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Occurrence of Anthropogenic Organic Compounds and Nutrients in Source and Finished Water in the Sioux Falls Area, South Dakota, 2009–10

Scientific Investigations Report 2012–5098

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

Cover photograph. Surface-water intake station on the Big Sioux River north of Sioux Falls, South Dakota.

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
mile (mi)	1.609	kilometer (km)
foot (ft)	0.3048	meter (m)
	Area	
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
cubic foot (ft^3)	0.02832	cubic meter (m^3)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)

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

$$°F=(1.8×°C)+32$$

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L). Values of stable isotopes of nitrogen and oxygen are given in per mil (‰).

Water year (WY) is the 12-month period, October 1 through September 30, and is designated by the calendar year in which it ends. Thus, the water year ending September 30, 2009, is called the "2009" water year.

Abbreviations and Acronyms

AIR	atmospheric nitrogen
AOC	anthropogenic organic compound
BQ	benchmark quotient
BQmax	maximum benchmark quotient
^{13}C	carbon-13
DEHP	bis(2-ethylhexyl) phthalate
GFF/C_{18}	glass-fiber filter / reverse phase octyldecyl surface-modified-silica embedded glass-fiber filter disk
HBSL	Health-Based Screening Level
HDPE	high-density polyethylene
IDS	isotope dilution standard
K_{ow}	octanol-water partitioning coefficient
LRL	laboratory reporting level
LT–MDL	long-term method detection level

MCL	Maximum Contaminant Level
mg/L as N	milligrams per liter as nitrogen
mL	milliliter
MRL	minimum reporting level
MSTFA	*N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide
N_2	nitrogen gas
NO_2+NO_3	nitrite plus nitrate
NWQL	National Water Quality Laboratory
OGRL	Organic Geochemistry Research Laboratory
RSIL	Reston Stable Isotope Laboratory
SPE	solid-phase extraction
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VSMOW	Vienna Standard Mean Ocean Water
$\delta^{15}N$	isotope ratio of ^{15}N to ^{14}N relative to atmospheric nitrogen
$\delta^{18}O$	isotope ratio of ^{18}O to ^{16}O relative to Vienna Standard Mean Ocean Water

Acknowledgments

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Abstract

Anthropogenic organic compounds (AOCs) in drinking-water sources commonly are derived from municipal, agricultural, and industrial wastewater sources, and are a concern for water-supply managers. A cooperative study between the city of Sioux Falls, S. Dak., and the U.S. Geological Survey was initiated in 2009 to (1) characterize the occurrence of anthropogenic organic compounds in the source waters (groundwater and surface water) to water supplies in the Sioux Falls area, (2) determine if the compounds detected in the source waters also are present in the finished water, and (3) identify probable sources of nitrate in the Big Sioux River Basin and determine if sources change seasonally or under different hydrologic conditions. This report presents analytical results of water-quality samples collected from source waters and finished waters in the Sioux Falls area.

The study approach included the collection of water samples from source and finished waters in the Sioux Falls area for the analyses of AOCs, nutrients, and nitrogen and oxygen isotopes in nitrate. Water-quality constituents monitored in this study were chosen to represent a variety of the contaminants known or suspected to occur within the Big Sioux River Basin, including pesticides, pharmaceuticals, sterols, household and industrial products, polycyclic aromatic hydrocarbons, antibiotics, and hormones. A total of 184 AOCs were monitored, of which 40 AOCs had relevant human-health benchmarks.

During 11 sampling visits, 45 AOCs (24 percent) were detected in at least one sample of source or finished water, and 13 AOCs were detected in at least 20 percent of all samples. Concentrations of detected AOCs were all less than 1 microgram per liter, except for two AOCs in multiple samples from the Big Sioux River, and one AOC in finished-water samples. Concentrations of AOCs were less than 0.1 microgram per liter in more than 75 percent of the detections. Nutrient concentrations varied seasonally in source-water samples from surface water and groundwater. In the Big Sioux River, nitrite plus nitrate concentrations were typically less than 1 milligram per liter as nitrogen, and reached a maximum of 4.06 milligrams per liter as nitrogen following a June 2010 storm. Nitrite plus nitrate concentrations in groundwater ranged from less than 0.1 to 0.701 milligram per liter as nitrogen.

Eight of the AOCs detected have a human-health benchmark that could be used to evaluate the concentrations in a human-health context. Four AOCs had maximum concentrations within an order of magnitude of the benchmark, indicating that additional monitoring of the compound may be warranted. Three herbicides (atrazine, metolachlor, and prometon) and one degradate (deethylatrazine) were detected in finished-water samples as frequently as in source-water samples. The concentrations of herbicides in source water varied by an order of magnitude from the period of peak use (early summer) to the winter months. Groundwater and finished-water concentrations of atrazine were similar for the six sampling dates when groundwater was the only source water used. Upstream wastewater discharges contributed a fairly small percentage of the flow to the Big Sioux River near Sioux Falls, but several AOCs associated with wastewater were frequently detected. The interpretation of all potential sources of nitrogen cannot be accomplished by use of nitrogen and oxygen isotopes in nitrate alone, but provides a qualitative indication that very little nitrate originates from excess fertilizer runoff, and most nitrate originates from municipal wastewater effluent, manure runoff (either from field application or feeding operations), or fertilizers mineralized by processes in the soil.

Introduction

Anthropogenic organic compounds (AOCs) in drinking-water sources commonly are derived from municipal, agricultural, and industrial wastewater sources, and are a concern for water-supply managers. Recent studies have documented the occurrence of AOCs at very low concentrations in source-water supplies and in finished water (Kingsbury and others, 2008; Focazio and others, 2008). Source water is defined as the raw water supply prior to treatment, and finished water is defined as water that has been through the treatment

process just prior to distribution. Although some of the most commonly used and toxic AOCs are regulated, most are unregulated, and human-health effects from many AOCs are uncertain. A better understanding of the occurrence of AOCs in drinking-water sources is important for water-treatment planning and for characterizing how activities on the landscape affect the quality of drinking-water sources.

During 2000–08, the city of Sioux Falls, S. Dak., observed an increase in nitrate concentrations in source-water samples from the Big Sioux River (Tim Stefanich, city of Sioux Falls, written comm., 2009), prompting questions about the causes of this increase. Water managers identified a need to investigate potential contaminant origins when peaks in nitrate concentrations occur in source water. AOCs may provide insight on the type of sources that lead to peak concentrations of regulated contaminants such as nitrate in public-water supplies. A cooperative study between the city of Sioux Falls and the U.S. Geological Survey (USGS) was initiated in 2009 to (1) characterize the occurrence of AOCs in source waters (groundwater and surface water) to water supplies in the Sioux Falls area, (2) determine if the compounds found in the source waters also are present in the finished water, and (3) identify probable sources of nitrate in the Big Sioux River Basin and determine if sources change seasonally or under different hydrologic conditions.

Purpose and Scope

This report presents analytical results of water-quality samples collected from source waters (groundwater and surface water) and finished water in the Sioux Falls area. Samples for analysis of AOCs and nutrients were collected on 11 days spaced monthly or bi-monthly between June 2009 and August 2010. On each sampling date, source-water samples were collected from one groundwater site, one surface-water site, or both sites depending on the source(s) to water supplies at the time of sampling; finished-water samples were collected from one site. Characterization of analytical results includes comparison of source-water occurrence to finished-water occurrence on the same day, temporal trends at each site during 2009–10, comparison of the detected concentrations to relevant benchmark standards, and evaluation of potential sources of water-quality constituents during different seasons or hydrologic conditions. This report is not intended to assess the efficacy of the water-treatment plant process for removal of organic compounds.

Description of Study Area

The Big Sioux River Basin (fig. 1) includes a contributing drainage area of about 3,130 square miles (mi^2) upstream from Sioux Falls. The annual mean streamflow for the USGS streamgage 06481000 (Big Sioux River near Dell Rapids, S. Dak., contributing drainage area = 3,057 mi^2) for water years 1972–2008 was 529 cubic feet per second (ft^3/s) (U.S. Geological Survey, 2011). The annual mean streamflow downstream at the USGS streamgage 06482020 (Big Sioux River at North Cliff Avenue at Sioux Falls, S. Dak., contributing drainage area = 3,778 mi^2) for water years 1972–2008 was 672 ft^3/s, which includes contribution from the 606-mi^2 Skunk Creek Basin and most of the urbanized area within Sioux Falls (U.S. Geological Survey, 2011). A diversion dam for flood control on the Big Sioux River near the northern edge of Sioux Falls allows the flow of the Big Sioux River to be partially routed through the diversion channel (fig. 1).

Hydrologic Conditions

The 2009–10 water-quality sampling period represented two extremes in terms of the prevailing hydrologic conditions. Water year 2009 (October 1, 2008, to September 30, 2009) was the driest year of the decade (table 1) for the Sioux Falls area, whereas water year 2010 had the most precipitation (43.1 inches (in.)) in the 120-year period of record (National Oceanic and Atmospheric Administration, 2000–10). In 2010, mean annual streamflow at USGS streamgage 06482020 (1,938 ft^3/s) was almost four times greater than the previous year (509 ft^3/s) (U.S. Geological Survey, 2011).

Maximum streamflow in the Big Sioux River Basin typically occurs in early spring as a result of snowmelt, when flooding conditions are frequent. Streamflow gradually decreases from summer until the following spring. Nearly two-thirds of the average yearly precipitation falls during the growing season of April through August, and thunderstorms are frequent during the late spring and summer with

Table 1. Precipitation totals and mean annual streamflow in the Big Sioux River in the Sioux Falls area, water years 2001–10.

[USGS, U.S. Geological Survey; ft^3/s, cubic feet per second]

Water year	Total precipitation[1] (inches)	Mean annual streamflow[2] at USGS streamgage 06482020 (ft^3/s)	Mean annual streamflow[2] at USGS streamgage 06481000 (ft^3/s)
2001	27.6	1,309	1,068
2002	26.6	348	306
2003	23.2	162	110
2004	34.4	244	156
2005	27.9	344	269
2006	29.1	679	485
2007	27.3	819	613
2008	25.6	605	464
2009	22.5	509	437
2010	43.1	1,938	1,535

[1]At National Weather Service station identified by international call sign KFSD (fig. 1). Data from National Oceanic and Atmospheric Administration (2000–10).

[2]Data from U.S. Geological Survey (2011).

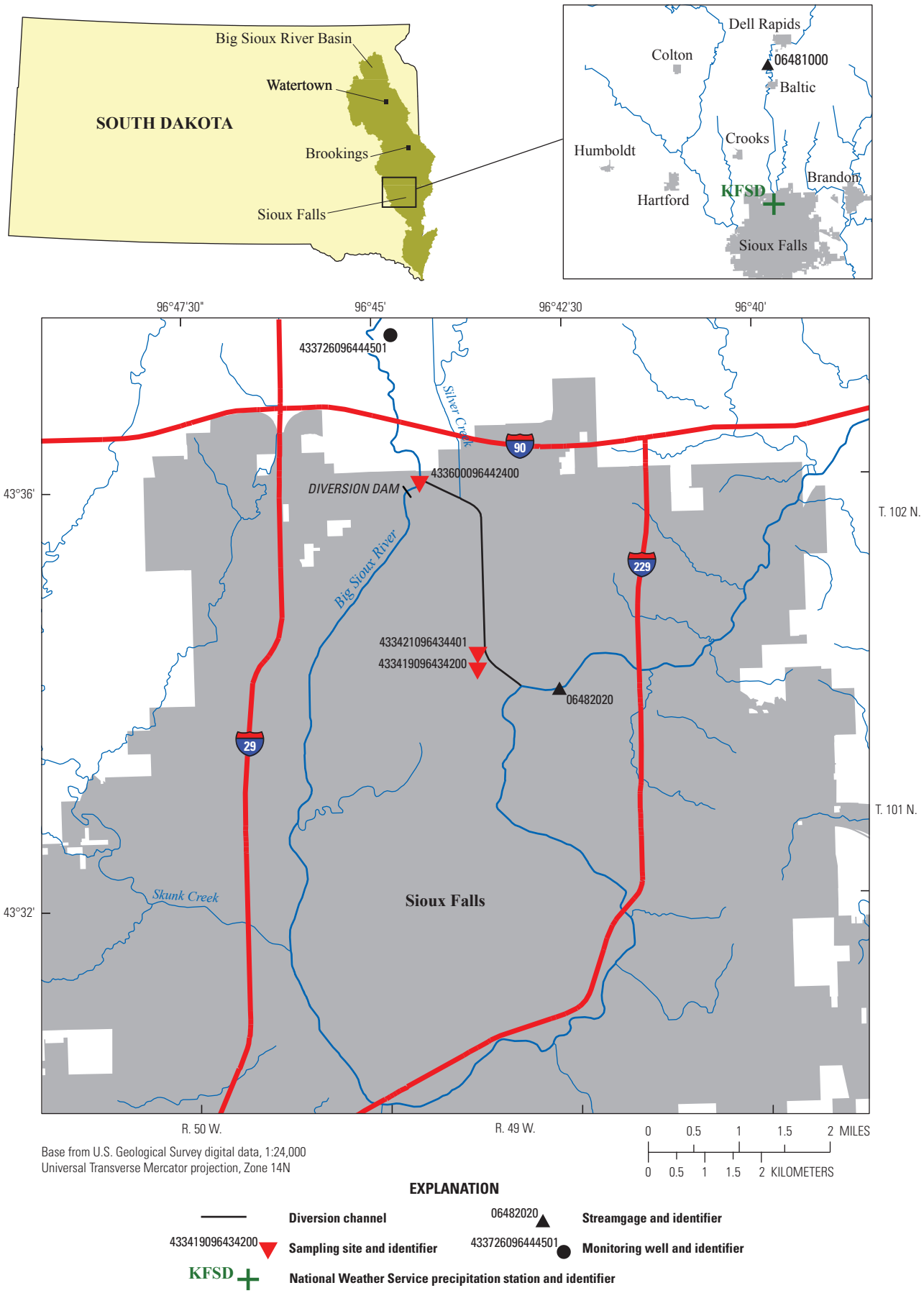

Figure 1. Location of Big Sioux River Basin and selected data-collection sites in the Sioux Falls area.

June and July the most active months (National Oceanic and Atmospheric Administration, 2000–10). October 2009 was an unusually wet month, with more than 5.5 in. of precipitation that caused a sustained increase in fall streamflow in the Big Sioux River (fig. 2). From June to August 2010, frequent intense thunderstorms maintained streamflow at more than 1,000 ft^3/s, typical of spring snowmelt conditions but uncommon for mid-summer streamflow in the Big Sioux River near Sioux Falls. June 2010 had 4 days with more than an inch of precipitation (total of 7.8 in. for June), July had two separate storms that produced more than 2 in. each day (total of 8.6 in. for July), and August had two separate storms with more than 1.5 in. of precipitation (total of 6.3 in. for August). Changes in groundwater levels in the Big Sioux aquifer at USGS monitoring well 433726096444501 correspond to changes in streamflow in the Big Sioux River (fig. 2; U.S. Geological Survey, 2011).

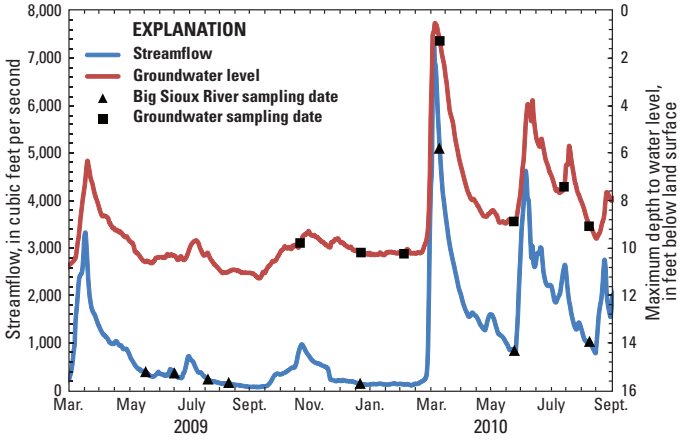

Figure 2. Streamflow in the Big Sioux River near Dell Rapids (streamgage 06481000) and groundwater levels in the Big Sioux aquifer (monitoring well 433726096444501), March 2009 to September 2010.

Land Use and Wastewater Discharge

Agricultural activities are extensive throughout the Big Sioux River Basin, and the largest cities in the basin have developed along the Big Sioux River, contributing urban runoff and wastewater effluent discharges. About 60 percent of the drainage basin is used for cultivated crops (fig. 3), and other agricultural activities in the basin include livestock and concentrated animal-feeding operations (Homer and others, 2004). Crops grown in the basin include predominantly corn, soybeans, wheat, and alfalfa; livestock raised in the basin primarily include dairy cattle, beef cattle, and hogs (Lawrence and Sando, 1991).

Sioux Falls is the largest city in South Dakota, and its population increased from 124,000 in 2000 to 154,000 in 2010 (U.S. Census Bureau, 2011). Brookings and Watertown (the 4th and 5th largest cities in the State, respectively) are upstream in the basin and discharge treated wastewater

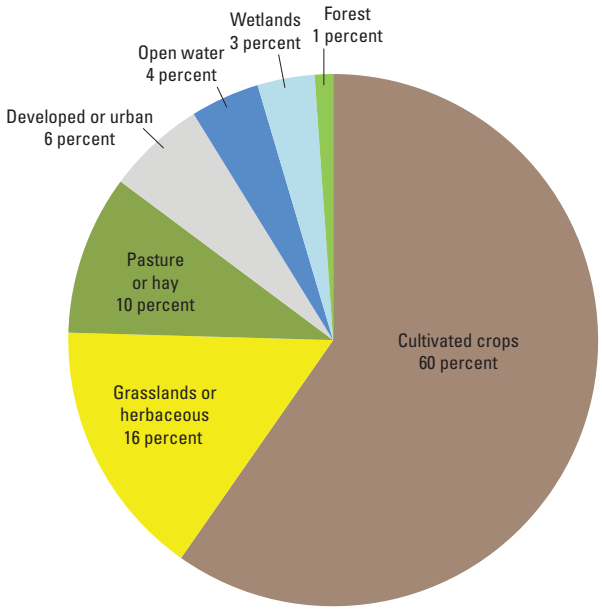

Figure 3. Land use in the Big Sioux River Basin (data from Homer and others, 2004).

effluent 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 (Sando and others, 2005). Other communities between Watertown and Sioux Falls contribute smaller intermittent wastewater discharges to the Big Sioux River from lagoons or holding ponds. During this study (2009–10), total wastewater discharges accounted for less than 23 percent of the flow in the Big Sioux River near Watertown, less than 15 percent of the flow near Brookings, and less than 10 percent of the flow near Dell Rapids (Mike Boerger, city of Watertown, written comm., 2011; Eric Witt, Brookings Municipal Utilities, written comm., 2011; U.S. Environmental Protection Agency, 2011c; U.S. Geological Survey, 2011). For the summer months (June–August), upstream wastewater discharges averaged 3.5 percent of the flow near Dell Rapids in 2009 and 0.8 percent of the flow in 2010.

Hydrogeology

Major aquifers in the Sioux Falls area (fig. 4) are described in this section of the report. Additional aquifers in the Sioux Falls area are described in Lindgren and Niehus (1992). Glacial outwash deposits along the Big Sioux River and its tributaries underlie much of the Big Sioux River Basin and are the major source of groundwater in the basin (Lawrence and Sando, 1991). Outwash deposits include the various units that contain the Big Sioux aquifer, which is one of the more extensively developed glacial aquifers in

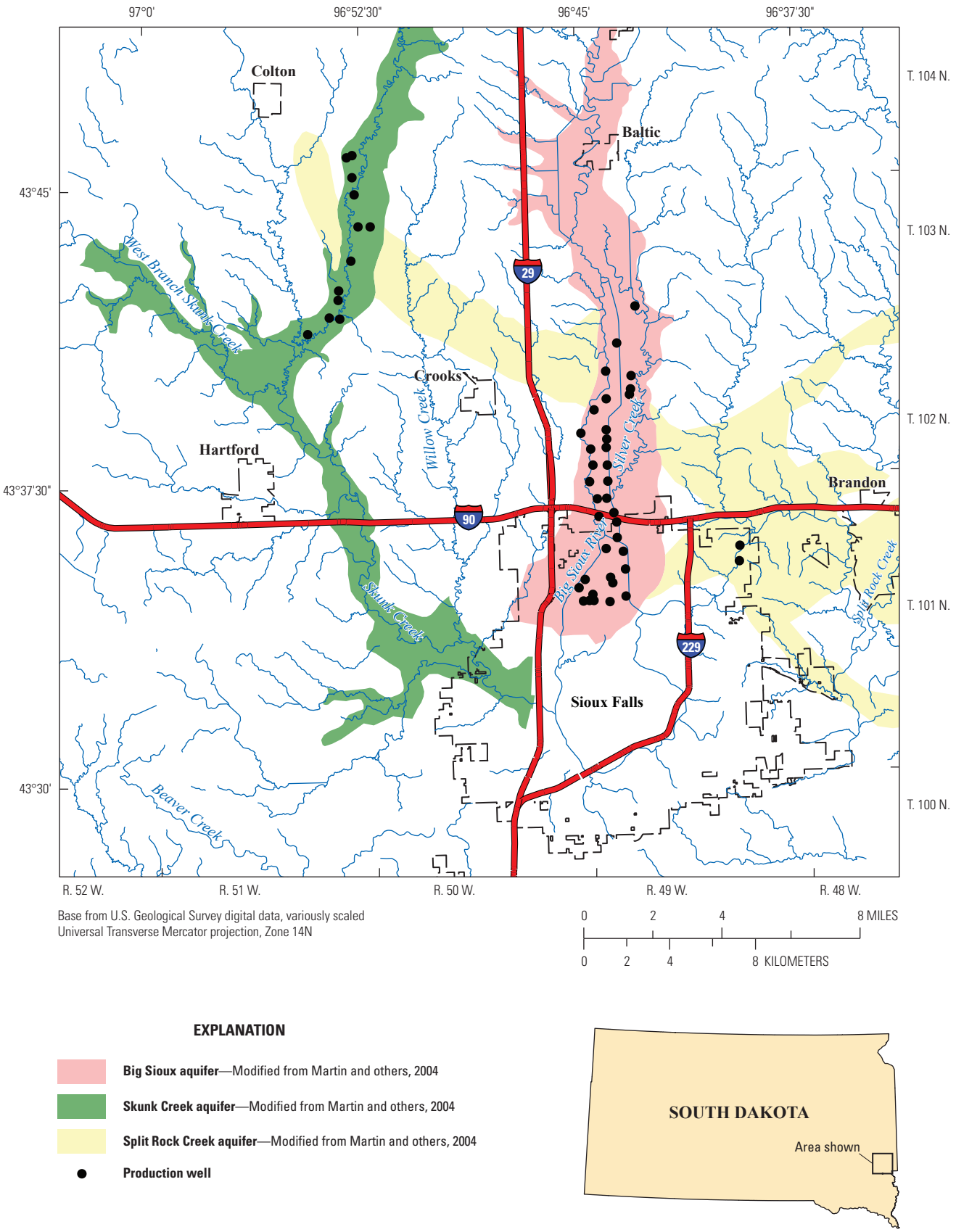

Figure 4. Surface drainage and approximate extent of aquifers used for water supplies in the Sioux Falls area.

South Dakota, the Skunk Creek aquifer, and several other glacial aquifers. The outwash deposits consist of cross-bedded gravel, sand, and silt that range in thickness from a few feet to about 200 feet (ft) and range in depth below land surface from about 1 to 100 ft (Lawrence and Sando, 1991). Many of the outwash deposits have areas where they are hydraulically connected to the Big Sioux River and can be sensitive to infiltration of surface contaminants (Sando and others, 2006).

The Split Rock Creek aquifer is a major bedrock aquifer in the Sioux Falls area. The Split Rock Creek aquifer is composed of layers of predominantly quartz sand interbedded with layers of siltstone, shale, and silty clay of the Late Cretaceous-age Split Rock Creek Formation (Lindgren and Niehus, 1992).

Source-Water Usage

Sources of groundwater used for water supplies in the Sioux Falls area include collection galleries or production wells completed in the shallow glacial or bedrock aquifers to the north and northwest of Sioux Falls (fig. 4). The city of Sioux Falls currently (2011) uses groundwater as its primary water source year-round (City of Sioux Falls, 2011) and supplements the supply with surface water from the Big Sioux River only during periods of increased demand (typically in the summer months). For days when the source water was blended in 2009–10, groundwater typically made up about two-thirds of the supply with water from the Big Sioux River making up the difference. Water from the Big Sioux aquifer accounted for nearly 90 percent of the groundwater pumped for public supply in 2009–10 and about 80 percent of the total water supply in the same period. Water from the Skunk Creek aquifer (fig. 4) made up about 10 percent of the groundwater supply in 2009–10, and water from the Split Rock Creek aquifer accounted for less than 1 percent of the groundwater supply in the same period. The Big Sioux River accounted for about 18 percent of the total water supply in 2009 but made up less than 3 percent of the total in 2010 because of a decreased demand during a very wet year (table 1). Usage of the surface-water source was higher in earlier years, such as 2008 when nearly 37 percent of the water supply came from the Big Sioux River.

Previous Investigations

Sando and others (2006) characterized the occurrence of compounds commonly associated with wastewater effluent in the finished water, wastewater effluent, and the Big Sioux River near Sioux Falls. During that study, only one AOC (the herbicide metolachlor) was detected in finished water at a concentration greater than laboratory reporting levels. Several other AOCs (primarily agricultural herbicides, pharmaceuticals, and wastewater compounds) were detected in samples from the Big Sioux River (USGS site 433600096442400, fig. 1). Sando and others (2005) documented the occurrence of selected wastewater compounds in the Big Sioux River Basin upstream from Sioux Falls. The city of Sioux Falls also conducts quarterly or annual monitoring of selected unregulated organic compounds in source and finished water (City of Sioux Falls, 2011).

Methods of Study

The study approach included the collection of water samples from source and finished water in the Sioux Falls area for the analyses of AOCs, nutrients, and nitrogen and oxygen isotopes in nitrate. Fifteen samples of source water and 11 samples of finished water were collected over a range of hydrologic conditions during an 18-month period (table 2). This section of the report describes the sampling sites, sample collection and analysis methods, and associated laboratory and field quality assurance/quality control used in this study.

Water-quality constituents monitored in this study were selected to represent a wide range of the compounds known or suspected to occur within the Big Sioux River Basin. These include AOCs and selected nutrients that may have anthropogenic and natural origins. Stable isotopes of nitrogen and oxygen in nitrate also were used to help identify probable sources of nitrate. In addition, selected physical properties were measured.

Table 2. Study sampling dates and source-water components used for day sampled.

["x" indicates sample collected; shading denotes source-water components for day sampled]

Date	Source water		Finished water (site 433419096434200)
	Big Sioux River (site 433600096442400)	Groundwater (site 433421096434401)	
6/1/2009	x		x
6/30/2009	x		x
8/3/2009	x		x
8/24/2009	x		x
11/4/2009		x	x
1/4/2010	x		
1/5/2010		x	x
2/17/2010		x	x
3/25/2010	x	x	x
6/9/2010	x	x	x
7/29/2010		x	x
8/26/2010	x	x	x
Total number of samples	8	7	11

Sampling Sites

Two source-water sites and one finished-water site were sampled during this study (fig. 1). One source-water site was the Big Sioux River (USGS site 433600096442400) at an intake just upstream from the diversion dam. The other source-water site (USGS site 433421096434401) was blended groundwater from multiple wells and collection galleries producing from the Big Sioux, Skunk Creek, and Split Rock Creek aquifers (fig. 4). Contributions of individual wells and galleries to the blended groundwater samples were not determined. Finished water (USGS site 433419096434200) was collected from a water line following water treatment but prior to distribution. During periods of high demand, surface water from the Big Sioux River undergoes a high-rate clarification process prior to blending with the raw groundwater. After blending, the water-treatment process is the same regardless of the presence of surface water, which includes conventional lime softening, re-carbonation, filtration, fluoridation, and disinfection and uses granular and powdered activated carbon in separate treatment steps (City of Sioux Falls, 2011). The treatment process is not designed to remove trace organic compounds.

Collection, Processing, and Analysis of Water Samples

Water-quality and isotope samples were collected according to standard USGS procedures (U.S. Geological Survey, variously dated; U.S. Geological Survey, Reston Stable Isotope Laboratory, 2008). All samples of raw groundwater and finished water were collected directly from flowing water lines. Raw surface water from the Big Sioux River was collected from a flowing water line when this source was being used for water supply. For sampling dates when the Big Sioux River was not being used as a source for water supply, samples were collected directly from the river using depth-integrating techniques at the screened intake along the bank just upstream from the diversion dam. Sample-collection techniques follow procedures described in detail in chapters A4 and A5 of the USGS National Water-Quality Field Manual (U.S. Geological Survey, variously dated). Equipment used in the collection and processing of samples analyzed for AOCs were composed of Teflon®, baked amber glass, high-density polyethylene (HDPE) plastic, or stainless steel and were rigorously cleaned according to standard USGS procedures. Equipment used in the collection and processing of samples analyzed for nutrients or stable isotopes of nitrogen and oxygen were composed of Teflon®, HDPE, or stainless steel. For all AOC laboratory analyses of finished water, samples were preserved with ascorbic acid or sodium thiosulfate to prevent degradation of organic compounds in the presence of free chlorine (U.S. Environmental Protection Agency, 2011a; Valder and others, 2008).

Samples for analyses of selected AOCs were filtered in the field using a 142-millimeter diameter stainless steel plate-filter assembly with 0.7-micrometer nominal pore size glass-fiber filter media and a valveless ceramic-piston pump. Samples for the analyses of nutrients and stable isotopes were filtered using a 0.45-micrometer pore size HDPE capsule filters and a peristaltic pump. Stable-isotope samples were further filtered using 0.2-micrometer pore size cellulose acetate membrane filters. Following collection and processing of samples for analyses of AOCs, nutrients, and stable isotopes, samples were packaged, placed on ice, and shipped to respective laboratories for analyses. Information on the measurement, laboratory analyses, and applicable human-health benchmarks of the constituents analyzed for this study follow.

Physical Properties

Physical properties of pH, specific conductance, water temperature, and dissolved oxygen were measured continuously during the spring and summer months from March 2009 to September 2010 at USGS streamgage 06481000 using an in-situ multi-parameter sonde according to standard USGS procedures (Wagner and others, 2006). The physical properties also were measured in the samples of source water and finished water on each sampling date using a multi-parameter sonde and flow-through chamber (U.S. Geological Survey, variously dated).

Anthropogenic Organic Compounds

Organic compounds that are derived from anthropogenic sources (such as wastewater discharges or agricultural runoff) and found in water samples can be used to infer potential sources of contaminants from a drainage basin. Samples were analyzed for 184 AOCs, including 16 compounds analyzed by multiple analytical methods. The compounds listed in appendix 1 are organized by an analytical method number, which generally contains similar compounds in terms of their typical source or use.

Analytical method 1 includes 64 major agricultural herbicides, insecticides, and selected degradates, including three major herbicides (atrazine, metolachlor, and acetochlor) widely used in the Big Sioux River Basin upstream from Sioux Falls (U.S. Department of Agriculture, 2012). Laboratory analyses for this method were performed at the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colo., using solid-phase extraction (SPE) columns that contain octadecyl-bonded porous silica to extract the analytes. The columns are dried by using nitrogen gas, and adsorbed analytes are eluted with ethyl acetate. Extracted analytes are determined by capillary-column gas chromatography/mass spectrometry (Sandstrom and others, 2001; Madsen and others, 2002).

Analytical method 2 includes 14 pharmaceuticals predominantly used by humans and that can be found in municipal wastewater discharges. Laboratory analyses for this method were conducted at NWQL using a chemically modified styrene-divinylbenzene resin-based SPE cartridge for analyte isolation and concentration, followed by a high-performance liquid chromatography/mass spectrometry system to separate the pharmaceuticals of interest from each other and coextracted material (Furlong and others, 2008).

Analytical method 3 includes 69 compounds from a broad range of sources including those typically found in wastewater effluents (sterol compounds and household and industrial products), agricultural runoff (herbicides and insecticides), and urban runoff (polycyclic aromatic hydrocarbons). Laboratory analyses of compounds in analytical method 3 were conducted at NWQL using extraction with continuous liquid–liquid extractors and methylene chloride solvent and then determined by capillary-column gas chromatography/mass spectrometry (Zaugg and others, 2006).

Analytical method 4 includes 33 human and veterinary antibiotics and degradates that can be found in human and animal wastes. Laboratory analyses of compounds in analytical method 4 were conducted at the USGS Kansas Organic Geochemistry Research Laboratory (OGRL) in Lawrence, Kans., using automated SPE and liquid chromatography/tandem mass spectrometry (Meyer and others, 2007).

Analytical method 5 includes 16 steroid hormones produced by warm-blooded animals and 4 other compounds that can be found in wastewater discharges or animal wastes. Laboratory analysis for analytical method 5 is currently (2011) under development at NWQL; an expanded method description is provided in appendix 2. Analytical methods 3 and 5 were performed on unfiltered samples, whereas all others were performed on field-filtered samples.

AOC concentrations detected below the lowest daily standard, or for information-rich methods, concentrations detected below the long-term method detection level (LT–MDL), are reported as estimated concentrations (Childress and others, 1999), coded with an "E" preceding the concentration. The laboratory reporting level (LRL) generally is equal to twice the yearly determined LT–MDL (Childress and others, 1999). The LT–MDL is a detection level derived by determining the standard deviation or a minimum of 24 method detection level spike-sample measurements throughout an extended time. The LT–MDL data are collected on a continuous basis to assess year-to-year variations in the LT–MDL. The chance of falsely reporting a concentration at or greater than the LT–MDL for a sample that did not contain the analyte is predicted to be less than or equal to 1 percent (Childress and others, 1999). Also, at low concentrations, especially concentrations less than the LRL, the variability of detection is high, false negatives are more likely, and greater variability in reported concentrations is expected (Martin, 2002). Results for analytical methods 1 and 3 also contain concentrations reported as "M," which indicates the presence of the compound was verified but not quantified. In most cases, results coded as "M" were detected at concentrations less than the LT-MDL and do not round to the LT-MDL using the significant figures signified by the LRL. The reporting of these data is subject to the discretion of the laboratory analyst (David Mueller, U.S. Geological Survey, written comm., 2011). Concentrations are reported as less than the LRL when the compound was not detected.

Appendix 1 also lists relevant U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Levels (MCLs) and USGS Health-Based Screening Levels (HBSLs). The HBSLs are benchmark concentrations of contaminants in water that may be of potential concern for human health, if exceeded. The HBSLs are non-enforceable benchmarks developed by the USGS in collaboration with the USEPA and others using (1) USEPA Office of Water methodologies for establishing drinking-water guidelines, and (2) the most recent USEPA peer-reviewed, publicly available human-health toxicity information (Toccalino, 2007). MCLs are available for 8 AOCs, HBSLs are available for 32 AOCs, and no applicable water-quality benchmarks are available for the remaining 144 AOCs.

Nutrients and Nitrogen and Oxygen Isotope Ratios in Nitrate

Selected nutrients (nitrate, nitrite, ammonia, and orthophosphate) were used to examine the variability of potential contaminant sources to the water supply in the Sioux Falls area. Nitrate originates from a variety of anthropogenic and natural sources, including wastewater, synthetic fertilizers, animal wastes, explosives, and decomposing organic matter (Clark and Fritz, 1997). In standard analytical techniques, nitrate and its intermediate transformation species, nitrite, are measured together. Concentrations of nitrite plus nitrate (NO_2+NO_3) in finished water are regulated by the USEPA MCL of 10 milligrams per liter as nitrogen (mg/L as N). NO_2+NO_3 concentrations greater than 10 mg/L as N may be injurious when used in feeding infants (U.S. Environmental Protection Agency, 2009). Ammonia and orthophosphate were used as supplementary measures of nutrient enrichment in the source water. Samples were analyzed for nutrients at NWQL using standard methods (Fishman, 1993). City of Sioux Falls personnel assisted in the collection of five source-water samples for nutrients and nitrogen and oxygen isotope ratios in nitrate following short-duration storms when USGS personnel could not collect samples. Laboratory analyses of NO_2+NO_3 for these samples were performed by the City of Sioux Falls Purification Plant Laboratory using ion chromatography according to standard methods (American Public Health Association, 2005).

Ratios of the stable isotopes of nitrogen (^{15}N and ^{14}N) and oxygen (^{18}O and ^{16}O) in nitrate can provide insights on the sources in water (typically differentiating fertilizer from animal waste or organic matter). The additional neutrons in ^{15}N and ^{18}O result in atomic weights for these isotopes that

are different from those of the more predominant isotopes ^{14}N and ^{16}O. Molecules with different atomic weights have different reaction rates, which leads to isotope partitioning or fractionation (Clark and Fritz, 1997). Stable isotope ratios are expressed in "delta notation," which compares the ratio between the heavy and light isotopes of a sample to that of a reference standard. Delta values are expressed as a difference, in parts per thousand, or per mil (‰), from the value reference standard. The nitrogen isotope ratio ($\delta^{15}N$) of a sample written in delta notation is:

$$\delta^{15}N_{sample} = \frac{{}^{15}N/{}^{14}N_{sample} - {}^{15}N/{}^{14}N_{standard}}{{}^{15}N/{}^{14}N_{standard}} \times 1{,}000 \text{ ‰ AIR} \quad (1)$$

The oxygen isotope ratio ($\delta^{18}O$) of a sample written in delta notation is expressed by replacing ^{15}N and ^{14}N with ^{18}O and ^{16}O, respectively, and atmospheric nitrogen (AIR) with Vienna Standard Mean Ocean Water (VSMOW) in equation 1.

The manufacture of fertilizer results in very little fractionation; therefore, $\delta^{15}N$ of synthetic mineralized fertilizer is about 0 ‰ (Clark and Fritz, 1997; Böhlke, 2002). Organic nitrogen fixation of soil organic matter has a minor fractionation effect on ^{15}N, resulting in enrichment of about 3–7 ‰. The complex fractionation of ^{15}N through the food web results in enriched $\delta^{15}N$ values in the waste from animals of about 10–20 ‰ (Clark and Fritz, 1997). Biologically formed nitrate generally is depleted in ^{18}O because only one oxygen atom comes from atmospheric oxygen with the remaining two molecules coming from water (Hollocher, 1984), which is considerably more depleted in ^{18}O. The oxygen in synthetic fertilizer is primarily from atmospheric oxygen. The $\delta^{18}O$ values for nitrate vary according to the $\delta^{18}O$ of local waters, so absolute ranges cannot be estimated. Isotopic composition of nitrate and oxygen was analyzed at the Reston Stable Isotope Laboratory (RSIL, in Reston, Va.) by using mass spectrometry to analyze the conversion of nitrate to nitrous oxide (Révész and Casciotti, 2007).

Quality Assurance / Quality Control

Quality-control samples were collected to identify possible cases of random or systemic errors in the field sampling, shipping, and laboratory analyses. Field-equipment blank samples and sequential replicate samples were used to determine the potential for sample contamination. Environmental matrix spike samples were used to monitor the performance of a given analytical method for a specific environmental matrix.

Field-equipment blank samples were collected at sites used for collection of environmental samples by passing analyte-free water through the collection and processing equipment used for the environmental samples and by using procedures identical to those used to collect and process the environmental samples. Constituent concentrations less than the minimum reporting level (MRL) in field-equipment blank samples indicate that the overall process of sample collection, processing, and laboratory analysis was free of substantial contamination. The MRL is the lowest measured concentration of a constituent that may be reliably reported from the use of a given analytical method (Timme, 1995). Sporadic, infrequent detections at concentrations near the MRL probably represent contamination from sample collection, processing, or shipping that is not likely to cause bias in the study results. Consistent detections in the field-equipment blank samples at concentrations within the range of concentrations in the environmental samples indicate that environmental concentrations need to be qualified or omitted from study results.

Field-equipment blank samples were collected with 5 of the 26 environmental samples. Four different compounds were detected, all analyzed by analytical method 3. Two compounds—bis(2-ethylhexyl) phthalate (DEHP) and triphenyl phosphate—were detected in the groundwater blank sample collected on November 4, 2009. Triphenyl phosphate was not detected in the corresponding environmental sample, but the DEHP detection in the corresponding environmental sample was censored from additional statistical analyses; analytical results that were censored were removed from the dataset. The compound 4-nonylphenol was detected in the surface-water blank sample on January 4, 2010 (but was not detected in the corresponding environmental sample), and isophorone was detected in both finished-water blank samples on June 30, 2009, and November 4, 2009. On the basis of previous quality-control results (Sandstrom and Delzer, 2007), the compounds benzophenone, isophorone, and 4-nonylphenol were censored in all finished-water environmental samples because of systematic contamination with the dechlorination reagent and pH buffer used in these samples.

Precision of analytical results for field replicate samples may be affected by numerous sources of potential variability in 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 variability associated with sample collection and analysis. One field replicate sample was analyzed for nutrients (15 environmental samples), and all relative percent differences (difference in concentration divided by mean concentration for the environmental/replicate pair) were less than 1 percent.

Environmental matrix spike samples consist of replicate samples that are collected and processed identically to the primary environmental sample but are fortified with known concentrations of method analytes at the laboratory. Concentrations of the method analytes in the primary environmental samples and matrix spikes are determined, and the ambient concentrations in the primary environmental sample are subtracted from the matrix-spike concentrations. The resulting

concentrations are compared to the expected concentrations to calculate the percent recoveries for the method analytes using the following equation:

$$Percent\ recovery = (C_{spiked} - C_{unspiked}) * 100 / [(C_{soln} * Amt) / Vol] \quad (2)$$

where

C_{spiked} is the measured concentration of the spiked sample,

$C_{unspiked}$ is the measured concentration of the unspiked sample,

C_{soln} is the concentration of the spike solution,

Amt is the amount of spike added, and

Vol is the sample volume.

If $C_{unspiked}$ is less than the LRL, a value of zero is used for this concentration. Recoveries less than 100 percent indicate loss (or transformation) of the target analyte during the sample-processing period, and recoveries greater than 100 percent indicate gain of the target analyte. The satisfactory range of median percent recoveries for environmental matrix spike samples typically is between 50–120 percent (Sando and others, 2006).

Matrix spike samples were collected with 5 of the 26 environmental samples. Percent recoveries for all matrix spike samples are shown in appendix 3. Recovery results indicated limited potential for loss or gain of target analytes during the field and laboratory processing for 85 percent of compounds, and no adjustment of analyte concentrations was made on the basis of unsatisfactory percent recoveries. For analytical method 1, five compounds had median percent recoveries less than 50 percent, 9 compounds had median recoveries greater than 120 percent, and the remaining 50 compounds had median percent recoveries within the satisfactory range. Median percent recoveries were less than 50 percent for 2 of the 14 analytes in analytical method 2 and for 9 of the 69 analytes in analytical method 3. Six analytes in analytical method 4 had median percent recoveries greater than 120 percent. All matrix recoveries were satisfactory for analytical method 5.

Occurrence of Anthropogenic Organic Compounds and Nutrients

Water-quality results are presented in separate sections for AOCs and nutrients. The occurrence of AOCs is presented according to the sampling sites (surface-water source, groundwater source, and finished water). The occurrence of nutrients is presented for source-water samples (not collected for finished water) and includes ratios of nitrogen and oxygen isotopes in nitrate. For brevity, sampling sites for the Big Sioux River, blended groundwater from multiple wells and collection galleries, and finished water (USGS sites 433600096442400, 433421096434401, and 433419096434200, respectively) will be referred to as the Big Sioux River, groundwater, and finished-water sites for the remainder of this report.

Physical Properties

The physical water-quality properties of pH, specific conductance, water temperature, and dissolved oxygen provide an initial characterization of water quality. The daily mean water temperature and specific conductance collected continuously from March 2009 to September 2010 at the Big Sioux River near Dell Rapids (USGS streamgage 06481000; U.S. Geological Survey, 2011), which is upstream from Sioux Falls (inset map in fig. 1), are shown on figure 5. Data for the physical water-quality properties for samples collected at source-water and finished-water sites are presented in appendix 4. Large increases in specific conductance indicate an increase in the dissolved solids concentration, which may correlate positively with concentrations of certain nutrients and AOCs associated with the same sources as the dissolved solids. Specific conductance and streamflow usually are inversely related in the Big Sioux River. Immediately following precipitation events in the Big Sioux River Basin, specific conductance typically decreases as a result of the precipitation with low dissolved solids entering the rivers. Shortly after the June 9 and August 24, 2010, sampling dates, prolonged rainfall events caused a rise in streamflow and groundwater levels (fig. 2), and the dilution of dissolved solids because of the precipitation is shown by the decrease in specific conductance following these sampling dates (fig. 5). Commonly, this decrease in specific conductance is followed by an increase during the subsequent weeks as the rainwater is replaced by surface runoff that has traveled farther distances from the river and contains various contaminants and dissolved solids accumulated along the way. Groundwater discharge into the river also could increase the specific conductance following storms, as groundwater with higher values of specific conductance mix with the snowmelt or runoff with lower values of specific conductance. For example, in the month following the snowmelt sample on March 25, 2010, specific conductance increased as the streamflows decreased (figs. 2 and 5). Water temperature typically follows the same pattern as specific conductance in the spring and summer because precipitation commonly is cooler than the antecedent river temperature. Other than the March 25, 2010, snowmelt sample, samples were collected from the Big Sioux River during base-flow conditions (fig. 2); no samples were representative of the conditions following spring and summer rainfall events when the probability of detecting higher concentrations of surface-runoff contaminants (such as pesticides) is greater.

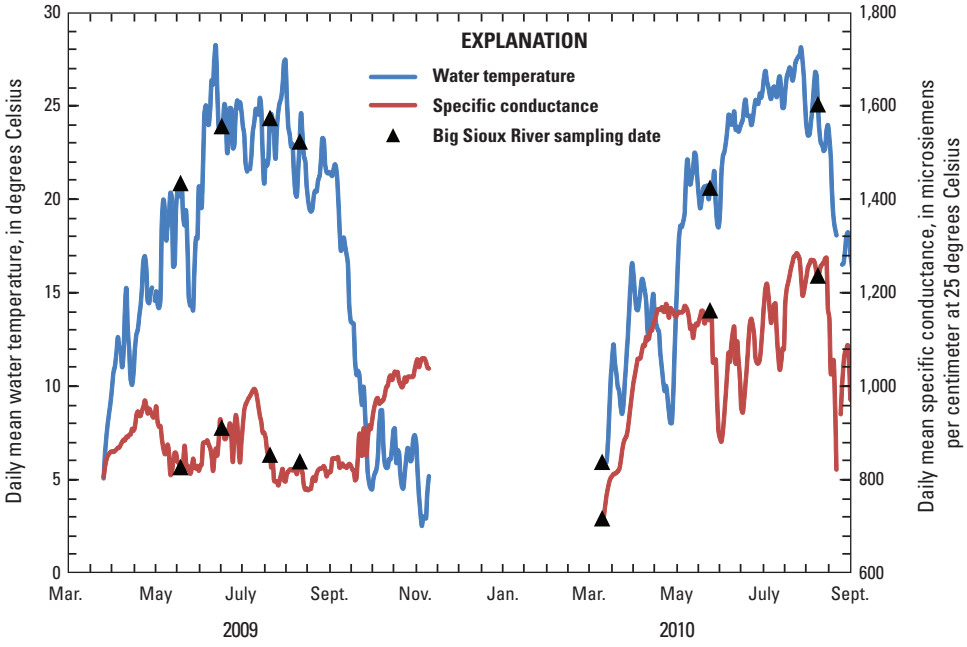

Figure 5. Daily mean water temperature and specific conductance at the Big Sioux River near Dell Rapids (streamgage 06481000), March 2009 to September 2010.

Anthropogenic Organic Compounds

The occurrence of AOCs is characterized separately for the Big Sioux River (source water), groundwater (source water), and finished water. The AOC concentrations for all samples are presented in appendix 4. Data that were censored because of potential contamination as indicated by quality-assurance samples were removed from the dataset and coded with a "C" in appendix 4. Data for all 184 AOCs are not available for every sample collected because a few bottles were broken during shipment to the laboratory and because some constituents were not analyzed in some samples because of laboratory quality-assurance issues. For the 184 AOCs analyzed, 45 compounds (24 percent) were detected in at least one sample of source or finished water (appendix 4), and 13 compounds were detected in at least 20 percent of all samples (table 3). Concentrations of AOCs detected were all less than 1 microgram per liter (µg/L), except for cholesterol and *beta*-sitosterol concentrations in the Big Sioux River, and one detection of DEHP in finished water. More than 75 percent of the detections of AOCs were at concentrations less than 0.1 µg/L. Concentrations coded as "M" in appendix 4 and table 3 indicate the presence of the analyte was verified but at a concentration less than reporting levels and could not be quantified.

To aid in evaluating water-quality data in the context of human health, benchmark quotient (BQ) values were calculated (Toccalino, 2007). A BQ value is the ratio of a measured concentration of a detected compound to its MCL or HBSL (BQ values cannot be calculated for compounds without a relevant human-health benchmark). For this study, the maximum concentration detected for each compound was used to calculate this ratio, called BQmax. A BQmax value greater than or equal to 0.1 (within an order of magnitude of the benchmark) was used to identify compounds that may merit additional study and to provide an early indication of contaminant concentrations of potential human-health concern.

Big Sioux River

Eight source-water samples were collected from the Big Sioux River. A total of 33 different AOCs were detected in at least one sample from the Big Sioux River (appendix 4), and 20 compounds were detected in at least 20 percent of the samples (table 3). Five compounds (atrazine, cholesterol, deethylatrazine, metolachlor, and prometon) were detected in every sample. For atrazine, the maximum concentration was about an order of magnitude less than its benchmark standard (table 3). Maximum concentrations of metolachlor and prometon were about four orders of magnitude less than benchmark standards (table 3). Cholesterol concentrations in the Big Sioux River ranged from 0.630 µg/L in the winter low-flow sample on January 4, 2010, to 11.5 µg/L in the late summer sample collected on August 3, 2009. The presence of cholesterol may be indicative of wastewater or livestock-waste runoff. The pesticide acetochlor was detected in 6 of 8 samples from the Big Sioux River; the maximum detected concentration of 0.146 µg/L was within an order of magnitude of the HBSL.

Groundwater

Seven source-water samples were collected from groundwater. A total of 30 different AOCs were detected in at least one groundwater sample (appendix 4), and 14 compounds were detected in at least 20 percent of groundwater samples (table 3). The same four herbicides or degradates detected in all Big Sioux River samples (atrazine, deethylatrazine,

Table 3. Detection frequency, maximum concentration, and maximum benchmark quotient for anthropogenic organic compounds detected in at least 20 percent of samples at any site.

[Big Sioux River, site 433600096442400; Groundwater, site 433421096434401; finished water, site 433419096434200; USEPA, U.S. Environmental Protection Agency; MCL, Maximum Contaminant Level; USGS, U.S. Geological Survey; HBSL, Health-Based Screening Level; µg/L, micrograms per liter; BQmax, maximum benchmark quotient; --, not available; E, estimated value; M, presence verified but not quantified]

Analyte	Analytical method(s)	Number of detections / samples			Maximum concentration (µg/L)			USEPA MCL or USGS HBSL (µg/L)	BQmax		
		Big Sioux River	Groundwater	Finished water	Big Sioux River	Groundwater	Finished water		Big Sioux River	Groundwater	Finished water
Pharmaceuticals, hormones, and antibiotics											
Caffeine	2, 3	2/6	1/7	0/10	E0.025	E0.024	--	--	--	--	--
Carbamazepine	2, 4	5/8	3/7	0/11	0.014	E0.002	--	--	--	--	--
Cholesterol	3, 5	8/8	1/7	1/11	11.5	M	M	--	--	--	--
Estrone	5	3/8	0/7	0/11	0.0014	--	--	--	--	--	--
Sulfamethoxazole	2, 4	7/8	2/7	0/11	0.052	0.011	--	--	--	--	--
Sterol compounds, household and industrial products											
4-Nonylphenol diethoxylate	3	1/7	2/7	0/9	M	M	--	--	--	--	--
5-Methyl-1H-benzotriazole	3	0/6	1/5	0/8	--	M	--	--	--	--	--
Benzophenone	3	1/7	3/7	--	M	M	--	--	--	--	--
beta-Sitosterol	3	4/7	1/7	0/9	E1	M	--	--	--	--	--
beta-Stigmastanol	3	2/7	0/6	0/8	M	--	--	--	--	--	--
Bis(2-ethylhexyl) phthalate (DEHP)	3	1/6	2/6	1/9	M	M	3	6	[1]0.02	[1]0.03	0.50
Bisphenol A	3, 5	2/6	2/7	0/9	M	M	--	--	--	--	--
Bromoform	3	1/7	2/7	9/9	M	E0.1	0.8	[2]80	[1]0.0002	0.0013	0.010
Diethyl phthalate	3	0/6	1/7	2/9	--	E0.1	E0.1	--	--	--	--
Isophorone	3	2/7	0/7	--	M	--	--	--	--	--	--
N,N-Diethyl-*meta*-toluamide (DEET)	3	5/7	2/7	2/9	M	M	E0.1	--	--	--	--
p-Cresol	3	1/7	2/7	0/9	M	M	--	--	--	--	--
Pentachlorophenol	3	1/5	0/6	0/8	M	--	--	1	[1]0.23	--	--
Tributyl phosphate	3	2/7	2/7	3/9	M	E0.1	M	--	--	--	--
Tris-(2-chloroethyl) phosphate	3	2/7	1/7	0/9	M	M	--	--	--	--	--
Pesticides and degradates											
2-Ethyl-6-methyl-aniline	1	0/8	4/7	0/11	--	E0.005	--	--	--	--	--
Acetochlor	1	6/8	1/7	4/11	0.146	0.023	0.010	1	0.15	0.023	0.010
Atrazine	1, 3	8/8	7/7	11/11	0.35	0.081	0.045	3	0.12	0.027	0.015
Chlorpyrifos	1, 3	2/8	0/7	0/11	E0.010	--	--	2	0.005	--	--
Deethylatrazine	1	8/8	7/7	9/11	E0.114	E0.064	E0.032	--	--	--	--
Desulfinylfipronil	1	2/8	0/7	0/11	E0.004	--	--	--	--	--	--
Metolachlor	1, 3	8/8	7/7	10/11	0.090	0.025	E0.010	700	0.0001	0.00004	0.00001
Prometon	1, 3	8/8	7/7	11/11	0.02	0.02	E0.01	400	0.00005	0.00005	0.00003

[1]Actual concentration used in BQmax calculation has high uncertainty and is not shown in appendix 4.

[2]MCL is for total trihalomethanes.

metolachlor, and prometon) also were detected in all groundwater samples. Atrazine concentrations in the groundwater ranged from 0.008 µg/L in the winter (Febuary 17, 2010) to 0.081 µg/L in the summer (July 29, 2010). Deethylatrazine was detected at similar concentrations, from 0.008–0.064 µg/L. Metolachlor was detected in the groundwater at a concentration range of 0.005–0.025 µg/L. Similar to the Big Sioux River concentrations, prometon concentrations for all groundwater samples were 0.02 µg/L or less.

Finished Water

Eleven finished-water samples were collected. A total of 14 AOCs were detected in at least one finished-water sample (appendix 4), and 9 compounds were detected in at least 20 percent of samples (table 3). The disinfection byproduct bromoform was detected in every finished-water sample, along with the herbicides atrazine and prometon. Bromoform concentrations ranged from 0.6 to 0.8 µg/L, which were much less than the MCL of 80 µg/L for total trihalomethanes (including bromoform). Atrazine concentrations in finished water were similar to those in groundwater (the dominant source water), ranging from 0.008–0.045 µg/L. Similar to the source-water concentrations, prometon concentrations in finished water were 0.01 µg/L or less. The relatively high concentration of DEHP in finished water on November 4, 2009 (3 µg/L) occurred on the same day the compound was detected in both the groundwater and blank sample associated with the groundwater sample. The DEHP concentration in the groundwater sample was not high enough to be quantified and was censored in appendix 4 because of the detection in the blank sample. The concentration in the groundwater blank sample was at a similar concentration (2 µg/L) as the finished-water sample. DEHP was detected in three other source-water samples and was not detected in the blank sample associated with the finished-water sample.

Nutrients

Nutrient samples were collected only at source-water sites (Big Sioux River and groundwater). Concentrations of nutrients and nitrogen and oxygen isotope ratios in nitrate for the source-water samples are presented in table 4. Nutrient concentrations varied seasonally in samples from the Big Sioux River and groundwater. The NO_2+NO_3 concentrations generally were lower in groundwater than the Big Sioux River, but ammonia concentrations typically were higher in groundwater than in the Big Sioux River. The NO_2+NO_3 concentrations in the Big Sioux River were lower in 2009–10 than in previous years (Tim Stefanich, city of Sioux Falls, written comm., 2010), and were always less than one-half of the MCL for drinking water (10 mg/L as N). In the Big Sioux River, NO_2+NO_3 concentrations were typically less than 1 mg/L as N for the summer months in 2009, increased to nearly 3 mg/L as N by January 2010, reached a maximum of 4.06 mg/L as N following a June 2010 runoff event, and decreased to 0.123 mg/L as N by August 2010. For groundwater, NO_2+NO_3 concentrations increased from 0.129 mg/L as N in November 2009 to 0.701 mg/L as N in March 2010, and then decreased to less than 0.100 mg/L as N in the summer months of 2010. During the fall and summer months, ammonia concentrations were greater than NO_2+NO_3 concentrations in groundwater samples. Orthophosphate concentrations generally were stable in the groundwater samples ranging between 0.010 and 0.020 mg/L as phosphorus. Orthophosphate concentrations were more variable in Big Sioux River samples than groundwater samples, ranging from 0.035 mg/L or less in the summer months of 2009 to 0.224 mg/L in the snowmelt sample collected in March 2010.

Isotopic ratios also varied seasonally in samples from the Big Sioux River but were somewhat less variable in groundwater samples (fig. 6). The $\delta^{15}N$ values for the Big Sioux River samples decreased from about 18.55 to 13.12 ‰ from June to July 2009, and reached a minimum value of 7.55 ‰ in the March 2010 snowmelt sample. From June to August 2010, the $\delta^{15}N$ values in the Big Sioux River samples increased from 9.36 to 21.59 ‰. Nitrogen and oxygen isotope ratios could not be determined for the June 1, August 3, and August 24, 2009, samples from the Big Sioux River because the concentrations of NO_2+NO_3 were less than analytical reporting levels. The $\delta^{18}O$ values mirrored the $\delta^{15}N$ values, as shown by the strong linear relation in figure 7. Groundwater $\delta^{15}N$ values were about 17–18 ‰ during the winter months (November 2009 to February 2010), but reached a maximum value of 22.84 ‰ on June 9, 2010, just prior to the sustained wet period in the summer of 2010. The late summer (July and August 2010) $\delta^{15}N$ values (10.54 and 13.22 ‰, respectively) in groundwater were lower than other groundwater samples.

Implications of Occurrence

Eight compounds were detected that have a human-health benchmark (USEPA MCL or USGS HBSL) that can be used to evaluate the concentrations in a human-health context. A plot of the BQmax for these compounds (fig. 8) shows no detections were at concentrations greater than relevant benchmarks (BQmax values were all less than 1). Four compounds had BQmax values greater than 0.1 (within an order of magnitude of the benchmark), indicating that additional monitoring of the compound may be warranted. Atrazine was detected at a maximum concentration of 0.35 µg/L (BQmax = 0.12) in the Big Sioux River, but BQmax values in groundwater and finished-water samples were less than 0.03. The occurrence of atrazine is not uncommon, as atrazine was detected in all samples at all sites during this study, and was detected in more than 50 percent of Big Sioux River samples during 2001–04 with a higher LRL (0.5 µg/L; Sando and others, 2006) than those used during this study (0.007 and 0.2 µg/L). Acetochlor had a BQmax value greater than 0.1 in Big Sioux River samples, but the BQmax value in finished water was two orders of magnitude less than the benchmark. Acetochlor was detected in 75 percent of the Big Sioux River samples, but in

Table 4. Concentrations of nutrients and nitrogen and oxygen isotope ratios in nitrate in source water.

[mg/L, milligrams per liter; N, nitrogen; P, phosphorus; per mil, difference in parts per thousand from value reference standard; E, estimated value; <, less than; --, not available]

Source water	Date	Nitrogen, ammonia, dissolved (mg/L as N) (00608)	Nitrogen, nitrite, dissolved (mg/L as N) (00613)	Nitrogen, nitrite plus nitrate, dissolved (mg/L as N) (00631)	Orthophosphate, dissolved (mg/L as P) (00671)	$\delta^{15}N$ in nitrate fraction, water (per mil) (82690)	$\delta^{18}O$ in nitrate fraction, water (per mil) (63041)
Big Sioux River (site 433600096442400)	6/1/2009	E0.011	<0.002	<0.016	E0.005	--	--
	6/19/2009	--	--	[1]0.26	--	[2]18.55	[2]9.66
	6/30/2009	<0.02	0.043	0.941	0.035	16.57	8.93
	7/10/2009	--	--	[1]1.08	--	[2]15.55	[2]7.68
	7/14/2009	--	--	[1]1.13	--	[2]13.12	[2]4.34
	8/3/2009	<0.02	<0.002	<0.016	0.011	--	--
	8/24/2009	<0.02	<0.002	<0.016	0.016	--	--
	1/4/2010	0.167	0.0142	2.92	0.129	9.65	3.08
	3/25/2010	0.138	0.058	2.34	0.224	7.55	4.31
	6/9/2010	E0.014	0.0196	1.08	0.127	11.93	4.28
	6/13/2010	--	--	[1]3.48	--	[2]9.36	[2]4.03
	6/16/2010	--	--	[1]4.06	--	[2]12.24	[2]5.87
	8/26/2010	<0.02	0.0057	0.123	0.189	21.59	12.35
Groundwater (site 433421096434401)	11/4/2009	0.245	0.0024	0.129	0.010	17.89	9.8
	1/5/2010	0.26	0.0081	0.363	0.019	16.95	6.16
	2/17/2010	0.248	0.0078	0.442	0.016	17.39	7.34
	3/25/2010	0.217	0.0085	0.701	0.019	14.45	7.12
	6/9/2010	0.192	0.0033	0.103	0.014	22.84	12.54
	7/29/2010	0.312	0.0029	0.092	0.017	10.54	5.15
	8/26/2010	0.291	0.0023	0.088	0.017	13.22	7.68

[1]Collection and laboratory analysis performed by city of Sioux Falls staff following short-duration storm.

[2]Collection performed by city of Sioux Falls staff following short-duration storm.

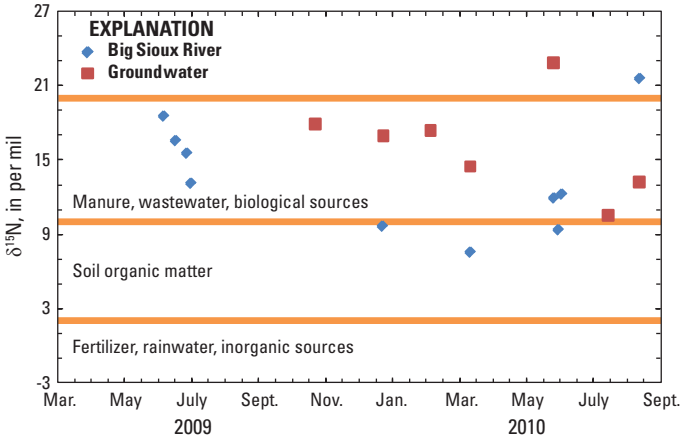

Figure 6. Nitrogen isotope ratios in nitrate for source-water samples in relation to the isotopic composition of nitrate sources, 2009–10.

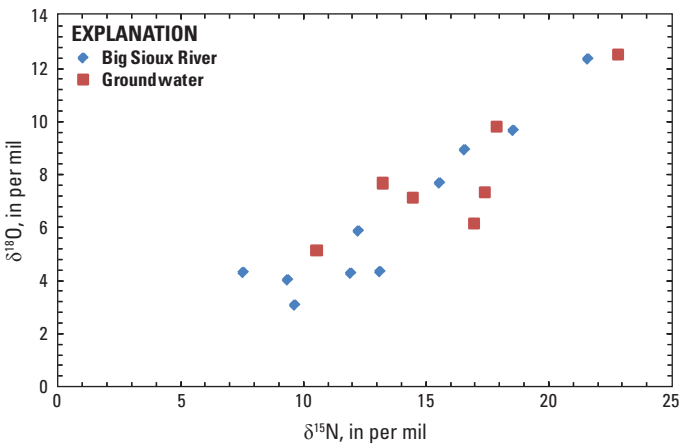

Figure 7. Nitrogen and oxygen isotope ratios in nitrate of source-water samples.

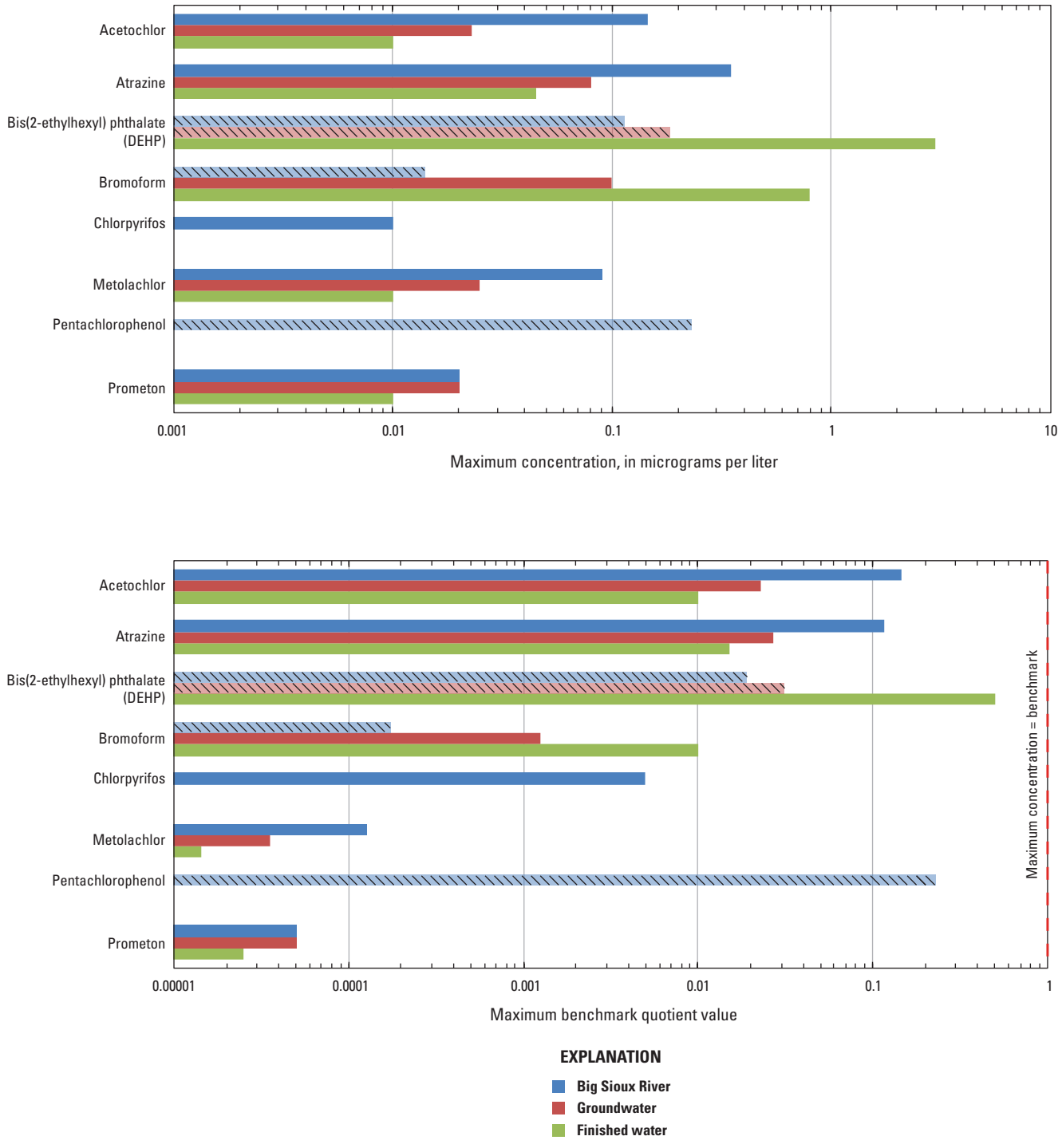

Figure 8. Maximum concentrations and benchmark quotient values for detected anthropogenic organic compounds that have a relevant benchmark. (Hatched bars for DEHP, bromoform, and pentachloraphenol indicate actual concentration was uncertain and not quantified in the text; presence of the compound was verified but not quantified).

only 14 percent of the groundwater samples, indicating a more sporadic occurrence trend. Pentachlorophenol was detected in one of five samples in the Big Sioux River (BQmax = 0.23), but was not detected in any sample of groundwater or finished water (three additional laboratory analyses of pentachlorophenol in the Big Sioux River were censored because of laboratory quality-control data). Pentachlorophenol was not detected in samples from the Big Sioux River and finished water in 2001–04, but was detected in two of six wastewater treatment-plant effluent samples (Sando and others, 2006). The plasticizer DEHP had the greatest BQmax value of any AOC (0.5) in finished water, but was not detected in any of the other eight finished-water samples and was detected in only 25 percent of the source-water samples. The compound was detected at a similar frequency (20 percent) in the Big Sioux River in 2001–04, and was detected at high concentrations (greater than 5 µg/L) in samples of wastewater effluent (Sando and others, 2006). Although it is plausible that the finished-water detection represents the presence of DEHP, this detection is somewhat uncertain on the basis of the concentration (2 µg/L) in one of the four blank samples.

Three herbicides (atrazine, metolachlor, and prometon) and one degradate (deethylatrazine) were detected in finished water as frequently as in source water (table 3). The occurrence of herbicides in surface water for drainage basins with predominantly agricultural land use is not uncommon. Atrazine and metolachlor are two of the most heavily used agricultural herbicides in the United States with much of the use for corn production, and prometon has considerable use for weed control in areas not associated with agriculture such as on turf-grass, lawns, and roadsides (Gilliom and others, 2006). Previous studies indicate that the herbicide degradates (such as deethylatrazine) typically occur with their parent compounds at concentrations similar to or greater than concentrations of their parent compounds (Gilliom and others, 2006; Kingsbury and others, 2008), but not all potential degradates of atrazine, metolachlor, and prometon were analyzed as part of this study. The concentrations of herbicides in source water can vary by an order of magnitude from the period of peak application (early summer) to the winter months (fig. 9).

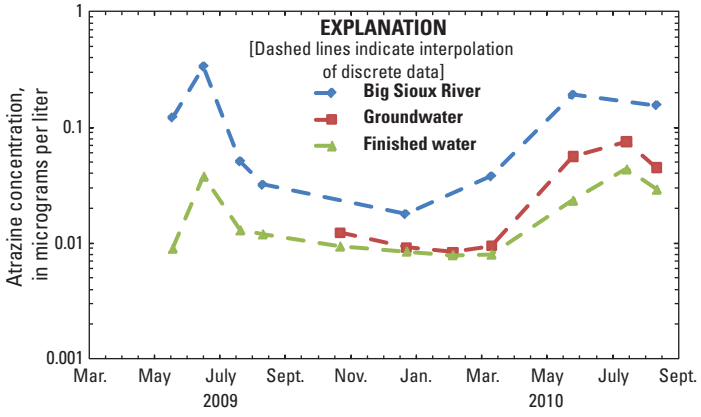

Figure 9. Atrazine concentration in source- and finished-water samples, 2009–10.

Chemical properties help explain the co-occurrence of certain AOCs in the Big Sioux River, groundwater, and finished water. The shallow setting of the Big Sioux aquifer provides a potential contaminant pathway to transport surface contaminants into the groundwater source because the Big Sioux River is hydraulically connected to the underlying aquifer in many areas. Atrazine, metolachlor, and prometon can be highly mobile in sandy soils and aquifers (Gilliom and others, 2006). Atrazine can remain in the environment for periods beyond the growing season when it was applied, with a half-life of about 60 days in the topsoil and substantially longer in the subsurface and aquatic environment (Christensen and Ziegler, 1998). These herbicides (along with acetochlor) have log octanol-water partitioning coefficients (log K_{ow}) less than 5 (U.S. Environmental Protection Agency, 2011b), which indicates their affinity for the dissolved phase. Contaminants with log K_{ow} in this range will not readily adsorb to sediments in the aquifer or other filtering materials in the transport process. Atrazine concentrations were lower in finished-water samples than in the source-water samples, although the concentration trends were similar (fig. 9). For the six sampling dates when groundwater was the only source water used (no blending with surface water; all groundwater samples except June 9, 2010), groundwater and finished-water concentrations of atrazine were similar (fig. 9). The samples collected for this study were not designed to assess the efficacy of the water treatment for removing herbicides, but demonstrate the potential for certain herbicides to persist throughout the treatment process.

Upstream wastewater discharges contributed a fairly small percentage of the flow to the Big Sioux River near Sioux Falls (usually less than 3 percent during the summer months), but several AOCs associated with wastewater were frequently detected. The large distance between major wastewater discharges and the sampling sites (Watertown and Brookings are about 176 and 76 river miles upstream from Sioux Falls, respectively) allows for substantial removal of these compounds by degradation and settling of particulate-bound contaminants, but bed sediments in the Big Sioux River also can be a source of AOCs (Sando and others, 2006). Carbamazapine (pharmaceutical) and sulfamethoxazole (antibiotic) were detected in more than one-half of the Big Sioux River samples but were detected at lower frequencies in groundwater and not detected in finished water (table 3). Three sterol compounds usually associated with wastewater discharges or manure runoff (cholesterol, *beta*-sitosterol, and 3-*beta*-coprostanol) had greater detection frequencies in the Big Sioux River samples (100, 57, and 13 percent, respectively) than in groundwater samples (14, 14, and 0 percent, respectively) and finished-water samples (9, 0, and 0 percent, respectively; table 3 and appendix 4). *Beta*-sitosterol (a plant sterol) also occurs in natural waters and sediments through the breakdown of native vegetation, and can be associated with nonpoint runoff as well as wastewater discharges. The compound 3-*beta*-coprostanol is a carnivore fecal sterol. The direct pathway to surface water explains the frequent occurrence of these

compounds in the Big Sioux River compared to groundwater and subsequently finished water. In addition, these compounds have log K_{ow} values greater than 8.0 (U.S. Environmental Protection Agency, 2011b), and are more susceptible to natural filtering in groundwater movement. Tributyl phosphate, a manufacturing additive and flame retardant, typically is associated with wastewater effluents and was detected at similar frequencies for the Big Sioux River, groundwater, and finished-water samples (29, 29, and 33 percent, respectively). The log K_{ow} for tributyl phosphate is less than 5 (Hansch and others, 1995), which may help explain the similar occurrence at all three sites. Sorption to aquifer materials is just one removal mechanism, and other environmental processes (such as volatilization or biological degradation) also will have a substantial effect on the fate and transport of organic compounds.

The measurements of isotopic ratios provide qualitative information regarding the nitrogen sources in the water supply (Cravotta, 2002), because the proportions of multiple nitrogen sources could not be sufficiently estimated using a single sampling location at the terminal point of the source water. The literature-reported range for $\delta^{15}N$ values indicative of fertilizers and inorganic sources is about -3–2 ‰, values for organic sources such as manure and wastewater range from about 10–20 ‰, and values for a combination of the two sources or for soil organic matter are in the intermediate range of 2–10 ‰ (fig. 6; Clark and Fritz, 1997; Katz and Böhlke, 2000; Tihansky and Sacks, 1997). Most (82 percent) of the $\delta^{15}N$ values in the source-water samples were greater than 10 ‰, indicating biological sources as the predominant component of nitrogen in the nitrate of the source water (fig. 6). Three samples of the Big Sioux River had $\delta^{15}N$ values between 7–10 ‰, indicating a greater proportion of soil organic material or inorganic sources. The varying isotopic composition of nitrogen and oxygen in nitrate in groundwater samples (fig. 7) is not only an effect of changing hydrologic conditions and seasonality, but also could be explained by the blending of groundwater from wells and collection galleries in several aquifers (fig. 4). For example, groundwater from a collection gallery near the Big Sioux River would likely have a much different isotopic signature than a well farther away from surface-water influence.

Source water sampled for this study was a mix of various water supplies within the Big Sioux River Basin that have undergone numerous chemical and biological transformations before reaching the sampling location. These processes (including volatilization, hydrolysis, assimilation, mineralization, nitrification, and denitrification) affect the isotopic signatures of nitrogen and oxygen in nitrate. Volatilization of urea or ammonia nitrogen, the typical form of nitrogen fertilizer in most agricultural areas, leaves the soil relatively enriched in ^{15}N (Böhlke, 2002). Nitrogen transformations in the soil further fractionate the isotopes of nitrogen and oxygen compounds and obscure the source signatures (Böhlke, 2003). Nitrification is the transformation of organic nitrogen, from manure or wastewater effluent, into nitrite and subsequently nitrate in an aerobic environment. Nitrogen that enters the aquatic environment in the form of nitrate (such as fertilizers) can denitrify into nitrite, nitric oxide, nitrous oxide, and eventually nitrogen gas (N_2) in an anaerobic environment. The denitrification process preferentially uses the lower $\delta^{15}N$ nitrate (from fertilizers), enriching the higher $\delta^{15}N$ nitrate (from wastewater and manure) in the remaining nitrate. Previous studies (McMahon and Böhlke, 2006; Böhlke, 2003) used a dissolved oxygen concentration of 2 mg/L as the maximum concentration for denitrification to occur. Dissolved oxygen concentrations in the Big Sioux River and groundwater samples were between 5 and 13 mg/L, thus denitrification was not likely, but cannot be adequately assessed without knowledge of oxic conditions throughout the basin. Denitrification could be quantified with analysis of dissolved gases (such as N_2) in the saturated zone (Böhlke, 2002), but dissolved gases were not sampled in this study.

Using the assumption that denitrification was not substantial, fertilizers and other inorganic sources probably are not the dominant source of nitrate in the source water because none of the $\delta^{15}N$ values from either surface water or groundwater was less than 7 ‰. Samples with high concentrations of dissolved oxygen, absence of N_2 gas, and constant values of $\delta^{18}O$ are most likely to have $\delta^{15}N$ values that reflect the actual nitrogen source characteristics (Böhlke, 2003). Values of $\delta^{18}O$ were not constant for varying values of $\delta^{15}N$ (fig. 7), so various transformation processes likely caused an enrichment of ^{15}N in the source water. The interpretation of all potential sources of nitrogen cannot be accomplished by use of nitrogen and oxygen isotopes in nitrate alone, but provides a qualitative indication that very little nitrate originates from excess fertilizer runoff, and most nitrate originates from municipal wastewater effluent, manure runoff (either from field application or feeding operations), or fertilizers mineralized by processes in the soil.

Summary and Conclusions

Anthropogenic organic compounds (AOCs) in drinking-water sources commonly are derived from municipal, agricultural, and industrial wastewater sources, and are a concern for water-supply managers. Although some of the most commonly used and toxic AOCs are regulated, most are unregulated and human-health effects from many AOCs are uncertain. The city of Sioux Falls, S. Dak., identified a need to investigate potential contaminant origins, including AOCs, when peak nitrate concentrations occur in source water. A cooperative study between the city of Sioux Falls and the U.S. Geological Survey (USGS) was initiated in 2009 to (1) characterize the occurrence of anthropogenic organic compounds in source waters (groundwater and surface water) to water supplies in the Sioux Falls area, (2) determine if the compounds found in the source waters also are present in the finished water, and (3) identify probable sources of nitrate in the Big Sioux River Basin and determine if sources change seasonally or

under different hydrologic conditions. This report presents analytical results of water-quality samples collected from source water (groundwater blended from multiple wells and collection galleries and surface water from the Big Sioux River) and finished water in the Sioux Falls area. Samples for analyses of AOCs and nutrients were collected on 11 days between June 2009 and August 2010. The 2009–10 period represented two extremes in terms of the prevailing hydrologic conditions. Water year 2009 (October 1, 2008, to September 30, 2009) was the driest year of the decade for the Sioux Falls area, whereas water year 2010 had the most precipitation (43.1 inches) in the 120-year period of record.

Extensive agricultural activities occur in the Big Sioux River Basin, and the largest cities in the basin have developed along the Big Sioux River, contributing urban runoff and wastewater effluent discharges to the river. Outwash deposits along the Big Sioux River and its tributaries underlie much of the Big Sioux River Basin, composing the glacial aquifers that serve as the primary source to water supplies in the Sioux Falls area. These aquifers have areas where they are hydraulically connected to the Big Sioux River, and can be sensitive to infiltration of surface contaminants. The city of Sioux Falls currently (2011) uses groundwater as its primary water source year-round, and supplements the supply with surface water from the Big Sioux River only during periods of increased demand (typically in the summer months).

The study approach included the collection of source- and finished-water samples for the analyses of AOCs, nutrients, and nitrogen and oxygen isotopes in nitrate. Two source-water sites and one finished-water site were sampled during this study. The two source-water sites were the Big Sioux River at an intake location and blended groundwater from multiple wells and collection galleries. Finished water was collected from a flowing water line following water treatment but prior to distribution. Water-quality constituents monitored in this study were chosen to represent a variety of the contaminants known or suspected to occur within the Big Sioux River Basin, including pesticides, pharmaceuticals, sterol compounds, household and industrial products, polycyclic aromatic hydrocarbons, antibiotics, and hormones. A total of 184 AOCs were monitored, of which 40 compounds had relevant U.S. Environmental Protection Agency Maximum Contaminant Levels (MCLs) or USGS Health-Based Screening Levels (HBSLs). The nutrients nitrate, nitrite, ammonia, and orthophosphorus, along with the ratios of the stable isotopes of nitrogen and oxygen in nitrate ($\delta^{15}N$ and $\delta^{18}O$), also were analyzed to assess the types of contaminants present in the water supplies in the Sioux Falls area.

Of the 184 AOCs analyzed, 45 compounds (24 percent) were detected in at least one sample of source or finished water, and 13 compounds were detected in at least 20 percent of all samples. Concentrations of detected AOCs were all less than 1 microgram per liter (µg/L), except for concentrations of cholesterol and *beta*-sitosterol in the Big Sioux River and one detection of bis-(2-ethylhexyl) phthalate in finished water. Concentrations of AOCs were less than 0.1 µg/L in more than 75 percent of the detections. Five compounds (atrazine, cholesterol, deethylatrazine, metolachlor, and prometon) were detected in every sample of source water from the Big Sioux River. The same four herbicides or degradates detected in all Big Sioux River samples also were detected in all groundwater samples. The disinfection byproduct bromoform was detected in every sample of finished water, along with the herbicides atrazine and prometon. Nutrient concentrations varied seasonally in the Big Sioux River and groundwater. In the Big Sioux River, nitrite plus nitrate concentrations typically were less than 1 milligram per liter as nitrogen (mg/L as N) for the summer months in 2009, increased to nearly 3 mg/L as N by January 2010, and reached a maximum of 4.06 mg/L as N following a June 2010 runoff event. For groundwater samples, nitrite plus nitrate concentrations increased from 0.13 mg/L as N in November 2009 to 0.70 mg/L as N in March 2010, and then decreased to less than 0.10 mg/L as N in the summer months of 2010.

Eight of the AOCs detected have a human-health benchmark (MCL or HBSL) that could be used to evaluate the concentrations in a human-health context. Four compounds had maximum concentrations within an order of magnitude of the benchmark, indicating that additional monitoring of the compound may be warranted. Three herbicides (atrazine, metolachlor, and prometon) and one degradate (deethylatrazine) were detected in finished-water samples as frequently as in source-water samples. The concentrations of herbicides in source water can vary by an order of magnitude from the period of peak application (early summer) to the winter months. Atrazine, metolachlor, and prometon can be highly mobile in sandy soils and aquifers. These herbicides (along with acetochlor) have log octanol-water partitioning coefficients (log K_{ow}) less than 5, which indicates their affinity for the dissolved phase. Contaminants with log K_{ow} in this range will not readily adsorb to sediments in the aquifer or other filtering materials in the transport process. Groundwater and finished-water concentrations of atrazine were similar for the six sampling dates when groundwater was the only source water used. Upstream wastewater discharges contributed a fairly small percentage of the flow to the Big Sioux River near Sioux Falls, but several AOCs associated with wastewater were frequently detected. The direct pathway to surface water explains the frequent occurrence of carbamazapine, sulfamethoxazole, cholesterol, *beta*-sitosterol, and 3-*beta*-coprostanol in the Big Sioux River compared to groundwater and subsequently finished water. In addition, three of these compounds have log K_{ow} values greater than 8.0 and are more susceptible to natural filtering in groundwater movement.

Most (82 percent) of the $\delta^{15}N$ values in the source-water samples were greater than 10 per mil, and none of the $\delta^{15}N$ values from either surface water or groundwater was less than 7 per mil, indicating biological sources as the predominant component of nitrogen in the nitrate of the source water. The varying isotopic composition of nitrogen and oxygen in nitrate in groundwater samples is not only an effect of

changing hydrologic conditions and seasonality, but also could be explained by the blending of groundwater from wells and collection galleries producing from several aquifers. Sourcewater samples were a mix of various water supplies within the Big Sioux River Basin that have undergone numerous chemical and biological transformations before reaching the sampling location, and varying $\delta^{18}O$ values support the conclusion that these processes likely caused an enrichment of ^{15}N in the source water. The interpretation of all potential sources of nitrogen cannot be accomplished by use of nitrogen and oxygen isotopes in nitrate alone, but provides a qualitative indication that very little nitrate originates from excess fertilizer runoff, and most nitrate originates from municipal wastewater effluent, manure runoff (either from field application or feeding operations), or fertilizers mineralized by processes in the soil.

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Appendixes 1–4

Appendix 1. Reporting levels and relevant benchmarks for anthropogenic organic compounds analyzed.

[USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number; MCL, Maximum Contaminant Level; HBSL, Health-Based Screening Level; µg/L, micrograms per liter; ng/L, nanograms per liter; --, not available]

Analyte	Analytical method	USGS parameter code	CASRN[1]	Reporting level before November 4, 2009	Reporting level after November 4, 2009	Units	MCL[2]	HBSL[3]
1-Naphthol	1	49295	90-15-3	0.04	0.036	µg/L	--	--
2-Chloro-2,6-diethylacetanilide	1	61618	6967-29-9	0.01	0.01	µg/L	--	--
2-Ethyl-6-methylaniline	1	61620	24549-06-2	0.01	0.01	µg/L	--	--
2,6-Diethylaniline	1	82660	579-66-8	0.006	0.006	µg/L	--	--
3,4-Dichloroaniline	1	61625	95-76-1	0.004	0.004	µg/L	--	--
4-Chloro-2-methylphenol	1	61633	1570-64-5	0.005	0.003	µg/L	--	--
Acetochlor	1	49260	34256-82-1	0.01	0.01	µg/L	--	1
Alachlor	1	46342	15972-60-8	0.008	0.008	µg/L	2	--
Atrazine	1	39632	1912-24-9	0.007	0.007	µg/L	3	--
Azinphos-methyl	1	82686	86-50-0	0.12	0.12	µg/L	--	10
Azinphos-methyl-oxon	1	61635	961-22-8	0.042	0.042	µg/L	--	--
Benfluralin	1	82673	1861-40-1	0.014	0.014	µg/L	--	4
Carbaryl	1	82680	63-25-2	0.2	0.06	µg/L	--	40
Chlorpyrifos	1	38933	2921-88-2	0.01	0.01	µg/L	--	2
Chlorpyrifos oxygen analog	1	61636	5598-15-2	0.05	0.05	µg/L	--	--
cis-Permethrin	1	82687	61949-76-6	0.014	0.014	µg/L	--	4
Cyfluthrin	1	61585	68359-37-5	0.016	0.016	µg/L	--	200
Cypermethrin	1	61586	52315-07-8	0.02	0.02	µg/L	--	40
Dacthal	1	82682	1861-32-1	0.006	0.008	µg/L	--	70
Deethylatrazine	1	04040	6190-65-4	0.014	0.014	µg/L	--	--
Desulfinylfipronil	1	62170	--	0.012	0.012	µg/L	--	--
Desulfinylfipronil amide	1	62169	--	0.029	0.029	µg/L	--	--
Diazinon	1	39572	333-41-5	0.005	0.005	µg/L	--	1
Diazoxon	1	61638	962-58-3	0.006	0.006	µg/L	--	--
Dichlorvos	1	38775	62-73-7	0.02	0.02	µg/L	--	0.4
Dicrotophos	1	38454	141-66-2	0.08	0.08	µg/L	--	0.05
Dieldrin	1	39381	60-57-1	0.009	0.009	µg/L	--	0.002
Dimethoate	1	82662	60-51-5	0.006	0.006	µg/L	--	2
Ethion	1	82346	563-12-2	0.012	0.008	µg/L	--	--
Ethion monoxon	1	61644	17356-42-2	0.021	0.021	µg/L	--	--
Fenamiphos	1	61591	22224-92-6	0.029	0.03	µg/L	--	0.7
Fenamiphos sulfone	1	61645	31972-44-8	0.053	0.053	µg/L	--	--
Fenamiphos sulfoxide	1	61646	31972-43-7	0.08	0.08	µg/L	--	--
Fipronil	1	62166	120068-37-3	0.04	0.018	µg/L	--	--
Fipronil sulfide	1	62167	120067-83-6	0.013	0.013	µg/L	--	--
Fipronil sulfone	1	62168	120068-36-2	0.024	0.024	µg/L	--	--
Fonofos	1	04095	944-22-9	0.01	0.004	µg/L	--	10
Hexazinone	1	04025	51235-04-2	0.008	0.008	µg/L	--	400
Iprodione	1	61593	36734-19-7	0.014	0.014	µg/L	--	0.8
Isofenphos	1	61594	25311-71-1	0.006	0.006	µg/L	--	6
Malaoxon	1	61652	1634-78-2	0.08	0.08	µg/L	--	--
Malathion	1	39532	121-75-5	0.02	0.016	µg/L	--	50
Metalaxyl	1	61596	57837-19-1	0.013	0.007	µg/L	--	--

Appendix 1. Reporting levels and relevant benchmarks for anthropogenic organic compounds analyzed.—Continued

[USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number; MCL, Maximum Contaminant Level; HBSL, Health-Based Screening Level; µg/L, micrograms per liter; ng/L, nanograms per liter; --, not available]

Analyte	Analytical method	USGS parameter code	CASRN[1]	Reporting level before November 4, 2009	Reporting level after November 4, 2009	Units	MCL[2]	HBSL[3]
Methidathion	1	61598	950-37-8	0.006	0.006	µg/L	--	1
Methyl parathion	1	82667	298-00-0	0.008	0.008	µg/L	--	--
Metolachlor	1	39415	51218-45-2	0.014	0.014	µg/L	--	700
Metribuzin	1	82630	21087-64-9	0.016	0.012	µg/L	--	90
Myclobutanil	1	61599	88671-89-0	0.01	0.01	µg/L	--	200
Paraoxon-methyl	1	61664	950-35-6	0.01	0.01	µg/L	--	--
Pendimethalin	1	82683	40487-42-1	0.012	0.012	µg/L	--	70
Phorate	1	82664	298-02-2	0.02	0.02	µg/L	--	--
Phorate oxygen analog	1	61666	2600-69-3	0.027	0.027	µg/L	--	--
Phosmet	1	61601	732-11-6	0.2	0.034	µg/L	--	8
Phosmet oxon	1	61668	3735-33-9	0.051	0.051	µg/L	--	--
Prometon	1	04037	1610-18-0	0.012	0.012	µg/L	--	400
Prometryn	1	04036	7287-19-6	0.006	0.006	µg/L	--	300
Pronamide	1	82676	23950-58-5	0.004	0.004	µg/L	--	1
Simazine	1	04035	122-34-9	0.01	0.006	µg/L	4	--
Tebuthiuron	1	82670	34014-18-1	0.02	0.028	µg/L	--	1,000
Terbufos	1	82675	13071-79-9	0.018	0.018	µg/L	--	0.4
Terbufos oxygen analog sulfone	1	61674	56070-15-6	0.045	0.045	µg/L	--	--
Terbuthylazine	1	04022	5915-41-3	0.006	0.006	µg/L	--	2
Tribufos	1	61610	78-48-8	0.035	0.018	µg/L	--	--
Trifluralin	1	82661	1582-09-8	0.012	0.018	µg/L	--	--
1,7-Dimethylxanthine	2	62030	611-59-6	0.12	0.1	µg/L	--	--
Acetaminophen	2	62000	103-90-2	0.08	0.12	µg/L	--	--
Albuterol	2	62020	18559-94-9	0.06	0.08	µg/L	--	--
Caffeine	2	50305	58-08-2	0.2	0.06	µg/L	--	--
Carbamazepine	2	62793	298-46-4	0.04	0.06	µg/L	--	--
Codeine	2	62003	76-57-3	0.04	0.046	µg/L	--	--
Cotinine	2	62005	486-56-6	0.026	0.038	µg/L	--	--
Dehydronifedipine	2	62004	67035-22-7	0.08	0.08	µg/L	--	--
Diltiazem	2	62008	42399-41-7	0.08	0.06	µg/L	--	--
Diphenhydramine	2	62796	147-24-0	0.04	0.036	µg/L	--	--
Sulfamethoxazole	2	62021	723-46-6	0.16	0.16	µg/L	--	--
Thiabendazole	2	62801	148-79-8	0.06	0.06	µg/L	--	--
Trimethoprim	2	62023	738-70-5	0.02	0.034	µg/L	--	--
Warfarin	2	62024	81-81-2	0.1	0.08	µg/L	--	--
1-Methylnaphthalene	3	81696	90-12-0	0.2	0.2	µg/L	--	--
1,4-Dichlorobenzene	3	34571	106-46-7	0.2	0.2	µg/L	75	--
2-Methylnaphthalene	3	30194	91-57-6	0.2	0.2	µg/L	--	--
2,6-Dimethylnaphthalene	3	62805	581-42-0	0.2	0.2	µg/L	--	--
3-*beta*-Coprostanol	3	62806	360-68-9	1.6	1.6	µg/L	--	--
3-Methyl-1H-indole	3	62807	83-34-1	0.2	0.2	µg/L	--	--
3-*tert*-Butyl-4-hydroxyanisole	3	61702	25013-16-5	0.2	0.2	µg/L	--	--
3,4-Dichlorophenyl isocyanate	3	63145	102-36-3	1.6	1.6	µg/L	--	--

Appendix 1. Reporting levels and relevant benchmarks for anthropogenic organic compounds analyzed.—Continued

[USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number; MCL, Maximum Contaminant Level; HBSL, Health-Based Screening Level; µg/L, micrograms per liter; ng/L, nanograms per liter; --, not available]

Analyte	Analytical method	USGS parameter code	CASRN[1]	Reporting level before November 4, 2009	Reporting level after November 4, 2009	Units	MCL[2]	HBSL[3]
4-Cumylphenol	3	62808	599-64-4	0.2	0.2	µg/L	--	--
4-*n*-Octylphenol	3	62809	1806-26-4	0.2	0.2	µg/L	--	--
4-Nonylphenol	3	62829	84852-15-3	1.6	1.6	µg/L	--	--
4-Nonylphenol diethoxylate	3	61703	26027–38–2	3.2	3.2	µg/L	--	--
4-Nonylphenol monoethoxylate	3	61704	--	1.6	1.6	µg/L	--	--
4-Octylphenol diethoxylate	3	62486	--	0.5	0.5	µg/L	--	--
4-Octylphenol monoethoxylate	3	62485	--	1	1	µg/L	--	--
4-*tert*-Octylphenol	3	62810	140-66-9	0.4	0.4	µg/L	--	--
5-Methyl-1H-benzotriazole	3	61944	136-85-6	1.6	1.6	µg/L	--	--
Acetophenone	3	62811	98-86-2	0.4	0.4	µg/L	--	--
Acetyl-hexamethyl-tetrahydro-naphthalene	3	62812	21145-77-7	0.2	0.2	µg/L	--	--
Anthracene	3	34220	120-12-7	0.2	0.2	µg/L	--	--
Anthraquinone	3	62813	84-65-1	0.2	0.2	µg/L	--	--
Atrazine	3	39630	1912-24-9	0.2	0.2	µg/L	3	--
BDE congener 47	3	63147	5436-43-1	0.3	0.3	µg/L	--	--
Benzo[a]pyrene	3	34247	50-32-8	0.2	0.2	µg/L	--	--
Benzophenone	3	62814	119-61-9	0.2	0.2	µg/L	--	--
beta-Sitosterol	3	62815	83-46-5	1.6	1.6	µg/L	--	--
beta-Stigmastanol	3	61948	19466-47-8	1.7	1.7	µg/L	--	--
Bis(2-ethylhexyl) phthalate	3	39100	117-81-7	2	2	µg/L	6	--
Bisphenol A	3	62816	80-05-7	0.4	0.4	µg/L	--	--
Bromacil	3	30234	314-40-9	0.8	0.8	µg/L	--	--
Bromoform	3	32104	75-25-2	0.2	0.2	µg/L	80	--
Caffeine	3	81436	58-08-2	0.2	0.2	µg/L	--	--
Camphor	3	62817	76-22-2	0.2	0.2	µg/L	--	--
Carbaryl	3	39750	63-25-2	0.2	0.2	µg/L	--	40
Carbazole	3	77571	86-74-8	0.2	0.2	µg/L	--	--
Chlorpyrifos	3	38932	2921-88-2	0.2	0.2	µg/L	--	2
Cholesterol	3	62818	57-88-5	1.6	1.6	µg/L	--	--
Cotinine	3	61945	486-56-6	0.8	0.8	µg/L	--	--
Diazinon	3	39570	333-41-5	0.2	0.2	µg/L	--	1
Dichlorvos	3	30218	62-73-7	0.2	0.2	µg/L	--	0.4
Diethyl phthalate	3	34336	84-66-2	0.2	0.2	µg/L	--	--
D-Limonene	3	62819	5989-27-5	0.2	0.2	µg/L	--	--
Fluoranthene	3	34376	206-44-0	0.2	0.2	µg/L	--	--
Hexahydrohexamethyl cyclopentabenzopyran	3	62823	1222-05-5	0.2	0.2	µg/L	--	--
Indole	3	62824	120-72-9	0.2	0.2	µg/L	--	--
Isoborneol	3	62825	124-76-5	0.2	0.2	µg/L	--	--
Isophorone	3	34408	78-59-1	0.2	0.2	µg/L	--	--
Isopropylbenzene	3	77223	98-82-8	0.2	0.2	µg/L	--	--
Isoquinoline	3	62826	119-65-3	0.2	0.2	µg/L	--	--
Menthol	3	62827	89-78-1	0.2	0.2	µg/L	--	--
Metalaxyl	3	04254	57837-19-1	0.2	0.2	µg/L	--	--

Appendix 1. Reporting levels and relevant benchmarks for anthropogenic organic compounds analyzed.—Continued

[USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number; MCL, Maximum Contaminant Level; HBSL, Health-Based Screening Level; µg/L, micrograms per liter; ng/L, nanograms per liter; --, not available]

Analyte	Analytical method	USGS parameter code	CASRN[1]	Reporting level before November 4, 2009	Reporting level after November 4, 2009	Units	MCL[2]	HBSL[3]
Methyl salicylate	3	62828	119-36-8	0.2	0.2	µg/L	--	--
Metolachlor	3	82612	51218-45-2	0.2	0.2	µg/L	--	700
Naphthalene	3	34696	91-20-3	0.2	0.2	µg/L	--	--
N,N-Diethyl-*meta*-toluamide (DEET)	3	61947	134-62-3	0.2	0.2	µg/L	--	--
p-Cresol	3	77146	106-44-5	0.2	0.2	µg/L	--	--
Pentachlorophenol	3	39032	87-86-5	0.8	0.8	µg/L	1	--
Phenanthrene	3	34461	85-01-8	0.2	0.2	µg/L	--	--
Phenol	3	34694	108-95-2	0.2	0.2	µg/L	--	--
Prometon	3	39056	1610-18-0	0.2	0.2	µg/L	--	400
Pyrene	3	34469	129-00-0	0.2	0.2	µg/L	--	--
Tetrachloroethylene	3	34475	127-18-4	0.4	0.4	µg/L	5	--
Tributyl phosphate	3	62832	126-73-8	0.2	0.2	µg/L	--	--
Triclosan	3	61708	3380-34-5	0.2	0.2	µg/L	--	--
Triethyl citrate	3	62833	77-93-0	0.2	0.2	µg/L	--	--
Triphenyl phosphate	3	62834	115-86-6	0.2	0.2	µg/L	--	--
Tris(2-butoxyethyl) phosphate	3	62830	78-51-3	0.2	0.2	µg/L	--	--
Tris(2-chloroethyl) phosphate	3	62831	115-96-8	0.2	0.2	µg/L	--	--
Tris(dichloroisopropyl) phosphate	3	61707	13674-87-8	0.2	0.2	µg/L	--	--
Azithromycin	4	62792	83905-01-05	0.005	0.005	µg/L	--	--
Carbamazepine	4	62793b	298-46-4	0.005	0.005	µg/L	--	--
Chloramphenicol	4	65194	56-75-7	0.1	0.1	µg/L	--	--
Chlorotetracycline	4	61744	57-62-5	0.01	0.01	µg/L	--	--
Ciprofloxacin	4	62898	85721-33-1	0.005	0.005	µg/L	--	--
Doxycycline	4	62694	564-25-0	0.01	0.01	µg/L	--	--
4-Epichlorotetracycline hydrochloride	4	63731	101342-45-4	0.01	0.01	µg/L	--	--
Isoepichlorotetracycline	4	64047	--	0.01	0.01	µg/L	--	--
4-Epioxytetracycline	4	63729	35259-39-3	0.01	0.01	µg/L	--	--
4-Epitetracycline hydrochloride	4	63727	23313-80-6	0.01	0.01	µg/L	--	--
Enrofloxacin	4	66495	93106-60-6	0.005	0.005	µg/L	--	--
Erythromycin	4	62797	114-07-8	0.008	0.008	µg/L	--	--
Anhydroerthromycin	4	63674	--	0.008	0.008	µg/L	--	--
Ibuprofen	4	62014	15687-27-1	0.05	0.05	µg/L	--	--
Isochlortetracycline	4	64175	514-53-4	0.01	0.01	µg/L	--	--
Lincomycin	4	62894	154-21-2	0.005	0.005	µg/L	--	--
Lomefloxacin	4	62900	98079-51-7	0.005	0.005	µg/L	--	--
Norfloxacin	4	62757	70458-96-7	0.005	0.005	µg/L	--	--
Ofloxacin	4	62899	83380-47-6	0.005	0.005	µg/L	--	--
Ormetoprim	4	62962	6981-18-6	0.005	0.005	µg/L	--	--
Oxytetracycline	4	61759	79-57-2	0.01	0.01	µg/L	--	--
Roxithromycin	4	62895	80214-83-1	0.005	0.005	µg/L	--	--
Sarafloxacin	4	62771	98105-99-8	0.005	0.005	µg/L	--	--
Sulfachloropyridazine	4	62774	80-32-0	0.005	0.005	µg/L	--	--
Sulfadiazine	4	62963	68-35-9	0.1	0.1	µg/L	--	--

Appendix 1. Reporting levels and relevant benchmarks for anthropogenic organic compounds analyzed.—Continued

[USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number; MCL, Maximum Contaminant Level; HBSL, Health-Based Screening Level; µg/L, micrograms per liter; ng/L, nanograms per liter; --, not available]

Analyte	Analytical method	USGS parameter code	CASRN[1]	Reporting level before November 4, 2009	Reporting level after November 4, 2009	Units	MCL[2]	HBSL[3]
Sulfadimethoxine	4	62776	122-11-2	0.005	0.005	µg/L	--	--
Sulfamethazine	4	61762	57-68-1	0.005	0.005	µg/L	--	--
Sulfamethoxazole	4	62775	723-46-6	0.005	0.005	µg/L	--	--
Sulfathiazole	4	62778	72-14-0	0.05	0.05	µg/L	--	--
Tetracycline	4	62781	60-54-8	0.01	0.01	µg/L	--	--
Trimethoprim	4	62023b	738-70-5	0.005	0.005	µg/L	--	--
Tylosin	4	62896	1401-69-0	0.008	0.008	µg/L	--	--
Virginiamycin	4	62897	21411-53-0	0.005	0.005	µg/L	--	--
3-*beta*-Coprostanol	5	64512	360-68-9	2,000	200	ng/L	--	--
4-Androstene-3,17-dione	5	64513	63-05-8	0.8	0.8	ng/L	--	--
11-Ketotestosterone	5	64507	564-35-2	2	2	ng/L	--	--
17-*alpha*-Estradiol	5	64508	57-91-0	0.8	0.8	ng/L	--	--
17-*alpha*-Ethynylestradiol	5	64509	57-63-6	0.8	0.8	ng/L	--	--
17-*beta*-Estradiol	5	64510	50-28-2	0.8	0.8	ng/L	--	--
Bisphenol A	5	67304	80-05-7	100	200	ng/L	--	--
Cholesterol	5	64514	57-88-5	2,000	200	ng/L	--	--
cis-Androsterone	5	64515	53-41-8	0.8	0.8	ng/L	--	--
Dihydrotestosterone	5	64524	521-18-6	4	4	ng/L	--	--
Epitestosterone	5	64517	481-30-1	4	4	ng/L	--	--
Equilenin	5	64518	517-09-9	2	2	ng/L	--	--
Equilin	5	64519	474-86-2	4	4	ng/L	--	--
Estriol	5	64520	50-27-1	2	2	ng/L	--	--
Estrone	5	64521	53-16-7	0.8	0.8	ng/L	--	--
Mestranol	5	64522	72-33-3	0.8	0.8	ng/L	--	--
Norethindrone	5	64511	68-22-4	0.8	0.8	ng/L	--	--
Progesterone	5	64523	57-83-0	8	8	ng/L	--	--
Testosterone	5	64525	58-22-0	0.8	0.8	ng/L	--	--
trans-Diethylstilbestrol	5	64516	56-53-1	0.8	0.8	ng/L	--	--

[1]This report uses CAS Registry Numbers®, which is a Registered Trademark of the American Chemical Society. The CAS recommends the verification of the CASRNs through CAS Client ServicesSM.

[2]From U.S. Environmental Protection Agency (2009).

[3]From Toccalino and others (2008).

Appendix 2. Detailed Description of Method for Analysis of Hormones

A research method (analytical method 5) under development at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) was used to analyze for 16 steroid hormones plus four other compounds, with an expanded method description provided herein (James Gray, Rhiannon ReVello, and William Foreman, National Water Quality Laboratory, written commun., 2011). Field samples for this method were collected using USGS protocols for organic contaminants, except that the samples were contained in 0.5-liter high-density polyethylene (HDPE) bottles. Samples not processed within 3 days at the NWQL were held frozen at no more than -5 degrees Celsius (°C) until the day preceding extraction when allowed to thaw at room temperature.

At the NWQL, samples were fortified with 50 milligrams of sodium chloride and isotopically labeled compounds that were used as isotope dilution standards (IDSs; see table 5). The sample was poured into a stainless-steel extraction tube fitted with a multigrade glass-fiber filter (GFF) positioned over a reverse phase octyldecyl surface-modified-silica embedded glass-fiber filter disk (C_{18} disk). The sample was passed through the combined GFF/C_{18} disk under pressure, as needed. Following compound isolation, the GFF/C_{18} disk was rinsed with 10 milliliters (mL) of 25-percent methanol in reagent water to remove polar compounds that interfere with gas-chromatography, tandem-quadrupole, mass-spectrometry analysis. Nitrogen gas was passed through the GFF/C_{18} disk to remove residual water, and the method compounds were eluted with two 20-mL additions of methanol. The eluent was evaporated to dryness at 25ºC with nitrogen gas and reconstituted in 2 mL of a 5-percent methanol in dichloromethane solution and allowed to sit for at least 30 minutes. The extract was passed through a 1-gram Florisil solid-phase extraction column and eluted with an additional 22 mL of 5-percent methanol/dichloromethane. The eluent was reduced in volume to about 1 mL with nitrogen gas, quantitatively transferred to a 5-mL reaction vial with 5-percent methanol/dichloromethane rinses, and evaporated to dryness. Processing of multi-level calibration standards contained in reaction vials was included beginning at this evaporation step. Ketone and alcohol groups on the analytes and IDSs were derivatized to trimethylsilyl or trimethylsilyl-enol ether analogs to increase compound volatility and minimize compound interactions with active sites in the gas-chromatography system. Derivation was accomplished by adding 200 microliters of *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide (MSTFA) activated with 2-(trimethylsilyl) ethanethiol and ammonium iodide, and heating the MSTFA solution to 65°C for 1 hour. The solution also contains cholestane-d_6 and chrysene-d_{12} as injection internal standards.

The extract was transferred to a gas-chromatography vial, and the analytes were separated by gas chromatography and detected by tandem quadrupole mass spectrometry using a Quattro-micro-GC (Waters Corp., Milford, Mass.). Compounds were separated by using a 30-meter long by 0.25-millimeter internal diameter Rxi XLB GC column with 0.25-micrometer film thickness (Restek Corp., Bellefonte, Pa.) and a multiple ramp temperature program. Analytes were detected by tandem-quadrupole mass spectrometry by monitoring the product ions of three specific precursor-to-product ion transitions. Positive analyte identification requires the presence of at least two unique transition product ions, with ion ratios not deviating from those in a standard by more than specified tolerances (Antignac and others, 2003).

Six of the original 13 IDS compounds—4-androstene-3,17-dione-d_7; dihydrotestosterone-d_4; estrone-d_4; norethindrone-d_6; testosterone-d_5; and progesterone-d_9—were found to be susceptible to deuterium-hydrogen exchange under non-routine sample-preparation conditions (water bath temperatures above ambient temperature of 25°C) or prolonged IDS standard storage periods (months) in methanol (Foreman and others, 2010). Loss of deuterium results in an underestimate of the IDS total mass in the sample extract and, thus, an underestimate of IDS absolute recovery, which produces a positive bias in the determined analyte concentration. Consequently, these six deuterium-labeled IDSs were removed from the method and were not used for samples collected after November 4, 2009. Reported concentrations of analytes normally determined using these six IDS were censored to the reporting level or a raised reporting level, if needed, or were quantified relative to 17-*alpha*-ethynylestradiol-d_4 to eliminate risk of positive bias in analyte concentration for those samples collected through November 4, 2009, when deuterium loss was evident or suspected.

Samples collected after November 4, 2009, were fortified with the 10 deuterium or carbon-13 (^{13}C) labeled IDSs shown in table 5, five of which were unchanged from those used previously. Replacement IDSs contained either carbon-13 or were non-direct analogs of the analytes that have deuterium labels in positions not adjacent to a ketone group and, thus, are not susceptible to deuterium-loss. In addition, 17-*beta*-estradiol-$^{13}C_6$ replaced 17-*beta*-estradiol-d_4 and 16-epiestriol-d_2 replaced estriol-d_3 to further minimize risk of IDS interference with the analyte's parent ion at concentrations near the instrumental detection level of the gas chromatography/tandem mass spectrometry. Six of the 10 IDS compounds were exact isotopic analogs of method analytes. The remaining 14 method analytes also were quantified using isotope dilution by using 1 of the other 4 IDSs that have similar related chemical functionality but are not a direct isotopic analog of the analyte.

All 20 method analytes were quantified relative to a specific IDS compound by using an isotope-dilution quantification procedure that automatically corrects for procedural losses in the reported analyte concentration on the basis of the absolute method recovery of the IDS. For samples collected through November 4, 2009, 13 deuterium-labeled IDS compounds were used that were exact isotopic analogs of method analytes (table 5). The remaining seven method analytes in these samples were quantified relative to one of the IDS compounds that has similar chemical functionality but is not a direct isotopic analog of the analyte (table 5).

Table 5. Analyte and the corresponding isotope dilution standard (IDS) used for its quantification.

[The six analytes with direct IDS analogs that were susceptible to deuterium loss (D-loss) are shown in bold italics. Four analytes quantified with non-direct IDS analogs susceptible to D-loss are shown in bold. Six IDSs that contain ketone functional groups (keto-IDSs) that can undergo deuterium loss (D-loss) are shown in bold. USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number; ng/L, nanograms per liter]

Analyte	USGS parameter code	CASRN[1]	Reporting level through November 4, 2009	Reporting level after November 4, 2009	Isotope dilution standard used for samples collected through November 4, 2009	Isotope dilution standard used for samples collected after November 4, 2009
11-ketotestosterone	64507	564-35-2	2	2	**testosterone-d_5**	nandrolone-16,16,17-d_3
17-*alpha*-Estradiol	64508	57-91-0	0.8	0.8	17-*beta*-estradiol-d_4	17-*beta*-estradiol-$^{13}C_6$
17-*alpha*-Ethynylestradiol	64509	57-63-6	0.8	0.8	17-*alpha*-ethynylestradiol-d_4	17-*alpha*-ethynylestradiol-d_4
17-*beta*-Estradiol	64510	50-28-2	0.8	0.8	17-*beta*-estradiol-d_4	17-*beta*-estradiol-$^{13}C_6$
norethindrone	64511	68-22-4	0.8	0.8	**norethindrone-d_6**	nandrolone-16,16,17-d_3
3-*beta*-Coprostanol	64512	360-68-9	2,000	200	cholesterol-d_7	cholesterol-d_7
4-androstene-3,17-dione	64513	63-05-8	0.8	0.8	**4-androstene-3,17-dione-d_7**	nandrolone-16,16,17-d_3
cholesterol	64514	57-88-5	2,000	200	cholesterol-d_7	cholesterol-d_7
***cis*-androsterone**	64515	53-41-8	0.8	0.8	**dihydrotestosterone-d_4**	nandrolone-16,16,17-d_3
trans-Diethylstilbestrol	64516	56-53-1	0.8	0.8	*trans*-diethylstilbestrol-d_8	*trans*-diethylstilbestrol-d_8
epitestosterone	64517	481-30-1	4	4	**testosterone-d_5**	nandrolone-16,16,17-d_3
equilenin	64518	517-09-9	2	2	17-*beta*-estradiol-d_4	17-*beta*-estradiol-$^{13}C_6$
equilin	64519	474-86-2	4	4	**estrone-d_4**	estrone-$^{13}C_6$
estriol	64520	50-27-1	2	2	estriol-d_3	16-epiestriol-d_2
estrone	64521	53-16-7	0.8	0.8	**estrone-d_4**	estrone-$^{13}C_6$
mestranol	64522	72-33-3	0.8	0.8	mestranol-d_4	mestranol-d_4
progesterone	64523	57-83-0	8	8	**progesterone-d_9**	medroxyprogesterone-d_3
dihydrotestosterone	64524	521-18-6	4	4	**dihydrotestosterone-d_4**	nandrolone-16,16,17-d_3
testosterone	64525	58-22-0	0.8	0.8	**testosterone-d_5**	nandrolone-16,16,17-d_3
bisphenol A	67304	80-05-7	100	200	bisphenol A-d_{16}	bisphenol A-d_{16}

[1]This report uses CAS Registry Numbers®, which is a Registered Trademark of the American Chemical Society. The CAS recommends the verification of the CASRNs through CAS Client Services℠.

Appendix 3. Percent recoveries of anthropogenic organic compounds for environmental matrix spike samples.

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

Analyte	Analytical method	USGS parameter code	Big Sioux River (site 433600096442400)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Median
			8/3/2009	8/3/2009	2/17/2010	2/17/2010	7/29/2010	
1-Naphthol	1	49295	18	16	38	45	92	38
2-Chloro-2,6-diethylacetanilide	1	61618	128	120	112	107	137	120
2-Ethyl-6-methylaniline	1	61620	94	83	77	79	97	83
2,6-Diethylaniline	1	82660	99	94	85	85	108	94
3,4-Dichloroaniline	1	61625	73	52	74	73	90	73
4-Chloro-2-methylphenol	1	61633	72	76	49	66	86	72
Acetochlor	1	49260	122	112	122	115	155	122
Alachlor	1	46342	119	110	121	115	138	119
Atrazine	1	39632	121	100	107	101	121	107
Azinphos-methyl	1	82686	158	139	136	130	235	139
Azinphos-methyl-oxon	1	61635	58	53	125	87	115	87
Benfluralin	1	82673	72	75	83	89	87	83
Carbamazepine	1	82687	88	113	79	86	141	88
Carbaryl	1	82680	136	137	121	124	141	136
Chlorpyrifos	1	38933	123	133	63	107	96	107
Chlorpyrifos oxygen analog	1	61636	0	28	23	108	64	28
Cyfluthrin	1	61585	116	135	82	117	117	117
Cypermethrin	1	61586	110	120	81	106	116	110
Dacthal	1	82682	120	112	116	112	119	116
Deethylatrazine	1	04040	71	58	83	82	139	82
Desulfinylfipronil	1	62170	105	96	118	113	159	113
Desulfinylfipronil amide	1	62169	110	109	124	136	105	110
Diazinon	1	39572	112	109	98	100	117	109
Diazoxon	1	61638	65	91	120	132	145	120
Dichlorvos	1	38775	5	38	8	78	47	38
Dicrotophos	1	38454	38	47	19	51	64	47
Dieldrin	1	39381	83	84	89	89	64	84
Dimethoate	1	82662	51	43	69	69	84	69
Ethion	1	82346	114	106	96	101	98	101

Appendix 3. Percent recoveries of anthropogenic organic compounds for environmental matrix spike samples.—Continued

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

Analyte	Analytical method	USGS parameter code	Big Sioux River (site 433600096442400)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Median
			8/3/2009	8/3/2009	2/17/2010	2/17/2010	7/29/2010	
Ethion monoxon	1	61644	97	108	118	127	102	108
Fenamiphos	1	61591	93	98	116	129	67	98
Fenamiphos sulfone	1	61645	147	143	127	142	116	142
Fenamiphos sulfoxide	1	61646	46	67	0	43	17	43
Fipronil	1	62166	130	120	133	131	184	131
Fipronil sulfide	1	62167	136	124	123	119	206	124
Fipronil sulfone	1	62168	86	85	107	112	114	107
Fonofos	1	04095	108	105	84	99	99	99
Hexazinone	1	04025	87	95	69	95	103	95
Iprodione	1	61593	127	124	104	111	136	124
Isofenphos	1	61594	152	141	121	117	192	141
Malaoxon	1	61652	55	104	112	135	153	112
Malathion	1	39532	114	119	113	115	155	115
Metalaxyl	1	61596	116	113	111	114	156	114
Methidathion	1	61598	94	93	111	116	115	111
Methyl parathion	1	82667	98	99	97	114	129	99
Metolachlor	1	39415	129	118	110	105	143	118
Metribuzin	1	82630	83	80	108	104	140	104
Myclobutanil	1	61599	105	103	112	117	117	112
Paraoxon-methyl	1	61664	27	73	67	112	116	73
Pendimethalin	1	82683	146	143	109	108	142	142
Phorate	1	82664	31	26	79	62	102	62
Phorate oxygen analog	1	61666	60	75	112	120	146	112
Phosmet	1	61601	42	47	95	93	72	72
Phosmet oxon	1	61668	22	29	115	94	40	40
Prometon	1	04037	102	94	104	99	125	102
Prometryn	1	04036	114	107	117	110	146	114
Pronamide	1	82676	113	106	102	99	133	106
Simazine	1	04035	110	102	108	102	144	108

Appendix 3. Percent recoveries of anthropogenic organic compounds for environmental matrix spike samples.—Continued

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

Analyte	Analytical method	USGS parameter code	Big Sioux River (site 433600096442400)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Median
			8/3/2009	8/3/2009	2/17/2010	2/17/2010	7/29/2010	
Tebuthiuron	1	82670	135	139	181	197	172	172
Terbufos	1	82675	74	71	91	93	113	91
Terbufos oxygen analog sulfone	1	61674	59	121	102	138	176	121
Terbuthylazine	1	04022	114	106	112	106	121	112
Tribufos	1	61610	101	99	78	87	83	87
Trifluralin	1	82661	79	81	87	94	95	87
1,7-Dimethylxanthine	2	62030	63	38	76	42	62	62
Acetaminophen	2	62000	44	20	60	25	50	44
Albuterol	2	62020	65	26	76	32	58	58
Caffeine	2	50305	86	71	116	87	72	86
Carbamazepine	2	62793	51	62	62	59	44	59
Codeine	2	62003	78	77	94	83	73	78
Cotinine	2	62005	60	48	69	41	65	60
Dehydronifedipine	2	62004	90	96	99	95	85	95
Diltiazem	2	62008	45	66	70	78	34	66
Diphenhydramine	2	62796	50	66	71	78	34	66
Sulfamethoxazole	2	62021	14	25	41	35	26	26
Thiabendazole	2	62801	55	66	62	75	21	62
Trimethoprim	2	62023	61	68	84	83	50	68
Warfarin	2	62024	62	84	89	77	72	77
1-Methylnaphthalene	3	81696	42	69	71	73	96	71
1,4-Dichlorobenzene	3	34571	37	65	65	68	91	65
2-Methylnaphthalene	3	30194	43	72	70	74	97	72
2,6-Dimethylnaphthalene	3	62805	41	73	67	73	94	73
3-*beta*-Coprostanol	3	62806	31	62	27	33	60	33
3-Methyl-1H-indole	3	62807	37	77	73	76	88	76
3-*tert*-Butyl-4-hydroxyanisole	3	61702	3	74	55	67	74	67
3,4-Dichlorophenyl isocyanate	3	63145	15	37	18	25	63	25
4-Cumylphenol	3	62808	62	94	67	81	114	81

Appendix 3. Percent recoveries of anthropogenic organic compounds for environmental matrix spike samples.—Continued

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

Analyte	Analytical method	USGS parameter code	Big Sioux River (site 433600096442400)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Median
			8/3/2009	8/3/2009	2/17/2010	2/17/2010	7/29/2010	
4-*n*-Octylphenol	3	62809	48	89	67	83	107	83
4-Nonylphenol	3	62829	48	76	66	76	116	76
4-Nonylphenol diethoxylate	3	61703	55	88	66	79	117	79
4-Nonylphenol monoethoxylate	3	61704	59	90	72	83	122	83
4-Octylphenol diethoxylate	3	62486	79	117	73	78	130	79
4-Octylphenol monoethoxylate	3	62485	80	112	74	86	118	86
4-*tert*-Octylphenol	3	62810	61	107	76	85	117	85
5-Methyl-1H-benzotriazole	3	61944	35	59	--	--	96	59
Acetophenone	3	62811	54	83	68	80	101	80
Acetyl-hexamethyl-tetrahydro-naphthalene	3	62812	43	83	59	69	110	69
Anthracene	3	34220	42	81	69	80	98	80
Anthraquinone	3	62813	78	94	75	82	121	82
Atrazine	3	39630	65	88	69	85	--	77
BDE congener 47	3	63147	39	90	43	56	96	56
Benzo[a]pyrene	3	34247	24	50	44	56	81	50
Benzophenone	3	62814	63	97	80	89	113	89
beta-Sitosterol	3	62815	18	52	27	33	64	33
beta-Stigmastanol	3	61948	32	50	29	37	65	37
Bis(2-ethylhexyl) phthalate	3	39100	25	73	1	46	0	25
Bisphenol A	3	62816	60	92	68	89	157	89
Bromacil	3	30234	68	102	65	82	122	82
Bromoform	3	32104	41	67	69	81	94	69
Caffeine	3	81436	45	71	51	69	103	69
Camphor	3	62817	46	73	71	75	96	73
Carbaryl	3	39750	98	126	113	139	194	126
Carbazole	3	77571	50	76	70	83	111	76
Chlorpyrifos	3	38932	36	67	58	68	95	67
Cholesterol	3	62818	4	62	28	33	65	33
Cotinine	3	61945	35	54	23	36	78	36

Appendix 3. Percent recoveries of anthropogenic organic compounds for environmental matrix spike samples.—Continued

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

Analyte	Analytical method	USGS parameter code	Big Sioux River (site 433600096442400)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Median
			8/3/2009	8/3/2009	2/17/2010	2/17/2010	7/29/2010	
Diazinon	3	39570	45	74	57	66	111	66
Dichlorvos	3	30218	57	86	74	81	127	81
Diethyl phthalate	3	34336	65	89	58	86	120	86
D-Limonene	3	62819	28	50	40	42	74	42
Fluoranthene	3	34376	40	79	69	79	105	79
Hexahydrohexamethyl cyclopentabenzopyran	3	62823	44	76	61	77	103	76
Indole	3	62824	34	70	61	69	93	69
Isoborneol	3	62825	43	71	70	77	91	71
Isophorone	3	34408	48	73	73	74	98	73
Isopropylbenzene	3	77223	30	54	46	56	81	54
Isoquinoline	3	62826	49	81	43	58	--	54
Menthol	3	62827	41	71	70	78	87	71
Metalaxyl	3	04254	61	89	66	85	119	85
Methyl salicylate	3	62828	53	84	74	78	105	78
Metolachlor	3	82612	53	88	69	85	113	85
Naphthalene	3	34696	47	77	71	76	95	76
N,N-Diethyl-*meta*-toluamide (DEET)	3	61947	64	84	77	91	124	84
p-Cresol	3	77146	41	80	66	76	100	76
Pentachlorophenol	3	39032	2	75	83	95	134	83
Phenanthrene	3	34461	42	78	68	81	97	78
Phenol	3	34694	-46	71	41	60	82	60
Prometon	3	39056	59	88	63	77	106	77
Pyrene	3	34469	37	79	66	79	106	79
Tetrachloroethylene	3	34475	18	40	34	40	64	40
Tributyl phosphate	3	62832	67	99	78	94	127	94
Triclosan	3	61708	53	76	62	73	114	73
Triethyl citrate	3	62833	60	92	71	87	121	87
Triphenyl phosphate	3	62834	51	79	61	70	108	70
Tris(2-butoxyethyl) phosphate	3	62830	55	78	63	78	110	78

Appendix 3. Percent recoveries of anthropogenic organic compounds for environmental matrix spike samples.—Continued

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

Analyte	Analytical method	USGS parameter code	Big Sioux River (site 433600096442400)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Median
			8/3/2009	8/3/2009	2/17/2010	2/17/2010	7/29/2010	
Tris(2-chloroethyl) phosphate	3	62831	58	84	65	79	120	79
Tris(dichloroisopropyl) phosphate	3	61707	52	76	56	69	117	69
4-Epioxytetracycline	4	63729	0	0	111	133	102	102
4-Epitetracycline hydrochloride	4	63727	7	6	90	108	94	90
Anhydroerthromycin	4	63674	98	103	116	118	129	116
Azithromycin	4	62792	52	89	130	197	105	105
Carbamazepine	4	62793	106	112	82	101	91	101
Chloramphenicol	4	65194	0	0	106	127	122	106
Chlortetracycline	4	61744	282	317	96	97	112	112
Ciprofloxacin	4	62898	101	115	142	164	127	127
Doxycycline	4	62694	102	110	64	76	82	82
Enrofloxacin	4	66495	96	97	61	77	66	77
Erythromycin	4	62797	44	48	140	140	156	140
Ibuprofen	4	62014	90	94	93	134	116	94
Lincomycin	4	62894	106	93	131	191	243	131
Lomefloxacin	4	62900	95	97	60	74	69	74
Norfloxacin	4	62757	92	91	55	71	69	71
Ofloxacin	4	62899	103	101	54	68	59	68
Ormetoprim	4	62962	106	111	105	118	116	111
Oxytetracycline	4	61759	145	157	128	151	129	145
Roxithromycin	4	62895	87	88	116	137	130	116
Sarafloxacin	4	62771	78	74	50	65	59	65
Sulfachlorpyridazine	4	62774	97	109	85	103	88	97
Sulfadiazine	4	62963	141	112	66	93	68	93
Sulfadimethoxine	4	62776	182	157	67	81	79	81
Sulfamethazine	4	61762	144	111	115	138	124	124
Sulfamethoxazole	4	62775	123	100	105	129	117	117
Sulfathiazole	4	62778	120	110	72	94	64	94
Tetracycline	4	62781	117	127	97	124	101	117

Appendix 3. Percent recoveries of anthropogenic organic compounds for environmental matrix spike samples.—Continued

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

Analyte	Analytical method	USGS parameter code	Big Sioux River (site 433600096442400)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Finished water (site 433419096434200)	Ground-water (site 433421096434401)	Median
			8/3/2009	8/3/2009	2/17/2010	2/17/2010	7/29/2010	
Trimethoprim	4	62023	90	109	105	129	117	109
Tylosin	4	62896	104	97	107	120	94	104
Virginiamycin	4	62897	51	213	126	168	190	168
4-Androstene-3,17-dione	5	64533	81	76	102	94	92	92
11-Ketotestosterone	5	64527	89	96	99	91	82	91
17-*alpha*-Estradiol	5	64528	101	97	101	110	86	101
17-*alpha*-Ethynylestradiol	5	64529	73	76	98	100	99	98
17-*beta*-Estradiol	5	64530	91	89	100	108	99	99
Bisphenol A	5	67305	72	73	80	76	88	76
Cholesterol	5	64534	98	77	65	77	95	77
cis-Androsterone	5	64535	134	111	103	101	126	111
Dihydrotestosterone	5	64544	87	102	95	95	134	95
Epitestosterone	5	64537	105	91	103	100	106	103
Equilenin	5	64538	44	91	49	95	68	68
Equilin	5	64539	139	134	73	97	76	97
Estriol	5	64540	89	92	99	102	63	92
Estrone	5	64541	96	87	116	109	104	104
Mestranol	5	64542	91	85	101	92	100	92
Norethindrone	5	64531	78	72	106	93	92	92
Progesterone	5	64543	152	76	93	92	86	92
Testosterone	5	64545	82	78	102	96	131	96
trans-Diethylstilbestrol	5	64536	60	76	8	98	89	76

Appendix 4. Physical Properties and Concentrations of Anthropogenic Organic Compounds in Source and Finished Water

The Excel file can be accessed at *http://pubs.usgs.gov/sir/2012/5098/downloads/appendix-4.xlsx*.

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Back cover inset photographs. Clockwise from left: Pump and sampling tap used at the surface-water intake station on the Big Sioux River. View of Big Sioux River north of Sioux Falls, showing the natural channel flowing from bottom left to right and diversion channel to the top left. Low-head dam on the Big Sioux River diversion channel north of Sioux Falls.

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