004
Time of sample collection	1045	1030	1200	1200	1305	0925	0930	1730	0915	1825
Human pharmaceutical compounds (HPCs)										
Number of compounds detected	1	0	1	0	3	2	3	1	3	1
Minimum detected concentration (µg/L)	e0.0047	0	e0.0027	0	e0.0035	0.017	e0.0054	e0.0066	e0.0039	e0.0051
Median detected concentration (µg/L)	e0.0047	0	e0.0027	0	0.034	0.026	0.039	e0.0066	e0.0090	e0.0051
Maximum detected concentration (µg/L)	e0.0047	0	e0.0027	0	0.049	0.036	0.087	e0.0066	0.042	e0.0051
Total detected concentration (µg/L)	e0.0047	0	e0.0027	0	e0.086	0.053	e0.13	e0.0066	e0.055	e0.0051
Total load (lb/d)	e0.0000	0	e0.0000	0	e0.0023	e0.0017	e0.0042	e0.0006	e0.0020	e0.0010
Human and veterinary antibiotic compounds (HVACs)										
Number of compounds detected	0	0	0	0	4	10	3	6	2	6
Minimum detected concentration (µg/L)	0	0	0	0	0.17	0.016	0.27	0.036	0.16	0.0060
Median detected concentration (µg/L)	0	0	0	0	1.1	0.26	0.31	0.16	0.42	0.063
Maximum detected concentration (µg/L)	0	0	0	0	1.7	5.7	0.56	0.85	0.67	0.30
Total detected concentration (µg/L)	0	0	0	0	4.0	9.0	1.1	1.5	0.83	0.59
Total load (lb/d)	0	0	0	0	e0.11	e0.30	e0.036	e0.14	e0.031	e0.11
Major agricultural herbicides (MAHs)										
Number of compounds detected	1	1	0	1	1	1	1	1	1	1
Minimum detected concentration (µg/L)	e0.10	e0.21	0	0.19	0.068	0.18	0.10	0.16	0.068	0.26
Median detected concentration (µg/L)	e0.10	e0.21	0	0.19	0.068	0.18	0.10	0.16	0.068	0.26
Maximum detected concentration (µg/L)	e0.10	e0.21	0	0.19	0.068	0.18	0.10	0.16	0.068	0.26
Total detected concentration (µg/L)	e0.10	e0.21	0	0.19	0.068	0.18	0.10	0.16	0.068	0.26
Total load (lb/d)	e0.0002	e0.025	0	e0.0090	e0.0018	e0.0059	e0.0032	e0.014	e0.0025	e0.050

Table 4. Statistical summaries of analytical results and load results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Watertown area.—Continued

[µg/L, micrograms per liter; lb/d, pounds per day; e, estimated]

	Station identification number and name (site label)									
	06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)		445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)		06479520 Big Sioux River below Watertown, SD (WT-DS2)	
Household, industrial, and minor agricultural use compounds (HIACs)										
Number of compounds detected	4	0	3	0	15	13	13	9	12	5
Minimum detected concentration (µg/L)	e0.036	0	e0.046	0	e0.034	e0.063	e0.024	e0.054	e0.033	e0.040
Median detected concentration (µg/L)	e0.080	0	e0.35	0	e0.15	e0.35	e0.11	e0.35	e0.078	e0.16
Maximum detected concentration (µg/L)	e0.19	0	0.55	0	28	1.6	12	e0.84	e0.23	e0.52
Total detected concentration (µg/L)	e0.39	0	e0.95	0	e32	e6.3	e14	e3.0	e1.2	e0.95
Total load (lb/d)	e0.0009	0	e0.0023	0	e0.83	e0.21	e0.46	e0.27	e0.046	e0.18
Polyaromatic hydrocarbons (PAHs)										
Number of compounds detected	0	0	0	1	0	0	0	0	0	0
Minimum detected concentration (µg/L)	0	0	0	e0.014	0	0	0	0	0	0
Median detected concentration (µg/L)	0	0	0	e0.014	0	0	0	0	0	0
Maximum detected concentration (µg/L)	0	0	0	e0.014	0	0	0	0	0	0
Total detected concentration (µg/L)	0	0	0	e0.014	0	0	0	0	0	0
Total load (lb/d)	0	0	0	e0.0007	0	0	0	0	0	0
Sterol compounds (SCs)										
Number of compounds detected	2	0	2	0	3	2	3	1	3	1
Minimum detected concentration (µg/L)	2.2	0	e1.6	0	e0.94	e1.2	e0.94	e1.8	e0.75	e1.5
Median detected concentration (µg/L)	2.7	0	e1.7	0	e1.3	e2.0	e1.0	e1.8	e1.7	e1.5
Maximum detected concentration (µg/L)	3.2	0	e1.8	0	3.0	2.9	e1.7	e1.8	2.3	e1.5
Total detected concentration (µg/L)	5.4	0	e3.4	0	e5.2	e4.1	e3.6	e1.8	e4.8	e1.5
Total load (lb/d)	e0.013	0	e0.0084	0	e0.14	e0.13	e0.12	e0.16	e0.18	e0.29

Table 4. Statistical summaries of analytical results and load results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Watertown area.—Continued

[µg/L, micrograms per liter; lb/d, pounds per day; e, estimated]

	Station identification number and name (site label)									
	06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)		445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)		06479520 Big Sioux River below Watertown, SD (WT-DS2)	
All organic wastewater compounds (OWCs)										
Number of compounds detected	8	1	6	2	26	28	23	18	21	14
Minimum detected concentration (µg/L)	e0.0047	e0.21	e0.0027	e0.014	e0.0035	0.016	e0.0054	e0.0066	e0.0039	e0.0051
Median detected concentration (µg/L)	e0.10	e0.21	e0.45	e0.10	e0.18	e0.32	e0.18	e0.19	e0.082	e0.10
Maximum detected concentration (µg/L)	3.2	e0.21	e1.8	e0.19	28	5.7	12	e1.8	2.3	e1.5
Total detected concentration (µg/L)	e5.9	e0.21	e4.3	e0.20	e41	e20	e19	e6.5	e6.9	e3.3
Total load (lb/d)	e0.014	e0.025	e0.011	e0.0097	e1.1	e0.65	e0.62	e0.58	e0.26	e0.63
Endocrine-disrupting compounds (EDCs) from all compound classes										
Number of compounds detected	2	1	1	1	4	7	4	6	5	3
Minimum detected concentration (µg/L)	e0.10	e0.21	0.55	e0.19	e0.078	e0.091	e0.068	e0.060	e0.033	e0.040
Median detected concentration (µg/L)	e0.14	e0.21	0.55	e0.19	e0.17	e0.54	e0.10	e0.45	e0.064	e0.16
Maximum detected concentration (µg/L)	e0.19	e0.21	0.55	e0.19	1.1	1.6	0.59	e0.84	e0.087	e0.26
Total detected concentration (µg/L)	e0.29	e0.21	0.55	e0.19	e1.4	e4.3	e0.86	e2.5	e0.32	e0.46
Total load (lb/d)	e0.0007	e0.025	e0.0014	e0.0090	e0.040	e0.14	e0.027	e0.22	e0.012	e0.088

Table 5. Detected organic wastewater compounds in wastewater effluent and the Big Sioux River in the Watertown area.

[Bold text for compound names indicates suspected endocrine-disrupting compounds (EDCs). AHTN, 7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene; DEET, N,N-diethyl-*meta*-toluamide; HHCB, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran; NP2EO, nonylphenol diethoxylate; NP1EO, nonylphenol monoethoxylate; NP, *para*-nonylphenol; --, not detected]

	Station identification number and name (site label)									
	06479500 Big Sioux River at Watertown, SD (WT-US1)		**06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)**		**445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)**		**445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)**		**06479520 Big Sioux River below Watertown, SD (WT-DS2)**	
Date of sample collection	08-18-2003	06-15-2004	08-18-2003	06-15-2004	08-19-2003	06-16-2004	08-19-2003	06-15-2004	08-20-2003	06-15-2004
Time of sample collection	1045	1030	1200	1200	1305	0925	0930	1730	0915	1825
Number of compounds detected	8	1	6	2	26	28	23	18	21	14
Human pharmaceutical compounds (HPCs)	Cotinine	--	Cotinine	--	Cotinine Dehydronifedipine Salbutamol	Cotinine Salbutamol	Caffeine Cotinine Salbutamol	Cotinine	Cotinine Dehydronifedipine Salbutamol	Cotinine
Human and veterinary antibiotic compounds (HVACs)	--	--	--	--	Ciprofloxacin Erythromycin-H_2O Ofloxacin Sulfamethoxazole	Ciprofloxacin Erythromycin Erythromycin-H_2O Norfloxacin Ofloxacin Roxithromycin Sulfadiazine Sulfamethoxazole Tetracycline Trimethoprim	Erythromycin-H_2O Ofloxacin Sulfamethoxazole	Ciprofloxacin Erythromycin Erythromycin-H_2O Ofloxacin Sulfamethoxazole Trimethoprim	Erythromycin-H_2O Sulfamethoxazole	Erythromycin Erythromycin-H_2O Sulfadiazine Sulfamethazine Sulfamethoxazole Trimethoprim
Major agricultural herbicides (MAHs)	**Atrazine**	**Atrazine**	--	**Atrazine**	Prometon	**Atrazine**	Prometon	**Atrazine**	Prometon	**Atrazine**

Table 5. Detected organic wastewater compounds in wastewater effluent and the Big Sioux River in the Watertown area.—Continued

[Bold text for compound names indicates suspected endocrine-disrupting compounds (EDCs). AHTN, 7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene; DEET, N,N-diethyl-*meta*-toluamide; HHCB, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran; NP2EO, nonylphenol diethoxylate; NP1EO, nonylphenol monoethoxylate; NP, *para*-nonylphenol; --, not detected]

	Station identification number and name (site label)									
	06479500 Big Sioux River at Watertown, SD (WT-US1)		**06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)**		**445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)**		**445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)**		**06479520 Big Sioux River below Watertown, SD (WT-DS2)**	
Household, industrial, and minor agricultural-use compounds (HIACs)	**Bisphenol-A** N,N-diethyl-*meta*-toluamide (DEET) Indole Isophorone	--	**Diethyl phthalate** Tributyl phosphate Tri(2-butoxyethyl) phosphate	--	5-methyl-1H-benzotriazole **AHTN** Acetophenone **Benzophenone** DEET **HHCB** Indole *para*-cresol Tributyl phosphate **Triclosan** Triethyl citrate (ethyl citrate) Triphenyl phosphate Tri(2-butoxyethyl) phosphate Tri(2-chloroethyl)phosphate Tri(dichloroisopropyl)phosphate	5-methyl-1H-benzotriazole **AHTN** **Benzophenone** DEET **HHCB** **NP2EO** **NP1EO** **NP** Tributyl phosphate Triethyl citrate (ethyl citrate) Triphenyl phosphate Tri(2-chloroethyl) phosphate Tri(dichloroisopropyl)phosphate	**AHTN** Acetophenone **Benzophenone** DEET **HHCB** Indole Tributyl phosphate **Triclosan** Triethyl citrate (ethyl citrate) Triphenyl phosphate Tri(2-butoxyethyl) phosphate Tri(2-chloroethyl) phosphate Tri(dichloroisopropyl)phosphate	**AHTN** **HHCB** **NP2EO** **NP1EO** **NP** Tributyl phosphate Triethyl citrate (ethyl citrate) Tri(2-butoxyethyl) phosphate Tri(2-chloroethyl) phosphate	**AHTN** Acetophenone **Benzophenone** **Bisphenol-A** DEET **HHCB** Indole Tributyl phosphate **Triclosan** Tri(2-butoxyethyl) phosphate Tri(2-chloroethyl) phosphate Tri(dichloroisopropyl)phosphate	**AHTN** DEET **HHCB** Triethyl citrate (ethyl citrate) Tri(2-butoxyethyl) phosphate
PAH compounds (PAHs)	--	--	--	Naphthalene	--	--	--	--	--	--
Sterol compounds (SCs)	*beta*-sitosterol Cholesterol	--	*beta*-sitosterol Cholesterol	--	3-*beta*-coprostanol *beta*-sitosterol Cholesterol	3-*beta*-coprostanol Cholesterol	3-*beta*-coprostanol *beta*-sitosterol Cholesterol	Cholesterol	3-*beta*-coprostanol *beta*-sitosterol Cholesterol	Cholesterol

MAHs were detected in samples collected from all sampling sites in the Watertown area (fig. 5, tables 4 and 5). Atrazine was detected in samples collected from the upstream sites WT-US1 and WT-US2 at estimated concentrations less than 0.2 µg/L and accounted for less than about 2 percent of the total OWC concentrations for August 2003 samples collected from these sites, but between about 95 and 100 percent for June 2004 samples. Two MAHs (atrazine and prometon) were detected in samples collected from WT-WWE with total estimated concentrations less than 0.2 µg/L, which accounted for less than about 1 percent of the total OWC concentration for any WT-WWE sample. The same two MAHs (atrazine and prometon) were detected in samples collected from the downstream sites WT-DS1 and WT-DS2 with total concentrations less than 0.3 µg/L, which accounted for less than about 8 percent of any sample. MAH concentrations at all sampling sites in the Watertown area were larger in June 2004 samples than in August 2003 samples.

HIACs were detected in samples from all sites in the Watertown area (fig. 5, tables 4 and 5). Seven HIACs were detected in samples from the upstream sites WT-US1 and WT-US2 with combined estimated concentrations as large as 0.95 µg/L. Bisphenol-A, diethyl phthalate, and tri(2-butoxyethyl)phosphate had the largest concentrations for the upstream sites, with maximum estimated concentrations of 0.19, 0.55, and 0.35 µg/L, respectively. All other individual HIACs had detected concentrations less than 0.2 µg/L. Total HIAC concentrations accounted for about 0 to 22 percent of the total OWC concentrations for the upstream sites. Eighteen HIACs were detected in samples from WT-WWE. For the August 2003 WT-WWE sample, 7-acetyl-1,1,2,4,4,6-hexamethyl tetrahydronaphthalene (AHTN) and tri(2-chloroethyl)phosphate had the largest concentrations (1.1 and 28 µg/L, respectively), and detected concentrations of all other individual HIACs were less than 0.5 µg/L. The total estimated HIAC concentration for the August 2003 WT-WWE sample was 32 µg/L and accounted for about 78 percent of the total OWC concentration. For the June 2004 WT-WWE sample, 5-methyl-1H-benzotriazole, AHTN, nonylphenol diethoxylate (NP2EO), NP1EO, and *para*-nonylphenol (NP) had the largest concentrations (about 0.89, 1.6, 0.91, 0.54, and 0.84 µg/L, respectively), and detected concentrations of all other individual HIACs were less than about 0.4 µg/L. The total HIAC concentration for the August 2003 WT-WWE sample was about 6.3 µg/L and accounted for about 32 percent of the total OWC concentration. Seventeen HIACs were detected in samples collected from the downstream sites WT-DS1 and WT-DS2 with total estimated HIAC concentrations ranging from 0.95 to 14 µg/L. For August 2003, HIACs with largest estimated concentrations included AHTN, tri(2-butoxyethyl)phosphate, and tri(2-chloroethyl)phosphate (0.59, 0.63, and 12 µg/L, respectively) for WT-DS1 and tri(2-butoxyethyl)phosphate, tri(2-chloroethyl)phosphate, and tri(dichloroisopropyl)phosphate (0.23, 0.20, and 0.18 µg/L, respectively) for WT-DS2. For August 2003, total HIAC concentrations accounted for about 74 and 17 percent of the total OWC concentrations for WT-DS1 and WT-DS2, respectively. For June 2004, HIACs with largest estimated concentrations included AHTN, NP2EO, NP1EO, and NP (0.51, 0.55, 0.39, and 0.84 µg/L, respectively) for WT-DS1 and AHTN (0.16 µg/L) for WT-DS2. Concentrations of HIACs in samples collected from downstream sites were larger during August 2003 than during June 2004 and probably reflect a greater fraction of the total flow of the Big Sioux River being derived from WWTP discharge during the August 2003 sampling period. For both August 2003 and June 2004, concentrations and loads of HIAC compounds were substantially smaller for WT-DS2 than for WT-DS1. This might be due to (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 (4) dilution that can directly reduce concentrations and can possibly reduce load estimates by decreasing concentrations to less than detectable levels.

One PAH (naphthalene) was detected in a single sample (June 2004) collected from a single site (WT-US2) in the Watertown area at an estimated concentration of 0.014 µg/L. The detection accounted for about 7 percent of the total OWC concentration for that sample.

SCs were detected in samples from all sites in the Watertown area (fig. 5, tables 4 and 5). Two SCs (*beta*-sitosterol and cholesterol) were detected in August 2003 samples collected from the upstream sites WT-US1 and WT-US2. No SCs were detected in June 2004 samples from the upstream sites. Total estimated SC concentrations were 5.4 and 3.4 µg/L, and accounted for about 92 and 79 percent of the total OWC concentration for the August 2003 WT-US1 and WT-US2 samples, respectively. Three SCs (3-*beta*-coprostanol, *beta*-sitosterol, and cholesterol) were detected in samples collected from WT-WWE (table 5). Total estimated SC concentrations were 5.2 and 4.1 µg/L, which accounted for about 13 and 20 percent of the total OWC concentration for the August 2003 and June 2004 WT-WWE samples, respectively. The same three SCs (3-*beta*-coprostanol, *beta*-sitosterol, and cholesterol) were detected in samples collected from downstream sites WT-DS1 and WT-DS2. Total estimated SC concentrations were 3.6 and 1.8 µg/L, and accounted for about 19 and 28 percent of the total OWC concentrations for the August 2003 and June 2004 WT-DS1 samples, respectively. Total estimated SC concentrations were 4.8 and 1.5 µg/L, and accounted for about 70 and 45 percent of the total OWC concentrations for the August 2003 and June 2004 WT-DS2 samples, respectively. SC loads for both WT-DS1 and WT-DS2 were larger for the June 2004 samples than for the August 2003 samples, primarily due to larger streamflow during the June sampling.

EDCs were detected in all samples from sampling sites in the Watertown area (fig. 6, tables 4 and 5). For both August 2003 and June 2004, the numbers of EDCs detected, and EDC concentrations and loads generally were larger for WT-WWE and downstream sites in the Watertown area (WT-DS1 and WT-DS2) than for upstream sites (WT-US1 and WT-US2). Three EDCs were detected in samples collected from upstream sites (atrazine, an MAH; and bisphenol-A and diethyl phthalate, HIACs). Total estimated EDC concentrations ranged from 0.19

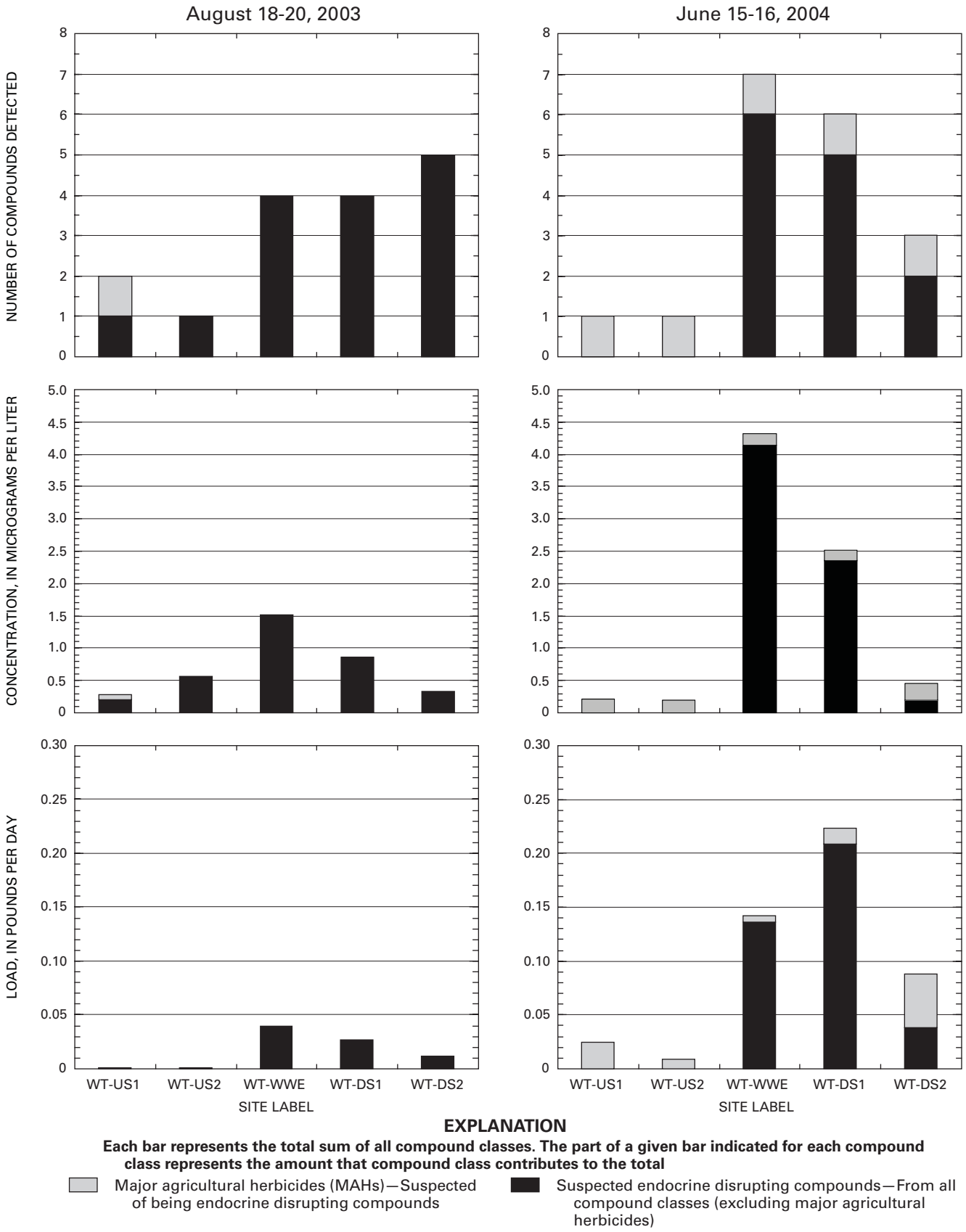

Figure 6. Summary of results for endocrine-disrupting compounds (EDCs) from all compound classes in wastewater effluent and the Big Sioux River in the Watertown area.

to 0.55 µg/L for upstream sites and were larger for August 2003 samples than for June 2004 samples. HIACs accounted for most of the total EDC concentration for August 2003, and an MAH (atrazine) accounted for all of the total EDC concentration for June 2004. Eight EDCs were detected in samples collected from WT-WWE (atrazine, an MAH; and AHTN, benzophenone, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), NP2EO, NP1EO, NP, and triclosan, which are HIACs). Total estimated EDC concentrations for WT-WWE were 1.4 and 4.3 µg/L for August 2003 and June 2004, respectively. HIACs accounted for more than about 96 percent of the total EDC concentration for WT-WWE samples. Nine EDCs were detected in samples collected from downstream sites (atrazine, an MAH; and AHTN, benzophenone, bisphenol-A, HHCB, triclosan, NP2EO, NP1EO, and NP, which are HIACs). Total estimated EDC concentrations were 0.86 and 2.5 µg/L for WT-DS1, and 0.32 and 0.46 µg/L for WT-DS2, for August 2003 and June 2004, respectively. Of the total EDC concentration, MAHs accounted for about 0 and 6 percent for WT-DS1, and for about 0 and 57 percent for WT-DS2 for August 2003 and June 2004, respectively. Of the total EDC concentration, HIACs accounted for about 100 and 94 percent for WT-DS1, and for about 100 and 43 percent for WT-DS2 for August 2003 and June 2004, respectively.

Volga Area Results

Sites in the Volga area were sampled during August 20–21, 2003, and October 21–22, 2003, when generally low-flow conditions prevailed, and during June 16–17, 2004, when runoff conditions prevailed. The Volga WWTP was not discharging to the Big Sioux River during the August 2003 or June 2004 sampling periods. Flow conditions during sampling periods are shown in figure 7. During August 20–22, 2003, streamflow at long-term USGS gaging station 06480000, located about 16 river miles downstream from sampling site VL-DS2/BK-US1, was about 32 percent of the long-term (1953–2004) median mid-August flow. During October 21–22, 2003, streamflow at station 06480000 was about 31 percent of the long-term median mid-October flow. During the October 2003 sampling period, the Volga WWTP was discharging continuously to the Big Sioux River, and the Volga WWTP discharge accounted for about 5 percent of the flow of the Big Sioux River from the confluence of the WWTP discharge to several miles downstream. During June 16–18, 2004, streamflow at station 06480000 was about 150 percent of the long-term median mid-June flow.

Field-Measured Properties and Constituents

Results for field-measured properties and constituents and auxiliary constituents in samples from sites in the Volga area are presented in figure 8 and table 17. Generally, results for field-measured properties and constituents and auxiliary constituents for the Volga area were within typical ranges for the upper Big Sioux River Basin (East Dakota Water Development District, 2004).

Organic Wastewater Constituents

OWCs in all compound classes except PAHs were detected in samples from sampling sites in the Volga area (fig. 9, tables 6 and 7). Differences in total OWC concentrations and loads between the upstream Big Sioux River site (VL-US1) and downstream sites (VL-DS1 and VL-DS2/BK-US1) were variable. For August 2003, the upstream site had larger total OWC concentrations and loads than downstream sites. SCs and HIACs accounted for about 90 percent and 8 percent, respectively, of the August 2003 VL-US1 total OWC concentration. SCs accounted for about 94 percent of the August 2003 VL-DS1 total OWC concentration, and SCs and HIACS accounted for about 83 and 10 percent, respectively, of the August 2003 VL-DS2/BK-US1 total OWC concentration. For October 2003, when the Volga WWTP was discharging to the Big Sioux River channel, total OWC concentrations and loads were larger for VL-DS1 than for VL-US1, and the estimated increase in load between VL-US1 and VL-DS1 corresponds well with the estimated load contributed by VL-WWE, especially for HIACs. HIACs and SCs accounted for about 64 and 33 percent, respectively, of the October 2003 VL-US1 total OWC concentration, and about 52 and 45 percent of the October 2003 VL-DS1 concentration. For June 2004, VL-US1 had a smaller total OWC concentration and load than downstream Big Sioux River sites. MAHs accounted for 90, 84, and 86 percent of the June 2004 total OWC concentrations for VL-US1, VL-DS1, and VL-DS2/BK-US1, respectively. Although confident conclusions cannot be made due to possible effects of non-Lagrangian sampling, OWC results for the Volga area might indicate that (1) for the August 2003 sampling period, nonpoint livestock agricultural and/or human wastewater sources (other than the Volga WWTP) primarily contributed to occurrence of OWCs at Big Sioux River sampling sites; (2) for the October 2003 sampling period, nonpoint livestock sources and/or human wastewater sources (including the Volga WWTP) primarily contributed to occurrence of OWCs at Big Sioux River sampling sites; (3) for the June 2004 sampling period, nonpoint crop agricultural sources primarily contributed to occurrence of OWCs at Big Sioux River sampling sites; (4) for the August 2003 and June 2004 sampling periods, seepage of water from the Volga WWTP had little effect on downstream OWC concentrations; and (5) for the October 2003 sampling period, the Volga wastewater effluent discharge contributed to downstream OWC concentrations.

HPCs were detected in samples from all sites in the Volga area (fig. 9, tables 6 and 7). Two HPCs (caffeine and cotinine) were detected in samples collected from all sites in the Volga area. In samples from VL-US1, total estimated HPC concentrations were less than 0.04 µg/L and accounted for less than 3 percent of the total OWC concentration in any sample collected from VL-US1. In samples from VL-WWE, total estimated HPC concentrations were less than 0.1 µg/L, and accounted for about 3 percent of the total OWC concentration in any sample collected from VL-WWE. In samples collected from VL-DS1 and VL-DS2/BK-US1, total estimated HPC concentrations were less than 0.1 µg/L and accounted for less than about 3 percent of the total OWC concentration in any sample collected from VL-DS1 or VL-DS2/BK-US1.

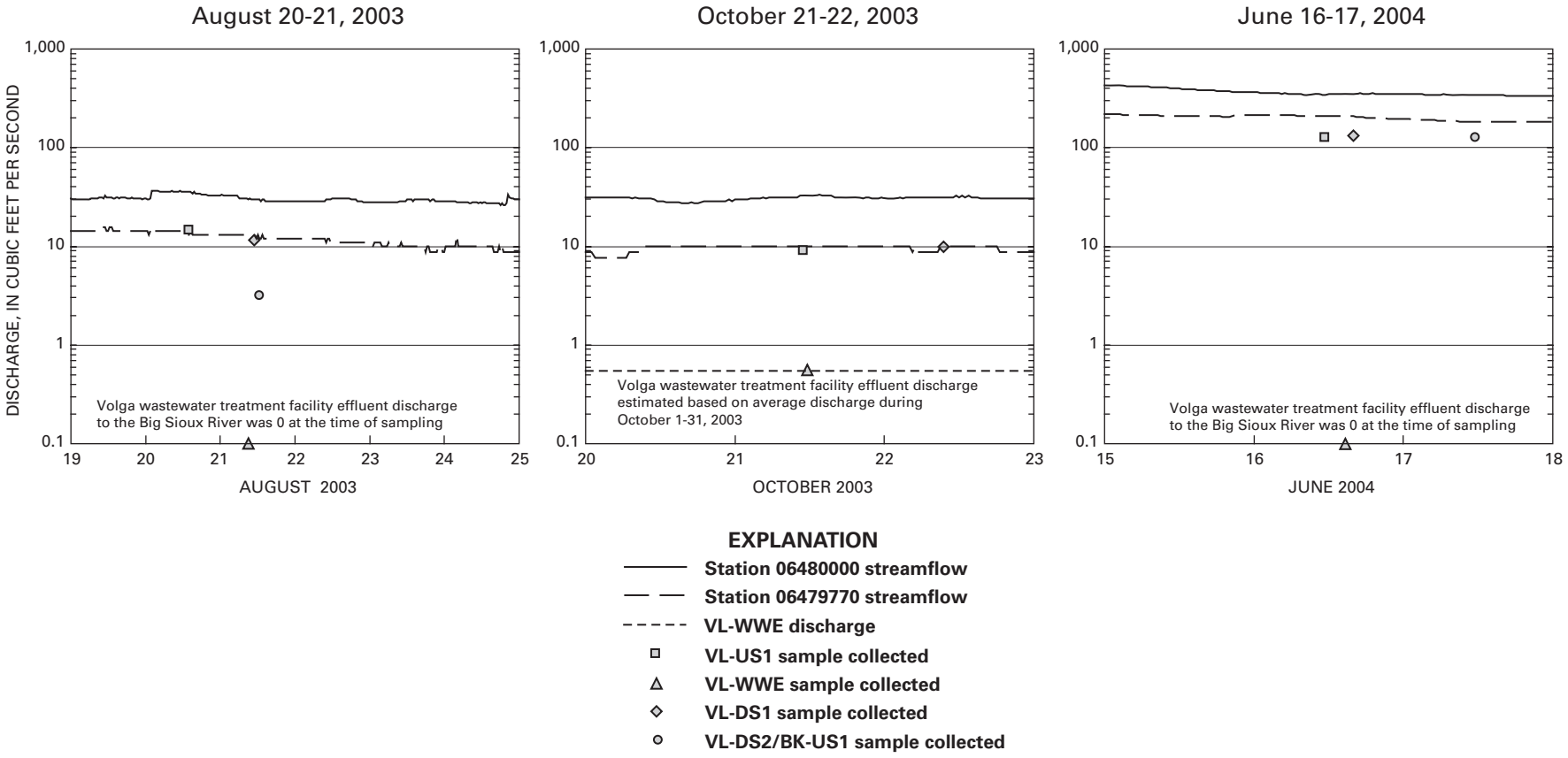

Figure 7. Flow conditions during sampling periods for sites in the Volga area.

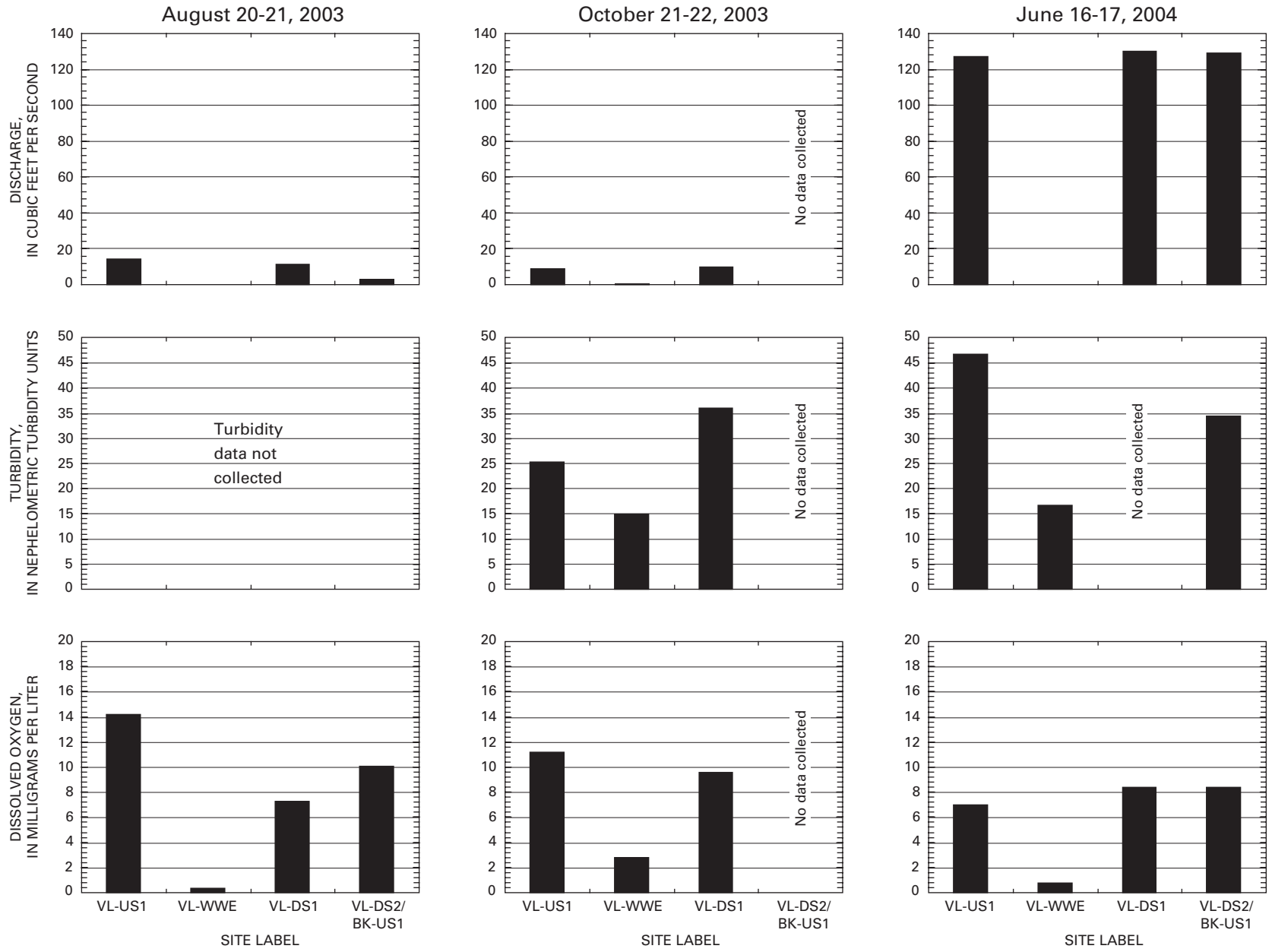

Figure 8. Results for selected field-measured properties and constituents and auxiliary constituents in wastewater effluent and the Big Sioux River in the Volga area.

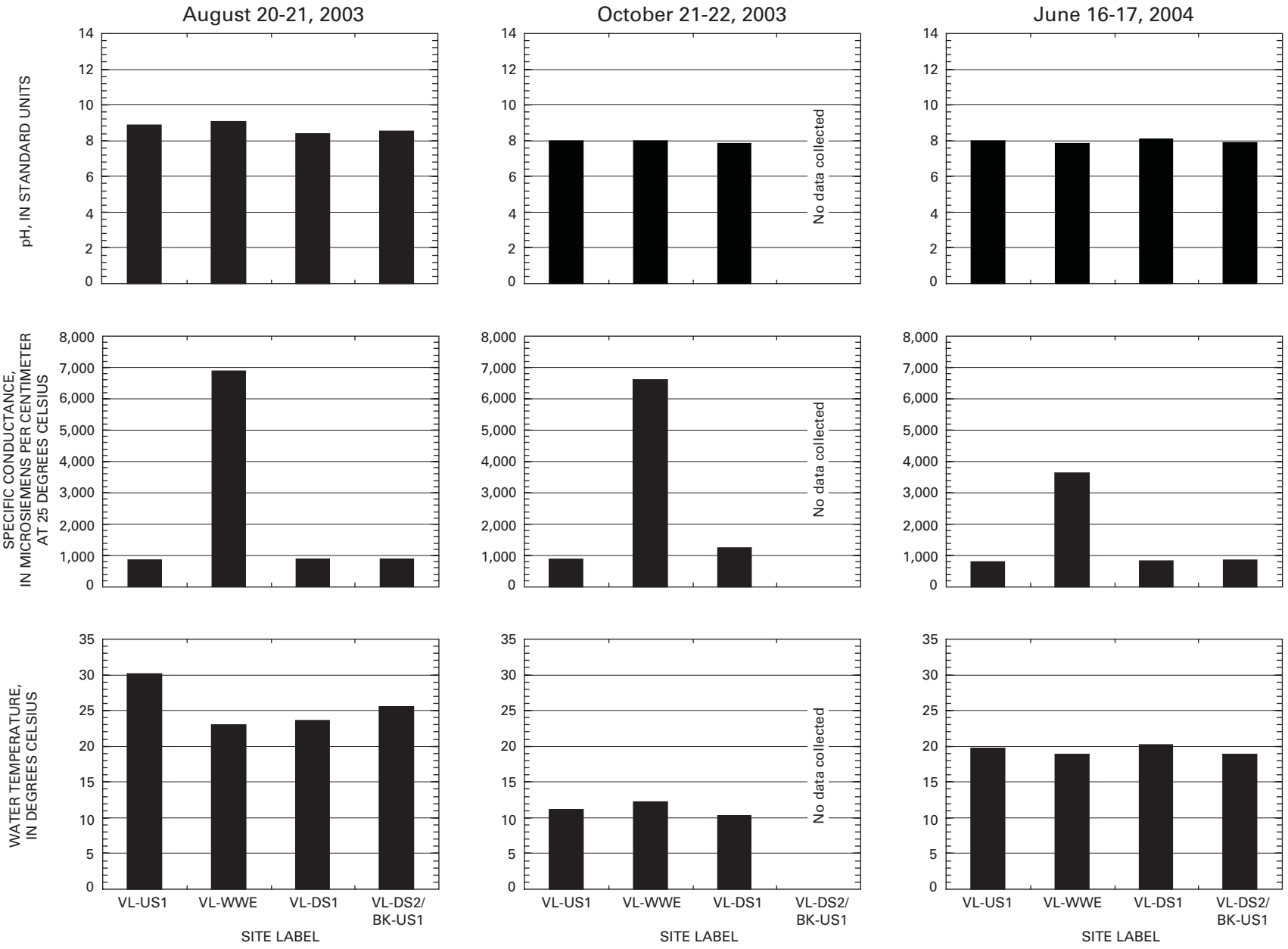

Figure 8. Results for selected field-measured properties and constituents and auxiliary constituents in wastewater effluent and the Big Sioux River in the Volga area.—Continued

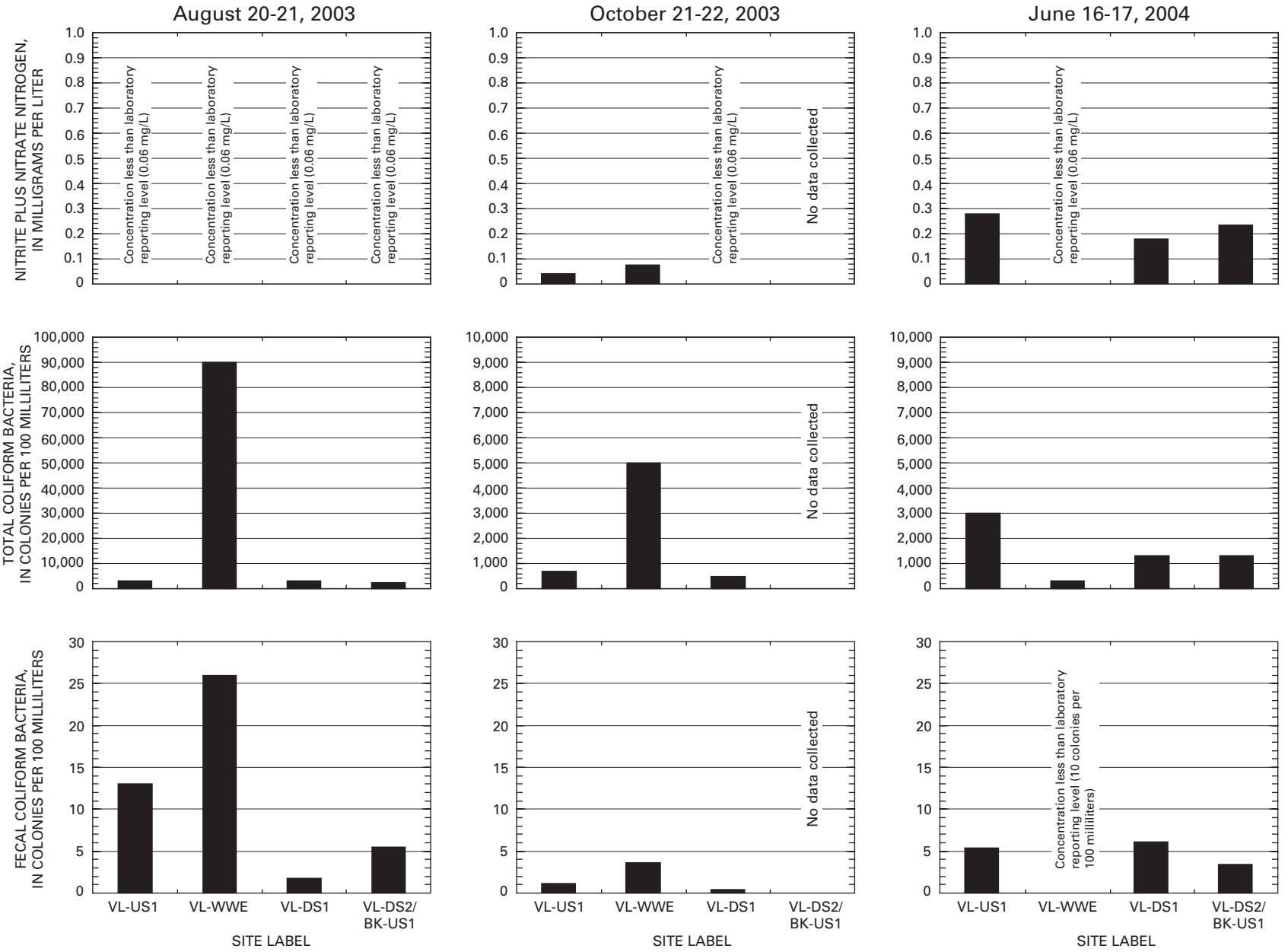

Figure 8. Results for selected field-measured properties and constituents and auxiliary constituents in wastewater effluent and the Big Sioux River in the Volga area.—Continued

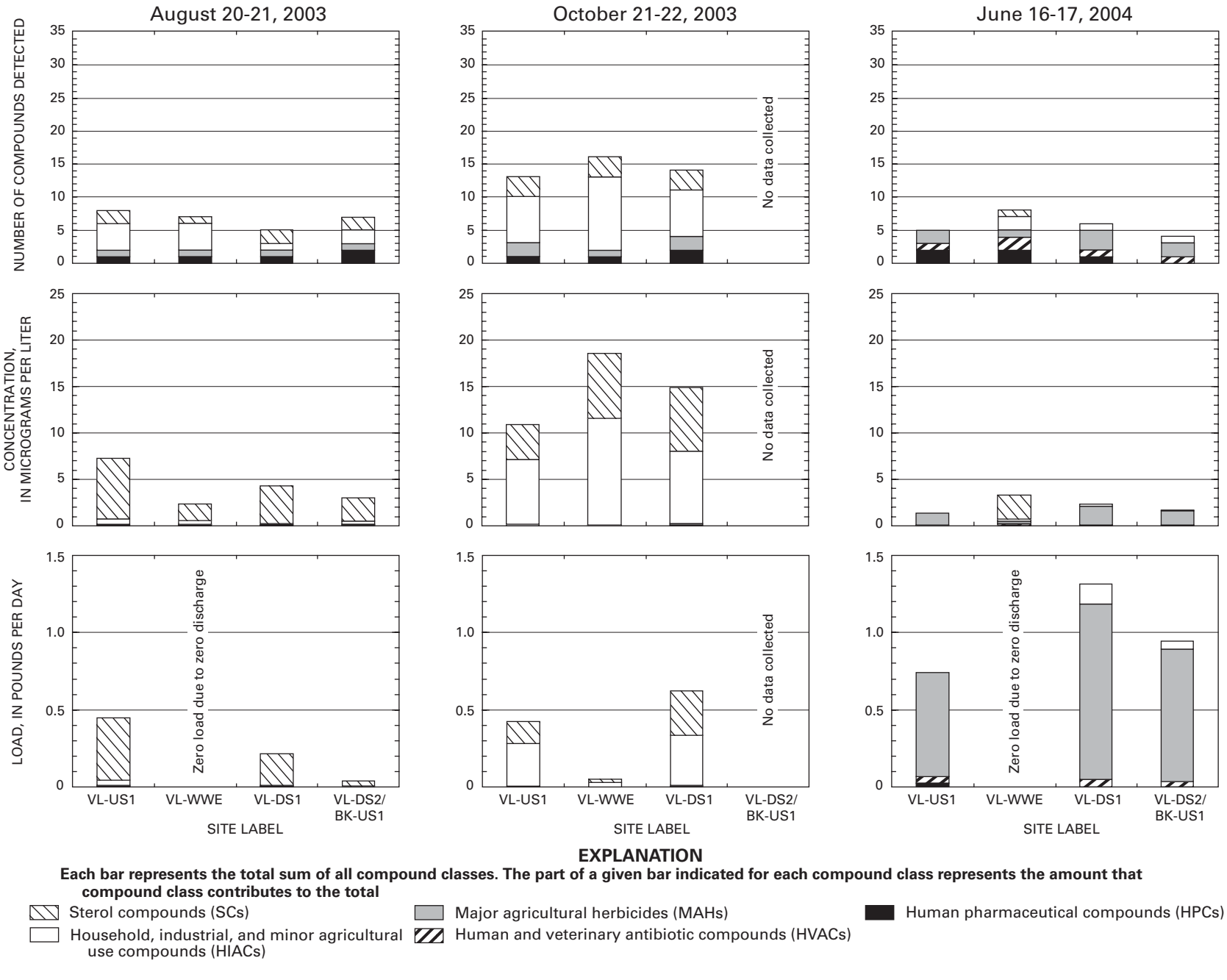

Figure 9. Summary of results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Volga area.

Table 6. Statistical summaries of analytical results and load results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Volga area.

[µg/L, micrograms per liter; lb/d, pounds per day; e, estimated; --, no data collected]

	Station identification number and name (site label)										
	442026096533600 Big Sioux River near Volga, SD (VL-US1)			441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)			441841096521400 Big Sioux River below wastewater wetland, near Volga, SD (VL-DS1)			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)	
Date of sample collection	08-20-2003	10-21-2003	06-16-2004	08-21-2003	10-21-2003	06-16-2004	08-21-2003	10-22-2003	06-16-2004	08-21-2003	06-17-2004
Time of sample collection	1400	1105	1145	0900	1240	1435	1100	0935	1615	1230	1140
Human pharmaceutical compounds (HPCs)											
Number of compounds detected	1	1	2	1	1	2	1	2	1	2	0
Minimum detected concentration (µg/L)	e0.035	e0.022	e0.0070	e0.049	e0.019	e0.0089	e0.038	0.024	e0.0030	0.029	0
Median detected concentration (µg/L)	e0.035	e0.022	e0.018	e0.049	e0.019	e0.042	e0.038	0.048	e0.0030	0.031	0
Maximum detected concentration (µg/L)	e0.035	e0.022	0.030	e0.049	e0.019	0.075	e0.038	0.073	e0.0030	0.033	0
Total detected concentration (µg/L)	e0.035	e0.022	e0.037	e0.049	e0.019	e0.084	e0.038	0.097	e0.0030	0.062	0
Total load (lb/d)	e0.0027	e0.0011	e0.025	--	e0.0001	--	e0.0023	e0.0051	e0.0021	e0.0011	0
Human and veterinary antibiotic compounds (HVACs)											
Number of compounds detected	0	0	1	0	0	2	0	0	1	0	1
Minimum detected concentration (µg/L)	0	0	0.060	0	0	0.043	0	0	0.063	0	0.048
Median detected concentration (µg/L)	0	0	0.060	0	0	0.057	0	0	0.063	0	0.048
Maximum detected concentration (µg/L)	0	0	0.060	0	0	0.071	0	0	0.063	0	0.048
Total detected concentration (µg/L)	0	0	0.060	0	0	0.11	0	0	0.063	0	0.048
Total load (lb/dd)	0	0	e0.041	--	0	--	0	0	e0.044	0	e0.033
Major agricultural herbicides (MAHs)											
Number of compounds detected	1	2	2	1	1	1	1	2	3	1	2
Minimum detected concentration (µg/L)	e0.093	e0.050	e0.035	e0.055	e0.059	e0.18	e0.076	e0.050	e0.055	e0.10	e0.035
Median detected concentration (µg/L)	e0.093	e0.053	e0.49	e0.055	e0.059	e0.18	e0.076	e0.056	e0.069	e0.10	e0.62
Maximum detected concentration (µg/L)	e0.093	e0.055	0.95	e0.055	e0.059	e0.18	e0.076	e0.061	1.5	e0.10	1.2
Total detected concentration (µg/L)	e0.093	e0.10	e0.99	e0.055	e0.059	e0.18	e0.076	e0.11	e1.6	e0.10	e1.2

Table 6. Statistical summaries of analytical results and load results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Volga area.—Continued

[µg/L, micrograms per liter; lb/d, pounds per day; e, estimated; --, no data collected]

	Station identification number and name (site label)										
	442026096533600 Big Sioux River near Volga, SD (VL-US1)			441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)			441841096521400 Big Sioux River below wastewater wetland, near Volga, SD (VL-DS1)			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)	
Total load (lb/d)	e0.0072	e0.0051	e0.67	--	e0.0002	--	e0.0047	e0.0058	e1.1	e0.0016	e0.86
Household, industrial, and minor agricultural use compounds (HIACs)											
Number of compounds detected	4	7	0	4	11	2	1	7	1	2	1
Minimum detected concentration (µg/L)	e0.043	e0.024	0	e0.029	e0.016	e0.085	e0.060	e0.083	e0.19	e0.056	e0.077
Median detected concentration (µg/L)	e0.068	e0.15	0	e0.058	e0.13	e0.098	e0.060	e0.16	e0.19	e0.12	e0.077
Maximum detected concentration (µg/L)	e0.29	e3.3	0	e0.23	e5.1	e0.11	e0.060	e3.4	e0.19	e0.19	e0.077
Total detected concentration (µg/L)	e0.47	e5.6	0	e0.38	e9.2	e0.20	e0.060	e6.3	e0.19	e0.25	e0.077
Total load (lb/d)	e0.036	e0.27	0	--	e0.030	--	e0.0037	e0.33	e0.13	e0.0042	e0.054
Polyaromatic hydrocarbons (PAHs)											
Number of compounds detected	0	0	0	0	0	0	0	0	0	0	0
Minimum detected concentration (µg/L)	0	0	0	0	0	0	0	0	0	0	0
Median detected concentration (µg/L)	0	0	0	0	0	0	0	0	0	0	0
Maximum detected concentration (µg/L)	0	0	0	0	0	0	0	0	0	0	0
Total detected concentration (µg/L)	0	0	0	0	0	0	0	0	0	0	0
Total load (lb/d)	0	0	0	0	0	--	0	0	0	0	0
Sterol compounds (SCs)											
Number of compounds detected	2	3	0	1	3	1	2	3	0	2	0
Minimum detected concentration (µg/L)	e1.6	e0.54	0	e1.4	e0.78	2.1	e1.4	e0.73	0	e1.0	0
Median detected concentration (µg/L)	e2.6	e1.1	0	e1.4	2.0	2.1	e1.6	2.3	0	e1.0	0
Maximum detected concentration (µg/L)	3.6	e1.3	0	e1.4	2.8	2.1	e1.9	2.4	0	e1.0	0
Total detected concentration (µg/L)	e5.2	e2.9	0	e1.4	e5.6	2.1	e3.3	e5.4	0	e2.0	0
Total load (lb/d)	e0.40	e0.14	0	--	e0.018	--	e0.20	e0.28	0	e0.034	0

Table 6. Statistical summaries of analytical results and load results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Volga area.—Continued

[µg/L, micrograms per liter; lb/d, pounds per day; e, estimated; --, no data collected]

	Station identification number and name (site label)										
	442026096533600 Big Sioux River near Volga, SD (VL-US1)			441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)			441841096521400 Big Sioux River below wastewater wetland, near Volga, SD (VL-DS1)			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)	
All organic wastewater compounds (OWCs)											
Number of compounds detected	8	13	5	7	16	8	5	14	6	7	4
Minimum detected concentration (µg/L)	e0.035	e0.022	e0.0070	e0.029	e0.016	e0.0089	e0.038	0.024	e0.0030	0.029	e0.035
Median detected concentration (µg/L)	e0.081	e0.15	e0.035	e0.055	e0.16	e0.080	e0.076	e0.14	e0.066	e0.095	e0.062
Maximum detected concentration (µg/L)	3.6	e3.3	0.95	e1.4	e5.1	2.1	e1.9	e3.4	1.5	e1.0	1.2
Total detected concentration (µg/L)	e5.8	e8.7	e1.1	e1.9	e15	e2.7	e3.5	e12	e1.9	e2.4	e1.4
Total load (lb/d)	e0.45	e0.42	e0.74	--	e0.048	--	e0.21	e0.62	e1.3	e0.041	e0.95
Endocrine-disrupting compounds (EDCs) from all compound classes											
Number of compounds detected	1	4	1	2	5	1	0	4	1	0	1
Minimum detected concentration (µg/L)	e0.069	e0.050	0.95	e0.029	e0.059	e0.18	0	e0.050	1.5	0	1.2
Median detected concentration (µg/L)	e0.069	e0.93	0.95	e0.042	e0.26	e0.18	0	e1.18	1.5	0	1.2
Maximum detected concentration (µg/L)	e0.069	e3.3	0.95	e0.055	e5.1	e0.18	0	e3.4	1.5	0	1.2
Total detected concentration (µg/L)	e0.069	e5.2	0.95	e0.084	e8.4	e0.18	0	e5.8	1.5	0	1.2
Total load (lb/d)	e0.0054	e0.25	e0.65	--	e0.027	--	0	e0.30	e1.1	0	e0.83

Table 7. Detected organic wastewater compounds in wastewater effluent and the Big Sioux River in the Volga area.

[Bold text for compound names indicates suspected endocrine-disrupting compounds (EDCs). NP2EO, nonylphenol diethoxylate; NP1EO, nonylphenol monoethoxylate; OP2EO, octylphenol diethoxylate; DEET, N,N-diethyl-*meta*-toluamide; --, not detected]

	Station identification number and name (site label)										
	442026096533600 Big Sioux River near Volga, SD (VL-US1)			**441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)**			**441841096521400 Big Sioux River below wastewater wetland, near Volga, SD (VL-DS1)**			**441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)**	
Date of sample collection	08-20-2003	10-21-2003	06-16-2004	08-21-2003	10-21-2003	06-16-2004	08-21-2003	10-22-2003	06-16-2004	08-21-2003	06-17-2004
Time of sample collection	1400	1105	1145	0900	1240	1435	1100	0935	1615	1230	1140
Number of compounds detected	8	13	5	7	16	8	5	14	6	7	4
Human pharmaceutical compounds (HPCs)	Cotinine	Cotinine	Caffeine Cotinine	Cotinine	Cotinine	Caffeine Cotinine	Cotinine	Caffeine Cotinine	Cotinine	Caffeine Cotinine	--
Human and veterinary antibiotic compounds (HVACs)	--	--	Erythromycin-H_2O	--	--	Erythromycin Erythromycin-H_2O	--	--	Erythromycin-H_2O	--	Erythromycin-H_2O
Major agricultural herbicides (MAHs)	Prometon	**Atrazine** Prometon	**Atrazine** Metolachlor	**Atrazine**	**Atrazine**	**Atrazine**	Prometon	**Atrazine** Prometon	**Atrazine** Metolachlor Prometon	Prometon	**Atrazine** Metolachlor
Household, industrial, and minor agricultural use compounds (HIACs)	**Bisphenol-A** Indole Tri(2-butoxyethyl) phosphate Tri(2-chloroethyl) phosphate	Acetophenone Indole **NP2EO** **NP1EO** **OP2EO** Tributyl phosphate Tri(2-chloroethyl) phosphate	--	**Benzophenone** DEET Isophorone Tri(2-chloroethyl) phosphate	5-methyl-1H-benzotriazole Acetophenone **Bisphenol-A** Camphor Indole Isophorone **NP2EO** **NP1EO** **OP2EO** *para*-cresol Tri(2-chloroethyl) phosphate	DEET Tri(2-chloroethyl) phosphate	Tri(2-chloroethyl) phosphate	Acetophenone Indole **NP2EO** **NP1EO** **OP2EO** Tributyl phosphate Tri(2-chloroethyl) phosphate	Tri(2-butoxyethyl) phosphate	Tri(2-butoxyethyl) phosphate Tri(2-chloroethyl) phosphate	DEET
PAH compounds (PAHs)	--	--	--	--	--	--	--	--	--	--	--
Sterol compounds (SCs)	*beta*-sitosterol Cholesterol	3-*beta*-coprostanol *beta*-sitosterol Cholesterol	--	Cholesterol	3-*beta*-coprostanol *beta*-sitosterol Cholesterol	Cholesterol	*beta*-sitosterol Cholesterol	3-*beta*-coprostanol *beta*-sitosterol Cholesterol	--	*beta*-sitosterol Cholesterol	--

HVACs were detected in June 2004 samples collected from all sampling sites in the Volga area (fig. 9, tables 6 and 7). No HVACs were detected in any August 2003 sample from sites in the Volga area. One HVAC (erythromycin-H_2O) was detected in the June 2004 VL-US1 sample at an estimated concentration of 0.06 µg/L and accounted for about 6 percent of the total OWC concentration. Two HVACs (erythromycin and erythromycin-H_2O) were detected in the June 2004 VL-WWE sample with a total estimated concentration of 0.11 µg/L, which accounted for about 4 percent of the total OWC concentration. One HVAC (erythromycin-H_2O) was detected in the June 2004 samples from the downstream sites VL-DS1 and VL-DS2/BK-DS1 at estimated concentrations less than 0.063 µg/L, which accounted for about 3 percent of the total OWC concentrations at both sites. The detections of HVACs in the June 2004 samples and the non-detections in the August 2003 and October 2003 samples might be related to changes in the analytical method that substantially reduced the LRLs for HVACs.

MAHs were detected in samples collected from all sampling sites in the Volga area (fig. 9, tables 6 and 7). Three MAHs (atrazine, metolachlor, and prometon) were detected in samples collected from the upstream site VL-US1 with total estimated concentrations of 0.093, 0.10, and 0.99 µg/L, which accounted for about 2, 1, and 91 percent of the total OWC concentrations for the August 2003, October 2003 samples, and June 2004 samples, respectively. Atrazine was the only MAH detected in samples collected from VL-WWE with concentrations less than 0.2 µg/L, which accounted for less than about 7 percent of the total OWC concentration for any VL-WWE sample. Three MAHs (atrazine, metolachlor, and prometon) were detected in samples collected from the downstream sites VL-DS1 and VL-DS2/BK-US1. Total estimated MAH concentrations ranged from 0.08 to 1.6 µg/L, which accounted for less than about 4 percent of the total OWC concentrations for the August 2003 and October 2003 samples, and about 84 and 86 percent for the June 2004 VL-DS1 and VL-DS2/BK-US1 samples, respectively. MAH concentrations at all sampling sites in the Volga area were larger in June 2004 samples than in August 2003 or October 2003 samples.

HIACs were detected in samples collected from all sites in the Volga area (fig. 9, tables 6 and 7). Eight HIACs were detected in August 2003 and October 2003 samples collected from upstream site VL-US1 with total estimated concentrations ranging from 0.47 to 5.6 µg/L. No HIACs were detected in the June 2004 VL-US1 sample. For VL-US1 samples, HIACs with the largest estimated concentrations were NP2EO and NP1EO (3.3 and 1.7 µg/L, respectively, for the October 2003 sample), and all other individual HIACs had detected concentrations less than 0.3 µg/L. Total HIAC concentrations accounted for about 8 and 64 percent of the total OWC concentrations for the August 2003 and October 2003 VL-US1 samples, respectively. Thirteen HIACs were detected in samples from VL-WWE with total estimated HIAC concentrations ranging from 0.20 to 9.2 µg/L. For VL-WWE samples, HIACs with the largest estimated concentrations were NP2EO and NP1EO (5.1 and 2.9 µg/L, respectively, for the October 2003 sample), and detected concentrations of all other individual HIACs were less than 0.4 µg/L. Total HIAC concentrations accounted for about 20, 61, and 7 percent of the total OWC concentration for the August 2003, October 2003, and June 2004 VL-WWE samples, respectively. Eight HIACs were detected in samples from VL-DS1, with total estimated concentrations ranging from 0.060 to 6.3 µg/L. HIACs with the largest estimated concentrations in samples from VL-DS1 were NP2EO and NP1EO (3.4 and 2.2 µg/L, respectively, for the October 2003 sample), and all other individual HIACs had detected concentrations less than 0.2 µg/L. Total estimated HIAC concentrations accounted for 2, 52, and 10 percent of the total OWC concentrations for the August 2003, October 2003, and June 2004 VL-DS1 samples, respectively. Three HIACs—N,N-diethyl-*meta*-toluamide (DEET), tri(2-butoxyethyl)phosphate, and tri(2-chloroethyl) phosphate)—were detected in samples from VL-DS2/BK-US1 with total HIAC concentrations of 0.25 µg/L or less, which accounted for about 10 and 6 percent of the total OWC concentrations for the August 2003 and June 2004 samples, respectively.

SCs were detected in samples collected from all sites in the Volga area (fig. 9, tables 6 and 7). Three SCs (3-*beta* coprostanol, *beta*-sitosterol, and cholesterol) were detected in August 2003 and October 2003 samples collected from VL-US1 with total estimated SC concentrations ranging from 2.9 to 5.2 µg/L. No SCs were detected in the June 2004 sample from VL-US1. Total SC concentrations accounted for about 90 and 33 percent of the total OWC concentration for the August 2003 and October 2003 VL-US1 samples, respectively. The same three SCs (3-*beta* coprostanol, *beta*-sitosterol, and cholesterol) were detected in samples collected from VL-WWE with total estimated SC concentrations ranging from 1.4 to 5.6 µg/L. Total SC concentrations accounted for about 74, 37, and 78 percent of the total OWC concentration for the August 2003, October 2003, and June 2004 VL-WWE samples, respectively. The same three SCs were detected in the August 2003 and October 2003 VL-DS1 samples with total estimated concentrations ranging from 3.3 to 5.4 µg/L. No SCs were detected in the June 2004 VL-DS1 sample. Total SC concentrations accounted for about 94 and 45 percent of the total OWC concentration for the August 2003 and October 2003 VL-DS1 samples, respectively. Two SCs (*beta*-sitosterol and cholesterol) were detected in the August 2003 VL-DS2/BK-US1 sample with a combined estimated concentration of 2.0 µg/L, which accounted for about 83 percent of the total OWC concentration. No SCs were detected in the June 2004 VL-DS1/BK-US1 sample.

EDCs were detected at all sampling sites in the Volga area (fig. 10, tables 6 and 7). Five different EDCs were detected in samples collected from VL-US1 (atrazine, an MAH; and bisphenol-A, NP2EO, NP1EO, and octylphenol diethoxylate (OP2EO), which are HIACs) with total estimated EDC concentrations ranging from 0.069 to 5.2 µg/L. Of the total EDC concentrations, HIACs accounted for 100, 99, and 0 percent, and MAHs accounted for 0, 1, and 100 percent for the August 2003, October 2003, and June 2004 VL-US1 samples, respectively. Six EDCs were detected in samples collected from VL-WWE

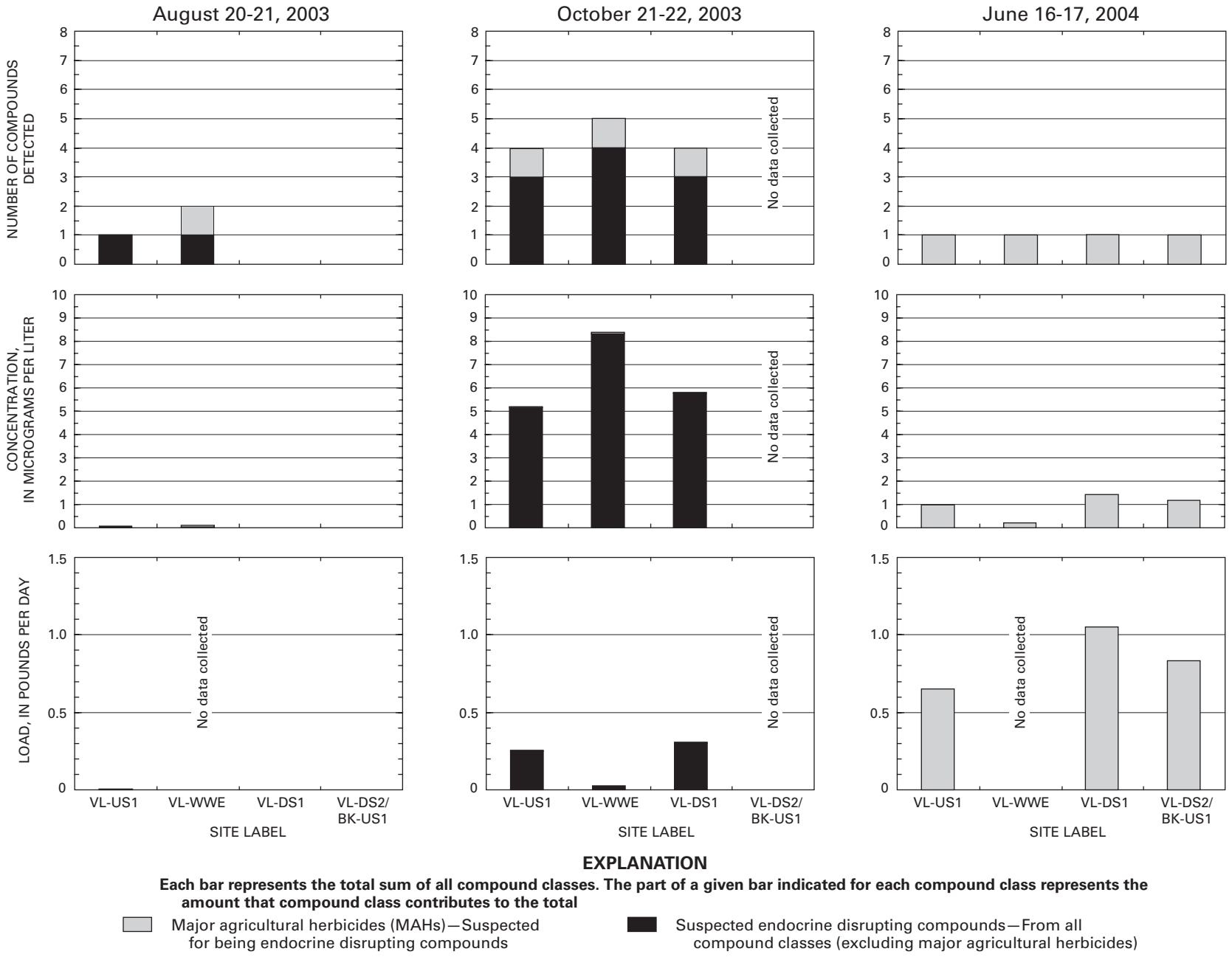

Figure 10. Summary of results for endocrine-disrupting compounds (EDCs) from all compound classes in wastewater effluent and the Big Sioux River in the Volga area.

(atrazine, which is an MAH; and benzophenone, bisphenol-A, NP2EO, NP1EO, and OP2EO, which are HIACs) with total estimated EDC concentrations ranging from 0.084 to 8.4 µg/L. Of the total EDC concentrations, HIACs accounted for about 35, 99, and 0 percent, and MAHs accounted for about 65, 1, and 100 percent for the August 2003, October 2003, and June 2004 VL-WWE samples, respectively. Four EDCs were detected in samples collected from VL-DS1 (atrazine, an MAH; and NP2EO, NP1EO, and OP2EO, which are HIACs) with total estimated EDC concentrations ranging from undetected to 5.8 µg/L. HIACs accounted for nearly all of the total EDC concentration at VL-DS1 for the October 2003 sample, and MAHs accounted for all of the total EDC concentration for the June 2004 sample. One EDC was detected in the June 2004 sample collected from VL-DS2/BK-US1 (atrazine, an MAH) at an estimated concentration of 1.2 µg/L.

Brookings Area Results

Sites in the Brookings area were sampled during August 21–22, 2003, when generally low-flow conditions prevailed and during June 17–18, 2004, when runoff conditions prevailed. Flow conditions during sampling periods are shown in figure 11. During August 20–22, 2003, streamflow at long-term USGS gaging station 06480000, located about 4.7 river miles downstream from sampling site BK-DS2, was about 32 percent of the long-term (1953–2004) median mid-August flow. During June 16–18, 2004, streamflow at station 06480000 was about 148 percent of the long-term median mid-June flow. The Brookings WWTP discharged continuously to the Big Sioux River during both sampling periods. During the August 2003 sampling period, the Brookings WWTP discharge accounted for about 10 to 40 percent of the flow of the Big Sioux River from the confluence of the WWTP discharge to several miles downstream. During the June 2004 sampling period, the Brookings WWTP discharge accounted for about 1 to 2 percent of the flow of the Big Sioux River from the confluence of the WWTP discharge to several miles downstream.

Field-Measured Properties and Constituents

Results for field-measured properties and constituents and auxiliary constituents in samples from sites in the Brookings area are presented in figure 12 and table 17. Generally, results for field-measured properties and constituents and auxiliary constituents for the Brookings area were within typical ranges for the upper Big Sioux River Basin (East Dakota Water Development District, 2004).

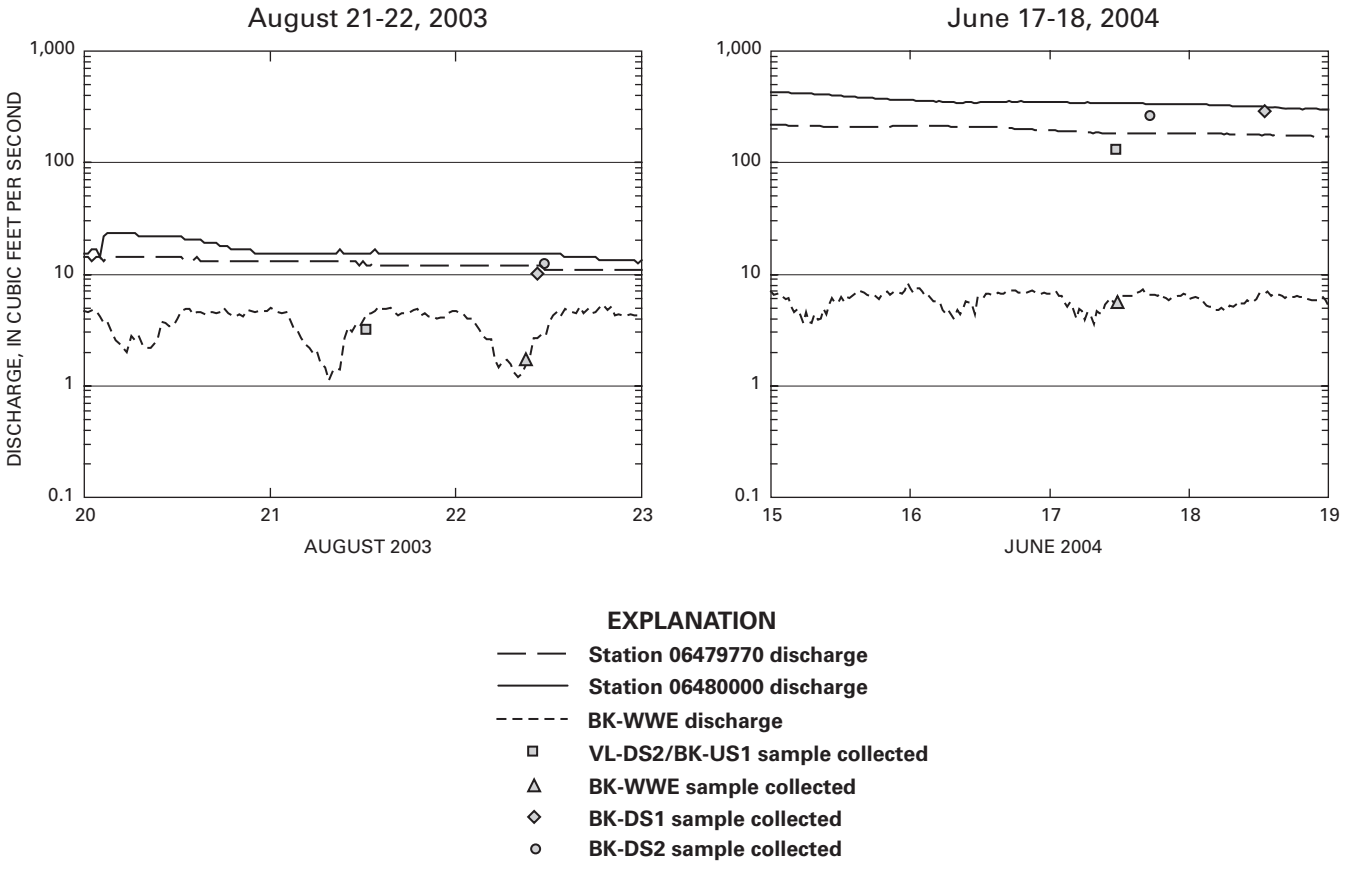

Figure 11. Flow conditions during sampling periods for sites in the Brookings area.

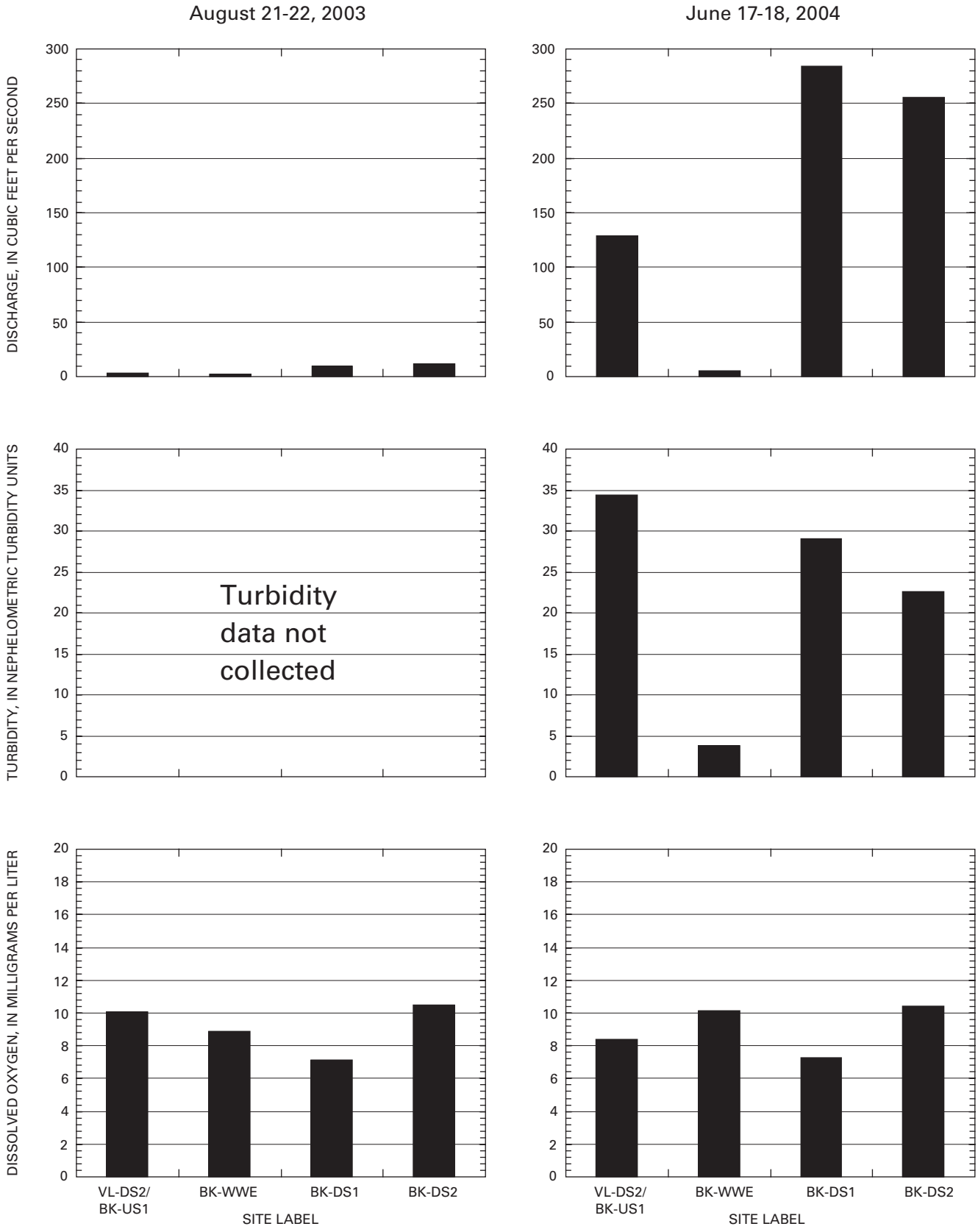

Figure 12. Results for selected field-measured properties and constituents and auxiliary constituents in wastewater effluent and the Big Sioux River in the Brookings area.

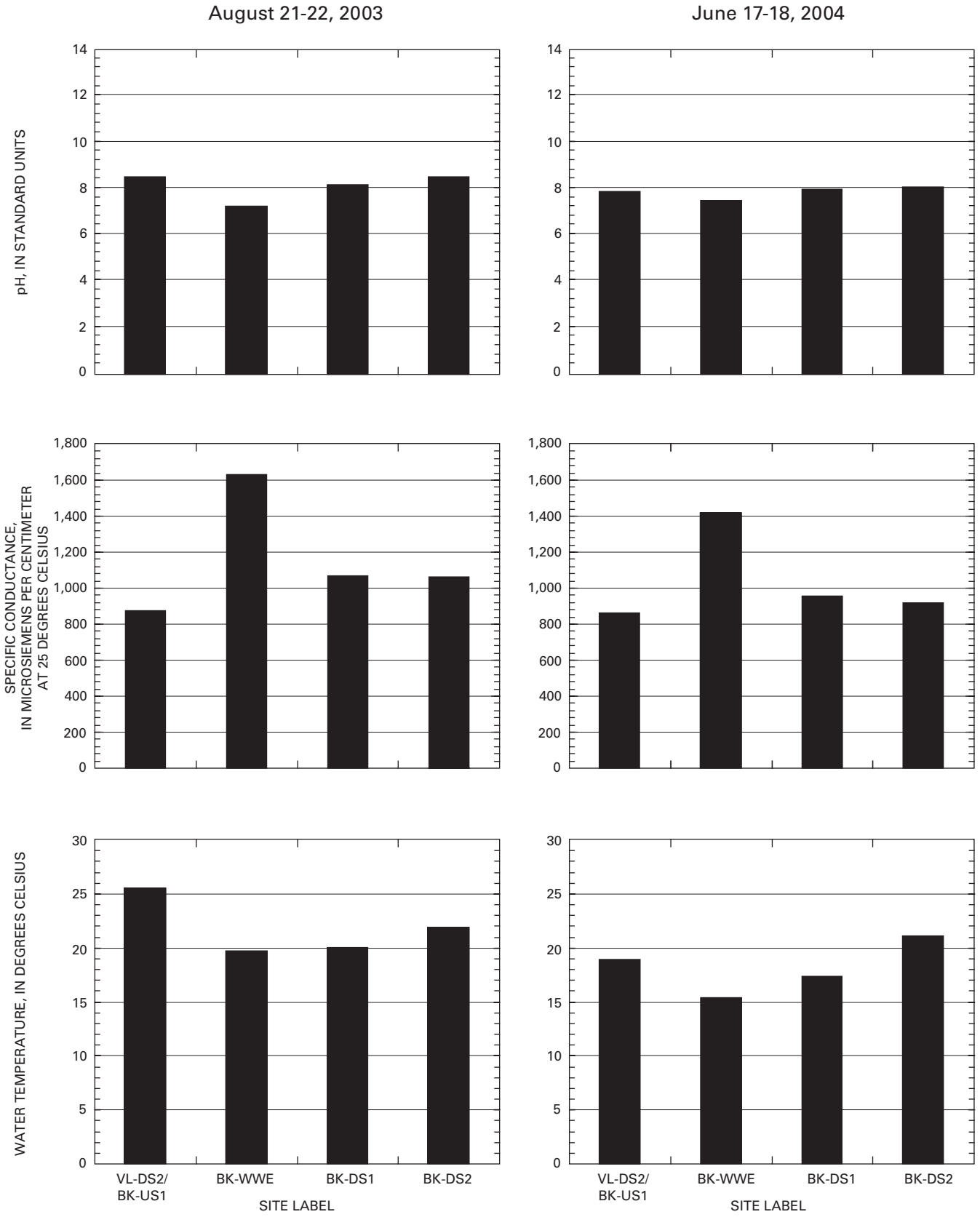

Figure 12. Results for selected field-measured properties and constituents and auxiliary constituents in wastewater effluent and the Big Sioux River in the Brookings area.—Continued

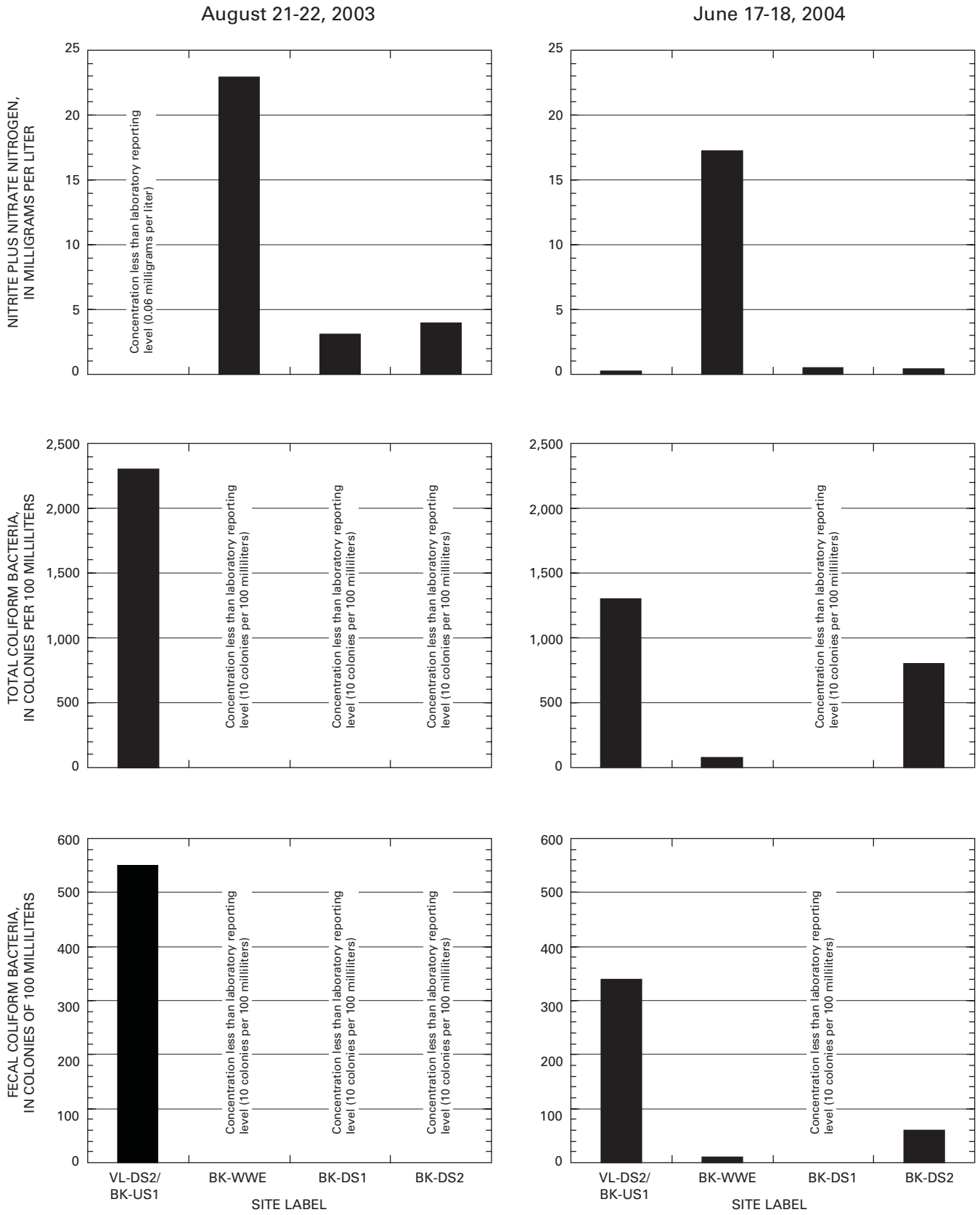

Figure 12. Results for selected field-measured properties and constituents and auxiliary constituents in wastewater effluent and the Big Sioux River in the Brookings area.—Continued

Organic Wastewater Constituents

OWCs in all compound classes except PAHs were detected in water samples from sampling sites in the Brookings area (fig. 13, tables 8 and 9). Differences in total OWC concentrations and loads between the upstream Big Sioux River site (VL-DS2/BK-US1) and downstream sites (BK-DS1 and BK-DS2) were variable. For August 2003, the upstream site had a slightly smaller total OWC concentration and load compared to the downstream sites. SCs and HIACs accounted for about 85 and 10 percent, respectively, for both VL-DS2/BK-US1 and BK-DS1 total OWC concentrations, and about 76 and 20 percent of the BK-DS2 total OWC concentration. Loads of total OWCs generally were similar for the August 2003 BK-WWE, BK-DS1, and BK-DS2 samples, but HIACs accounted for more of the total OWC load for BK-WWE than for BK-DS1 and BK-DS2. This might be due to (1) contribution of SCs in water entering the Big Sioux River channel downstream from the Brookings WWTP effluent discharge; (2) degradation of HIACs in the Big Sioux River; (3) adsorption of HIACs to particulate material and sedimentation from the water column; (4) diurnal variability in wastewater effluent discharges and relative concentrations of SCs and HIACs in the wastewater effluent combined with effects of non-Lagrangian sampling; and (5) dilution of HIAC concentrations that can directly reduce concentrations and can possibly reduce load estimates by decreasing concentrations to less than detectable levels. For June 2004, VL-DS2/BK-US1 generally had a smaller total OWC concentration and load than the downstream sites. MAHs accounted for about 86, 91, and 54 percent of the June 2004 total OWC concentrations for VL-DS2/BK-US1, BK-DS1, and BK-DS2, respectively. SCs accounted for about 40 percent of the June 2004 total OWC concentration for BK-DS2. Although confident conclusions cannot be made due to possible effects of non-Lagrangian sampling, OWC results for the Brookings area might indicate that (1) for the August 2003 sampling period, nonpoint livestock agricultural and/or human wastewater sources probably primarily contributed to occurrence of OWCs at all Big Sioux River sampling sites, and the Brookings WWTP wastewater effluent discharge contributed but did not have a substantial effect on concentrations at downstream sites; (2) for the June 2004 sampling period, nonpoint crop agricultural sources primarily contributed to occurrence of OWCs at all of the Big Sioux River sites, a substantial amount of SCs were contributed to the Big Sioux River downstream between BK-DS1 and BK-DS2, and the Brookings WWTP wastewater effluent discharge probably did not substantially contribute to total OWC concentrations at downstream sampling sites.

HPCs were detected in samples from all sites in the Brookings area (fig. 13, tables 8 and 9). Two HPCs (caffeine and cotinine) were detected in the August 2003 VL-DS2/BK-US1 sample with a total estimated concentration less than 0.1 µg/L, which accounted for less than about 3 percent of the total OWC concentration. No HPCs were detected in the June 2004 VL-DS2/BK-US1 sample. Two HPCs (cotinine and dehydronifedipine) were detected in samples collected from BK-WWE with total estimated concentrations less than 0.03 µg/L, which accounted for less than about 0.3 percent of the total OWC concentration. Two HPCs (caffeine and cotinine) were detected in samples collected from downstream sites BK-DS1 and BK-DS2 with total estimated concentrations less than 0.1 µg/L, which accounted for no more than about 5 percent of the total OWC concentrations.

HVACs were detected in all June 2004 samples collected from sampling sites in the Brookings area (fig. 13, tables 8 and 9). No HVACs were detected in any August 2003 samples. The increase in HVAC detections and total HVAC concentrations for the June 2004 samples relative to the August 2003 samples for all of the sampling sites in the Brookings area might be related to changes in the analytical method that substantially reduced the LRLs for HVACs. One HVAC (erythromycin-H_2O) was detected in the June 2004 VL-DS2/BK-US1 sample at an estimated concentration of 0.048 µg/L, and accounted for about 3 percent of the total OWC concentration. Eight HVACs were detected in the June 2004 BK-WWE sample with a total estimated concentration of 3.6 µg/L, which accounted for about 28 percent of the total OWC concentration. Erythromycin, erythromycin-H_2O, and sulfamethoxazole had the largest estimated concentrations (0.71, 2.0, and 0.50 µg/L, respectively) in the BK-WWE sample. Two HVACs (erythromycin-H_2O and sulfamethoxazole) were detected in the June 2004 samples collected from downstream sites BK-DS1 and BK-DS2 with total estimated concentrations less than 0.1 µg/L, which accounted for about 6 and 3 percent of the total OWC concentrations for the June 2004 BK-DS1 and BK-DS2 samples, respectively.

MAHs were detected in samples collected from all sampling sites in the Brookings area (fig. 13, tables 8 and 9). Three MAHs (atrazine, metolachlor, and prometon) were detected in samples collected from VL-DS2/BK-US1 with total estimated concentrations ranging from 0.10 to 1.2 µg/L, which accounted for about 4 and 86 percent of the total OWC concentrations for the August 2003 and June 2004 samples, respectively. Two MAHs (atrazine and prometon) were detected in samples collected from BK-WWE with total estimated concentrations less than 0.1 µg/L, which accounted for less than 1 percent of the total OWC concentrations. Three MAHs (atrazine, metolachlor, and prometon) were detected in samples collected from BK-DS1 and BK-DS2 with total estimated concentrations ranging from 0.081 to 1.3 µg/L. These total MAH concentrations accounted for about 3 percent of the total OWC concentrations for the August 2003 samples and about 91 and 54 percent of the total OWC concentration for the June 2004 BK-DS1 and BK-DS2 samples, respectively.

HIACs were detected in samples from all sites in the Brookings area (fig. 13, tables 8 and 9). Three HIACs—DEET, tri(2-butoxyethyl)phosphate, and tri(2-chloroethyl)phosphate—were detected in samples from VL-DS2/BK-US1 with total estimated concentrations of less than 0.25 µg/L, which accounted for about 10 and 6 percent of the total OWC concentrations for the August 2003 and June 2004 samples,

respectively. Sixteen HIACs were detected in samples from BK-WWE with total estimated concentrations ranging from 5.4 to 7.2 µg/L, which accounted for about 60 percent of the total OWC concentrations for both the August 2003 and June 2004 samples. AHTN had concentrations of 2.0 and 2.3 µg/L for the August 2003 and June 2004 BK-WWE samples, respectively, and NP2EO had a concentration of 1.2 µg/L for the June 2004 sample. All other individual HIACs had estimated concentrations less than 0.8 µg/L for all BK-WWE samples. Seven HIACs were detected in the August 2003 BK-DS1 and BK-DS2 samples with total estimated concentrations ranging from 0.33 to 0.67 µg/L, which accounted for about 11 and 20 percent of the total OWC concentrations for the August 2003 samples, respectively. Concentrations of individual HIACs for the August 2003 BK-DS1 and BK-DS2 samples were all less than about 0.25 µg/L. No HIACs were detected in the June 2004 BK-DS1 or BK-DS2 samples.

SCs were detected in samples from all sites in the Brookings area (fig. 13, tables 8 and 9). Two SCs (*beta*-sitosterol and cholesterol) were detected in the August 2003 VL-DS2/BK-US1 sample with a total estimated concentration of 2.0 µg/L, which accounted for about 83 percent of the total OWC concentration. No SCs were detected in the June 2004 VL-DS1/BK-US1 sample. Three SCs (3-*beta*-coprostanol, *beta*-sitosterol, and cholesterol) were detected in samples from BK-WWE samples with total estimated concentrations ranging from 1.8 to 3.6 µg/L, which accounted for about 40 and 14 percent of the total OWC concentration for the August 2003 and June 2004 samples, respectively. Two SCs (*beta*-sitosterol and cholesterol) were detected in August 2003 samples collected from the downstream sites BK-DS1 and BK-DS2 with total estimated concentrations ranging from 2.5 to 2.7 µg/L, which accounted for about 87 and 76 percent of the total OWC concentration for the August 2003 BK-DS1 and BK-DS2 samples, respectively. No SCs were detected in the June 2004 BK-DS1 sample and the June 2004 BK-DS2 sample had one SC detection (cholesterol) at an estimated concentration of 0.96 µg/L, which accounted for about 40 percent of the total OWC concentration.

EDCs were detected in all samples collected from sampling sites in the Brookings area except the August 2003 sample from VL-DS2/BK-US1 (fig. 14, tables 8 and 9). For August 2003, the numbers of EDCs detected, and EDC concentrations and loads generally were larger for BK-WWE than for downstream sampling sites BK-DS1 and BK-DS2. For June 2004, EDC concentrations were similar among Big Sioux River sites, and loads were larger for downstream Big Sioux River sites than for the upstream site, but the EDCs detected for June 2004 Big Sioux River samples consist entirely of MAHs and probably were contributed primarily by nonpoint sources. One EDC was detected in samples collected from VL-DS2/BK-US1 (atrazine, an MAH) with an estimated concentration of 1.2 µg/L. Nine EDCs were detected in samples collected from BK-WWE (atrazine, an MAH; and AHTN, benzophenone, bisphenol-A, HHCB, NP2EO, NP1EO, NP, and triclosan, which are HIACs) with total estimated concentrations ranging from 3.0 to 5.4 µg/L. HIACs accounted for greater than about 98 percent of the total EDC concentrations for both the August 2003 and June 2004 BK-WWE samples. Four EDCs (atrazine, an MAH; and AHTN, benzophenone, and HHCB, which are HIACs) were detected in samples collected from BK-DS1 and BK-DS2 with total estimated concentrations ranging from 0.15 to 1.3 µg/L. HIACs accounted for about 100 percent of the total EDC concentration for the August 2003 BK-DS1 sample, and MAHs accounted for about 100 percent of the total EDC concentration for the June 2004 BK-DS1 sample. HIACs accounted for about 100 percent of the total EDC concentration for the August 2003 BK-DS2 sample, and MAHs accounted for about 100 percent of the total EDC concentration for the June 2004 BK-DS2 sample.

Synopsis of Results

Several previous 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 upper Big Sioux River generally were within ranges of concentrations reported in these previous studies. Maximum concentrations of detected OWCs found in water samples collected from the upper Big Sioux River 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-H_2O, sulfamethoxazole, and trimethoprim) were detected in water samples collected from the Big Sioux River downstream from Watertown at concentrations about 2 to 8 times 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.

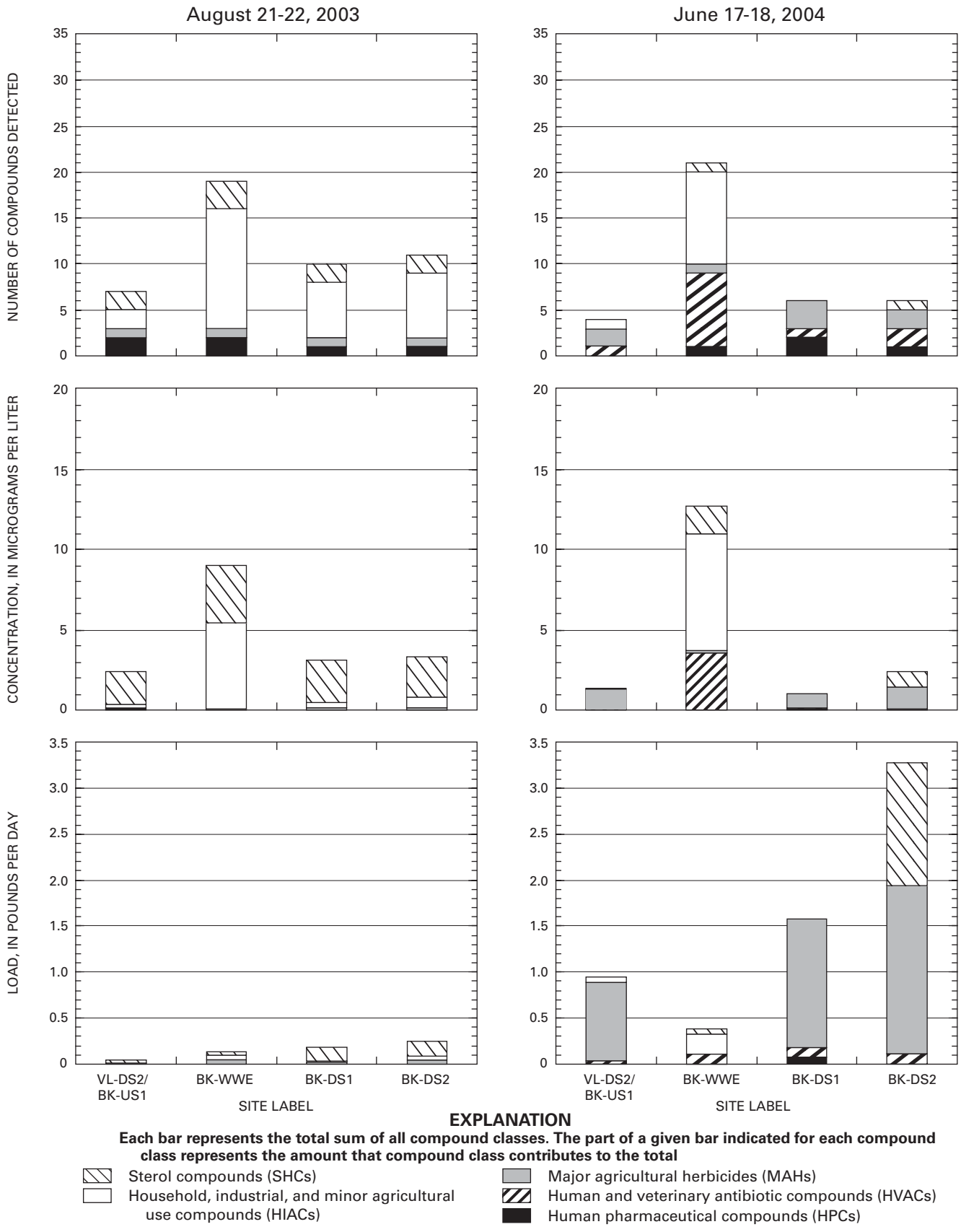

Figure 13. Summary of results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Brookings area.

Table 8. Statistical summaries of analytical results and load results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Brookings area.

[µg/L, micrograms per liter; lb/d, pounds per day; e, estimated; --, no data collected]

	Station identification number and name (site label)							
	441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)		441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)		441316096483300 Big Sioux River below wastewater effluent, near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)	
Date of sample collection	08-21-2003	06-17-2004	08-22-2003	06-17-2004	08-22-2003	06-18-2004	08-22-2003	06-17-2004
Time of sample collection	1230	1140	0915	0950	1015	1215	1140	1645
Human pharmaceutical compounds (HPCs)								
Number of compounds detected	2	0	2	1	1	2	1	1
Minimum detected concentration (µg/L)	e0.029	0	e0.0052	0.022	0.030	e0.0023	0.030	e0.0011
Median detected concentration (µg/L)	e0.031	0	e0.013	0.022	0.030	e0.025	0.030	e0.0011
Maximum detected concentration (µg/L)	e0.033	0	e0.021	0.022	0.030	0.048	0.030	e0.0011
Total detected concentration (µg/L)	e0.062	0	e0.026	0.022	0.030	e0.050	0.030	e0.0011
Total load (lb/d)	e0.0011	0	e0.0002	e0.0007	e0.0016	e0.077	e0.0020	e0.0015
Human and veterinary antibiotic compounds (HVACs)								
Number of compounds detected	0	1	0	8	0	1	0	2
Minimum detected concentration (µg/L)	0	0.048	0	0.0090	0	0.065	0	0.020
Median detected concentration (µg/L)	0	0.048	0	0.12	0	0.065	0	0.040
Maximum detected concentration (µg/L)	0	0.048	0	2.0	0	0.065	0	0.060
Total detected concentration (µg/L)	0	0.048	0	3.6	0	0.065	0	0.080
Total load (lb/d)	0	e0.033	0	e0.11	0	e0.10	0	e0.11
Major agricultural herbicides (MAHs)								
Number of compounds detected	1	2	1	1	1	3	1	2
Minimum detected concentration (µg/L)	e0.10	e0.035	e0.050	e0.086	e0.081	e0.030	e0.10	e0.028
Median detected concentration (µg/L)	e0.10	e0.62	e0.050	e0.086	e0.081	e0.044	e0.10	e0.66
Maximum detected concentration (µg/L)	e0.10	1.2	e0.050	e0.086	e0.081	0.84	e0.10	1.3
Total detected concentration (µg/L)	e0.10	e1.2	e0.050	e0.086	e0.081	e0.91	e0.10	e1.3
Total load (lb/d)	e0.0016	e0.86	e0.0005	e0.0026	e0.0043	e1.4	e0.0065	e1.8

Table 8. Statistical summaries of analytical results and load results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Brookings area.—Continued

[µg/L, micrograms per liter; lb/d, pounds per day; e, estimated; --, no data collected]

	Station identification number and name (site label)							
	441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)		441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)		441316096483300 Big Sioux River below wastewater effluent, near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)	
Household, industrial, and minor agricultural use compounds (HIACs)								
Number of compounds detected	2	1	13	10	6	0	7	0
Minimum detected concentration (µg/L)	e0.056	e0.077	e0.017	e0.13	e0.032	0	e0.041	0
Median detected concentration (µg/L)	e0.12	e0.077	e0.27	e0.54	e0.054	0	e0.059	0
Maximum detected concentration (µg/L)	e0.19	e0.077	e2.0	2.3	e0.078	0	e0.24	0
Total detected concentration (µg/L)	e0.25	e0.077	e5.4	e7.2	e0.33	0	e0.67	0
Total load (lb/d)	e0.0042	e0.054	e0.049	e0.22	e0.018	0	e0.044	0
Polyaromatic hydrocarbons (PAHs)								
Number of compounds detected	0	0	0	0	0	0	0	0
Minimum detected concentration (µg/L)	0	0	0	0	0	0	0	0
Median detected concentration (µg/L)	0	0	0	0	0	0	0	0
Maximum detected concentration (µg/L)	0	0	0	0	0	0	0	0
Total detected concentration (µg/L)	0	0	0	0	0	0	0	0
Total load (lb/d)	0	0	0	0	0	0	0	0
Sterol compounds (SCs)								
Number of compounds detected	2	0	3	1	2	0	2	1
Minimum detected concentration (µg/L)	e1.0	0	e0.89	e1.8	e1.2	0	e1.1	e0.96
Median detected concentration (µg/L)	e1.0	0	e1.1	e1.8	e1.4	0	e1.2	e0.96
Maximum detected concentration (µg/L)	e1.0	0	e1.6	e1.8	e1.5	0	e1.4	e0.96
Total detected concentration (µg/L)	e2.0	0	e3.6	e1.8	e2.7	0	e2.5	e0.96
Total load (lb/d)	e0.034	0	e0.033	e0.054	e0.14	0	e0.16	e1.3

Table 8. Statistical summaries of analytical results and load results for organic wastewater compounds in wastewater effluent and the Big Sioux River in the Brookings area.—Continued

[µg/L, micrograms per liter; lb/d, pounds per day; e, estimated; --, no data collected]

	Station identification number and name (site label)							
	441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)		441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)		441316096483300 Big Sioux River below wastewater effluent, near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)	
All organic wastewater compounds (OWCs)								
Number of compounds detected	7	4	19	21	10	6	11	6
Minimum detected concentration (µg/L)	0.029	e0.035	e0.0052	e0.0090	e0.030	e0.0023	e0.030	e0.0011
Median detected concentration (µg/L)	e0.095	e0.062	e0.27	e0.36	e0.067	e0.046	e0.096	e0.044
Maximum detected concentration (µg/L)	e1.0	1.2	e2.0	e2.3	e1.5	0.84	e1.4	1.3
Total detected concentration (µg/L)	e2.4	e1.4	e9.0	e13	e3.1	e1.0	e3.3	e2.4
Total load (lb/d)	e0.041	e0.95	e0.083	e0.38	e0.17	e1.6	e0.22	e3.3
Endocrine-disrupting compounds (EDCs) from all compound classes								
Number of compounds detected	0	1	5	7	3	1	3	1
Minimum detected concentration (µg/L)	0	1.2	e0.13	e0.086	e0.032	0.84	e0.041	1.3
Median detected concentration (µg/L)	0	1.2	e0.26	e0.69	e0.042	0.84	e0.054	1.3
Maximum detected concentration (µg/L)	0	1.2	e2.0	2.3	e0.074	0.84	e0.24	1.3
Total detected concentration (µg/L)	0	1.2	e3.0	e5.4	e0.15	0.84	e0.34	1.3
Total load (lb/d)	0	e0.83	e0.027	e0.16	e0.0079	e1.3	e0.021	e1.8

Table 9. Detected organic wastewater compounds in wastewater effluent and the Big Sioux River in the Brookings area.

[Bold text for compound names indicates suspected endocrine-disrupting compounds (EDCs). AHTN, 7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene; HHCB, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran; NP2EO, nonylphenol diethoxylate; NP1EO, nonylphenol monoethoxylate; NP, *para*-nonylphenol; --, not detected]

	Station identification number and name (site label)							
	441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)		**441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)**		**441316096483300 Big Sioux River below wastewater effluent, near Brookings, SD (BK-DS1)**		**441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)**	
Date of sample collection	08-21-2003	06-17-2004	08-22-2003	06-17-2004	08-22-2003	06-18-2004	08-22-2003	06-17-2004
Time of sample collection	1230	1140	0915	0950	1015	1215	1140	1645
Number of compounds detected	7	4	19	21	10	6	11	6
Human pharmaceutical compounds (HPCs)	Caffeine Cotinine	--	Cotinine Dehydronifedipine	Cotinine	Cotinine	Caffeine Cotinine	Cotinine	Cotinine
Human and veterinary antibiotic compounds (HVACs)	--	Erythromycin-H_2O	--	Ciprofloxacin Erythromycin Erythromycin-H_2O Ofloxacin Sulfadiazine Sulfamethazine Sulfamethoxazole Trimethoprim	--	Erythromycin-H_2O	--	Erythromycin-H_2O Sulfamethoxazole
Major agricultural herbicides (MAHs)	Prometon	**Atrazine** Metolachlor	Prometon	**Atrazine**	Prometon	**Atrazine** Metolachlor Prometon	Prometon	**Atrazine** Metolachlor

Table 9. Detected organic wastewater compounds in wastewater effluent and the Big Sioux River in the Brookings area.—Continued

[Bold text for compound names indicates suspected endocrine-disrupting compounds (EDCs). AHTN, 7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene; HHCB, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran; NP2EO, nonylphenol diethoxylate; NP1EO, nonylphenol monoethoxylate; NP, *para*-nonylphenol; --, not detected]

	Station identification number and name (site label)							
	441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)		**441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)**		**441316096483300 Big Sioux River below wastewater effluent, near Brookings, SD (BK-DS1)**		**441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)**	
Household, industrial, and minor agricultural use compounds (HIACs)	Tri(2-butoxyethyl) phosphate Tri(2-chloroethyl) phosphate	N,N-diethyl-meta-toluamide (DEET)	5-methyl-1H-benzotriazole **AHTN** Acetophenone **Benzophenone** **Bisphenol-A** **HHCB** Tributyl phosphate **Triclosan** Triethyl citrate (ethyl citrate) Triphenyl phosphate Tri(2-butoxyethyl) phosphate Tri(2-chloroethyl) phosphate Tri(dichloroisopropyl)phosphate	5-methyl-1H-benzotriazole **AHTN** **Benzophenone** **HHCB** **NP2EO** **NP1EO** **NP** Tributyl phosphate Triethyl citrate (ethyl citrate) Tri(2-chloroethyl) phosphate	**AHTN** **Benzophenone** **HHCB** Tributyl phosphate Tri(2-chloroethyl) phosphate Tri(dichloroisopropyl)phosphate	--	**AHTN** **Benzophenone** **HHCB** Tributyl phosphate Triethyl citrate (ethyl citrate) Tri(2-chloroethyl) phosphate Tri(dichloroisopropyl)phosphate	--
PAH compounds (PAHs)	--	--	--	--	--	--	--	--
Sterol compounds (SCs)	*beta*-sitosterol Cholesterol	--	3-*beta*-coprostanol *beta*-sitosterol Cholesterol	Cholesterol	*beta*-sitosterol Cholesterol	--	*beta*-sitosterol Cholesterol	Cholesterol

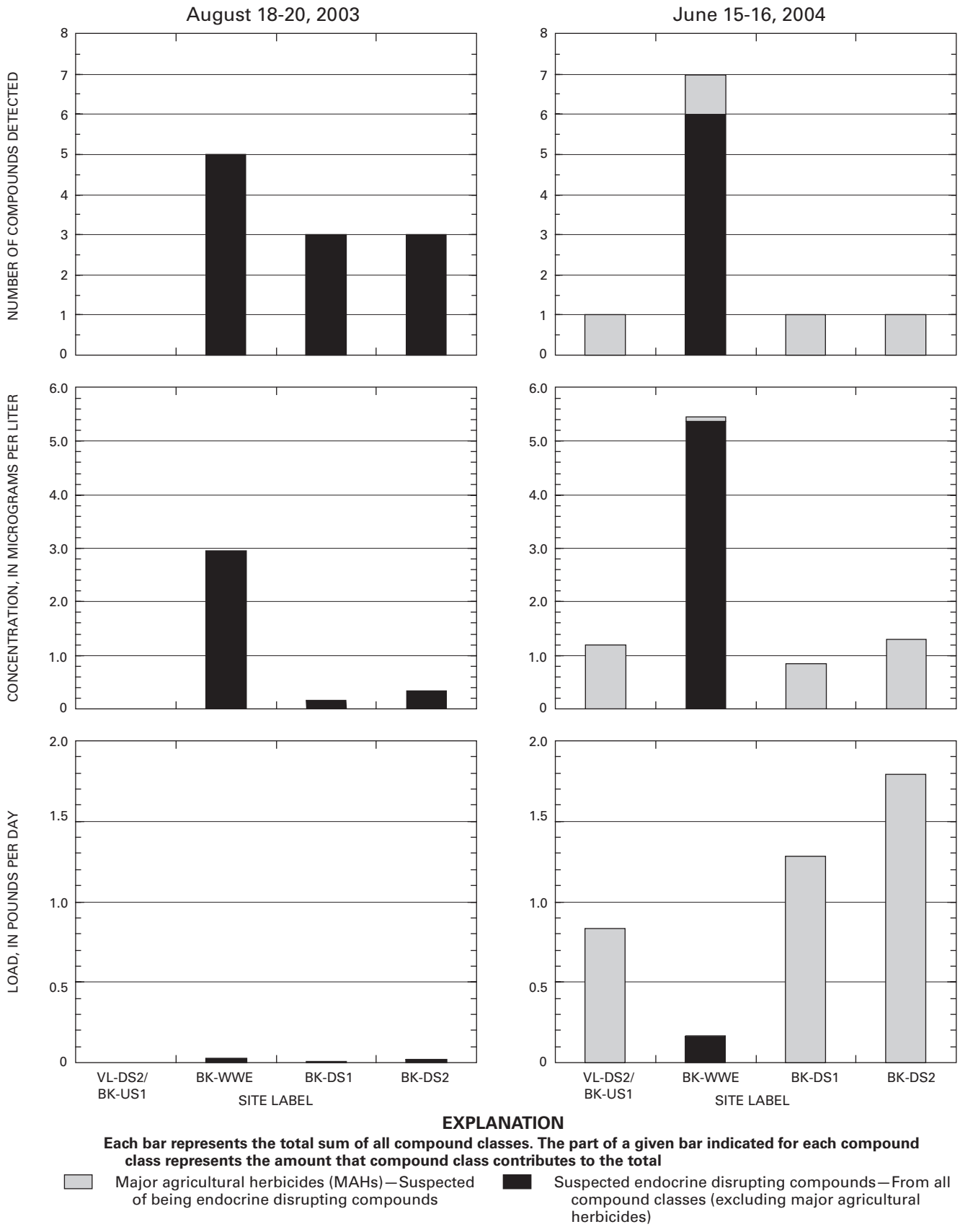

Figure 14. Summary of results for endocrine-disrupting compounds (EDCs) from all compound classes in wastewater effluent and the Big Sioux River in the Brookings area.

In the upper Big Sioux River Basin, the location and size of the WWTPs relative to the flow of the Big Sioux River where the effluent is discharged clearly affects concentrations of OWCs in the Big Sioux River. Watertown is the largest city included in this study and has the largest capacity WWTP (table 1). Watertown is located near the upstream part of the Big Sioux River Basin, where the mean annual flow of the Big Sioux River is less than 100 ft^3/s. Watertown WWTP discharges commonly can account for greater than 50 percent of the flow of the Big Sioux River, especially during low-flow periods. Effects of the Watertown WWTP wastewater effluent discharges on the occurrence of OWCs in the Big Sioux River downstream were apparent during both the low-flow and runoff sampling periods. For Volga and Brookings, which are farther downstream in the Big Sioux River where the mean annual flow of the Big Sioux River exceeds 400 ft^3/s, wastewater effluent discharges from the Volga and Brookings WWTPs probably influenced the occurrence of OWCs in the Big Sioux River, but probably did not substantially contribute to total OWC concentrations or loads, especially during the runoff sampling period.

For the Watertown and Brookings areas, relative contributions from major probable sources of OWCs to the Big Sioux River at sites downstream from WWTP effluent discharges varied with different flow conditions. During low-flow conditions, OWCs that probably primarily were contributed by WWTP effluent discharges generally comprised a larger proportion of the total concentration of OWCs than during runoff conditions. During runoff conditions, OWCs that probably primarily were contributed by nonpoint source crop and animal agricultural sources generally comprised a larger proportion of the total concentration of OWCs than during low-flow conditions. Seasonal factors relating to timing of pesticide applications probably also contributed to this pattern. The combined effects of varied OWC sources and differences in the types of hydrologic conditions that govern the contributions from the OWC sources might result in moderate to substantial inputs of OWCs to the upper Big Sioux River under a wide range of flow conditions.

Occurrence of EDCs in aquatic systems is a very complex and sensitive issue. A complete assessment of potential effects of EDCs in the upper Big Sioux River based on the results of this study is not possible for several reasons. Sex hormones, which are the most potent EDCs, were not reported for this study. Also, a relatively small number of water-quality samples were collected in the Big Sioux River Basin during this study. WWTP effluent discharges vary with time, and concentrations of EDCs in wastewaters vary seasonally and interannually (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 small number of samples collected during a single year. Also, mixtures of individual EDCs, like those that typically were found in samples collected in the upper Big Sioux River Basin, 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). There might be EDCs that occur in the upper Big Sioux River for which there currently is no knowledge of endocrine-disrupting effects. 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 most of the EDCs determined in this study, concentrations that result in substantial 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 definitive assessment on EDC effects in the upper Big Sioux River Basin, a brief synopsis of research on the occurrence of EDCs in aquatic environments might be useful in providing a context for the EDC results for the upper Big Sioux River Basin and also to illustrate 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 on aquatic ecosystems. However, in some studies, skewed sex ratios and gonadal histology indicate that individual and population level effects on reproductive success are possible (Desbrow and others, 1998).

Potential EDCs detected in the upper Big Sioux River Basin probably were derived from two general types of sources—WWTP discharges (the EDCs AHTN, benzophenone, bisphenol A, diethyl phthalate, HHCB, NP2EO, NP1EO, OP2EO, NP, and triclosan were detected in the upper Big Sioux River Basin and generally were attributable to WWTP discharges); and nonpoint crop agricultural sources (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 both of 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 17B estradiol and ethynyl estradiol) generally are regarded as the most potent EDCs, can produce substantial atypical sexual characteristics in fish at concentrations less than about 0.025 µg/L (Sumpter and Johnson, 2005), and in some studies have been implicated as the primary com-

pounds contributing to feminization of male fish (Huggett and others, 2003) as a result of exposure to WWTP effluents. Analytical results for sex hormones for the upper Big Sioux River Basin are not reported for this study. However, sex hormones commonly are found in WWTP effluent discharges, so it is possible that they occur in the upper Big Sioux River.

AP ethoxylates and their shorter chain metabolites are complex nonionic surfactants. Of the various APs and AP ethoxylates, 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 upper Big Sioux River Basin at concentrations greater than the SRL include NP2EO, NP1EO, NP, and OP2EO. The largest combined concentration for these compounds in any water sample collected from the Big Sioux River was 5.8 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 Basin 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 Basin that have shown endocrine-disrupting effects include: AHTN (Bitsch and others, 2002; Richard and others, 2002; Richard and others, 2004); benzophenone (Schlumpf and others, 2001); bisphenol A (Jobling and others, 1995; Jobling and others, 1998; Andersen and others, 1999; Fisher and others, 1999; Oehlmann and others, 2000; Sheehan, 2000; Rajapakse and others, 2001; and Sohoni and others, 2001); diethyl phthalate (Jobling and others, 1995; Harris and others, 1997; Jobling and others, 1998), HHCB (Richard and others, 2002; Richard and others, 2004); and triclosan (Foran and others, 2000; Latch and others, 2003). Generally, these compounds have much less potent endocrine disruptive 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 0.59 µg/L (AHTN was detected at this concentration in a water sample collected from WT-DS1).

Although it is not possible to definitively assess the effects of WWTP EDCs from the data that were collected in the upper Big Sioux River Basin, studies performed in the United Kingdom might provide information that could help in evaluating the potential for WWTP-related endocrine disruption effects in the Big Sioux River Basin. From these studies, researchers have concluded that EDCs are present in most, if not all, treated sewage effluents (Jobling and Tyler, 2003). Dilution effects from introduction of the WWTP effluents into receiving streams substantially reduce the effects of the EDCs present in sewage effluents. British research on a variety of types of WWTPs has found that WWTP effluents start to show statistically significant estrogenic effects in fish populations in receiving waters when the WWTP effluent accounts for between about 25 and 50 percent of the total flow of the receiving water (Harries and others, 1999; Rodgers-Gray and others, 2000) for relatively short periods (about 1 month). Further, when the time of exposure is increased to 4 months, significant estrogenic effects occurred when the WWTP effluent accounted for as little as 10 percent of the total flow of the receiving water (Rodgers-Gray and others, 2000). Based on these observations, it is possible that the WWTP effluents in the Big Sioux River might produce estrogenic effects in aquatic organisms. This is especially true for the Watertown area, because the Watertown WWTP effluent commonly accounts for greater than 25 percent of the downstream flow of the Big Sioux River for extended periods of time (that is, several months). For example, assuming an average discharge from the Watertown WWTP of 4 ft^3/s, during water years 1977 through 2004, this level of effluent discharge would have accounted for about 25 percent or more of the flow of the Big Sioux River about 45 percent of the time, and would have accounted for about 10 percent or more of the flow of the Big Sioux River about 65 percent of the time. Based on these observations, it is possible that the Watertown WWTP effluent discharges to the Big Sioux River might produce endocrine-disrupting effects in aquatic organisms. However, it should be noted that concentrations and loads of EDCs decreased substantially between sites WT-DS1 and WT-DS2, so any endocrine-disrupting effects on organisms in the Big Sioux River resulting from WWTP effluent discharges probably would be restricted to a relatively short reach. Also, results of studies conducted in Britain on potential estrogenic effects of WWTP effluents on fish populations in receiving waters do not necessarily have direct application in the Big Sioux River Basin primarily 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 WWTP effluents; and (2) EDC effects on fish are species dependent (Sumpter and Johnson, 2005), and fish species present in the Big Sioux River Basin are different than the fish species studied in the United Kingdom and might respond differently to EDC exposure.

Atrazine is a herbicide contributed to the Big Sioux River primarily from nonpoint crop agricultural sources 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. Bringolf 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. Based on the lack of definitive research establishing endocrine-disruptive effect levels for atrazine, 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.

Summary and Conclusions

The U.S. Geological Survey (USGS) in cooperation with the East Dakota Water Development District conducted a reconnaissance study to determine the occurrence of organic wastewater compounds (OWCs) in wastewater effluent and the Big Sioux River in the upper Big Sioux River Basin during August 2003 through June 2004. Water samples were collected at 12 sites to investigate the occurrence of OWCs in wastewater effluent and the Big Sioux River at or near the cities of Watertown, Volga, and Brookings. For each city, samples were collected from the wastewater treatment plant (WWTP) effluent, and from the Big Sioux River at sites upstream and downstream from where the wastewater effluent enters the Big Sioux River. For Watertown and Brookings, samples were collected during a low-flow period (August 2003) and a runoff period (June 2004). For Volga, samples were collected during two low-flow periods (August 2003 and October 2003) and a runoff period (June 2004).

A total of 125 different OWCs were analyzed for in this study using three 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 analyzed for in this study are classified into the following six compound classes: (1) human pharmaceutical compounds (HPCs), which are commonly used prescription and non-prescription pharmaceutical drugs; (2) human and veterinary antibiotic compounds (HVACs), which are prescription drugs used in the treatment of infectious diseases; (3) major agricultural herbicides (MAHs), which include atrazine, metolachlor, and prometon; (4) 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); (5) polyaromatic hydrocarbons (PAHs), which are compounds often occurring in fossil fuels or produced by the combustion of fossil fuels; and (6) 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). Of the 125 different OWCs analyzed for in this study, 73 OWCs had one or more detections in environmental samples reported by the laboratories, and of those 73 OWCs, 45 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 wastewater effluents and the Big Sioux River.

OWCs in all compound classes were detected in water samples collected in August 2003 and June 2004 from sampling sites in the Watertown area. The Watertown WWTP discharged continuously to the Big Sioux River during both sampling periods. Total OWC concentrations for upstream Big Sioux River sites generally were small, less than about 6 μg/L for both sampling periods. SCs accounted for nearly all of the total OWC concentration for upstream Big Sioux River sites for the August 2003 sample, and MAHs accounted for nearly all of the total OWC concentrations for the June 2004 sample. Total OWC concentrations for the Watertown wastewater effluent (WT-WWE) were relatively large for both sampling periods. Major OWC classes contributing to total OWC concentrations for WT-WWE included HIACs, SCs, and HVACs. Total OWC concentrations for downstream site WT-DS1 were relatively large for August 2003 and smaller for June 2004, and probably reflect a greater fraction of the total flow of the Big Sioux River being derived from WWTP discharge during the August 2003 sampling period. Major OWC classes contributing to total OWC concentrations for WT-DS1 were HIACs, SCs, and HVACs. Total OWC concentrations were substantially smaller for the most downstream site WT-DS2 than for WT-WWE and WT-DS1. Major OWC classes contributing to total OWC concentrations for WT-DS2 were SCs, HIACs, and HVACs. Although confident conclusions could not be made because of possible effects of non-Lagrangian sampling, OWC results for the Watertown area might indicate that (1) OWCs for upstream Big Sioux River sites probably were primarily contributed by nonpoint source agricultural sources, with livestock agriculture accounting for most of the total OWC concentration for the August 2003 (low-flow) sampling period, and crop agriculture accounting for most of the total OWC concentration for the June 2004 (runoff) sampling period; (2) OWCs for downstream Big Sioux River sites were strongly influenced by contributions from the Watertown WWTP during both the August 2003 (low-flow) and June 2004 (runoff) sampling periods; and (3) contributions of OWCs that might be derived from nonpoint livestock agricultural sources accounted for a larger proportion of OWCs for WT-DS2 than for WT-DS1 for both the August 2003 (low-flow) and June 2004 (runoff) sampling periods. EDCs were detected in all Big Sioux River samples in the Watertown area. For both August 2003 and June 2004, the numbers of EDCs detected, and EDC concentrations and loads generally were larger in samples from downstream Big Sioux River sites than from upstream Big Sioux River sites. Total estimated EDC concentrations ranged from 0.19 to 0.55 μg/L for upstream Big Sioux River sites and consisted mostly of HIACs for low-flow samples and MAHs for runoff samples. Total estimated EDC concentrations for downstream Big Sioux River sites ranged from about 0.32 to 2.5 μg/L, and consisted mostly of HIACs for low-flow samples and both HIACs and MAHs for runoff samples.

OWCs in all compound classes except PAHs were detected in samples from sites in the Volga area. For the August 2003 and June 2004 sampling periods, the Volga WWTP was not discharging to the Big Sioux River, but for the October 2003 sampling period, the Volga WWTP was discharging continuously to the Big Sioux River. For August 2003, the upstream Big Sioux River site had larger total OWC concentrations and loads than downstream Big Sioux River sites, and SCs accounted for most of the total OWC concentration for all Big

Sioux River sites. For October 2003, when the Volga WWTP was discharging to the Big Sioux River channel, total OWC concentrations and loads were larger for the downstream Big Sioux River site, than for the upstream site and the increase in load corresponds well with the load contributed by the Volga wastewater effluent discharge, especially for HIACs. HIACs and SCs accounted for most of the total OWC concentration for Big Sioux River sites. For June 2004, the upstream site had smaller total OWC concentrations and loads than downstream Big Sioux River sites. MAHs accounted for most of the total OWC concentrations for Big Sioux River sites. Although confident conclusions cannot be made due to possible effects of non-Lagrangian sampling, the data might indicate that (1) for the August 2003 sampling period, nonpoint livestock agricultural and/or human wastewater sources might have been the primary contributor to occurrence of OWCs at Big Sioux River sampling sites; (2) for the October 2003 sampling period, nonpoint livestock sources and upstream human wastewater sources primarily contributed to the occurrence of OWCs at Big Sioux River sampling sites; (3) for the June 2004 sampling period, nonpoint crop agricultural sources primarily contribute to occurrence of OWCs at Big Sioux River sampling sites; (4) for the August 2003 and June 2004 sampling periods, seepage of water from the Volga WWTP had little effect on downstream OWC concentrations; and (5) for the October 2003 sampling period, the Volga wastewater effluent discharge contributed to downstream OWC concentrations. EDCs were detected in all samples collected from sampling sites in the Volga area. For all sampling periods, total EDC concentrations generally were similar between upstream and downstream Big Sioux River sites. Total estimated EDC concentrations for the upstream site ranged from 0.069 to 5.2 μg/L and consisted of HIACs and MAHs. Total estimated EDC concentrations for downstream sites ranged from undetected to 5.8 μg/L and consisted of HIACs and MAHs. HIACs accounted for most of the total EDC concentrations for the August 2003 and October 2003 sampling periods, and MAHs accounted for most of the total EDC concentrations for the June 2004 sampling period for all Big Sioux River sites.

OWCs in all compound classes except PAHs were detected in water samples collected in August 2003 and June 2004 from sampling sites in the Brookings area. The Brookings WWTP discharged continuously to the Big Sioux River during both sampling periods. For August 2003, the upstream site had slightly smaller total OWC concentrations and loads compared to the downstream Big Sioux River sites. SCs and HIACs accounted for most of the total OWC concentrations in all Big Sioux River sampling sites, but the proportion of SCs increased at the most downstream site. For June 2004, the upstream site generally had smaller total OWC concentrations and loads than downstream Big Sioux River sites. MAHs accounted for most of the total OWC concentrations for all Big Sioux River sites, but the proportion of SCs increased at the most downstream site. Although confident conclusions could not be made due to possible effects of non-Lagrangian sampling, the data might indicate that (1) for the August 2003 sampling period, nonpoint livestock agricultural and/or human wastewater sources probably primarily contributed to occurrence of OWCs at all Big Sioux River sampling sites, and the Brookings WWTP wastewater effluent discharge contributed but did not have a substantial effect on concentrations at downstream sites; (2) for the June 2004 sampling period, nonpoint crop agricultural and/or human wastewater sources primarily contributed to occurrence of OWCs at all of the Big Sioux River sites, a substantial amount of SCs were contributed to the Big Sioux River downstream between BK-DS1 and BK-DS2, and the Brookings WWTP wastewater effluent discharge probably did not substantially contribute to total OWC concentrations at downstream sampling sites. EDCs were detected in all samples collected from sampling sites in the Brookings area. Total estimated EDC concentrations for one sample from the upstream site was 1.2 μg/L and consisted of MAHs. Total estimated EDC concentrations for downstream sites ranged from 0.15 to 1.3 μg/L and consisted of MAHs and HIACs. HIACs accounted for all of the total EDC concentrations for the August 2003 sampling period, and MAHs accounted for all of the total EDC concentrations for the June 2004 sampling period for downstream Big Sioux River sites.

Detected concentrations of individual OWCs found in water samples collected from the Big Sioux River generally were within ranges of concentrations reported for other streams in the United States. However, concentrations of some HVACs (including ciprofloxacin, erythromycin-H_2O, sulfamethoxazole, and trimethoprim) in water samples collected from the Big Sioux River downstream from Watertown generally were large relative to reported concentrations for other streams in the United States.

In the upper Big Sioux River Basin, the location and size of the WWTPs relative to the discharge of the Big Sioux River where the effluent is discharged clearly affects concentrations of OWCs in the Big Sioux River. The city of Watertown is located near the upstream part of the Big Sioux River Basin, where the mean annual flow of the Big Sioux River is less than 100 ft^3/s. Watertown WWTP discharges can account for a substantial part of the flow in the Big Sioux River, especially during low-flow periods. Effects of the Watertown WWTP wastewater effluent discharges on the occurrence of OWCs in the Big Sioux River downstream were apparent during both the low-flow and runoff sampling periods. For Volga and Brookings, which are farther downstream in the Big Sioux River where the mean annual flow of the Big Sioux River exceeds 400 ft^3/s, wastewater effluent discharges from the Volga and Brookings WWTPs probably influenced the occurrence of OWCs in the Big Sioux River, but probably did not substantially contribute to total OWC concentrations, especially during the runoff sampling period.

For the Watertown and Brookings areas, relative contributions from major probable sources of OWCs to the Big Sioux River at sites downstream from WWTP effluent discharges varied with different flow conditions. During low-flow conditions, OWCs that probably primarily were contributed by WWTP effluent discharges generally comprised a larger pro-

portion of the total concentration of OWCs than during runoff conditions. During runoff conditions, OWCs that probably primarily were contributed by nonpoint source crop and animal agricultural sources generally comprised a larger proportion of the total concentration of OWCs than during low-flow conditions. Seasonal factors related to timing of pesticide applications probably also contributed to this pattern. The combination of the different major sources of OWCs in the upper Big Sioux River might result in maintenance of fairly substantial levels of OWCs under a wide range in flow conditions.

Occurrence of EDCs in aquatic systems is a very complex and sensitive issue. Accurate assessment of potential effects of EDCs in the upper Big Sioux River based on the results of this study is not possible.

References

American Public Health Association, 1998, Standard methods for the examination of water and wastewater (20th ed.): Washington, D.C., American Public Health Association, 1,220 p.

Andersen, H.R., Halling-Sorensen, B., and Kusk, K.O., 1999, A parameter for detecting estrogenic exposure in the copepod *Acartia tonsa*: Ecotoxicology and Environmental Safety, v. 44, p. 56–61.

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 (available only online at *http://toxics.usgs.gov/pubs/OFR-02-94/*).

Bitsch, N., Dudas, C., Koerner, W., Failing, K., Biselli, S., Rimkus, B., and Brunn, H., 2002, Estrogenic activity of musk fragrances detected by the E-screen assay using human MCF-7 cells: Archives of Environmental Contaminant Toxicology, v. 43, p. 257–264.

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.

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.

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.

Fisher, J.S., Turner, K.J., Brown, D., and Sharpe, R.M., 1999, Effect of neonatal exposure to estrogenic compounds on development of the excurrent ducts of the rat testis through puberty to adulthood: Environmental Health Perspectives, v. 107, p. 397–405.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.

Flint, R.F., 1971, Glacial and Quaternary geology: New York, John Wiley and Sons, 892 p.

Foran, C.M., Bennett, E.R., and Benson, W.H., 2000, Developmental evaluation of a potential non-steroidal estrogen—triclosan: Marine Environmental Research, v. 50, p. 153–156.

Gies, Andreas; Gottschalk, Christa; Greiner, Petra; Heger, Wolfgang; Kolossa, Marike; Rechenberg, Bettina; Robkamp, Elke; Schroeter-Kermani, Christa; Steinhauser, 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), accessed on August 1, 2005, at *http://www.umweltdaten.de/down-e/chempol2.pdf 8/5/2005*, 53 p.

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., Henttu, P., Parker, M.G., and Sumpter, J.P., 1997, The estrogenic activity of phthalate esters in vitro: Environmental Health Perspectives, v. 105, p. 802–811.

Harris, C.A., Santos, E.M., Janbakhsh, A., Pottinger, T.G., Tyler, C.R., 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, no. 4, 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; Nolan, Monique; Tyler, C.R.; Brighty, Geoff; and Sumpter, J.P., 1998, Widespread sexual disruption in wild fish: Environmental Science & Technology, v. 32, no. 17, p. 2498–2506.

Jobling, Susan; Reynolds, Tracey; White, Roger; Parker, M.G.; and Sumpter, J.P., 1995, A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic: Environmental Health Perspectives, v. 103, p. 582–587.

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.

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.

Latch, D.E., Packer, J.L., Arnold, W.A., McNeill, K., 2003, Photochemical conversion of triclosan to 2,8-dichlorodibenzo-p-dioxin in aqueous solution: Journal of Photochemistry and Photobiology, v. 158, p. 63–66.

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.

Meyer, M.T., Bumgarner, J.E., Varns, J.L., Daughtridge, J.V., Thurman, E.M., and Hostetler, K.A., 2000, Use of radioimmunoassay as a screen for antibiotics in confined feeding operations and confirmation by liquid chromatography/mass spectrometry: Science of the Total Environment, v. 248, p. 181–187.

Oehlmann, Jörg; Schulte-Oehlmann, Ulrike; Tillmann, Michaela; and Markert, Bernd, 2000, Effects of endocrine disruptors on prosobranch snails (Mollusca: Gastropoda) in the laboratory—Part I—bisphenol A and octylphenol as xeno-estrogens: Ecotoxicology, v. 9, p. 383–397.

Rajapakse, N., Ong, D., and Kortenkamp, A., 2001, Defining the impact of weakly estrogenic chemicals on the action of steroidal estrogens: Toxicological Sciences, v. 60, p. 296–304.

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; 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 ERα and ERβ 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, p. 515–519.

Sheehan, D.M., 2000, Activity of environmentally relevant low doses of endocrine disruptors and the bisphenol A controversy—Initial results confirmed: Experimental Biology and Medicine, v. 224, p. 57–60.

Sohoni, P., Tyler, C.R., Hurd, K., Caunter, J., Hetheridge, M., Williams, T., Woods, C., Evans, M., Toy, R., Gargas, M., Sumpter, J.P., 2001, Reproductive effects of long-term exposure to bisphenol A in the fathead minnow (*Pimephales promelas*): Environmental Science & Technology, v. 35, no. 14, p. 2917–2481.

South Dakota Department of Environment and Natural Resources, 2004, The 2004 South Dakota integrated report for surface water quality assessment: accessed on May 2, 2005, at *http://www.state.sd.us/denr/Documents/04IRFinal.pdf*

South Dakota State University, 2005a, South Dakota climate and weather—temperature normals (1971–2000): accessed April 7, 2005, at *http://climate.sdstate.edu/data/tempnormals.shtm*

South Dakota State University, 2005b, South Dakota climate and weather—precipitation normals (1971–2000): accessed April 7, 2005, at *http://climate.sdstate.edu/data/pptnormals.shtm*

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.

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., 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: 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 online 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*.]

U.S. Geological Survey, 2005, Surface water data for South Dakota: accessed July 28, 2005, at *http://waterdata.usgs.gov/sd/nwis/sw*

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.

Supplemental Information

Table 10. Field-measured properties and constituents and analytical constituents.

[Bold text indicates suspected endocrine-disrupting compound (EDC). Units are micrograms per liter unless otherwise noted. CAS RN, Chemical Abstracts Service Registry Number; ft, feet; ft^3/s, cubic feet per second; mm Hg, millimeter of mercury; mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degree Celsius; col/100 mL, colonies per 100 milliliters; NTU, Nephelometric Turbidity Unit; ND, not determined; --, no data]

Constituent or property	Footnote	Analytical method number	Field or laboratory reporting level	Study reporting level for data summary and analysis	CAS RN	Typical use or source
Field-measured properties and constituents						
Gage height	--	--	0.01 ft	0.01 ft	--	--
Discharge, instantaneous	--	--	0.1 ft^3/s	0.1 ft^3/s	--	--
Turbidity	--	--	1 NTU	1 NTU	--	--
Barometric pressure	--	--	1 mm Hg	1 mm Hg	--	--
Dissolved oxygen	--	--	0.1 mg/L	0.1 mg/L	--	--
pH	--	--	0.1 standard unit	0.1 standard unit	--	--
Specific conductance	--	--	5 µS/cm	5 µS/cm	--	--
Air temperature	--	--	0.1°C	0.1°C	--	--
Water temperature	--	--	0.1°C	0.1°C	--	--
Auxiliary constituents						
Nitrite plus nitrate nitrogen	--	--	0.06 mg/L	0.06 mg/L	--	--
Total coliform concentration, most probable number	--	--	10 col/100 mL	10 col/100 mL	--	--
Fecal coliform concentration, membrane filter	--	--	10 col/100 mL	10 col/100 mL	--	--
Human pharmaceutical compounds (HPCs)						
1,7-dimethylxanthine, dissolved	2	1	0.144	0.05	611-59-6	caffeine metabolite
Acetaminophen, dissolved	2, 3	1	0.036	ND	103-90-2	antipyretic (nonprescription)
Caffeine, dissolved	1, 4	1	0.016	0.022	58-08-2	stimulant (nonprescription)
Caffeine, whole water	1	3	0.5	0.12	58-08-2	stimulant (nonprescription)
Carbamazepine, dissolved	1, 3	1	0.011	ND	298-46-4	anticonvulsant, antineuralgic (prescription)
Cimetidine, dissolved	1, 3	1	0.012	ND	51481-61-9	antacid (nonprescription)
Codeine, dissolved	1, 3	1	0.015	ND	76-57-3	analgesic (prescription)
Cotinine, dissolved	1, 4	1	0.014	0.0008	486-56-6	nicotine metabolite
Cotinine, whole water	1	3	1	0.18	486-56-6	nicotine metabolite
Dehydronifedipine, dissolved	1, 4	1	0.015	0.0035	67035-22-7	antianginal (prescription)
Diltiazem, dissolved	1, 3	1	0.016	ND	42399-41-7	antihypertensive (prescription)
Diphenhydramine, dissolved	1, 3	1	0.015	ND	58-73-1	antihistamine (prescription)
Fluoxetine, dissolved	2, 3	1	0.014	ND	54910-89-3	antidepressant (prescription)
Furosemide, dissolved	2, 3	1	0.039	ND	54-31-9	diuretic (prescription)

Table 10. Field-measured properties and constituents and analytical constituents.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Units are micrograms per liter unless otherwise noted. CAS RN, Chemical Abstracts Service Registry Number; ft, feet; ft^3/s, cubic feet per second; mm Hg, millimeter of mercury; mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degree Celsius; col/100 mL, colonies per 100 milliliters; NTU, Nephelometric Turbidity Unit; ND, not determined; --, no data]

Constituent or property	Footnote	Analytical method number	Field or laboratory reporting level	Study reporting level for data summary and analysis	CAS RN	Typical use or source
Human pharmaceutical compounds (HPCs)—Continued						
Gemfibrozil, dissolved	2, 3	1	0.013	ND	25812-30-0	antihyperlipidemic (prescription)
Ibuprofen, dissolved	2, 3	1	0.042	ND	15687-27-1	anti-inflamatory (nonprescription)
Metformin, dissolved	2, 3	1	ND	ND	1115-70-4	antidiabetic (prescription)
Miconazole, dissolved	2, 3	1	0.018	ND	22916-47-8	antifungal (nonprescription)
Ranitidine, dissolved	1, 3	1	0.013	ND	66357-35-5	antacid (nonprescription)
Salbutamol, dissolved	1, 4	1	0.023	0.0054	18559-94-9	antiasthmatic (prescription)
Thiabendazole, dissolved	2, 3	1	0.011	ND	148-79-8	human and veterinary antihelminthic (prescription)
Warfarin, dissolved	2, 3	1	0.012	ND	81-81-2	anticoagulant (prescription)
Human and veterinary antibiotic compounds (HVACs)						
Amoxicilin, dissolved	2	2	0.01	0.05	26787-78-0	antibiotic (human and veterinary; penicillin class)
Ampicillin, dissolved	2	2	0.01	0.01	69-53-4	antibiotic (human and veterinary; penicillin class)
Anhd-Cl-tetracycline, dissolved	2	2	0.01	0.3	13803-65-1	tetracycline metabolite
Anhydrotetracycline, dissolved	2	2	0.01	0.15	--	tetracycline metabolite
Azithromycin, dissolved	2, 3	1	0.004	ND	83905-01-5	antibiotic (human and veterinary; macrolide class)
Cefotaxime, dissolved	2	2	0.01	0.01	63527-52-6	antibiotic (human and veterinary; cephalosporin class)
Chlorotetracycline, dissolved	2	2	0.01	0.05	57-62-5	antibiotic (veterinary; tetracycline class)
Ciprofloxacin, dissolved	1, 4	2	0.005	0.036	85721-33-1	antibiotic (human and veterinary; fluoroquinolone class)
Clinafloxacin, dissolved	2	2	0.005	0.01	105956-97-6	antibiotic (human and veterinary; fluoroquinolone class)
Cloxacillin, dissolved	2	2	0.01	0.01	61-72-3	antibiotic (human and veterinary; penicillin class)
Demeclocycline, dissolved	2	2	0.01	0.08	127-33-3	antibiotic (human and veterinary; tetracycline class)
Doxycycline, dissolved	2	2	0.01	0.05	564-25-0	antibiotic (human and veterinary; tetracycline class)
Erythromycin (method 1), dissolved	2, 3	1	0.009	ND	114-07-8	antibiotic (human and veterinary; macrolide class)
Erythromycin (method 2), dissolved	1, 4	2	0.02	0.025	114-07-8	antibiotic (human and veterinary; macrolide class)

Table 10. Field-measured properties and constituents and analytical constituents.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Units are micrograms per liter unless otherwise noted. CAS RN, Chemical Abstracts Service Registry Number; ft, feet; ft^3/s, cubic feet per second; mm Hg, millimeter of mercury; mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degree Celsius; col/100 mL, colonies per 100 milliliters; NTU, Nephelometric Turbidity Unit; ND, not determined; --, no data]

Constituent or property	Footnote	Analytical method number	Field or laboratory reporting level	Study reporting level for data summary and analysis	CAS RN	Typical use or source
Human and veterinary antibiotic compounds (HVACs)—Continued						
Erythromycin-H_2O, dissolved	1, 4	2	0.005	0.046	114-07-8	erythromycin metabolite
Flumequine, dissolved	2	2	0.005	0.005	42835-25-6	antibiotic (veterinary; fluoroquinolone class)
Lincomycin, dissolved	2	2	0.005	0.005	154-21-2	antibiotic (veterinary; lincosamide class)
Lomefloxacin, dissolved	2	2	0.005	0.005	98079-51-7	antibiotic (veterinary; fluoroquinolone class)
Minocycline, dissolved	2	2	0.01	0.25	10118-90-8	antibiotic (human and veterinary; tetracycline class)
Norfloxacin, dissolved	1, 4	2	0.005	0.02	70458-96-7	antibiotic (human and veterinary; fluoroquinolone class)
Ofloxacin, dissolved	1, 4	2	0.005	0.03	83380-47-6	antibiotic (human and veterinary; fluoroquinolone class)
Ormetoprim, dissolved	2	2	0.005	0.005	6981-18-6	antibiotic (veterinary; sulfonamide class)
Oxacillin, dissolved	2	2	0.01	0.01	66-79-5	antibiotic (human and veterinary; penicillin class)
Oxolinic acid, dissolved	2	2	0.005	0.005	14698-29-4	antibiotic (veterinary; fluoroquinolone class)
Oxytetracycline, dissolved	2	2	0.01	0.15	79-57-2	antibiotic (veterinary; tetracycline class)
Penicillin G, dissolved	2	2	0.01	0.01	69-57-8	antibiotic (human and veterinary; penicillin class)
Penicillin V, dissolved	2	2	0.01	0.01	87-08-1	antibiotic (human and veterinary; penicillin class)
Roxithromycin, dissolved	1, 4	2	0.005	0.005	80214-83-1	antibiotic (human and veterinary; macrolide class)
Sarafloxacin, dissolved	2	2	0.005	0.03	98105-99-8	antibiotic (veterinary; fluoroquinolone class)
Sulfachlorpyridazine, dissolved	2	2	0.005	0.005	80-32-0	antibiotic (veterinary; sulfonamide class)
Sulfadiazine, dissolved	1, 4	2	0.005	0.005	68-35-9	antibiotic (veterinary; sulfonamide class)
Sulfadimethoxine, dissolved	2	2	0.005	0.005	122-11-2	antibiotic (veterinary; sulfonamide class)
Sulfamerazine, dissolved	2	2	0.005	0.005	127-79-7	antibiotic (veterinary; sulfonamide class)

Table 10. Field-measured properties and constituents and analytical constituents.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Units are micrograms per liter unless otherwise noted. CAS RN, Chemical Abstracts Service Registry Number; ft, feet; ft^3/s, cubic feet per second; mm Hg, millimeter of mercury; mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degree Celsius; col/100 mL, colonies per 100 milliliters; NTU, Nephelometric Turbidity Unit; ND, not determined; --, no data]

Constituent or property	Footnote	Analytical method number	Field or laboratory reporting level	Study reporting level for data summary and analysis	CAS RN	Typical use or source
Human and veterinary antibiotic compounds (HVACs)—Continued						
Sulfamethazine, dissolved	1, 4	2	0.005	0.005	57-68-1	antibiotic (veterinary; sulfonamide class)
Sulfamethoxazole (method 1), dissolved	1, 3	1	0.064	ND	723-46-6	antibiotic (human and veterinary; sulfonamide class)
Sulfamethoxazole (method 2), dissolved	1, 4	2	0.005	0.02	723-46-6	antibiotic (human and veterinary; sulfonamide class)
Sulfathiazole, dissolved	2	2	0.005	0.005	72-14-0	antibiotic (veterinary; sulfonamide class)
Tetracycline, dissolved	1, 4	2	0.01	0.064	60-54-8	antibiotic (human and veterinary; tetracycline class)
Trimethoprim (method 1), dissolved	1, 3	1	0.013	ND	738-70-5	antibiotic (human and veterinary; folic acid inhibitor class)
Trimethoprim (method 2), dissolved	1, 4	2	0.01	0.02	738-70-5	antibiotic (human and veterinary; folic acid inhibitor class)
Tylosin, dissolved	2	2	0.005	0.07	1401-69-0	antibiotic (veterinary; macrolide class)
Virginiamycin, dissolved	2	2	0.005	0.005	21411-53-0	antibiotic (veterinary; streptogramin class)
Major agricultural herbicides (MAHs)						
Atrazine, whole water	1, 4	3	0.5	0.0002	1912-24-9	herbicide
Metolachlor, whole water	1, 4	3	0.5	0.028	98-82-8	herbicide
Prometon, whole water	1, 4	3	0.5	0.02	1610-18-0	herbicide
Household, industrial, and minor agricultural-use compounds (HIACs)						
1,4-dichlorobenzene, whole water	2, 3	3	0.5	ND	106-46-7	deodorizer, moth repellent
2,2′,4,4′-tetrabromodiphenyl ether, whole water	2	3	0.5	0.5	5436-43-1	fire retardant
3,4-dichlorophenyl isocyanate, whole water	2, 3	3	0.5	ND	102-36-3	manufacturing intermediate
3-methyl-1H-indole (skatol), whole water	2	3	1	0.02	83-34-1	fragrance
3-*tert*-butyl-4-hydroxy anisole (BHA), whole water	2, 3	3	5	ND	121-00-6	antioxidant
4-cumylphenol, whole water	2	3	1	1	599-64-4	detergent metabolite
4-*normal*-octylphenol, whole water	2	3	1	1	1806-26-4	detergent metabolite
4-*tert*-octylphenol, whole water	2	3	1	0.26	140-66-9	detergent metabolite

Table 10. Field-measured properties and constituents and analytical constituents.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Units are micrograms per liter unless otherwise noted. CAS RN, Chemical Abstracts Service Registry Number; ft, feet; ft^3/s, cubic feet per second; mm Hg, millimeter of mercury; mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degree Celsius; col/100 mL, colonies per 100 milliliters; NTU, Nephelometric Turbidity Unit; ND, not determined; --, no data]

Constituent or property	Footnote	Analytical method number	Field or laboratory reporting level	Study reporting level for data summary and analysis	CAS RN	Typical use or source
Household, industrial, and minor agricultural-use compounds (HIACs)—Continued						
5-methyl-1H-benzotriazole, whole water	1, 4	3	2	0.33	136-85-6	anticorrosive
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN), whole water	1, 4	3	0.5	0.048	21145-77-7	fragrance
Acetophenone, whole water	1, 4	3	0.5	0.08	98-86-2	fragrance
Anthraquinone, whole water	2	3	0.5	0.96	84-65-1	manufacturing, pesticide
Benzophenone, whole water	1, 4	3	0.5	0.025	119-61-9	fixative
Bis(2-ethylhexyl) phthalate, whole water	2, 3	3	2	ND	117-81-7	plasticizer
Bisphenol-A, whole water	1, 4	3	1	0.069	80-05-7	plasticizer
Bromacil, whole water	2	3	0.5	0.068	314-40-9	herbicide
Camphor, whole water	1, 4	3	0.5	0.07	76-22-2	fumigant and flavorant
Carbaryl, whole water	2, 3	3	1	ND	63-25-2	insecticide
Chlorpyrifos, whole water	2	3	0.5	0.5	2921-88-2	insecticide
N,N-diethyl-*meta*-toluamide (DEET), whole water	1, 4	3	0.5	0.08	134-62-3	insect repellent
Diazinon, whole water	2	3	0.5	0.027	333-41-5	insecticide
Dichlorvos, whole water	2	3	1	1	62-73-7	insecticide
Diethyl phthalate, whole water	1, 4	3	0.5	0.55	84-66-2	plasticizer
D-Limonene, whole water	2, 3	3	0.5	ND	5989-27-5	solvent
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), whole water	1, 4	3	0.5	0.032	1222-05-5	fragrance
Indole, whole water	1, 4	3	0.5	0.015	120-72-9	amino-acid metabolite
Isoborneol, whole water	2	3	0.5	0.5	124-76-5	fragrance, flavorant
Isophorone, whole water	1, 4	3	0.5	0.047	78-59-1	solvent
Isoquinoline, whole water	2	3	0.5	0.5	119-65-3	manufacturing
Menthol, whole water	2	3	0.5	0.5	89-78-1	pharmaceutical additive, fragrance
Metalaxyl, whole water	2	3	0.5	0.5	57837-19-1	agricultural fungicide
Methyl salicylate, whole water	2	3	0.5	0.5	119-36-8	flavoring agent, liniment
Nonylphenol diethoxylate (NP2EO), whole water	1, 4	3	5	0.55	26027-38-2	detergent/surfactant or metabolite

Table 10. Field-measured properties and constituents and analytical constituents.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Units are micrograms per liter unless otherwise noted. CAS RN, Chemical Abstracts Service Registry Number; ft, feet; ft^3/s, cubic feet per second; mm Hg, millimeter of mercury; mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degree Celsius; col/100 mL, colonies per 100 milliliters; NTU, Nephelometric Turbidity Unit; ND, not determined; --, no data]

Constituent or property	Footnote	Analytical method number	Field or laboratory reporting level	Study reporting level for data summary and analysis	CAS RN	Typical use or source
Household, industrial, and minor agricultural-use compounds (HIACs)—Continued						
Nonylphenol monoethoxylate (NP1EO), whole water	1, 4	3	2	0.39	27986-36-3	detergent/surfactant or metabolite
Octylphenol diethoxylate (OP2EO), whole water	1, 4	3	1	0.14	26636-32-8	detergent/surfactant or metabolite
Octylphenol monoethoxylate (OP1EO), whole water	2	3	1	1	26636-32-8	detergent/surfactant or metabolite
para-cresol, whole water	1, 4	3	1	0.03	106-44-5	wood preservative
***para*-nonylphenol (NP)**, whole water	1, 4	3	5	0.64	84852-15-3	detergent/surfactant or metabolite
Pentachlorophenol, whole water	2	3	2	2	87-86-5	wood preservative
Phenol, whole water	2	3	0.5	0.94	108-95-2	resin and pharmaceutical manufacturing, disinfectant,
Tetrachloroethylene, whole water	2, 3	3	0.5	ND	127-18-4	solvent, degreaser
Tributyl phosphate, whole water	1, 4	3	0.5	0.02	126-73-8	fire retardant
Triclosan, whole water	1, 4	3	1	0.084	3380-34-5	antimicrobial disinfectant
Triethyl citrate (ethyl citrate), whole water	1, 4	3	0.5	0.048	77-93-0	cosmetics
Triphenyl phosphate, whole water	1, 4	3	0.5	0.015	115-86-6	plasticizer
Tri(2-butoxyethyl)phosphate, whole water	1, 4	3	0.5	0.13	78-51-3	plasticizer
Tri(2-chloroethyl)phosphate, whole water	1, 4	3	0.5	0.056	115-96-8	fire retardant
Tri(dichloroisopropyl)phosphate, whole water	1, 4	3	0.5	0.047	13674-87-8	fire retardant
Polyaromatic hydrocarbons (PAHs)						
1-methylnaphthalene, whole water	2	3	0.5	0.5	90-12-0	fossil fuel combustion
2,6-dimethylnaphthalene, whole water	2	3	0.5	0.5	58-14-2	fossil fuel combustion
2-methylnaphthalene, whole water	2	3	0.5	0.5	91-57-6	fossil fuel combustion
Anthracene, whole water	2	3	0.5	0.5	120-12-7	preservative, component of tar
Benzo[*a*]pyrene, whole water	2	3	0.5	0.5	50-32-8	fossil fuel combustion
Carbazole, whole water	2	3	0.5	0.22	86-74-8	chemical manufacturing
Fluoranthene, whole water	2	3	0.5	0.15	206-44-0	component of coal tar and asphalt
Isopropylbenzene (cumene), whole water	2, 3	3	0.5	ND	98-82-8	fuels and paint thinners
Naphthalene, whole water	1, 4	3	0.5	0.01	91-20-3	moth repellent, major component in gasoline

Table 10. Field-measured properties and constituents and analytical constituents.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Units are micrograms per liter unless otherwise noted. CAS RN, Chemical Abstracts Service Registry Number; ft, feet; ft^3/s, cubic feet per second; mm Hg, millimeter of mercury; mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degree Celsius; col/100 mL, colonies per 100 milliliters; NTU, Nephelometric Turbidity Unit; ND, not determined; --, no data]

Constituent or property	Footnote	Analytical method number	Field or laboratory reporting level	Study reporting level for data summary and analysis	CAS RN	Typical use or source
Polyaromatic hydrocarbons (PAHs)—Continued						
Phenanthrene, whole water	2	3	0.5	0.1	85-01-8	fossil fuel combustion
Pyrene, whole water	2	3	0.5	0.04	129-00-0	fossil fuel combustion
Sterol compounds (SCs)						
3-*beta*-coprostanol, whole water	1, 4	3	2	0.26	360-68-9	fecal sterol
beta-sitosterol, whole water	1, 4	3	2	0.57	83-46-5	plant sterol
beta-stigmastanol, whole water	2, 3	3	2	ND	19466-47-8	plant sterol
Cholesterol, whole water	1, 4	3	2	0.64	57-88-5	plant/animal sterol
Laboratory quality-assurance/quality-control surrogate compounds						
Bisphenol-A-d3 (surrogate), whole water	--	3	0.1 percent recovery	0.1 percent recovery	--	laboratory analytical surrogate
Bisphenol-A-d3 (surrogate), whole water	--	3	0.1 percent recovery	0.1 percent recovery	--	laboratory analytical surrogate
Caffeine-c13 (surrogate), whole water	--	3	0.1 percent recovery	0.1 percent recovery	--	laboratory analytical surrogate
Decafluorobiphenyl (surrogate), whole water	--	3	0.1 percent recovery	0.1 percent recovery	434-90-2	laboratory analytical surrogate
Ethyl-nicontinate-d4 (surrogate), dissolved	--	1	0.1 percent recovery	0.1 percent recovery	--	laboratory analytical surrogate
Fluoranthene-d10 (surrogate), whole water	--	3	0.1 percent recovery	0.1 percent recovery	93951-69-0	laboratory analytical surrogate

[1]Constituent detected in one or more environmental samples at concentration(s) greater than study reporting level.

[2]Constituent not detected in any environmental samples at concentration(s) greater than study reporting level.

[3]Results for laboratory reagent-spike samples and/or matrix-spike samples unacceptable; constituent excluded from analyses.

[4]Constituent included in summary analyses and discussion related to occurrence of organic wastewater compounds in wastewater effluent.

Table 11. Statistical summaries of analytical results for detected compounds in laboratory method-blank samples.

[Bold text indicates suspected endocrine-disrupting compound (EDC). µg/L, micrograms per liter; ND, not determined; --, not available]

Compound	Footnote	Analytical method number	Number of method-blank samples	Number of method-blank samples with detections	Minimum detected concentration (µg/L)	Median detected concentration (µg/L)	Maximum detected concentration (µg/L)	Study reporting level for data summary and analysis (µg/L)
Human pharmaceutical compounds (HPCs)								
Acetaminophen, dissolved	3	1	7	1	0.0040	0.0040	0.0040	ND
Caffeine, whole water	1	3	5	1	.0020	.0020	.0020	.12
Human and veterinary antibiotic compounds (HVACs)								
Amoxicilin, dissolved	3, 4	2	20	1	--	0.03	--	0.05
Anhd-Cl-tetracycline, dissolved	3, 4	2	20	2	--	.21	--	.3
Anhydrotetracycline, dissolved	3, 4	2	20	6	--	.09	--	.15
Chlorotetracycline, dissolved	3, 4	2	20	5	--	.03	--	.05
Ciprofloxacin, dissolved	1, 4	2	20	3	--	.02	--	.036
Demeclocycline, dissolved	3, 4	2	20	8	--	.04	--	.08
Doxycycline, dissolved	3, 4	2	20	10	--	.03	--	.05
Erythromycin-H2O, dissolved	1, 4	2	20	9	--	.02	--	.046
Minocycline, dissolved	3, 4	2	20	4	--	.14	--	.25
Norfloxacin, dissolved	1, 4	2	20	1	--	.01	--	.02
Ofloxacin, dissolved	1, 4	2	20	4	--	.02	--	.03
Oxytetracycline, dissolved	3, 4	2	20	2	--	.08	--	.15
Sarafloxacin, dissolved	3, 4	2	20	1	--	.02	--	.03
Tetracycline, dissolved	1, 4	2	20	9	--	.03	--	.064
Trimethoprim, dissolved	1, 4	2	20	1	--	--	--	.02
Household, industrial, and minor agricultural-use compounds (HIACs)								
4-*tert*-octylphenol, whole water	3	3	5	5	0.024	0.048	0.079	0.26
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN), whole water	1	3	5	1	.0021	.0021	.0021	.048
Acetophenone, whole water	2	3	5	5	.022	.054	.11	.08
Benzophenone, whole water	1	3	5	1	.0074	.0074	.0074	.015
Bis(2-ethylhexyl) phthalate, whole water	1	3	3	3	.16	.59	.63	ND
Camphor, whole water	1	3	5	1	.020	.020	.020	.07

Table 11. Statistical summaries of analytical results for detected compounds in laboratory method-blank samples.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). µg/L, micrograms per liter; ND, not determined; --, not available]

Compound	Footnote	Analytical method number	Number of method-blank samples	Number of method-blank samples with detections	Minimum detected concentration (µg/L)	Median detected concentration (µg/L)	Maximum detected concentration (µg/L)	Study reporting level for data summary and analysis (µg/L)
Household, industrial, and minor agricultural-use compounds (HIACs)—Continued								
N,N-diethyl-*meta*-toluamide (DEET), whole water	1	3	5	1	0.0040	0.0040	0.0040	0.08
Diethyl phthalate, whole water	1	3	3	3	.045	.066	.33	.55
Nonylphenol diethoxylate (NP2EO), whole water	2	3	5	1	1.4	1.4	1.4	.55
Nonylphenol monoethoxylate (NP1EO), whole water	2	3	3	1	.72	.72	.72	.39
Octylphenol diethoxylate (OP2EO), whole water	1	3	5	1	.072	.072	.072	.14
Octylphenol monoethoxylate (OP1EO), whole water	3	3	5	2	.31	.32	.32	1
Methyl salicylate, whole water	3	3	5	1	.0051	.0051	.0051	.5
Phenol, whole water	3	3	5	3	.018	.033	.13	.94
Triphenyl phosphate, whole water	1	3	5	2	.0024	.0062	.0099	.015
Tri(2-butoxyethyl)phosphate, whole water	1	3	5	1	.10	.10	.10	.13
Tri(dichloroisopropyl) phosphate, whole water	1	3	5	1	.0080	.0080	.0080	.047
Polyaromatic hydrocarbons (PAHs)								
1-methylnaphthalene, whole water	3	3	5	3	0.0029	0.0041	0.0082	0.5
2,6-dimethylnaphthalene, whole water	3	3	5	1	.0021	.0021	.0021	.5
2-methylnaphthalene, whole water	3	3	5	3	.0044	.0045	.0079	.5
Fluoranthene, whole water	3	3	5	1	.0017	.0017	.0017	.15
Isopropylbenzene (cumene), whole water	3	3	5	1	.0012	.0012	.0012	ND
Naphthalene, whole water	1	3	5	2	.0050	.0050	.0050	.01
Phenanthrene, whole water	3	3	5	1	.0032	.0032	.0032	.1
Pyrene, whole water	3	3	5	1	.0006	.0006	.0006	.04

Table 11. Statistical summaries of analytical results for detected compounds in laboratory method-blank samples.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). µg/L, micrograms per liter; ND, not determined; --, not available]

Compound	Footnote	Analytical method number	Number of method-blank samples	Number of method-blank samples with detections	Minimum detected concentration (µg/L)	Median detected concentration (µg/L)	Maximum detected concentration (µg/L)	Study reporting level for data summary and analysis (µg/L)
Sterol compounds (SCs)								
3-*beta*-coprostanol, whole water	1	3	5	1	0.19	0.19	0.19	0.26
Cholesterol, whole water	1	3	5	1	.21	.21	.21	.64

[1]Compound detected in one or more method-blank samples but at concentrations generally substantially less than study reporting level.

[2]Compound detected infrequently in method-blank samples; compound was not detected in environmental samples associated with method-blank samples with detections, or compound was detected in method-blank samples at concentrations substantially less than detected concentrations in environmental samples associated with the method-blank samples with detections.

[3]Compound detected in method-blank samples but not detected in any environmental samples at concentrations greater than study reporting level or compound excluded from analyses based on unacceptable results for laboratory-reagent spike or matrix-spike samples.

[4]Raw data for laboratory method blank samples for analytical method 2 were not available; the laboratory only reported median concentrations for laboratory method blank samples.

Table 12. Statistical summaries of analytical results for laboratory reagent-spike samples.

[Bold text indicates suspected endocrine-disrupting compound (EDC). RSD, relative standard deviation]

Compound	Footnote	Analytical method number	Number of reagent-spike samples	Minimum percent recovery	Median percent recovery	Maximum percent recovery	Percent recovery RSD
Human pharmaceutical compounds (HPCs)							
1,7-dimethylxanthine, dissolved	1	1	7	78	98	150	24
Acetaminophen, dissolved	1	1	7	76	85	120	18
Caffeine, dissolved	1	1	7	73	87	120	19
Caffeine, whole water	1	3	5	80	90	95	9
Carbamazepine, dissolved	1	1	7	58	93	110	21
Cimetidine, dissolved	2	1	7	6	41	53	45
Codeine, dissolved	1	1	7	59	91	110	20
Cotinine, dissolved	1	1	7	60	89	110	27
Cotinine, whole water	1	3	5	39	64	83	26
Dehydronifedipine, dissolved	1	1	7	67	95	120	19
Diltiazem, dissolved	1	1	7	34	61	69	25
Diphenhydramine, dissolved	1	1	7	40	65	80	24
Fluoxetine, dissolved	1	1	7	26	40	52	19
Furosemide, dissolved	2	1	7	0	0	0	0
Gemfibrozil, dissolved	1	1	7	30	57	63	20
Ibuprofen, dissolved	2	1	7	14	32	110	77
Metformin, dissolved	2	1	7	0	0	0	0
Miconazole, dissolved	2	1	7	5	12	21	42
Ranitidine, dissolved	1	1	7	34	57	66	22
Salbutamol, dissolved	1	1	7	36	69	99	30
Thiabendazole, dissolved	2	1	7	16	20	86	73
Warfarin, dissolved	1	1	7	61	77	120	22
Human and veterinary antibiotic compounds (HVACs)							
Azithromycin, dissolved	2	1	7	0	4	13	99
Erythromycin, dissolved	2	1	7	1	6	15	86
Sulfamethoxazole, dissolved	1	1	7	42	94	100	30
Trimethoprim, dissolved	1	1	7	46	65	79	17
Major agricultural herbicides (MAHs)							
Atrazine, whole water	1	3	3	120	130	140	10
Metolachlor, whole water	1	3	5	75	85	100	14
Prometon, whole water	1	3	5	85	100	120	14

Table 12. Statistical summaries of analytical results for laboratory reagent-spike samples.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). RSD, relative standard deviation]

Compound	Footnote	Analytical method number	Number of reagent-spike samples	Minimum percent recovery	Median percent recovery	Maximum percent recovery	Percent recovery RSD
Household, industrial, and minor agricultural-use compounds (HIACs)							
1,4-dichlorobenzene, whole water	1	3	5	34	35	44	14
2,2′,4,4′-tetrabromodiphenyl ether, whole water	1	3	3	75	110	130	27
3,4-dichlorophenyl isocyanate, whole water	2	3	3	40	150	150	56
3-methyl-1H-indole (skatol), whole water	1	3	5	75	85	90	7
3-*tert*-butyl-4-hydroxy anisole (BHA), whole water	2	3	5	4	14	31	74
4-cumylphenol, whole water	1	3	5	85	85	95	6
4-*normal*-octylphenol, whole water	1	3	5	80	95	110	12
4-*tert*-octylphenol, whole water	1	3	5	80	90	95	6
5-methyl-1H-benzotriazole, whole water	1	3	5	100	120	200	32
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN), whole water	1	3	5	80	80	90	5
Acetophenone, whole water	1	3	5	65	90	110	18
Anthraquinone, whole water	1	3	5	75	85	130	24
Benzophenone, whole water	1	3	5	75	85	90	7
Bis(2-ethylhexyl) phthalate, whole water	1	3	3	95	110	110	8
Bisphenol-A, whole water	1	3	5	70	85	95	11
Bromacil, whole water	1	3	5	76	88	96	9
Camphor, whole water	1	3	5	70	90	95	12
Carbaryl, whole water	2	3	5	25	35	80	49
Chlorpyrifos, whole water	1	3	5	75	75	80	4
N,N-diethyl-*meta*-toluamide (DEET), whole water	1	3	5	80	95	95	7
Diazinon, whole water	1	3	5	80	85	90	6
Dichlorvos, whole water	1	3	5	60	80	100	18
Diethyl phthalate, whole water	1	3	3	85	90	90	3
D-Limonene, whole water	2	3	5	9	14	21	31
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), whole water	1	3	5	85	95	100	8
Indole, whole water	1	3	5	70	80	85	8
Isoborneol, whole water	1	3	5	65	85	90	12
Isophorone, whole water	1	3	5	70	85	100	15
Isoquinoline, whole water	1	3	5	60	65	80	13

Table 12. Statistical summaries of analytical results for laboratory reagent-spike samples.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). RSD, relative standard deviation]

Compound	Footnote	Analytical method number	Number of reagent-spike samples	Minimum percent recovery	Median percent recovery	Maximum percent recovery	Percent recovery RSD
Household, industrial, and minor agricultural-use compounds (HIACs)—Continued							
Menthol, whole water	1	3	5	60	80	85	13
Metalaxyl, whole water	1	3	5	85	90	95	5
Methyl salicylate, whole water	1	3	5	65	80	90	11
Nonylphenol diethoxylate (NP2EO), whole water	1	3	5	88	88	110	12
Nonylphenol monoethoxylate (NP1EO), whole water	1	3	3	94	100	120	12
Octylphenol diethoxylate (OP2EO), whole water	1	3	5	71	79	93	12
Octylphenol monoethoxylate (OP1EO), whole water	1	3	5	68	79	79	7
para-**cresol**, whole water	1	3	5	70	85	100	15
***para*-nonylphenol** (NP), whole water	1	3	5	75	94	110	14
Pentachlorophenol, whole water	1	3	5	43	53	55	12
Phenol, whole water	1	3	5	70	75	95	13
Tetrachloroethylene, whole water	2	3	5	5	13	16	38
Tributyl phosphate, whole water	1	3	5	80	90	100	8
Triclosan, whole water	1	3	5	70	75	100	16
Triethyl citrate (ethyl citrate), whole water	1	3	5	80	90	110	14
Triphenyl phosphate, whole water	1	3	5	80	95	100	10
Tri(2-butoxyethyl)phosphate, whole water	1	3	5	85	100	100	8
Tri(2-chloroethyl)phosphate, whole water	1	3	5	80	90	100	10
Tri(dichloroisopropyl)phosphate, whole water	1	3	5	90	105	140	21
Polyaromatic hydrocarbons (PAHs)							
1-methylnaphthalene, whole water	1	3	5	50	60	65	10
2,6-dimethylnaphthalene, whole water	1	3	5	44	55	60	13
2-methylnaphthalene, whole water	1	3	5	50	60	60	8
Anthracene, whole water	1	3	5	75	90	95	10
Benzo[*a*]pyrene, whole water	1	3	5	75	80	85	5
Carbazole, whole water	1	3	5	75	95	100	12
Fluoranthene, whole water	1	3	5	80	90	100	8
Isopropylbenzene (cumene), whole water	2	3	5	14	20	22	19
Naphthalene, whole water	1	3	5	50	55	60	7
Phenanthrene, whole water	1	3	5	65	85	85	11
Pyrene, whole water	1	3	5	65	75	85	10

Table 12. Statistical summaries of analytical results for laboratory reagent-spike samples.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). RSD, relative standard deviation]

Compound	Footnote	Analytical method number	Number of reagent-spike samples	Minimum percent recovery	Median percent recovery	Maximum percent recovery	Percent recovery RSD
Sterol compounds (SCs)							
3-*beta*-coprostanol, whole water	1	3	5	78	85	95	8
beta-sitosterol, whole water	1	3	5	60	78	95	16
beta-stigmastanol, whole water	1	3	5	59	80	99	18
Cholesterol, whole water	1	3	5	71	85	88	9

[1]Median percent recovery for reagent-spike samples within acceptable range (30-120 percent), and percent recovery RSD acceptable (less than 40 percent).

[2]Median percent recovery for reagent-spike samples outside of acceptable range (30-120 percent) or percent recovery RSD unacceptable (greater than 40 percent); compound excluded from analyses and discussion related to occurrence of emerging contaminants in wastewater effluents and the Big Sioux River.

Table 13. Statistical summaries of analytical results for laboratory surrogate samples.

[RSD, relative standard deviation]

Compound	Footnote	Analytical method number	Number of spiked environmental samples	Minimum percent recovery	Median percent recovery	Maximum percent recovery	Percent recovery RSD
Bisphenol-A-d3 (surrogate)	1	3	30	48	100	160	30
Caffeine-c13 (surrogate)	1	3	30	46	87	110	18
Decafluorobiphenyl (surrogate)	1	3	30	30	59	82	22
Ethyl-nicontinate-d4 (surrogate)	1	1	30	72	94	160	21
Fluoranthene-d10 (surrogate)	1	3	30	46	87	130	24

[1]Median percent recovery for reagent-spike samples within acceptable range (30 to 120 percent), and percent recovery RSD acceptable (less than 40 percent).

Table 14. Statistical summaries of analytical results for detected compounds in field equipment-blank samples.

[Bold text indicates suspected endocrine-disrupting compound (EDC). µg/L, micrograms per liter; e, estimated; ND, not determined]

Compound	Analytical method number	Number of field equipment-blank samples	Number of field equipment-blank samples with detections	Minimum detected concentration (µg/L)	Median detected concentration (µg/L)	Maximum concentration (µg/L)	Study reporting level (µg/L)
Human pharmaceutical compounds (HPCs)							
Acetaminophen, dissolved	1	9	3	e0.0058	e0.0091	e0.022	ND
Caffeine, dissolved	1	9	2	e.011	e.013	e.015	.022
Diphenhydramine, dissolved	1	9	1	e.0004	e.0004	e.0004	ND
Fluoxetine, dissolved	1	9	1	.018	.018	.018	ND
Human and veterinary antibiotic compounds (HVACs)							
Ciprofloxacin, dissolved	2	9	1	0.011	0.011	0.011	0.036
Clinafloxacin, dissolved	2	9	1	.0060	.0060	.0060	.01
Erythromycin-H2O, dissolved	2	9	1	.019	.019	.019	.025
Sulfamethoxazole, dissolved	2	9	1	.017	.017	.017	.02
Household, industrial, and minor agricultural-use compounds (HIACs)							
1,4-dichlorobenzene, whole water	3	8	1	e0.38	e0.38	e0.38	ND
4-*tert*-octylphenol, whole water	3	8	1	e.13	e.13	e.13	.26
Acetophenone, whole water	3	8	1	e.057	e.057	e.057	.08
Anthraquinone, whole water	3	8	2	e.060	e.27	e.48	.96
Benzophenone, whole water	3	8	1	e.017	e.017	e.017	.025
Bis(2-ethylhexyl) phthalate, whole water	3	8	1	e1.3	e1.3	e1.3	ND
N,N-diethyl-*meta*-toluamide (DEET), whole water	3	8	1	e.043	e.043	e.043	.08
Isophorone, whole water	3	8	1	e.024	e.024	e.024	.047
Isoquinoline, whole water	3	8	1	e.090	e.090	e.090	.5
Phenol, whole water	3	8	2	e.45	e.46	e.47	.94
Polyaromatic hydrocarbons (PAHs)							
Anthracene, whole water	3	8	1	e0.030	e0.030	e0.030	0.5
Benzo[*a*]pyrene, whole water	3	8	1	e.056	e.056	e.056	.5
Carbazole, whole water	3	8	1	e.21	e.21	e.21	.22
Fluoranthene, whole water	3	8	1	e.030	e.030	e.030	.15
Phenanthrene, whole water	3	8	2	e.017	e.048	e.079	.1
Pyrene, whole water	3	8	2	e.011	e.024	e.037	.04
Sterol compounds (SCs)							
Cholesterol, whole water	3	8	1	e0.56	e0.56	e0.56	0.64

Table 15. Statistical summaries for field replicate samples for organic wastewater compounds (OWCs) detected in any sample for any primary/replicate sample pair.

[Bold text indicates suspected endocrine-disrupting compound (EDC)]

Compound	Footnote	Number of field primary/ replicate sample pairs	Number of field primary/ replicate sample pairs in which compound was detected at concentration greater than study reporting level		Summary statistics for relative percent differences for primary/replicate sample pairs in which the compound was detected in both samples		
			In either sample	In both samples	Minimum	Median	Maximum
Human pharmaceutical compounds (HPCs)							
Caffeine, dissolved	2	9	5	4	4.1	8.3	53
Caffeine, whole water	1	9	2	2	8.2	23	37
Carbamazepine, dissolved	1	9	2	2	5.9	7.3	8.8
Codeine, dissolved	1	9	1	1	16	16	16
Cotinine, dissolved	1	9	7	7	0	7.8	63
Diltiazem, dissolved	1	9	1	1	12	12	12
Diphenhydramine, dissolved	1	9	2	2	5.7	7.1	8.5
Metformin, dissolved	1	9	1	1	5.3	5.3	5.3
Salbutamol, dissolved	1	9	1	1	40	40	40
Human and veterinary antibiotic compounds (HVACs)							
Ciprofloxacin, dissolved	1	13	1	1	12	12	12
Erythromycin, dissolved	1	13	3	3	1.1	7.5	13
Erythromycin-H2O, dissolved	1	13	6	6	2.4	9.5	19
Ofloxacin, dissolved	1	13	2	2	22	26	30
Sulfamethoxazole, dissolved	1	9	1	1	6.5	6.5	6.5
Sulfamethoxazole, dissolved	1	13	6	6	13	26	121
Trimethoprim, dissolved	1	10	3	3	3.7	8.0	21
Trimethoprim, dissolved	1	13	3	3	3.6	13	22
Tylosin, dissolved	1	13	1	1	39	39	39
Major agricultural herbicides (MAHs)							
Atrazine, whole water	1	10	7	7	2.0	9.5	17
Metolachlor, whole water	1	10	5	5	1.6	7.2	14
Prometon, whole water	2	10	3	2	1.7	5.6	9.5
Household, industrial, and minor agricultural-use compounds (HIACs)							
1,4-dichlorobenzene, whole water	1	10	3	3	3.2	17	79
3,4-dichlorophenyl isocyanate, whole water	4	9	3	3	23	46	86
4-*tert*-octylphenol, whole water	1	10	2	2	5.4	12	19
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN), whole water	2	10	4	3	5.4	11	39

Table 15. Statistical summaries for field replicate samples for organic wastewater compounds (OWCs) detected in any sample for any primary/replicate sample pair.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC)]

Compound	Footnote	Number of field primary/ replicate sample pairs	Number of field primary/ replicate sample pairs in which compound was detected at concentration greater than study reporting level		Summary statistics for relative percent differences for primary/replicate sample pairs in which the compound was detected in both samples		
			In either sample	In both samples	Minimum	Median	Maximum
Household, industrial, and minor agricultural-use compounds (HIACs)—Continued							
Acetophenone, whole water	3	10	2	2	20	50	81
Anthraquinone, whole water	1	10	1	1	18	18	18
Benzophenone, whole water	1	10	1	1	37	37	37
N,N-diethyl-*meta*-toluamide (DEET), whole water	1	10	4	4	0	19	40
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), whole water	1	10	3	3	15	21	50
Indole, whole water	1	10	2	2	26	29	32
Nonylphenol diethoxylate (NP2EO), whole water	1	10	2	2	11	14	16
Nonylphenol monoethoxylate (NP1EO), whole water	3	10	1	1	44	44	44
Octylphenol diethoxylate (OP2EO), whole water	1	10	1	1	13	13	13
***para*-nonylphenol (NP)**, whole water	1	10	1	1	12	12	12
Tributyl phosphate, whole water	1	10	5	5	0	5.2	17
Triclosan, whole water	1	10	1	1	14	14	14
Triethyl citrate (ethyl citrate), whole water	1	10	3	3	1.2	11	26
Triphenyl phosphate, whole water	1	10	2	2	5.9	16	25
Tri(2-butoxyethyl)phosphate, whole water	2	10	3	2	4.5	12	19
Tri(2-chloroethyl)phosphate, whole water	1	10	4	4	0	.85	30
Tri(dichloroisopropyl)phosphate, whole water	1	10	3	3	7.4	22	38
Polyaromatic hydrocarbons (PAHs)							
1-methylnaphthalene, whole water	1	10	1	1	9.5	9.5	9.5
2-methylnaphthalene, whole water	1	10	1	1	23	23	23
Phenanthrene, whole water	1	10	2	2	4.3	31	58
Pyrene, whole water	3	10	1	1	68	68	68

Table 15. Statistical summaries for field replicate samples for organic wastewater compounds (OWCs) detected in any sample for any primary/replicate sample pair.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC)]

Compound	Footnote	Number of field primary/ replicate sample pairs	Number of field primary/ replicate sample pairs in which compound was detected at concentration greater than study reporting level		Summary statistics for relative percent differences for primary/replicate sample pairs in which the compound was detected in both samples		
			In either sample	In both samples	Minimum	Median	Maximum
Sterol compounds (SCs)							
3-*beta*-coprostanol, whole water	1	10	4	4	1.0	20	33
beta-sitosterol, whole water	2	10	2	1	4.1	4.1	4.1
Cholesterol, whole water	2	10	9	7	1.9	29	49

[1]When compound was detected at concentrations above the study reporting level in either sample of a primary/replicate sample pair, compound was always detected in both samples; median relative percent difference acceptable (less than 40 percent); field replicate results judged to be acceptable.

[2]Infrequently, compound was detected at a concentration greater than the study reporting level in either the primary or replicate sample, but not both; median relative percent difference acceptable (less than 40 percent); all other quality-assurance/quality control results for compound were acceptable; field replicate results judged to be acceptable.

[3]Compound was detected at a concentration above the study reporting level in both samples of a single primary/replicate sample pair; relative percent difference exceeded 40 percent; all other quality-assurance/quality-control results for compound were acceptable; field replicate results judged to be acceptable.

[4]Compound was detected at a concentration above the study reporting level in multiple primary/replicate sample pairs; median relative percent difference exceeded 40 percent; replicate results unacceptable; however, compound was excluded from analyses and discussion related to occurrence of emerging contaminants in Big Sioux River and wastewater effluents based on unacceptable laboratory reagent-spike and/or matrix-spike sample results.

Table 16. Statistical summaries for environmental matrix spikes for wastewater effluent and Big Sioux River samples collected in the Sioux Falls area during 2002–2004.

[Bold text indicates suspected endocrine-disrupting compound (EDC). RSD, relative standard deviation]

Compound	Footnote	Number of matrix spike samples	Minimum percent recovery	Median percent recovery	Maximum percent recovery	Percent recovery RSD
Human pharmaceutical compounds (HPCs)						
1,7-dimethylxanthine, dissolved	1	10	42	60	71	16
Acetaminophen, dissolved	3	10	-9.3	40	52	46
Caffeine (method 1), dissolved	1	10	29	33	45	15
Caffeine (method 3), whole water	1	3	89	94	100	7.7
Carbamazepine, dissolved	3	10	4.9	19	33	48
Cimetidine, dissolved	3	10	8.3	23	32	44
Codeine, dissolved	3	10	38	70	140	49
Cotinine (method 1), dissolved	1	10	31	41	56	23
Cotinine (method 3), whole water	1	3	48	63	73	21
Dehydronifedipine, dissolved	1	10	39	46	81	27
Diltiazem, dissolved	3	10	5.9	12	30	60
Diphenhydramine, dissolved	3	10	8.2	11	29	55
Fluoxetine, dissolved	3	10	0	.22	20	250
Furosemide, dissolved	3	10	0	8.0	49	120
Gemfibrozil, dissolved	3	10	0	0	17	210
Ibuprofen, dissolved	3	10	0	0	35	320
Metformin, dissolved	3	10	0	1.5	9.3	120
Miconazole, dissolved	3	10	0	0	30	320
Ranitidine, dissolved	3	10	0	11	42	78
Salbutamol, dissolved	1	10	33	51	64	24
Thiabendazole, dissolved	3	10	0	7.7	22	83
Warfarin, dissolved	3	10	0	29	46	54
Human and veterinary antibiotic compounds (HVACs)						
Azithromycin, dissolved	3	10	0	3.3	16	110
Erythromycin (method 1), dissolved	3	10	0	9.6	46	120
Sulfamethoxazole (method 1), dissolved	3	10	0	11	42	92
Trimethoprim (method 1), dissolved	3	9	10	18	32	40
Major agricultural herbicides (MAHs)						
Atrazine, whole water	1	3	110	120	160	19
Metolachlor, whole water	1	3	53	69	82	21
Prometon, whole water	1	3	80	100	110	15

Table 16. Statistical summaries for environmental matrix spikes for wastewater effluent and Big Sioux River samples collected in the Sioux Falls area during 2002–2004.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). RSD, relative standard deviation]

Compound	Footnote	Number of matrix spike samples	Minimum percent recovery	Median percent recovery	Maximum percent recovery	Percent recovery RSD
Household, industrial, and minor agricultural-use compounds (HIACs)						
1,4-dichlorobenzene, whole water	3	3	23	23	45	42
2,2′,4,4′-tetrabromodiphenyl ether, whole water	1	3	58	72	72	12
3,4-dichlorophenyl isocyanate, whole water	3	3	39	110	230	78
3-methyl-1H-indole (skatol), whole water	1	3	62	81	85	16
3-*tert*-butyl-4-hydroxy anisole (BHA), whole water	3	3	3.0	7.2	63	140
4-cumylphenol, whole water	1	3	71	98	100	19
4-*normal*-octylphenol, whole water	1	3	84	85	98	8.9
4-*tert*-octylphenol, whole water	1	3	71	94	94	15
5-methyl-1H-benzotriazole, whole water	2	3	130	140	200	23
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN), whole water	1	3	58	71	72	12
Acetophenone, whole water	1	3	67	81	98	20
Anthraquinone, whole water	1	3	80	81	90	6.4
Benzophenone, whole water	1	3	67	85	90	15
Bis(2-ethylhexyl) phthalate, whole water	3	3	89	94	220	51
Bisphenol-A, whole water	1	3	93	120	130	17
Bromacil, whole water	1	3	78	110	110	17
Bromoform, whole water	1	3	36	45	67	32
Camphor, whole water	1	3	62	81	94	20
Carbaryl, whole water	3	3	140	150	170	10
Chlorpyrifos, whole water	1	3	44	63	72	23
N,N-diethyl-*meta*-toluamide (DEET), whole water	1	3	67	92	99	20
Diazinon, whole water	1	3	62	81	90	18
Dichlorvos, whole water	1	3	75	94	94	12
Diethyl phthalate, whole water	1	3	71	90	94	15
D-Limonene, whole water	3	3	7.1	7.6	24	75
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), whole water	1	3	53	79	81	22
Indole, whole water	1	3	58	63	72	11

Table 16. Statistical summaries for environmental matrix spikes for wastewater effluent and Big Sioux River samples collected in the Sioux Falls area during 2002–2004.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). RSD, relative standard deviation]

Compound	Footnote	Number of matrix spike samples	Minimum percent recovery	Median percent recovery	Maximum percent recovery	Percent recovery RSD
Household, industrial, and minor agricultural-use compounds (HIACs)—Continued						
Isoborneol, whole water	1	3	62	81	90	18
Isophorone, whole water	1	3	67	90	94	18
Isopropylbenzene (cumene), whole water	3	3	10	10	26	57
Isoquinoline, whole water	1	3	62	76	81	13
Menthol, whole water	1	3	67	81	85	13
Metalaxyl, whole water	1	3	62	94	100	25
Methyl salicylate, whole water	1	3	58	76	85	19
Nonylphenol diethoxylate (NP2EO), whole water	1	3	80	98	100	13
Nonylphenol monoethoxylate (NP1EO), whole water	1	3	89	100	110	10
Octylphenol diethoxylate (OP2EO), whole water	1	3	72	84	91	12
Octylphenol monoethoxylate (OP1EO), whole water	1	3	54	69	77	18
para-cresol, whole water	1	3	75	85	85	6.9
***para*-nonylphenol (NP)**, whole water	1	3	76	85	92	9.3
Pentachlorophenol, whole water	1	3	83	85	85	1.7
Phenol, whole water	1	3	58	72	90	22
Tetrachloroethylene, whole water	3	3	5.8	6.3	17.5	67
Tributyl phosphate, whole water	1	3	62	81	94	20
Triclosan, whole water	1	3	110	110	120	4.9
Triethyl citrate (ethyl citrate), whole water	1	3	80	93	99	11
Triphenyl phosphate, whole water	1	3	71	90	110	20
Tri(2-butoxyethyl)phosphate, whole water	1	3	80	88	90	6.1
Tri(2-chloroethyl)phosphate, whole water	1	3	80	100	100	14
Tri(dichloroisopropyl)phosphate, whole water	1	3	98	110	110	7.0
Polyaromatic hydrocarbons (PAHs)						
1-methylnaphthalene, whole water	1	3	44	49	72	26
2,6-dimethylnaphthalene, whole water	1	3	43	44	72	31
2-methylnaphthalene, whole water	1	3	44	45	76	33
Anthracene, whole water	1	3	75	76	98	16
Benzo[*a*]pyrene, whole water	1	3	53	63	67	12

Table 16. Statistical summaries for environmental matrix spikes for wastewater effluent and Big Sioux River samples collected in the Sioux Falls area during 2002–2004.—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). RSD, relative standard deviation]

Compound	Footnote	Number of matrix spike samples	Minimum percent recovery	Median percent recovery	Maximum percent recovery	Percent recovery RSD
Polyaromatic hydrocarbons (PAHs)—Continued						
Carbazole, whole water	1	3	84	99	110	14
Fluoranthene, whole water	1	3	71	75	95	16
Naphthalene, whole water	1	3	40	44	67	29
Phenanthrene, whole water	1	3	70	71	87	13
Pyrene, whole water	1	3	58	62	82	19
Sterol compounds (SCs)						
3-*beta*-coprostanol, whole water	1	3	73	100	100	20
beta-sitosterol, whole water	2	3	140	160	210	21
beta-stigmastanol, whole water	3	3	100	200	240	38
Cholesterol, whole water	1	3	82	90	120	21

[1]Median spike recovery within acceptable range (30-120 percent) and median spike recovery RSD acceptable (less than 40 percent); matrix-spike results judged to be acceptable.

[2]Median spike recovery greater than 120 percent, but median spike recovery RSD acceptable (less than 40 percent) and all other quality-assurance/quality-control results acceptable; matrix-spike results judged to be acceptable.

[3]Median spike recovery outside of acceptable range (30 to 120 percent) and/or median spike recovery RSD unacceptable (greater than 40 percent).

Table 17. Results for field-measured properties and constituents and auxiliary constituents.

[LE, analytical results unavailable due to laboratory error. ft, feet; ft^3/s, cubic feet per second; NTU, Nephelometric Turbidity Units; mm Hg, millimeter of mercury; mg/L, milligrams per liter; pH, negative base-10 logarithm of hydrogen ion activity, in moles per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; col/100 mL, colonies per 100 milliliters; e, estimated; <, less than; --, no data collected]

	Station identification and name (site label)												
	06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)		445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)		06479520 Big Sioux River below Watertown, SD (WT-DS2)		442026096533600 Big Sioux River near Volga, SD (VL-US1)		
Date of sample collection	08-18-2003	06-15-2004	08-18-2003	06-15-2004	08-19-2003	06-16-2004	08-19-2003	06-15-2004	08-20-2003	06-15-2004	08-20-2003	10-21-2003	06-16-2004
Time of sample collection	1045	1030	1200	1200	1305	0925	0930	1730	0915	1825	1400	1105	1145
Property or constituent													
Discharge, instantaneous (ft^3/s)	.45	21.8	.46	8.8	e4.9	e6.1	5.89	16.5	6.88	35.5	14.4	9.05	127
Turbidity (NTU)	--	20.4	--	11.8	--	5.0	--	13.6	--	33.2	--	25.2	46.7
Barometric pressure (mm Hg)	717	721	718	719	719	724	719	719	716	717	718	726	724
Dissolved oxygen (mg/L)	7.5	4.5	12.1	4.9	9.4	10.1	6.3	8.4	6.3	7.5	14.2	11.2	7.0
pH (standard units)	8.3	7.8	7.9	7.8	7.7	7.4	7.7	7.7	8.6	8.0	8.9	8.0	8.0
Specific conductance (µS/cm)	616	780	822	786	1,223	1,280	1,055	996	1,134	908	852	877	810
Air temperature (°C)	26.5	18.5	30.5	22.0	30.5	15.6	21.0	26.0	23.5	26.5	34.5	16.0	15.0
Water temperature (°C)	25.0	19.8	24.1	20.9	20.1	15.6	20.1	19.5	22.2	21.8	30.1	11.2	19.8
Nitrite plus nitrate nitrogen (mg/L)	<.060	<.060	<.060	.224	13.4	18.9	7.72	5.62	6.00	2.13	<.060	e.041	.278
Total coliform concentration, most probable number (col/100 mL)	1,100	300	3,000	1,700	8,000	1,300	50,000	8,000	8,000	1,300	3,000	700	3,000
Fecal coliform concentration, membrane filter (col/100 mL)	60	280	450	340	30	40	1300	250	1,600	200	1,300	110	540

Table 17. Results for field-measured properties and constituents and auxiliary constituents.—Continued

[LE, analytical results unavailable due to laboratory error. ft, feet; ft^3/s, cubic feet per second; NTU, Nephelometric Turbidity Units; mm Hg, millimeter of mercury; mg/L, milligrams per liter; pH, negative base-10 logarithm of hydrogen ion activity, in moles per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; col/100 mL, colonies per 100 milliliters; e, estimated; <, less than; --, no data collected]

	Station identification and name (site label)													
	441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)			441841096521400 Big Sioux River below wastewater wetland, near Volga, SD (VL-DS1)			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)		441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)		441316096483300 Big Sioux River below wastewater effluent, near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)	
Date of sample collection	08-21-2003	10-21-2003	06-16-2004	08-21-2003	10-22-2003	06-16-2004	08-21-2003	06-17-2004	08-22-2003	06-17-2004	08-22-2003	06-18-2004	08-22-2003	06-17-2004
Time of sample collection	0900	1240	1435	1100	0935	1615	1230	1140	0915	0950	1015	1215	1140	1645
Property or constituent														
Discharge, instantaneous (ft^3/s)	--	e.6	<.2	11.4	9.7	130	3.18	129	e1.7	e5.6	9.89	284	12.1	256
Turbidity (NTU)	--	15.0	16.6	--	36.0	--	--	34.4	--	3.8	--	29.0	--	22.6
Barometric pressure (mm Hg)	724	723	725	726	726	728	726	729	729	729	729	733	729	728
Dissolved oxygen (mg/L)	.3	2.8	.8	7.3	9.6	8.4	10.1	8.4	8.9	10.1	7.1	7.3	10.5	10.4
pH (standard units)	9.1	8.0	7.9	8.4	7.8	8.1	8.6	7.9	7.3	7.5	8.2	8.0	8.6	8.1
Specific conductance (µS/cm)	6,890	6,600	3,650	885	1,240	843	878	861	1,630	1,420	1,066	956	1,060	921
Air temperature (°C)	22.0	19.0	19.0	20.0	6.5	19.0	28.0	20.5	23.0	20.0	23.0	11.0	25.0	27.0
Water temperature (°C)	23.0	12.2	18.9	23.6	10.3	20.2	25.5	18.9	19.7	15.4	20.0	17.3	21.9	21.1
Nitrite plus nitrate nitrogen (mg/L)	<.060	.077	<.060	<.060	<.060	.181	<.060	.233	22.9	17.2	3.07	.533	3.94	.448
Total coliform concentration, most probable number (col/100 mL)	90,000	5,000	300	3,000	500	1,300	2,300	1,300	LE	80	LE	LE	LE	800
Fecal coliform concentration, membrane filter (col/100 mL)	2,600	360	<10	180	40	610	550	340	LE	10	LE	LE	LE	60

Table 18. Analytical results for human pharmaceutical compounds (HPCs).

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. ND, not determined; UD, undetected, laboratory reporting level not determined; <, less than; e, estimated]

	Analytical method number	Study reporting level	Station identification and name (site label)					
			06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)	
Date of sample collection			08-18-2003	06-15-2004	08-18-2003	06-15-2004	08-19-2003	06-16-2004
Time of sample collection			1045	1030	1200	1200	1305	0925
Compound								
1,7-dimethylxanthine, dissolved	1	0.05	<0.144	<0.144	<0.144	<0.144	<0.144	<0.144
Acetaminophen, dissolved	1	ND	.129	e.0094	<.036	e.0031	<.036	<.036
Caffeine, dissolved	1	.022	<.016	<.016	<.016	<.016	e.0069	<.016
Caffeine, whole water	3	.12	<.5	<.5	<.5	<.5	<.5	<.5
Carbamazepine, dissolved	1	ND	<.011	<.011	<.011	<.011	.091	.073
Cimetidine, dissolved	1	ND	<.012	<.012	<.012	<.012	.033	.14
Codeine, dissolved	1	ND	<.015	<.015	<.015	<.015	.036	.022
Cotinine, dissolved	1	.0008	e.0047	<.014	e.0027	<.014	.049	.017
Cotinine, whole water	3	.18	<1	<1	<1	<1	<1	<1
Dehydronifedipine, dissolved	1	.0035	<.015	<.015	<.015	<.015	e.0035	<.015
Diltiazem, dissolved	1	ND	<.016	<.016	<.016	<.016	.030	.057
Diphenhydramine, dissolved	1	ND	<.015	<.015	<.015	e.0085	.062	.084
Fluoxetine, dissolved	1	ND	<.014	<.014	<.014	<.014	<.014	<.014
Furosemide, dissolved	1	ND	<.039	<.039	<.039	<.039	<.039	<.039
Gemfibrozil, dissolved	1	ND	<.013	<.013	<.013	<.013	<.013	<.013
Ibuprofen, dissolved	1	ND	<.042	<.042	<.042	<.042	<.042	<.042
Metformin, dissolved	1	ND	UD	UD	UD	UD	UD	UD
Miconazole, dissolved	1	ND	<.018	<.018	<.018	<.018	<.018	<.018
Ranitidine, dissolved	1	ND	<.013	<.013	<.013	<.013	.038	.16
Salbutamol, dissolved	1	.0054	<.023	<.023	<.023	<.023	.034	.036
Thiabendazole, dissolved	1	ND	<.011	<.011	<.011	<.011	<.011	<.011
Warfarin, dissolved	1	ND	<.012	<.012	<.012	<.012	<.012	<.012

Table 18. Analytical results for human pharmaceutical compounds (HPCs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. ND, not detected, laboratory reporting level not determined; <, less than; e, estimated]

	Analytical method number	Study reporting level	Station identification and name (site label)						
			445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)		06479520 Big Sioux River below Watertown, SD (WT-DS2)		442026096533600 Big Sioux River near Volga, SD (VL-US1)		
Date of sample collection			08-19-2003	06-15-2004	08-20-2003	06-15-2004	08-20-2003	10-21-2003	06-16-2004
Time of sample collection			0930	1730	0915	1825	1400	1105	1145
Compound									
1,7-dimethylxanthine, dissolved	1	0.05	<0.144	<0.144	<0.144	<0.144	<0.144	<0.144	<0.144
Acetaminophen, dissolved	1	ND	e.002	e.014	e.011	e.0060	<.036	<.036	e.021
Caffeine, dissolved	1	.022	.087	<.016	e.0092	e.0095	<.016	<.016	.030
Caffeine, whole water	3	.12	e.24	<.5	<.5	<.5	<.5	e.011	<.5
Carbamazepine, dissolved	1	ND	.023	e.0069	.078	<.011	<.011	.023	<.011
Cimetidine, dissolved	1	ND	<.012	e.0054	.017	<.012	<.012	<.012	<.012
Codeine, dissolved	1	ND	.015	<.015	.020	<.015	<.015	<.015	<.015
Cotinine, dissolved	1	.0008	.039	e.0066	.042	e.0051	.035	e.022	e.007
Cotinine, whole water	3	.18	<1	<1	<1	<1	<1	e.18	<1
Dehydronifedipine, dissolved	1	.0035	<.015	<.015	e.0039	<.015	<.015	<.015	<.015
Diltiazem, dissolved	1	ND	<.016	e.010	<.016	e.0030	<.016	<.016	<.016
Diphenhydramine, dissolved	1	ND	<.015	e.0027	<.015	e.0035	<.015	<.015	e.0013
Fluoxetine, dissolved	1	ND	<.014	<.014	<.014	<.014	<.014	<.014	<.014
Furosemide, dissolved	1	ND	<.039	<.039	<.039	<.039	<.039	<.039	<.039
Gemfibrozil, dissolved	1	ND	<.013	<.013	<.013	<.013	<.013	<.013	<.013
Ibuprofen, dissolved	1	ND	<.042	<.042	<.042	<.042	<.042	<.042	<.042
Metformin, dissolved	1	ND	UD	UD	UD	UD	UD	UD	UD
Miconazole, dissolved	1	ND	<.018	<.018	<.018	<.018	<.018	<.018	<.018
Ranitidine, dissolved	1	ND	<.013	.020	<.013	<.013	<.013	<.013	<.013
Salbutamol, dissolved	1	.0054	e.0054	<.023	e.0090	<.023	<.023	<.023	<.023
Thiabendazole, dissolved	1	ND	.011	<.011	<.011	<.011	<.011	<.011	<.011
Warfarin, dissolved	1	ND	<.012	<.012	<.012	<.012	<.012	<.012	<.012

Table 18. Analytical results for human pharmaceutical compounds (HPCs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. ND, not detected, laboratory reporting level not determined; <, less than; e, estimated]

	Analytical method number	Study reporting level	Station identification and name (site label)					
			441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)			441841096521400 Big Sioux River below wastewater wetland, near Volga, SD (VL-DS1)		
Date of sample collection			08-21-2003	10-21-2003	06-16-2004	08-21-2003	10-22-2003	06-16-2004
Time of sample collection			0900	1240	1435	1100	0935	1615
Compound								
1,7-dimethylxanthine, dissolved	1	0.05	<0.144	<0.144	<0.144	<0.144	e0.049	<0.144
Acetaminophen, dissolved	1	ND	<.036	<.036	.20	<.036	.058	<.036
Caffeine, dissolved	1	.022	<.016	<.016	.075	<.016	.073	<.016
Caffeine, whole water	3	.12	<.5	e.034	<.5	<.5	<.5	<.5
Carbamazepine, dissolved	1	ND	.019	.019	<.011	.015	.021	<.011
Cimetidine, dissolved	1	ND	<.012	<.012	<.012	<.012	<.012	<.012
Codeine, dissolved	1	ND	<.015	<.015	<.015	<.015	<.015	<.015
Cotinine, dissolved	1	.0008	.049	e.0188	e.0089	.038	.024	e.003
Cotinine, whole water	3	.18	<1	<1	<1	<1	<1	<1
Dehydronifedipine, dissolved	1	.0035	<.015	<.015	<.015	<.015	<.015	<.015
Diltiazem, dissolved	1	ND	<.016	<.016	<.016	<.016	<.016	<.016
Diphenhydramine, dissolved	1	ND	<.015	<.015	<.015	<.015	<.015	e.0006
Fluoxetine, dissolved	1	ND	<.014	<.014	<.014	<.014	<.014	<.014
Furosemide, dissolved	1	ND	<.039	<.039	<.039	<.039	<.039	<.039
Gemfibrozil, dissolved	1	ND	<.013	<.013	<.013	<.013	<.013	<.013
Ibuprofen, dissolved	1	ND	<.042	<.042	<.042	<.042	<.042	<.042
Metformin, dissolved	1	ND	UD	UD	UD	UD	UD	UD
Miconazole, dissolved	1	ND	<.018	<.018	<.018	<.018	<.018	<.018
Ranitidine, dissolved	1	ND	<.013	<.013	<.013	<.013	<.013	<.013
Salbutamol, dissolved	1	.0054	<.023	<.023	<.023	<.023	<.023	<.023
Thiabendazole, dissolved	1	ND	<.011	<.011	<.011	<.011	<.011	<.011
Warfarin, dissolved	1	ND	<.012	<.012	<.012	<.012	<.012	<.012

Table 18. Analytical results for human pharmaceutical compounds (HPCs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. ND, not detected, laboratory reporting level not determined; <, less than; e, estimated]

	Analytical method number	Study reporting level	Station identification and name (site label)							
			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)		441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)		441316096483300 Big Sioux River below wastewater effluent, near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)	
Date of sample collection			08-21-2003	06-17-2004	08-22-2003	06-17-2004	08-22-2003	06-18-2004	08-22-2003	06-17-2004
Time of sample collection			1230	1140	0915	0950	1015	1215	1140	1645
Compound										
1,7-dimethylxanthine, dissolved	1	0.05	<0.144	<0.144	<0.144	<0.144	<0.144	<0.144	<0.144	<0.144
Acetaminophen, dissolved	1	ND	e.014	<.036	<.036	<.036	<.036	.48	<.036	<.036
Caffeine, dissolved	1	.022	.029	<.016	<.016	<.016	<.016	.048	<.016	<.016
Caffeine, whole water	3	.12	<.5	e.13	<.5	<.5	<.5	<.5	<.5	<.5
Carbamazepine, dissolved	1	ND	.013	<.011	.24	.18	.053	<.011	.075	<.011
Cimetidine, dissolved	1	ND	<.012	<.012	<.012	<.012	<.012	<.012	<.012	<.012
Codeine, dissolved	1	ND	<.015	<.015	e.0047	<.015	<.015	<.015	<.015	<.015
Cotinine, dissolved	1	.0008	.033	<.014	e.021	.022	.030	e.0023	.030	e.0011
Cotinine, whole water	3	.18	<1	<1	<1	<1	<1	<1	<1	<1
Dehydronifedipine, dissolved	1	.0035	<.015	<.015	e.0052	<.015	<.015	<.015	<.015	<.015
Diltiazem, dissolved	1	ND	<.016	<.016	<.016	e.0004	<.016	<.016	<.016	<.016
Diphenhydramine, dissolved	1	ND	<.015	<.015	.059	.068	<.015	<.015	<.015	<.015
Fluoxetine, dissolved	1	ND	<.014	<.014	<.014	<.014	<.014	<.014	<.014	<.014
Furosemide, dissolved	1	ND	<.039	<.039	<.039	<.039	<.039	<.039	<.039	<.039
Gemfibrozil, dissolved	1	ND	<.013	<.013	<.013	<.013	<.013	<.013	<.013	<.013
Ibuprofen, dissolved	1	ND	<.042	<.042	<.042	<.042	<.042	<.042	<.042	<.042
Metformin, dissolved	1	ND	UD	UD	UD	UD	UD	UD	UD	UD
Miconazole, dissolved	1	ND	<.018	<.018	<.018	<.018	<.018	<.018	<.018	<.018
Ranitidine, dissolved	1	ND	<.013	<.013	<.013	<.013	<.013	<.013	<.013	<.013
Salbutamol, dissolved	1	.0054	<.023	<.023	<.023	<.023	<.023	<.023	<.023	<.023
Thiabendazole, dissolved	1	ND	<.011	<.011	<.011	<.011	<.011	<.011	<.011	<.011
Warfarin, dissolved	1	ND	<.012	<.012	<.012	<.012	<.012	<.012	<.012	<.012

Table 19. Analytical results for human and veterinary antibiotic compounds (HVACs).

[Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. All compounds are dissolved. <, less than; e, estimated; ND, not determined]

	Analytical method number	Study reporting level	Station identification and name (site label)					
			06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)	
Date of sample collection			08-18-2003	06-15-2004	08-18-2003	06-15-2004	08-19-2003	06-16-2004
Time of sample collection			1045	1030	1200	1200	1305	0925
Compound								
Amoxicilin	2	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ampicillin	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Anhd-Cl-tetracycline	2	.3	<.01	<.01	<.01	<.01	<.01	<.01
Anhydrotetracycline	2	.15	<.01	<.01	<.01	<.01	<.01	<.01
Azithromycin	1	ND	<.004	<.004	<.004	<.004	<.004	<.004
Cefotaxime	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Chlorotetracycline	2	.05	<.01	<.01	<.01	<.01	<.01	<.01
Ciprofloxacin	2	.036	<.005	<.005	<.005	<.005	.17	.17
Clinafloxacin	2	.01	<.005	<.005	<.005	<.005	<.005	<.005
Cloxacillin	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Demeclocycline	2	.08	<.01	<.01	<.01	<.01	<.01	<.01
Doxycycline	2	.05	<.01	<.01	<.01	<.01	<.01	.012
Erythromycin (method 1)	1	ND	<.009	<.009	<.009	<.009	<.009	<.009
Erythromycin (method 2)	2	.025	<.005	<.005	<.005	<.005	<.005	1.3
Erythromycin-H_2O	2	.046	<.005	<.005	<.005	<.005	1.7	5.7
Flumequine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Lincomycin	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Lomefloxacin	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Minocycline	2	.25	<.01	<.01	<.01	<.01	<.01	<.01
Norfloxacin	2	.02	<.005	<.005	<.005	<.005	<.005	.064
Ofloxacin	2	.03	<.005	<.005	<.005	<.005	.97	.34
Ormetoprim	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Oxacillin	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Oxolinic acid	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Oxytetracycline	2	.15	<.01	<.01	<.01	<.01	<.01	<.01
Penicillin G	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Penicillin V	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Roxithromycin	2	.005	<.005	<.005	<.005	<.005	<.005	.016
Sarafloxacin	2	.03	<.005	<.005	<.005	<.005	<.005	<.005
Sulfachlorpyridazine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfadiazine	2	.005	<.005	<.005	<.005	<.005	<.005	.16
Sulfadimethoxine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfamerazine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfamethazine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfamethoxazole (method 1)	1	ND	<.064	<.064	<.064	<.064	<.064	.16
Sulfamethoxazole (method 2)	2	.02	<.005	<.005	<.005	<.005	1.2	.79
Sulfathiazole	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Tetracycline	2	.064	<.01	<.01	<.01	<.01	<.01	.087
Trimethoprim (method 1)	1	ND	<.013	<.013	<.013	<.013	.047	.30
Trimethoprim (method 2)	2	.02	<.005	<.005	<.005	<.005	<.005	.37
Tylosin	2	.07	<.005	<.005	<.005	<.005	<.005	<.005
Virginiamycin	2	.005	<.005	<.005	<.005	<.005	<.005	<.005

Table 19. Analytical results for human and veterinary antibiotic compounds (HVACs).—Continued

[Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. All compounds are dissolved. <, less than; e, estimated; ND, not determined]

	Analytical method number	Study reporting level	Station identification and name (site label)						
			445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)		06479520 Big Sioux River below Watertown, SD (WT-DS2)		442026096533600 Big Sioux River near Volga, SD (VL-US1)		
Date of sample collection			08-19-2003	06-15-2004	08-20-2003	06-15-2004	08-20-2003	10-21-2003	06-16-2004
Time of sample collection			0930	1730	0915	1825	1400	1105	1145
Compound									
Amoxicilin	2	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ampicillin	2	.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Anhd-Cl-tetracycline	2	.3	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Anhydrotetracycline	2	.15	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Azithromycin	1	ND	<.004	<.004	<.004	<.004	<.004	<.004	<.004
Cefotaxime	2	.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Chlorotetracycline	2	.05	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Ciprofloxacin	2	.036	<.005	.036	<.005	<.005	<.005	<.005	<.005
Clinafloxacin	2	.01	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Cloxacillin	2	.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Demeclocycline	2	.08	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Doxycycline	2	.05	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Erythromycin (method 1)	1	ND	<.009	<.009	<.009	<.009	<.009	<.009	<.009
Erythromycin (method 2)	2	.025	<.005	.25	<.005	.081	<.005	<.005	<.005
Erythromycin-H_2O	2	.046	.31	.85	.16	.30	<.005	<.005	.060
Flumequine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Lincomycin	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Lomefloxacin	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Minocycline	2	.25	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Norfloxacin	2	.02	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Ofloxacin	2	.03	.27	.067	<.005	<.005	<.005	<.005	<.005
Ormetoprim	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Oxacillin	2	.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Oxolinic acid	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Oxytetracycline	2	.15	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Penicillin G	2	.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Penicillin V	2	.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Roxithromycin	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Sarafloxacin	2	.03	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfachlorpyridazine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfadiazine	2	.005	<.005	<.005	<.005	.044	<.005	<.005	<.005
Sulfadimethoxine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfamerazine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfamethazine	2	.005	<.005	<.005	<.005	.0060	<.005	<.005	<.005
Sulfamethoxazole (method 1)	1	ND	<.064	<.064	e.042	<.064	<.064	<.064	<.064
Sulfamethoxazole (method 2)	2	.02	.56	.22	.67	.12	<.005	<.005	.014
Sulfathiazole	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Tetracycline	2	.064	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Trimethoprim (method 1)	1	ND	.013	.049	.016	e.010	<.013	<.013	<.013
Trimethoprim (method 2)	2	.02	<.005	.11	<.005	.042	<.005	<.005	<.005
Tylosin	2	.07	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Virginiamycin	2	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005

Table 19. Analytical results for human and veterinary antibiotic compounds (HVACs).—Continued

[Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. All compounds are dissolved. <, less than; e, estimated; ND, not determined]

	Analytical method number	Study reporting level	Station identification and name (site label)					
			441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)			441841096521400 Big Sioux River below wastewater wetland, near Volga, SD (VL-DS1)		
Date of sample collection			08-21-2003	10-21-2003	06-16-2004	08-21-2003	10-22-2003	06-16-2004
Time of sample collection			0900	1240	1435	1100	0935	1615
Compound								
Amoxicilin	2	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ampicillin	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Anhd-Cl-tetracycline	2	.3	<.01	<.01	<.01	<.01	<.01	<.01
Anhydrotetracycline	2	.15	<.01	<.01	<.01	<.01	<.01	<.01
Azithromycin	1	ND	<.004	<.004	<.004	<.004	<.004	<.004
Cefotaxime	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Chlorotetracycline	2	.05	<.01	<.01	<.01	<.01	<.01	<.01
Ciprofloxacin	2	.036	<.005	<.005	<.005	<.005	<.005	<.005
Clinafloxacin	2	.01	<.005	<.005	<.005	<.005	<.005	<.005
Cloxacillin	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Demeclocycline	2	.08	<.01	<.01	<.01	<.01	<.01	<.01
Doxycycline	2	.05	<.01	<.01	<.01	<.01	<.01	<.01
Erythromycin (method 1)	1	ND	<.009	<.009	<.009	<.009	<.009	<.009
Erythromycin (method 2)	2	.025	<.005	<.005	.043	<.005	<.005	.014
Erythromycin-H_2O	2	.046	<.005	<.005	.071	<.005	<.005	.063
Flumequine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Lincomycin	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Lomefloxacin	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Minocycline	2	.25	<.01	<.01	<.01	<.01	<.01	<.01
Norfloxacin	2	.02	<.005	<.005	<.005	<.005	<.005	<.005
Ofloxacin	2	.03	<.005	<.005	<.005	<.005	<.005	<.005
Ormetoprim	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Oxacillin	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Oxolinic acid	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Oxytetracycline	2	.15	<.01	<.01	<.01	<.01	<.01	<.01
Penicillin G	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Penicillin V	2	.01	<.01	<.01	<.01	<.01	<.01	<.01
Roxithromycin	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Sarafloxacin	2	.03	<.005	<.005	<.005	<.005	<.005	<.005
Sulfachlorpyridazine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfadiazine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfadimethoxine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfamerazine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfamethazine	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Sulfamethoxazole (method 1)	1	ND	<.064	<.064	<.064	<.064	<.064	<.064
Sulfamethoxazole (method 2)	2	.02	<.005	<.005	<.005	<.005	<.005	.012
Sulfathiazole	2	.005	<.005	<.005	<.005	<.005	<.005	<.005
Tetracycline	2	.064	<.01	<.01	<.01	<.01	<.01	<.01
Trimethoprim (method 1)	1	ND	<.013	<.013	<.013	<.013	<.013	<.013
Trimethoprim (method 2)	2	.02	<.005	<.005	<.005	<.005	<.005	.0060
Tylosin	2	.07	<.005	<.005	<.005	<.005	<.005	<.005
Virginiamycin, dissolved	2	.005	<.005	<.005	<.005	<.005	<.005	<.005

Table 19. Analytical results for human and veterinary antibiotic compounds (HVACs).—Continued

[Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. All compounds are dissolved. <, less than; e, estimated; ND, not determined]

	Analytical method number	Study reporting level	Station identification and name (site label)			
			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)		441434096482500 Brookings wastwater effluent near Brookings, SD (BK-WWE)	
Date of sample collection			08-21-2003	06-17-2004	08-22-2003	06-17-2004
Time of sample collection			1230	1140	0915	0950
Compound						
Amoxicilin	2	0.05	<0.01	<0.01	<0.01	<0.01
Ampicillin	2	.01	<.01	<.01	<.01	<.01
Anhd-Cl-tetracycline	2	.3	<.01	<.01	<.01	<.01
Anhydrotetracycline	2	.15	<.01	<.01	<.01	<.01
Azithromycin	1	ND	<.004	<.004	<.004	<.004
Cefotaxime	2	.01	<.01	<.01	<.01	<.01
Chlorotetracycline	2	.05	<.01	<.01	<.01	<.01
Ciprofloxacin	2	.036	<.005	<.005	<.005	.051
Clinafloxacin	2	.01	<.005	<.005	<.005	<.005
Cloxacillin	2	.01	<.01	<.01	<.01	<.01
Demeclocycline	2	.08	<.01	<.01	<.01	<.01
Doxycycline	2	.05	<.01	<.01	<.01	<.01
Erythromycin (method 1)	1	ND	<.009	<.009	<.009	<.009
Erythromycin (method 2)	2	.025	<.005	<.005	<.005	.71
Erythromycin-H_2O	2	.046	<.005	.048	<.005	2.0
Flumequine	2	.005	<.005	<.005	<.005	<.005
Lincomycin	2	.005	<.005	<.005	<.005	<.005
Lomefloxacin	2	.005	<.005	<.005	<.005	<.005
Minocycline	2	.25	<.01	<.01	<.01	<.01
Norfloxacin	2	.02	<.005	<.005	<.005	<.005
Ofloxacin	2	.03	<.005	<.005	<.005	.051
Ormetoprim	2	.005	<.005	<.005	<.005	<.005
Oxacillin	2	.01	<.01	<.01	<.01	<.01
Oxolinic acid	2	.005	<.005	<.005	<.005	<.005
Oxytetracycline	2	.15	<.01	<.01	<.01	<.01
Penicillin G	2	.01	<.01	<.01	<.01	<.01
Penicillin V	2	.01	<.01	<.01	<.01	<.01
Roxithromycin	2	.005	<.005	<.005	<.005	<.005
Sarafloxacin	2	.03	<.005	<.005	<.005	<.005
Sulfachlorpyridazine	2	.005	<.005	<.005	<.005	<.005
Sulfadiazine	2	.005	<.005	<.005	<.005	.084
Sulfadimethoxine	2	.005	<.005	<.005	<.005	<.005
Sulfamerazine	2	.005	<.005	<.005	<.005	<.005
Sulfamethazine	2	.005	<.005	<.005	<.005	.01
Sulfamethoxazole (method 1)	1	ND	<.064	<.064	<.064	.14
Sulfamethoxazole (method 2)	2	.02	<.005	.013	<.005	.50
Sulfathiazole	2	.005	<.005	<.005	<.005	<.005
Tetracycline	2	.064	<.01	<.01	<.01	<.01
Trimethoprim (method 1)	1	ND	<.013	<.013	.013	.11
Trimethoprim (method 2)	2	.02	<.005	<.005	<.005	.16
Tylosin	2	.07	<.005	<.005	<.005	<.005
Virginiamycin	2	.005	<.005	<.005	<.005	<.005

Table 19. Analytical results for human and veterinary antibiotic compounds (HVACs).—Continued

[Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. All compounds are dissolved. <, less than; e, estimated; ND, not determined]

	Analytical method number	Study reporting level	Station identification and name (site label)			
			441316096483300 Big Sioux River below wastewater effluent, near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)	
Date of sample collection			08-22-2003	06-18-2004	08-22-2003	06-17-2004
Time of sample collection			1015	1215	1140	1645
Compound						
Amoxicilin	2	0.05	<0.01	<0.01	<0.01	<0.01
Ampicillin	2	.01	<.01	<.01	<.01	<.01
Anhd-Cl-tetracycline	2	.3	<.01	<.01	<.01	<.01
Anhydrotetracycline	2	.15	<.01	<.01	<.01	<.01
Azithromycin	1	ND	<.004	<.004	<.004	<.004
Cefotaxime	2	.01	<.01	<.01	<.01	<.01
Chlorotetracycline	2	.05	<.01	<.01	<.01	<.01
Ciprofloxacin	2	.036	<.005	<.005	<.005	<.005
Clinafloxacin	2	.01	<.005	<.005	<.005	<.005
Cloxacillin	2	.01	<.01	<.01	<.01	<.01
Demeclocycline	2	.08	<.01	<.01	<.01	<.01
Doxycycline	2	.05	<.01	<.01	<.01	<.01
Erythromycin (method 1)	1	ND	<.009	<.009	<.009	<.009
Erythromycin (method 2)	2	.025	<.005	.017	<.005	.017
Erythromycin-H_2O	2	.046	<.005	.065	<.005	.060
Flumequine	2	.005	<.005	<.005	<.005	<.005
Lincomycin	2	.005	<.005	<.005	<.005	<.005
Lomefloxacin	2	.005	<.005	<.005	<.005	<.005
Minocycline	2	.25	<.01	<.01	<.01	<.01
Norfloxacin	2	.02	<.005	<.005	<.005	<.005
Ofloxacin	2	.03	<.005	<.005	<.005	<.005
Ormetoprim	2	.005	<.005	<.005	<.005	<.005
Oxacillin	2	.01	<.01	<.01	<.01	<.01
Oxolinic acid	2	.005	<.005	<.005	<.005	<.005
Oxytetracycline	2	.15	<.01	<.01	<.01	<.01
Penicillin G	2	.01	<.01	<.01	<.01	<.01
Penicillin V	2	.01	<.01	<.01	<.01	<.01
Roxithromycin	2	.005	<.005	<.005	<.005	<.005
Sarafloxacin	2	.03	<.005	<.005	<.005	<.005
Sulfachlorpyridazine	2	.005	<.005	<.005	<.005	<.005
Sulfadiazine	2	.005	<.005	<.005	<.005	<.005
Sulfadimethoxine	2	.005	<.005	<.005	<.005	<.005
Sulfamerazine	2	.005	<.005	<.005	<.005	<.005
Sulfamethazine	2	.005	<.005	<.005	<.005	<.005
Sulfamethoxazole (method 1)	1	ND	<.064	<.064	<.064	<.064
Sulfamethoxazole (method 2)	2	.02	<.005	.014	<.005	.020
Sulfathiazole	2	.005	<.005	<.005	<.005	<.005
Tetracycline	2	.064	<.01	<.01	<.01	<.01
Trimethoprim (method 1)	1	ND	<.013	<.013	<.013	<.013
Trimethoprim (method 2)	2	.02	<.005	<.005	<.005	<.005
Tylosin	2	.07	<.005	<.005	<.005	<.005
Virginiamycin	2	.005	<.005	<.005	<.005	<.005

Table 20. Analytical results for major agricultural herbicides (MAHs).

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)							
			06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)		445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)	
Date of sample collection			08-18-2003	06-15-2004	08-18-2003	06-15-2004	08-19-2003	06-16-2004	08-19-2003	06-15-2004
Time of sample collection			1045	1030	1200	1200	1305	0925	0930	1730
Compound										
Atrazine	3	0.0002	e0.10	e0.21	<0.5	e0.19	<0.5	e0.18	<0.5	e0.16
Metolachlor	3	.028	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Prometon	3	.02	<.5	<.5	<.5	<.5	e.068	<.5	e.10	<.5

	Analytical method number	Study reporting level	Station identification and name (site label)							
			06479520 Big Sioux River below Watertown, SD (WT-DS2)		442026096533600 Big Sioux River near Volga, SD (VL-US1)			441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)		
Date of sample collection			08-20-2003	06-15-2004	08-20-2003	10-21-2003	06-16-2004	08-21-2003	10-21-2003	06-16-2004
Time of sample collection			0915	1825	1400	1105	1145	0900	1240	1435
Compound										
Atrazine	3	0.0002	<0.5	e0.26	<0.5	e0.050	0.95	e0.055	e0.059	e0.18
Metolachlor	3	.028	<.5	<.5	<.5	<.5	e.035	<.5	<.5	<.5
Prometon	3	.02	e.068	<.5	e.093	e.055	<.5	<.5	<.5	<.5

	Analytical method number	Study reporting level	Station identification and name (site label)				
			441841096521400 Big Sioux River below wastewater wetland, near Volga, SD (VL-DS1)			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)	
Date of sample collection			08-21-2003	10-22-2003	06-16-2004	08-21-2003	06-17-2004
Time of sample collection			1100	0935	1615	1230	1140
Compound							
Atrazine	3	0.0002	<0.5	e0.050	1.5	<0.5	1.2
Metolachlor	3	.028	<.5	<.5	e.055	<.5	e.035
Prometon	3	.02	e.076	e.061	e.069	e.095	<.5

	Analytical method number	Study reporting level	Station identification and name (site label)					
			441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)		441316096483300 Big Sioux River below Wastewater effluent, near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)	
Date of sample collection			08-22-2003	06-17-2004	08-22-2003	06-18-2004	08-22-2003	06-17-2004
Time of sample collection			0915	0950	1015	1215	1140	1645
Compound								
Atrazine	3	0.0002	<0.5	e0.086	<0.5	0.84	<0.5	1.3
Metolachlor	3	.028	<.5	<.5	<.5	e.030	<.5	e.028
Prometon	3	.02	e.05	<.5	e.081	e.044	e.099	<.5

Table 21. Analytical results for household, industrial, and minor agricultural-use compounds (HIACs).

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)							
			06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)		445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)	
Date of sample collection			08-18-2003	06-15-2004	08-18-2003	06-15-2004	08-19-2003	06-16-2004	08-19-2003	06-15-2004
Time of sample collection			1045	1030	1200	1200	1305	0925	0930	1730
Compound										
1,4-dichlorobenzene, whole water	3	ND	<0.5	<0.5	<0.5	<0.5	e0.068	e0.28	<0.5	<0.5
2,2′,4,4′-tetrabromodiphenyl ether, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
3,4-dichlorophenyl isocyanate, whole water	3	ND	<.5	<.5	<.5	<.5	<.5	e0.16	<.5	<.5
3-methyl-1H-indole (skatol), whole water	3	.02	<1	<1	<1	<1	<1	<1	<1	<1
3-*tert*-butyl-4-hydroxy anisole (BHA), whole water	3	ND	<5	<5	<5	<5	<5	<5	<5	<5
4-cumylphenol, whole water	3	1	<1	<1	<1	<1	<1	<1	<1	<1
4-*normal*-octylphenol, whole water	3	1	<1	<1	<1	<1	<1	<1	<1	<1
4-*tert*-octylphenol, whole water	3	.26	<1	<1	<1	<1	<1	<1	e.14	<1
5-methyl-1H-benzotriazole, whole water	3	.33	<2	<2	<2	<2	e.45	e.89	<2	<2
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN), whole water	3	.048	<.5	<.5	<.5	<.5	1.1	1.6	.59	.51
Acetophenone, whole water	3	.08	<.5	<.5	<.5	<.5	e.12	<.5	e.18	<.5
Anthraquinone, whole water	3	.96	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Benzophenone, whole water	3	.025	<.5	<.5	<.5	<.5	e.078	e.091	e.068	<.5
Bis(2-ethylhexyl) phthalate, whole water	3	ND	<2	7.2	<2	<2	e1.9	<2	<2	<2
Bisphenol-A, whole water	3	.069	e.19	<1	<1	<1	<1	<1	<1	<1
Bromacil, whole water	3	.068	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Camphor, whole water	3	.07	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Carbaryl, whole water	3	ND	<1	<1	<1	<1	<1	<1	<1	<1
Chlorpyrifos, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
N,N-diethyl-*meta*-toluamide (DEET), whole water	3	.08	e.11	<.5	e.058	<.5	e.083	e.090	e.11	e.052
Diazinon, whole water	3	.027	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Dichlorvos, whole water	3	1	<1	<1	<1	<1	<1	<1	<1	<1
Diethyl phthalate, whole water	3	.55	<.5	<.5	.55	<.5	<.5	<.5	<.5	<.5
D-Limonene, whole water	3	ND	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5

Table 21. Analytical results for household, industrial, and minor agricultural-use compounds (HIACs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)							
			06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)		445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)	
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), whole water	3	0.032	<0.5	<0.5	<0.5	<0.5	e0.19	e0.16	e0.11	e0.060
Indole, whole water	3	.015	e.036	<.5	<.5	<.5	e.034	<.5	e.043	<.5
Isoborneol, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Isophorone, whole water	3	.047	e.050	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Isoquinoline, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Menthol, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Metalaxyl, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Methyl salicylate, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Nonylphenol diethoxylate (NP2EO), whole water	3	.55	<5	<5	<5	<5	<5	e.91	<5	e.55
Nonylphenol monoethoxylate (NP1EO), whole water	3	.39	<2	<2	<2	<2	<2	e.54	<2	e.39
Octylphenol diethoxylate (OP2EO), whole water	3	.14	<1	<1	<1	<1	<1	<1	<1	<1
Octylphenol monoethoxylate (OP1EO), whole water	3	1	<1	<1	<1	<1	<1	<1	<1	<1
para-cresol, whole water	3	.03	<1	<1	<1	<1	e.084	<1	<1	<1
***para*-nonylphenol (NP)**, whole water	3	.64	<5	<5	<5	<5	<5	e.84	<5	e.84
Pentachlorophenol, whole water	3	2	<2	<2	<2	<2	<2	<2	<2	<2
Phenol, whole water	3	.94	<.5	<.5	<.5	<.5	<.5	<.5	e0.22	<.5
Tetrachloroethylene, whole water	3	ND	<.5	<.5	<.5	<.5	<.5	e.41	<.5	e.22
Tributyl phosphate, whole water	3	.02	<.5	<.5	e.046	<.5	e.15	e.11	e.11	e.054
Triclosan, whole water	3	.084	<1	<1	<1	<1	e.15	<1	e.096	<1
Triethyl citrate (ethyl citrate), whole water	3	.048	<.5	<.5	<.5	<.5	e.34	e.35	e.20	e.097
Triphenyl phosphate, whole water	3	.015	<.5	<.5	<.5	<.5	e.047	e.063	e.024	<.5
Tri(2-butoxyethyl)phosphate, whole water	3	.13	<.5	<.5	e.35	<.5	e.23	<.5	.63	e.35
Tri(2-chloroethyl)phosphate, whole water	3	.056	<.5	<.5	<.5	<.5	28	e.35	12	e.13
Tri(dichloroisopropyl)phosphate, whole water	3	.047	<.5	<.5	<.5	<.5	e.49	e.30	e.28	<.5

Table 21. Analytical results for household, industrial, and minor agricultural-use compounds (HIACs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)							
			06479520 Big Sioux River below Watertown, SD (WT-DS2)		442026096533600 Big Sioux River near Volga, SD (VL-US1)			441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)		
Date of sample collection			08-20-2003	06-15-2004	08-20-2003	10-21-2003	06-16-2004	08-21-2003	10-21-2003	06-16-2004
Time of sample collection			0915	1825	1400	1105	1145	0900	1240	1435
Compound										
1,4-dichlorobenzene, whole water	3	ND	<0.5	<0.5	e0.47	e0.083	<0.5	<0.5	<0.5	<0.5
2,2′,4,4′-tetrabromodiphenyl ether, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
3,4-dichlorophenyl isocyanate, whole water	3	ND	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
3-methyl-1H-indole (skatol), whole water	3	.02	<1	<1	<1	<1	<1	<1	<1	<1
3-*tert*-butyl-4-hydroxy anisole (BHA), whole water	3	ND	<5	<5	e.16	<5	<5	<5	<5	<5
4-cumylphenol, whole water	3	1	<1	<1	<1	<1	<1	<1	<1	<1
4-*normal*-octylphenol, whole water	3	1	<1	<1	<1	<1	<1	<1	<1	<1
4-*tert*-octylphenol, whole water	3	.26	<1	<1	e.14	<1	<1	<1	e.091	<1
5-methyl-1H-benzotriazole, whole water	3	.33	<2	<2	<2	<2	<2	<2	e.36	<2
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN), whole water	3	.048	e.053	e.16	<.5	<.5	<.5	<.5	<.5	<.5
Acetophenone, whole water	3	.08	e.082	<.5	<.5	e.23	<.5	<.5	e.18	<.5
Anthraquinone, whole water	3	.96	<.5	<.5	<.5	<.5	<.5	e.092	<.5	<.5
Benzophenone, whole water	3	.025	e.064	<.5	<.5	<.5	<.5	e.029	<.5	<.5
Bis(2-ethylhexyl) phthalate, whole water	3	ND	<2	<2	<2	<2	<2	<2	<2	<2
Bisphenol-A, whole water	3	.069	e.087	<1	e.069	<1	<1	<1	e.072	<1
Bromacil, whole water	3	.068	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Camphor, whole water	3	.07	<.5	<.5	<.5	<.5	<.5	<.5	e.070	<.5
Carbaryl, whole water	3	ND	<1	<1	<1	<1	<1	<1	<1	<1
Chlorpyrifos, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
N,N-diethyl-*meta*-toluamide (DEET), whole water	3	.08	e.075	e.18	e.063	e.029	<.5	e.23	e.20	e.085
Diazinon, whole water	3	.027	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Dichlorvos, whole water	3	1	<1	<1	<1	<1	<1	<1	<1	<1
Diethyl phthalate, whole water	3	.55	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
D-Limonene, whole water	3	ND	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5

Table 21. Analytical results for household, industrial, and minor agricultural-use compounds (HIACs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)							
			06479520 Big Sioux River below Watertown, SD (WT-DS2)		442026096533600 Big Sioux River near Volga, SD (VL-US1)			441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)		
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), whole water	3	0.032	e0.033	e0.040	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Indole, whole water	3	.015	e.070	<.5	e.043	e.024	<.5	<.5	e.016	<.5
Isoborneol, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Isophorone, whole water	3	.047	<.5	<.5	e.035	e.026	<.5	e.050	e.047	<.5
Isoquinoline, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Menthol, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Metalaxyl, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Methyl salicylate, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Nonylphenol diethoxylate (NP2EO), whole water	3	.55	<5	<5	<5	e3.3	<5	<5	e5.1	<5
Nonylphenol monoethoxylate (NP1EO), whole water	3	.39	<2	<2	<2	e1.7	<2	<2	e2.9	<2
Octylphenol diethoxylate (OP2EO), whole water	3	.14	<1	<1	<1	e.15	<1	<1	e.26	<1
Octylphenol monoethoxylate (OP1EO), whole water	3	1	<1	<1	<1	<1	<1	<1	<1	<1
para-cresol, whole water	3	.03	<1	<1	<1	<1	<1	<1	e.030	<1
***para*-nonylphenol (NP)**, whole water	3	.64	<5	<5	<5	<5	<5	<5	<5	<5
Pentachlorophenol, whole water	3	2	<2	<2	<2	<2	<2	<2	<2	<2
Phenol, whole water	3	.94	e.19	<.5	e.23	<.5	<.5	<.5	<.5	<.5
Tetrachloroethylene, whole water	3	ND	<.5	e.020	<.5	<.5	<.5	<.5	<.5	<.5
Tributyl phosphate, whole water	3	.02	e.073	<.5	<.5	e.12	<.5	<.5	<.5	<.5
Triclosan, whole water	3	.084	e.084	<1	<1	<1	<1	<1	<1	<1
Triethyl citrate (ethyl citrate), whole water	3	.048	<.5	e.048	<.5	<.5	<.5	<.5	<.5	<.5
Triphenyl phosphate, whole water	3	.015	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Tri(2-butoxyethyl)phosphate, whole water	3	.13	e.23	0.52	e.29	<.5	<.5	<.5	<.5	<.5
Tri(2-chloroethyl)phosphate, whole water	3	.056	e.20	<.5	e.066	e.11	<.5	e.067	e.13	e.11
Tri(dichloroisopropyl)phosphate, whole water	3	.047	e.18	<.5	<.5	<.5	<.5	<.5	<.5	<.5

Table 21. Analytical results for household, industrial, and minor agricultural-use compounds (HIACs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)				
			441841096521400 Big Sioux River below wastewater wetland, near Volga, SD (VL-DS1)			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)	
Date of sample collection			08-21-2003	10-22-2003	06-16-2004	08-21-2003	06-17-2004
Time of sample collection			1100	0935	1615	1230	1140
Compound							
1,4-dichlorobenzene, whole water	3	ND	e0.18	e0.093	<0.5	e0.32	<0.5
2,2′,4,4′-tetrabromodiphenyl ether, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
3,4-dichlorophenyl isocyanate, whole water	3	ND	<.5	<.5	<.5	<.5	<.5
3-methyl-1H-indole (skatol), whole water	3	.02	<1	<1	<1	<1	<1
3-*tert*-butyl-4-hydroxy anisole (BHA), whole water	3	ND	<5	<5	<5	<5	<5
4-cumylphenol, whole water	3	1	<1	<1	<1	<1	<1
4-*normal*-octylphenol, whole water	3	1	<1	<1	<1	<1	<1
4-*tert*-octylphenol, whole water	3	.26	<1	e.085	<1	<1	<1
5-methyl-1H-benzotriazole, whole water	3	.33	<2	<2	<2	<2	<2
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN), whole water	3	.048	<.5	<.5	<.5	<.5	<.5
Acetophenone, whole water	3	.08	<.5	e.17	<.5	<.5	<.5
Anthraquinone, whole water	3	.96	e.062	<.5	<.5	<.5	<.5
Benzophenone, whole water	3	.025	<.5	<.5	<.5	<.5	<.5
Bis(2-ethylhexyl) phthalate, whole water	3	ND	<2	<2	<2	<2	<2
Bisphenol-A, whole water	3	.069	<1	<1	<1	<1	<1
Bromacil, whole water	3	.068	<.5	<.5	<.5	<.5	<.5
Camphor, whole water	3	.07	<.5	<.5	<.5	<.5	<.5
Carbaryl, whole water	3	ND	<1	<1	<1	<1	<1
Chlorpyrifos, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
N,N-diethyl-*meta*-toluamide (DEET), whole water	3	.08	e.052	e.043	e.036	e.048	e.077
Diazinon, whole water	3	.027	<.5	<.5	<.5	<.5	<.5
Dichlorvos, whole water	3	1	<1	<1	<1	<1	<1
Diethyl phthalate, whole water	3	.55	<.5	<.5	<.5	<.5	<.5
D-Limonene, whole water	3	ND	<.5	<.5	<.5	<.5	<.5

Table 21. Analytical results for household, industrial, and minor agricultural-use compounds (HIACs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)				
			441841096521400 Big Sioux River below wastewater wetland, near Volga, SD (VL-DS1)			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)	
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), whole water	3	0.032	<0.5	<0.5	<0.5	<0.5	<0.5
Indole, whole water	3	.015	<.5	e.083	<.5	<.5	<.5
Isoborneol, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
Isophorone, whole water	3	.047	<.5	e.028	<.5	<.5	<.5
Isoquinoline, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
Menthol, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
Metalaxyl, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
Methyl salicylate, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
Nonylphenol diethoxylate (NP2EO), whole water	3	.55	<5	e3.4	<5	<5	<5
Nonylphenol monoethoxylate (NP1EO), whole water	3	.39	<2	e2.2	<2	<2	<2
Octylphenol diethoxylate (OP2EO), whole water	3	.14	<1	e.16	<1	<1	<1
Octylphenol monoethoxylate (OP1EO), whole water	3	1	<1	<1	<1	<1	<1
para-cresol, whole water	3	.03	<1	<1	<1	<1	<1
***para*-nonylphenol (NP)**, whole water	3	.64	<5	<5	<5	<5	<5
Pentachlorophenol, whole water	3	2	<2	<2	<2	<2	<2
Phenol, whole water	3	.94	<.5	<.5	<.5	e.13	<.5
Tetrachloroethylene, whole water	3	ND	<.5	<.5	<.5	<.5	<.5
Tributyl phosphate, whole water	3	.02	<.5	e.13	<.5	<.5	<.5
Triclosan, whole water	3	.084	<1	<1	<1	<1	<1
Triethyl citrate (ethyl citrate), whole water	3	.048	<.5	<.5	<.5	<.5	<.5
Triphenyl phosphate, whole water	3	.015	<.5	<.5	<.5	<.5	<.5
Tri(2-butoxyethyl)phosphate, whole water	3	.13	<.5	<.5	e.19	e.19	<.5
Tri(2-chloroethyl)phosphate, whole water	3	.056	e.060	e.12	<.5	e.056	<.5
Tri(dichloroisopropyl)phosphate, whole water	3	.047	<.5	<.5	<.5	<.5	<.5

Table 21. Analytical results for household, industrial, and minor agricultural-use compounds (HIACs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)					
			441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)		441316096483300 Big Sioux River below Wastewater effluent, near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)	
Date of sample collection			08-22-2003	06-17-2004	08-22-2003	06-18-2004	08-22-2003	06-17-2004
Time of sample collection			0915	0950	1015	1215	1140	1645
Compound								
1,4-dichlorobenzene, whole water	3	ND	e0.13	e0.16	e0.22	<0.5	e0.25	<0.5
2,2′,4,4′-tetrabromodiphenyl ether, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
3,4-dichlorophenyl isocyanate, whole water	3	ND	<.5	<.5	<.5	<.5	<.5	<.5
3-methyl-1H-indole (skatol), whole water	3	.02	<1	<1	<1	<1	<1	<1
3-*tert*-butyl-4-hydroxy anisole (BHA), whole water	3	ND	<5	<5	<5	<5	<5	<5
4-cumylphenol, whole water	3	1	<1	<1	<1	<1	<1	<1
4-*normal*-octylphenol, whole water	3	1	<1	<1	<1	<1	<1	<1
4-*tert*-octylphenol, whole water	3	.26	<1	<1	<1	<1	<1	<1
5-methyl-1H-benzotriazole, whole water	3	.33	e.80	e.84	<2	<2	<2	<2
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN), whole water	3	.048	2	2.3	e.074	<.5	e.24	<.5
Acetophenone, whole water	3	.08	e.083	<.5	<.5	<.5	<.5	<.5
Anthraquinone, whole water	3	.96	e.058	<.5	<.5	<.5	<.5	<.5
Benzophenone, whole water	3	.025	e.26	e.13	e.042	<.5	e.041	<.5
Bis(2-ethylhexyl) phthalate, whole water	3	ND	<2	<2	<2	<2	<2	<2
Bisphenol-A, whole water	3	.069	e.13	<1	<1	<1	<1	<1
Bromacil, whole water	3	.068	<.5	<.5	<.5	<.5	<.5	<.5
Camphor, whole water	3	.07	<.5	<.5	<.5	<.5	<.5	<.5
Carbaryl, whole water	3	ND	<1	<1	<1	<1	<1	<1
Chlorpyrifos, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
N,N-diethyl-*meta*-toluamide (DEET), whole water	3	.08	e.042	e.038	e.050	e.042	e.051	e.069
Diazinon, whole water	3	.027	<.5	<.5	<.5	<.5	<.5	<.5
Dichlorvos, whole water	3	1	<1	<1	<1	<1	<1	<1
Diethyl phthalate, whole water	3	.55	<.5	<.5	<.5	<.5	<.5	<.5
D-Limonene, whole water	3	ND	<.5	<.5	<.5	<.5	<.5	<.5

Table 21. Analytical results for household, industrial, and minor agricultural-use compounds (HIACs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)					
			441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)		441316096483300 Big Sioux River below Wastewater effluent, near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)	
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), whole water	3	0.032	e0.44	e0.33	e0.032	<0.5	e0.054	<0.5
Indole, whole water	3	.015	<.5	<.5	<.5	<.5	<.5	<.5
Isoborneol, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
Isophorone, whole water	3	.047	<.5	<.5	<.5	<.5	<.5	<.5
Isoquinoline, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
Menthol, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
Metalaxyl, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
Methyl salicylate, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
Nonylphenol diethoxylate (NP2EO), whole water	3	.55	<5	e1.2	<5	<5	<5	<5
Nonylphenol monoethoxylate (NP1EO), whole water	3	.39	<2	e.69	<2	<2	<2	<2
Octylphenol diethoxylate (OP2EO), whole water	3	.14	<1	<1	<1	<1	<1	<1
Octylphenol monoethoxylate (OP1EO), whole water	3	1	<1	<1	<1	<1	<1	<1
para-cresol, whole water	3	.03	<1	<1	<1	<1	<1	<1
***para*-nonylphenol (NP)**, whole water	3	.64	<5	e.71	<5	<5	<5	<5
Pentachlorophenol, whole water	3	2	<2	<2	<2	<2	<2	<2
Phenol, whole water	3	.94	e.22	0.50	<.5	<.5	<.5	<.5
Tetrachloroethylene, whole water	3	ND	<.5	<.5	<.5	<.5	<.5	<.5
Tributyl phosphate, whole water	3	.02	e.38	e.28	e.060	<.5	e.096	<.5
Triclosan, whole water	3	.084	e.13	<1	<1	<1	<1	<1
Triethyl citrate (ethyl citrate), whole water	3	.048	e.33	e.36	<.5	<.5	e.052	<.5
Triphenyl phosphate, whole water	3	.015	e.017	<.5	<.5	<.5	e.0094	<.5
Tri(2-butoxyethyl)phosphate, whole water	3	.13	e.27	<.5	<.5	<.5	<.5	<.5
Tri(2-chloroethyl)phosphate, whole water	3	.056	e.32	e.40	e.078	<.5	e.13	<.5
Tri(dichloroisopropyl)phosphate, whole water	3	.047	e.19	<.5	e.047	<.5	e.059	<.5

Table 22. Analytical results for polyaromatic hydrocarbons (PAHs).

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)							
			06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)		445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)	
Date of sample collection			08-18-2003	06-15-2004	08-18-2003	06-15-2004	08-19-2003	06-16-2004	08-19-2003	06-15-2004
Time of sample collection			1045	1030	1200	1200	1305	0925	0930	1730
Compound										
1-methylnaphthalene, whole water	3	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2,6-dimethylnaphthalene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
2-methylnaphthalene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Anthracene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Benzo[*a*]pyrene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Carbazole, whole water	3	.22	<.5	<.5	<.5	<.5	<.5	<.5	e.048	<.5
Fluoranthene, whole water	3	.15	<.5	<.5	e.027	.031	<.5	<.5	<.5	e.027
Isopropylbenzene (cumene), whole water	3	ND	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Naphthalene, whole water	3	.01	<.5	<.5	<.5	e.014	<.5	<.5	<.5	<.5
Phenanthrene, whole water	3	.1	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Pyrene, whole water	3	.04	<.5	<.5	e.026	e.027	<.5	<.5	e.014	e.028

Table 22. Analytical results for polyaromatic hydrocarbons (PAHs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)							
			06479520 Big Sioux River below Watertown, SD (WT-DS2)		442026096533600 Big Sioux River near Volga, SD (VL-US1)			441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)		
Date of sample collection			08-20-2003	06-15-2004	08-20-2003	10-21-2003	06-16-2004	08-21-2003	10-21-2003	06-16-2004
Time of sample collection			0915	1825	1400	1105	1145	0900	1240	1435
Compound										
1-methylnaphthalene, whole water	3	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2,6-dimethylnaphthalene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
2-methylnaphthalene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Anthracene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Benzo[*a*]pyrene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Carbazole, whole water	3	.22	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Fluoranthene, whole water	3	.15	e.035	e.025	<.5	<.5	<.5	<.5	<.5	<.5
Isopropylbenzene (cumene), whole water	3	ND	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Naphthalene, whole water	3	.01	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Phenanthrene, whole water	3	.1	e.023	e.031	<.5	<.5	<.5	<.5	<.5	<.5
Pyrene, whole water	3	.04	e.031	e.023	<.5	<.5	<.5	<.5	<.5	<.5

Table 22. Analytical results for polyaromatic hydrocarbons (PAHs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)				
			441841096521400 Big Sioux River below wastewater wetland near Volga, SD (VL-DS1)			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)	
Date of sample collection			08-21-2003	10-22-2003	06-16-2004	08-21-2003	06-17-2004
Time of sample collection			1100	0935	1615	1230	1140
Compound							
1-methylnaphthalene, whole water	3	0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2,6-dimethylnaphthalene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
2-methylnaphthalene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
Anthracene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
Benzo[*a*]pyrene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5
Carbazole, whole water	3	.22	<.5	<.5	<.5	<.5	<.5
Fluoranthene, whole water	3	.15	<.5	<.5	<.5	<.5	<.5
Isopropylbenzene (cumene), whole water	3	ND	<.5	<.5	<.5	<.5	<.5
Naphthalene, whole water	3	.01	<.5	<.5	<.5	<.5	<.5
Phenanthrene, whole water	3	.1	<.5	<.5	<.5	<.5	<.5
Pyrene, whole water	3	.04	<.5	<.5	<.5	<.5	<.5

Table 22. Analytical results for polyaromatic hydrocarbons (PAHs).—Continued

[Bold text indicates suspected endocrine-disrupting compound (EDC). Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; ND, not determined; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)					
			441434096482500 Brookings wastewater effluent near Brookings, SD (BK-WWE)		441316096483300 Big Sioux River below wastewater effluent, near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek at Medary, SD (BK-DS2)	
Date of sample collection			08-22-2003	06-17-2004	08-22-2003	06-18-2004	08-22-2003	06-17-2004
Time of sample collection			0915	0950	1015	1215	1140	1645
Compound								
1-methylnaphthalene, whole water	3	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2,6-dimethylnaphthalene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
2-methylnaphthalene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
Anthracene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
Benzo[*a*]pyrene, whole water	3	.5	<.5	<.5	<.5	<.5	<.5	<.5
Carbazole, whole water	3	.22	<.5	<.5	<.5	<.5	<.5	<.5
Fluoranthene, whole water	3	.15	<.5	<.5	<.5	<.5	<.5	<.5
Isopropylbenzene (cumene), whole water	3	ND	<.5	<.5	<.5	<.5	<.5	<.5
Naphthalene, whole water	3	.01	<.5	<.5	<.5	<.5	<.5	<.5
Phenanthrene, whole water	3	.1	e.012	<.5	<.5	<.5	<.5	<.5
Pyrene, whole water	3	.04	<.5	<.5	<.5	<.5	<.5	<.5

Table 23. Analytical results for sterol compounds (SCs).

[Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. ND, not determined; e, estimated; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)							
			06479500 Big Sioux River at Watertown, SD (WT-US1)		06479512 Big Sioux River at Broadway, at Watertown, SD (WT-US2)		445301097055900 Watertown wastewater effluent at Watertown, SD (WT-WWE)		445234097054800 Big Sioux River below wastewater effluent, near Watertown, SD (WT-DS1)	
Date of sample collection			08-18-2003	06-15-2004	08-18-2003	06-15-2004	08-19-2003	06-16-2004	08-19-2003	06-15-2004
Time of sample collection			1045	1030	1200	1200	1305	0925	0930	1730
Compound										
3-*beta*-coprostanol	3	0.26	<2	<2	<2	<2	e1.3	e1.2	e1.0	<2
beta-sitosterol	3	.57	2.2	<2	e1.6	<2	e.94	<2	e.94	<2
beta-stigmastanol	3	ND	<2	<2	<2	<2	<2	<2	<2	<2
Cholesterol	3	.64	3.2	<2	e1.8	<2	3.0	2.9	e1.7	e1.8

	Analytical method number	Study reporting level	Station identification and name (site label)							
			06479520 Big Sioux River below Watertown, SD (WT-DS2)		442026096533600 Big Sioux River near Volga, SD (VL-US1)			441913096533400 Volga wastewater wetland at Volga, SD (VL-WWE)		
Date of sample collection			08-20-2003	06-15-2004	08-20-2003	10-21-2003	06-16-2004	08-21-2003	10-21-2003	06-16-2004
Time of sample collection			0915	1825	1400	1105	1145	0900	1240	1435
Compound										
3-*beta*-coprostanol	3	0.26	e0.75	<2	<2	e0.54	<2	<2	e0.78	<2
beta-sitosterol	3	.57	e1.7	<2	e1.6	e1.1	<2	<2	2	<2
beta-stigmastanol	3	ND	<2	<2	<2	e.88	<2	<2	e1.8	<2
Cholesterol	3	.64	2.3	e1.5	3.6	e1.3	<2	e1.4	2.8	2.1

Table 23. Analytical results for sterol compounds (SCs).—Continued

[Shaded cells indicate concentrations greater than study reporting levels for compounds with acceptable quality assurance/quality control, and were used in analyses related to occurrence of organic wastewater compounds. Units are micrograms per liter. e, estimated; <, less than]

	Analytical method number	Study reporting level	Station identification and name (site label)				
			441841096521400 Big Sioux River below wastewater wetland, near Volga (VL-DS1)			441421096491200 Big Sioux River above wastewater effluent, near Brookings, SD (VL-DS2/BK-US1)	
Date of sample collection			08-21-2003	10-22-2003	06-16-2004	08-21-2003	06-17-2004
Time of sample collection			1100	0935	1615	1230	1140
Compound							
3-*beta*-coprostanol	3	0.26	<2	e0.73	<2	<2	<2
beta-sitosterol	3	.57	e1.4	2.4	<2	e1.0	<2
beta-stigmastanol	3	ND	<2	e1.3	<2	<2	<2
Cholesterol	3	.64	e1.9	2.3	<2	e1.0	<2

	Analytical method number	Study reporting level	Station identification and name (site label)					
			441434096482500 Brookings wastwater effluent near Brookings, SD (BK-WWE)		441316096483300 Big Sioux River below wastewater effluent near Brookings, SD (BK-DS1)		441151096472200 Big Sioux River above Medary Creek, at Medary, SD (BK-DS2)	
Date of sample collection			08-22-2003	06-17-2004	08-22-2003	06-18-2004	08-22-2003	06-17-2004
Time of sample collection			0915	0950	1015	1215	1140	1645
Compound								
3-*beta*-coprostanol	3	0.26	e1.1	<2	<2	<2	<2	<2
beta-sitosterol	3	.57	e.89	<2	e1.2	<2	e1.1	<2
beta-stigmastanol	3	ND	<2	<2	<2	<2	<2	<2
Cholesterol	3	.64	e1.6	e1.8	e1.5	<2	e1.4	e.96

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