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Steroidal Hormones and Other Related Compounds in Shallow Groundwater in Nonagricultural Areas of Minnesota—Study Design, Methods, and Data, 2009–10

Data Series 663

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

Cover. Water-level measurement in a domestic well, White Bear Lake, Minnesota, March 2011. Photograph by Perry M. Jones, U.S Geological Survey.

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U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
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Conversion Factors

Inch/Pound to SI (used for well characteristics)

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)

SI to Inch/Pound (used for analytical methods)

Multiply	By	To obtain
	Length	
meter (m)	3.281	foot (ft)
millimeter (mm)	0.03937	inch (in)
micrometer (μm)	0.00003937	inch (in)
	Volume	
liter (L)	0.2642	gallon (gal)
milliliter (mL)	0.0338	ounce, fluid (fl. oz)
microliter (μL)	0.0000338	ounce, fluid (fl. oz)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
milligram (mg)	0.00003527	ounce, avoirdupois (oz)

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

$$°F=(1.8×°C)+32$$

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Concentrations of chemical constituents in water are given in nanograms per liter (ng/L).

Abbreviations and Acronyms

^{13}C	carbon-13
C_{18} disk	reverse-phase, octyldecyl, surface-modified, silica-embedded, glass-fiber filter disk
D-loss	deuterium loss
EAC	endocrine active compound
IDS	isotope dilution standard
GC/MS/MS	gas chromatography/tandem mass spectrometry
GFF	glass-fiber filter
MeOH/DCM	methanol in dichloromethane solution
MPCA	Minnesota Pollution Control Agency
MSTFA	*N*-methyl-*N*-trimethylsilyl trifluoroacetamide
NFM	National Field Manual for the Collection of Water-Quality Data
ng	nanogram
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
PCFF	Personal Computer Field Forms
RSD	relative standard deviation
USGS	U.S. Geological Survey

Steroidal Hormones and Other Related Compounds in Shallow Groundwater in NonAgricultural Areas of Minnesota—Study Design, Methods, and Data, 2009–10

By Melinda L. Erickson

Abstract

The U.S. Geological Survey, in cooperation with the Minnesota Pollution Control Agency, completed a study on the occurrence of steroidal hormones and other endocrine active compounds in shallow groundwater in nonagricultural areas of Minnesota during 2009–10. This report describes the study design and methods, and presents the data collected on steroidal hormones and other related compounds. Environmental and quality-control samples were collected from 40 wells as part of this study. Samples were analyzed by the U.S. Geological Survey National Water Quality Laboratory for 16 steroidal hormones and 4 other related compounds, of which all but 2 compounds are endocrine active compounds. Most of the water samples did not contain detectable concentrations of any of the 20 compounds analyzed. Water samples from three wells had detectable concentrations of one or more compounds. Bisphenol A was detected in samples from three wells, and *trans*-diethylstilbestrol was detected in one of the samples in which bisphenol A also was detected.

Introduction

Several recent studies have documented endocrine active compounds (EACs) and other contaminants of emerging interest in Minnesota surface water (Lee and others, 2004; Lee, Schoenfuss, and others, 2008; Lee, Yaeger, and others, 2008). Additionally, these contaminants have been detected in groundwater in Minnesota (Lee and others, 2004; Tornes and others, 2007) and nationwide (Zogorski and others, 2006; DeSimone and others, 2009). Understanding the occurrence and distribution of these compounds in Minnesota groundwater is important for source-water protection efforts and to better understand the connections between land use and water quality. Wastewater treatment systems, including domestic septic systems, are not designed to remove these types of compounds (Herberer, 2002; Ternes, 2002), potentially providing a transport path for these compounds to groundwater.

Lee and others (2004) collected samples from 11 monitoring or production wells, which were located in a variety of land-use settings, including sewered residential/commercial/industrial, residential septic, landfill, and feedlot. Although few groundwater sites were sampled, the detections of pharmaceuticals, antibiotics, disinfectants, personal-care products (such as sunscreen, insect repellent, and fragrances), plasticizers, pesticides, solvents, detergents, flame retardants, and polycyclic aromatic hydrocarbons in the groundwater samples were notable.

In November 2008, Minnesota voters approved a three-eighths of 1 percent increase in the State sales tax rate under the Clean Water, Land and Legacy Amendment (State of Minnesota, 2008). During the 2009 legislative session, the Minnesota Legislature appropriated funds for the Minnesota Pollution Control Agency (MPCA) to expand its monitoring of shallow groundwater to assess long-term water-quality trends in nonagricultural parts of the State. The MPCA's ambient groundwater monitoring network is planned to include a network of 200 shallow wells completed in Quaternary-age deposits and located in nonagricultural parts of the State (Minnesota Pollution Control Agency, 2009). The wells will be selected or installed to represent typical urban land-use settings in large and small urban areas throughout Minnesota; selected and installed wells will be screened near the water table. Approximately 40 of these wells will be sampled annually for EACs and other organic contaminants of emerging interest on a rotating basis.

The U.S. Geological Survey (USGS), in cooperation with the MPCA, conducted a study on the occurrence of steroidal hormones and other EACs in shallow groundwater in nonagricultural areas of Minnesota. As part of this study, the MPCA collected groundwater samples from 40 wells during 2009–10. The water samples were analyzed for steroidal hormones, pharmaceuticals, antibiotics, and organic wastewater compounds by the USGS National Water Quality laboratory (NWQL) in Denver, Colo., or the USGS Organic Geochemistry Research Laboratory in Lawrence, Kans.

The purposes of this report are to describe the study design and methods of sample collection and analysis, and to present quality-assurance and analytical data for 16 steroidal hormones and 4 other related compounds in groundwater samples collected from 40 wells during 2009–10. Of these 20 compounds, all except cholesterol and coprostanol are EACs (James Gray, National Water Quality Laboratory, written commun., 2011). All samples included in this report were analyzed by the USGS NWQL using research method schedule 2434 for hormones in filtered water. Analytical results for pharmaceuticals, antibiotics, and wastewater compounds in samples analyzed by the NWQL or Organic Geochemistry Research Laboratory using approved methods, are published in the USGS National Water Information System (NWIS) (U.S. Geological Survey, 2011) and are not included in this report.

Study Design

The study was designed to determine the magnitude of contamination from steroidal hormones, other EACs, and other organic contaminants of emerging interest in shallow groundwater in nonagricultural areas of Minnesota. EACs and other organic compounds analyzed in groundwater samples for this study include compounds typically found in wastewater, including steroidal hormones, pharmaceuticals, antibiotics, and other organic compounds.

MPCA staff, in consultation with other State agencies (Departments of Natural Resources, Health, and Agriculture) and the USGS, selected a subset of 40 shallow wells (less than 200 feet deep) from the State's ambient groundwater monitoring network for sampling as part of the first year of this study. The 40 sampled wells (fig. 1, table 1) are located primarily in nonagricultural areas in proximity to human alterations, such as housing development or industrial activities. Water samples were collected from the 40 wells during the months November 2009, and April through June 2010. The water samples were analyzed for steroidal hormones, human-use pharmaceutical compounds, human and animal-use antibiotics, and a broad suite of organic compounds associated with wastewater. Samples were sent to the USGS NWQL and the USGS Organic Chemistry Research Laboratory for analysis. Only the methods and analytical results of samples analyzed for 16 steroidal hormones and 4 other related compounds using research method schedule 2434 are included in this report.

Methods

This section of the report describes the methods used to collect the groundwater samples and the analytical methods for the analysis of 16 steroidal hormones and 4 other related compounds. Quality-assurance and quality-control samples collected for this study also are described.

Groundwater Sample Collection

USGS staff provided training to MPCA hydrologic technicians on USGS sampling protocols and on the use of the USGS Personal Computer Field Forms (PCFF) computer program, which is used to record field data. An experienced USGS hydrologic technician accompanied MPCA staff during the first week of sampling to fully train and assist MPCA staff. MPCA staff collected samples from 40 of the wells in the State's ambient network during November 2009 through June 2010. Water samples were collected by MPCA staff according to the USGS National Field Manual for the Collection of Water-Quality Data (NFM) (U.S. Geological Survey, variously dated). USGS staff verified sample integrity and labeling, shipped all samples to the USGS laboratories, and entered necessary site and sample information into USGS databases.

Each monitoring well was purged using a peristaltic pump and Teflon® tubing. Field properties, such as water temperature, pH, and specific conductance, were measured and recorded in PCFF as specified in the NFM. Samples for analysis by schedule 2434 were collected using USGS protocols for organic contaminants (section 5.6.1.F of Wilde and others, 2004), except that the samples were contained in new 0.5-liter (L; or 0.13-gallon) high-density polyethylene bottles. Samples for analysis by schedule 2434 were filtered in the field using the procedures summarized in Wilde and others (2004). Samples that were not processed within 3 days of receipt by the NWQL were stored in a freezer at -5 degrees Celsius (°C) or less, until the day preceding extraction when allowed to thaw at room temperature. Sampling equipment was decontaminated between sampling sites using, in sequence, Liqui-Nox®, tap water, deionized water, methanol, and organic-free blank water. Sampling personnel refrained from using personal-care products (for example, mosquito repellent containing *N*,*N*-diethyl-*meta*-toluamide [DEET]) to avoid contamination of the samples during collection.

Field quality-assurance samples collected for this study included duplicate and blank samples. Field-duplicate samples were collected randomly at four wells during the sampling. Matrix spike/matrix spike duplicate samples were collected at 2 of the 40 wells, but these samples were used as field-duplicates, as described in the Quality Assurance and Control section of the report. Field equipment-blank samples were collected at 4 of the 40 wells to characterize any contamination potentially introduced during field activities.

Analytical Methods

Groundwater samples were analyzed for 16 steroidal hormones and 4 other related compounds (diethylstilbestrol, bisphenol A, cholesterol, and coprostanol) using schedule 2434, which is under method research development at the USGS NWQL. Because this USGS research method is under development, long-term quality-assurance information is not available. Field-filtered water samples (typically 0.5-L volume) were fortified (spiked) with 50 milligrams (mg) of

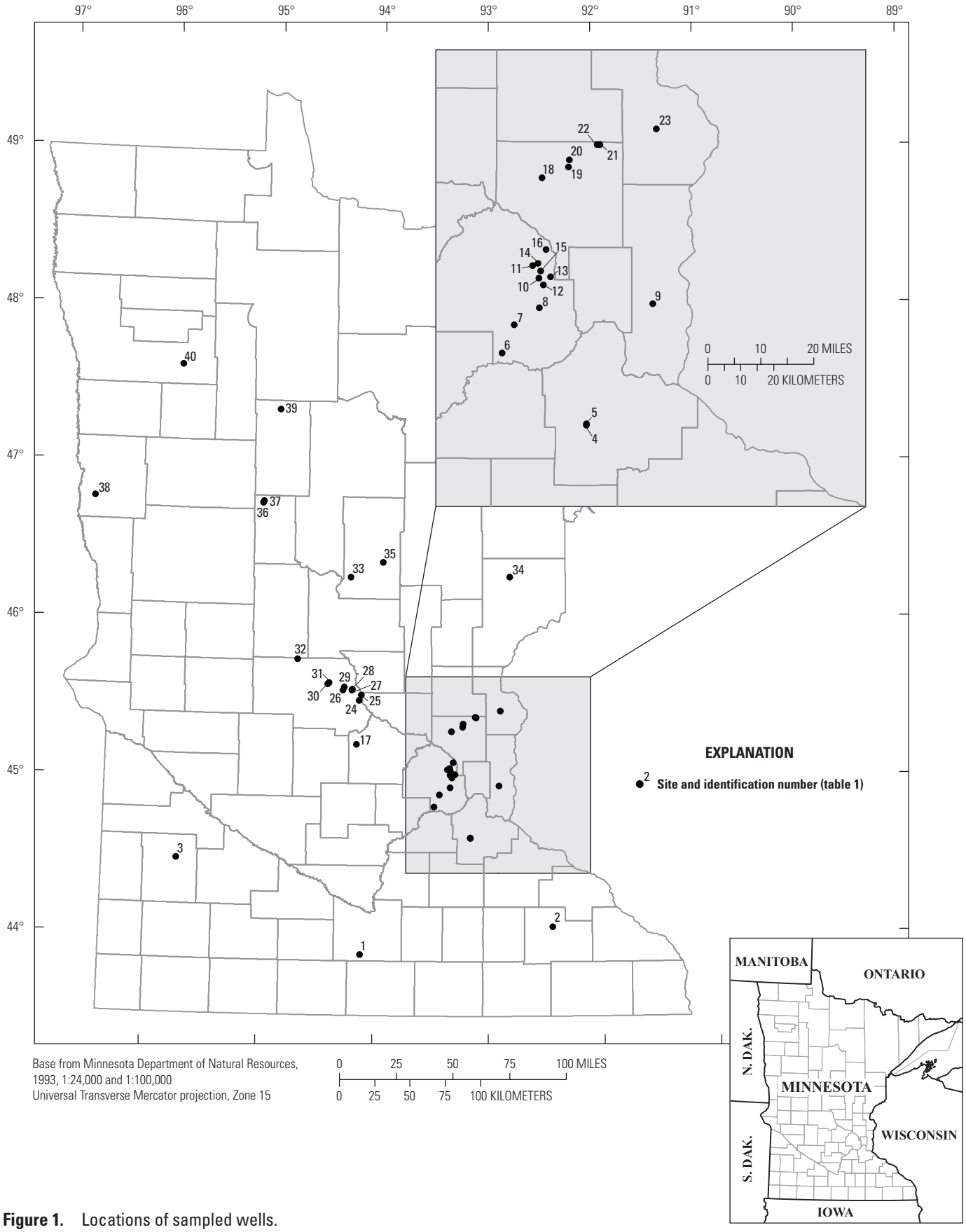

Figure 1. Locations of sampled wells.

Table 1. Selected information for sampled wells.

[ID, identification; MUN, Minnesota unique well number; ft bgs, feet below ground surface; USGS, U.S. Geological Survey; PADC, Prairie Du Chien Group; GSSG, glacial surficial sand or gravel; MN040, Minnesota County Well Index; JRDN, Jordan Sandstone; PLSC, Pleistocene series]

Agency code	Station number	Site ID number (fig. 1)	MUN	Well type	Aquifer	Well depth (ft bgs)	Open or screened interval of well (ft bgs)
USGS	435328094080601	1	444696	Domestic	PADC	128	126–128
USGS	440417092254501	2	220775	Domestic	PADC	145	127–145
USGS	442913095465601	3	427800	Domestic	GSSG	71	Unknown.
USGS	443811093093301	4	639315	Monitoring	GSSG	10	5–10
USGS	443825093093401	5	639314	Monitoring	GSSG	10	5–10
MN040	445003093290501	6	194919	Domestic	PADC	183	160–183
MN040	445443093261401	7	204590	Domestic	GSSG	112	Unknown.
USGS	445732093203201	8	639311	Monitoring	GSSG	19	14–20
MN040	445815092541101	9	404244	Domestic	PADC	133	93–133
USGS	450122093193801	10	560426	Monitoring	GSSG	19	14–19
USGS	450226093203901	11	560423	Monitoring	GSSG	29	24–29
USGS	450236093175801	12	560425	Monitoring	GSSG	17	12–17
USGS	450333093201701	13	560418	Monitoring	GSSG	9	4–9
USGS	450430093220801	14	560417	Monitoring	GSSG	22.5	17.5–22.5
USGS	450448093205301	15	560415	Monitoring	GSSG	18	13–18
USGS	450702093185101	16	560408	Monitoring	GSSG	24	19–24
USGS	451346094111901	17	757565	Monitoring	GSSG	20	10–20
USGS	451855093195901	18	245653	Monitoring	GSSG	27.6	Unknown.
MN040	452043093134801	19	148184	Domestic	JRDN	109	Unknown.
USGS	452153093133501	20	W30009	Monitoring	GSSG	18	Unknown.
USGS	452422093063301	21	639312	Monitoring	GSSG	25	20–25
USGS	452425093071001	22	Unknown	Monitoring	GSSG	23.5	Unknown.
USGS	452657092531801	23	500773	Monitoring	GSSG	87	82–87
USGS	453042094102201	24	594125	Monitoring	GSSG	23.5	18.5–23.5
USGS	453247094085701	25	561099	Monitoring	GSSG	25	15–25
USGS	453431094190301	26	440156	Domestic	GSSG	60	56–60
USGS	453436094141901	27	588392	Monitoring	GSSG	22	17–22
USGS	453453094140501	28	507162	Domestic	GSSG	58	54–58
USGS	453537094182901	29	540955	Monitoring	GSSG	31	Unknown.
USGS	453646094272301	30	403748	Domestic	GSSG	32	28–32
USGS	453717094264101	31	415618	Domestic	GSSG	31	28–31
USGS	454610094440101	32	646144	Monitoring	GSSG	19	14–19
USGS	461743094154301	33	649961	Monitoring	GSSG	16	11–16
USGS	461809092481301	34	Unknown	Monitoring	Unknown	28.6	Unknown.
USGS	462337093575601	35	582082	Monitoring	PLSC	23.5	20.3–22.3
USGS	464538095050101	36	438559	Domestic	GSSG	40	36–40
USGS	464616095043101	37	646145	Monitoring	GSSG	28	27.5–30
USGS	464631096384101	38	437602	Domestic	GSSG	72	68–72
MN040	472129094562901	39	243852	Monitoring	GSSG	21	Unknown.
USGS	473750095521601	40	132701	Domestic	GSSG	60	56–60

sodium chloride and with 10 to 10,000 nanograms (ng) of isotopically labeled compounds that were used as isotope dilution standards (IDSs; see table 2). 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 mass spectrometry (GC/MS/MS) 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 (MeOH). The eluent was evaporated to dryness at 25°C with nitrogen gas and reconstituted in 2 mL of a 5-percent methanol in dichloromethane solution (5-percent MeOH/DCM) 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 MeOH/DCM. The eluent was reduced in volume to about 1 mL with nitrogen gas, quantitatively transferred to a 5-mL reaction vial with 5-percent MeOH/DCM 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 compounds 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 addition of 200 microliters of *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide (MSTFA) activated with 2-(trimethylsilyl) ethanethiol and ammonium iodide, and heating of the MSTFA solution to 65°C for 1 hour. The MSTFA solution also contains cholestane-d_6 and chrysene-d_{12} as injection internal standards (Foreman and others, 2010).

The extract was transferred to a gas-chromatography vial, and the method compounds were determined by GC/MS/MS using a Quattro-micro-GC® (Waters Corp., Milford, Mass.). Compounds were separated by using a 30-meter by 0.25-millimeter internal diameter Rxi XLB gas chromatography column with 0.25-micrometer film thickness (Restek Corp., Bellefonte, Pa.) and a multiple ramp temperature program. Compounds were detected by tandem mass spectrometry by monitoring the product ions of three specific precursor-to-product ion transitions. Positive compound 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).

All 20 method compounds 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 based on the absolute method recovery of the IDS. For samples collected through November 2009, 13 deuterium-labeled IDS compounds were used that were exact isotopic analogs of method compounds (table 2). The remaining seven method compounds in these samples were quantified relative to one of the IDS compounds that have similar chemical functionality, but is not a direct isotopic analog of the compound (table 2).

Six of the original 13 IDS compounds—4-androstene-3,17-dione-d_7, dihydrotestosterone-d_4, estrone-d_4, norethindrone-d_7, testosterone-d_5, and progesterone-d_9—were determined to be susceptible to deuterium-hydrogen exchange (deuterium loss, D-loss) under nonroutine 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 (and, thus, IDS absolute recovery) in the sample extract, which produces a positive bias in the determined compound concentration. Consequently, these six deuterium-labeled IDS compounds were removed from the method, and not used for samples collected after November 2009. Reported concentrations of compounds normally determined using these six IDS compounds 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 compound concentration for those samples collected through November 2009 where D-loss was evident or suspected.

Samples collected after November 2009 were fortified (spiked) with the 10 deuterium- or carbon-13 (^{13}C)-labeled IDS compounds shown in table 2, five of which were unchanged from those used previously. Replacement IDS compounds contained either ^{13}C or were nondirect analogs of the analytes that have deuterium labels in positions not adjacent to a ketone group and, thus, are not susceptible to D-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 compound's parent ion at concentrations near the GC/MS/MS instrumental detection level. Six of the 10 IDS compounds were exact isotopic analogs of method compounds. The remaining 14 method compounds also were quantified using isotope dilution by using one of the IDS compounds that has similar related chemical functionality, but is not a direct isotopic analog of the compound.

Quality assurance was monitored, in part, by evaluation of IDS recoveries in each sample matrix, which represent absolute recoveries for the method. In addition, two laboratory quality-control samples were prepared and analyzed with each set of environmental samples (typically 10–16 samples in a set): (1) a laboratory reagent-water blank sample that was fortified with the IDS compounds only, and (2) a laboratory reagent-water spike sample that also was fortified with approximately 25–2,500 ng/L of the method compounds. The laboratory reagent blank was used to monitor for interferences and the possible introduction of method compounds during sample preparation or analysis. The laboratory reagent spike was used to assess recovery performance for method compounds.

The IDS compounds are reported (in percent recovery) along with the compounds' concentrations in the environmental samples or the compounds' recoveries in the laboratory reagent-spike or optional matrix-spike samples. However, these IDS measurements reflect absolute recoveries achieved during sample preparation, and are only corrected for injection variability by quantitation compared to internal injection standard compounds chrysene-d_{12} or cholestane-d_6. Reported compound concentrations (or recoveries in quality-control spike samples) are automatically recovery-corrected by using this isotope dilution quantification procedure (Foreman and others, 2010).

Quality Assurance and Control

Quality-assurance samples were collected consistent with the USGS NFM (U.S. Geological Survey, variously dated). The collected field quality-assurance samples included duplicates and blanks (table 3). Sample duplicates were collected randomly at four wells during the sampling, and samples from two additional wells were used as duplicates. Field equipment-blank samples were collected at four wells. Analytical results of the field quality-assurance samples are presented in table 4 as a separate Adobe Portable Document Format (PDF) file and a Microsoft© Excel spreadsheet.

Quality-assurance plans were established to evaluate laboratory and field sampling techniques, assess possible sources of contamination, and assure representative samples. All field personnel were familiar with study design and sampling protocols before field sampling or data processing to assure sample integrity.

Laboratory quality-control samples were used to validate and interpret the environmental data. Laboratory quality-control samples included laboratory blanks, reagent spikes, and surrogates. At least 1 fortified laboratory spike and 1 laboratory blank was analyzed with each set of 10–16 environmental samples. Laboratory reagent-water blank samples were used to assess potential sample contamination. Target compounds were not detected in the laboratory reagent-water blank samples at concentrations greater than the reporting level.

Table 2. Compound and corresponding isotope dilution standard (IDS) used for its quantification in filtered water samples analyzed by U.S. Geological Survey National Water Quality Laboratory schedule 2434.

[The six compounds with direct IDS analogs that were susceptible to deuterium loss (D-loss) are shown in ***bold italics***. The four compounds quantified with nondirect IDS analogs susceptible to D-loss are shown in **bold**. The six IDS compounds that contain ketone functional groups (keto-IDS compounds) that can undergo deuterium loss (D-loss) are shown in **bold**. d, deuterium; ^{13}C, carbon-13]

Compound	Isotope dilution standard used for samples collected through November 2009	Isotope dilution standard used for samples collected after November 2009
17-*alpha*-ethynylestradiol	17-*alpha*-ethynylestradiol-d_4	no change.
17-*alpha*-estradiol	17-*beta*-estradiol-d_4	17-*beta*-estradiol-$^{13}C_6$.
17-*beta*-estradiol	17-*beta*-estradiol-d_4	17-*beta*-estradiol-$^{13}C_6$.
equilenin	17-*beta*-estradiol-d_4	17-*beta*-estradiol-$^{13}C_6$.
4-androstene-3,17-dione	**4-androstene-3,17-dione-d_7**	nandrolone-16,16,17-d_3.
bisphenol A	bisphenol A-d_{16}	no change.
3-*beta*-coprostanol	cholesterol-d_7	no change.
cholesterol	cholesterol-d_7	no change.
***cis*-androsterone**	**dihydrotestosterone-d_4**	nandrolone-16,16,17-d_3.
dihydrotestosterone	**dihydrotestosterone-d_4**	nandrolone-16,16,17-d_3.
estriol	estriol-d_3	16-epiestriol-d_2.
equilin	**estrone-d_4**	estrone-$^{13}C_6$.
estrone	**estrone-d_4**	estrone-$^{13}C_6$.
mestranol	mestranol-d_4	no change.
norethindrone	**norethindrone-d_6**	nandrolone-16,16,17-d_3.
progesterone	**progesterone-d_9**	medroxyprogesterone-d_3.
11-ketotestosterone	**testosterone-d_5**	nandrolone-16,16,17-d_3.
epitestosterone	**testosterone-d_5**	nandrolone-16,16,17-d_3.
testosterone	**testosterone-d_5**	nandrolone-16,16,17-d_3.
trans-diethylstilbestrol	*trans*-diethylstilbestrol-d_8	no change.

Recoveries for compounds spiked into reagent water, and surrogate compounds spiked into environmental samples indicate the general proficiency of the laboratory methods. This method had surrogate compounds added to samples before extraction to monitor method performance, as described in the "Analytical Methods" section. Surrogates are chemicals that have similar properties to the analytes of interest, but do not interfere with quantitation of the compounds of interest.

Matrix interference was to be assessed by laboratory spikes in groundwater samples. Two matrix spike samples with associated duplicate samples were collected at two wells and shipped to the NWQL for assessment of matrix interference. The laboratory did not spike the samples, so the samples were used instead as duplicate samples.

Potential contamination of water samples during sample collection, processing, and laboratory analysis was assessed with field-blank samples. Field equipment-blank samples were prepared at selected sites before collecting a scheduled-environmental sample. Field equipment-blank samples were prepared by processing high-performance liquid chromatography organic-free grade water (certified by the USGS to be free of the compounds of interest) through the same equipment used to collect and process environmental samples. Four field equipment-blank samples were collected and analyzed to assess contamination introduced during sample collection and processing and laboratory analysis for water samples. None of the method compounds were detected in any of the field equipment-blank samples (table 4).

Duplicate samples are used to quantify the variability of detection and corresponding concentrations that result from sample processing (sample splitting, filtration, and transport) and laboratory techniques. Eight duplicate samples were collected. The duplicate sample pairs consisted of a primary environmental field sample and a duplicate sample collected immediately after the environmental sample; the two samples should be nearly identical in composition. Duplicate water samples were collected at six wells. Concentrations of detected compounds in duplicate samples were compared by calculating the relative standard deviation (RSD) for each detected compound. The RSD is calculated by dividing the standard deviation of the samples by the mean of the samples, and then multiplying by 100. Only the two duplicate samples collected at site 18 (station number 451855093195901) had detections of one compound (bisphenol A) making calculation of the RSD possible. The RSDs were 6.6 and 1.8.

Data for Steroidal Hormones and Other Endocrine Active Compounds

The concentration data for the 16 steroidal hormones and 4 other related compounds in groundwater samples collected from 40 wells in Minnesota during 2009–10 are presented in table 4 (PDF; Microsoft© Excel spreadsheet), along with the associated IDS percent recoveries. Most of the water samples did not contain detectable concentrations of any of the 20 method compounds analyzed using USGS NWQL schedule 2434. Environmental samples from three wells had detectable concentrations of one or more compounds (sites 18, 20, and 31; fig. 1). Bisphenol A was detected in samples from those three wells, and *trans*-diethylstilbestrol was detected in the sample from one of the wells (site 20) at which bisphenol A also was detected.

Table 3. Field quality-assurance sample descriptions.

[ID, identification; OAQ, field equipment blank quality-assurance sample; WGQ, groundwater quality-assurance sample]

Station number	Site ID number (fig. 1)	Date sampled	Time sampled	Medium code	Sample description
442913095465601	3	06/17/2010	1030	OAQ	Field equipment blank.
443811093093301	4	04/26/2010	1311	WGQ	Duplicate of environmental sample collected at 12:50.
443811093093301	4	04/26/2010	1312	WGQ	Duplicate of environmental sample collected at 12:50.
443825093093401	5	11/09/2009	1125	OAQ	Field equipment blank.
450122093193801	10	06/24/2010	1406	WGQ	Duplicate of environmental sample collected at 11:50.
451855093195901	18	06/25/2010	844	WGQ	Duplicate of environmental sample collected at 8:40.
451855093195901	18	06/25/2010	845	WGQ	Duplicate of environmental sample collected at 8:40.
453042094102201	24	06/08/2010	1116	WGQ	Duplicate of environmental sample collected at 11:15.
461809092481301	34	06/16/2010	1040	OAQ	Field equipment blank.
464631096384101	38	06/21/2010	1135	OAQ	Field equipment blank.
464631096384101	38	06/21/2010	1151	WGQ	Duplicate of environmental sample collected at 11:50.
473750095521601	40	06/29/2010	931	WGQ	Duplicate of environmental sample collected at 9:30.

Summary

The U.S. Geological Survey, in cooperation with the Minnesota Pollution Control Agency, completed a study on the occurrence of steroidal hormones and other endocrine active compounds in shallow groundwater in nonagricultural areas of Minnesota during 2009–10. As part of this study, the Minnesota Pollution Control Agency collected groundwater samples from 40 wells during 2009–10. The water samples were analyzed for steroidal hormones, pharmaceuticals, antibiotics, and organic wastewater compounds. This report describes the study design and methods, and presents the data collected on 16 steroidal hormones and 4 other related compounds that were analyzed by the U.S. Geological Survey National Water Quality Laboratory using research method schedule 2434 for hormones in filtered water. Of these 20 compounds analyzed, all except 2 are endocrine active compounds. Most of the water samples did not contain detectable concentrations of any of the 20 compounds analyzed using this laboratory schedule. Water samples from three wells had detectable concentrations of one or more compounds. Bisphenol A was detected in samples from three wells, and *trans*-diethylstilbestrol was detected in one of the samples in which bisphenol A also was detected.

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