

Presence and Distribution of Organic Wastewater Compounds in Wastewater, Surface, Ground, and Drinking Waters, Minnesota, 2000–02

By Kathy E. Lee, Larry B. Barber, Edward T. Furlong, Jeffery D. Cahill, Dana W. Kolpin, Michael T. Meyer, and Steven D. Zaugg

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Conversion Factors and Water-Quality Units

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
gallon (gal)	3.785	liter (L)
cubic yard (yd ³)	0.7646	cubic meter (m ³)
Flow rate		
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m ³ /s)

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

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

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PRESENCE AND DISTRIBUTION OF ORGANIC WASTEWATER COMPOUNDS IN WASTEWATER, SURFACE, GROUND, AND DRINKING WATERS, MINNESOTA, 2000-02

By Kathy E. Lee, Larry B. Barber, Edward T. Furlong, Jeffery D. Cahill, Dana W. Kolpin, Michael T. Meyer, and Steven D. Zaugg

ABSTRACT

Selected organic wastewater compounds (OWCs) such as household, industrial, and agricultural-use compounds, pharmaceuticals, antibiotics, and sterols and hormones were measured at 65 sites in Minnesota as part of a cooperative study among the Minnesota Department of Health, Minnesota Pollution Control Agency, and the U.S. Geological Survey. Samples were collected in Minnesota during October 2000 through November 2002 and analyzed for the presence and distribution of 91 OWCs at sites including wastewater treatment plant influent and effluent; landfill and feedlot lagoon leachate; surface water; ground water (underlying sewered and unsewered mixed urban land use, a waste dump, and feedlots); and the intake and finished drinking water from drinking water facilities

There were 74 OWCs detected that represent a wide variety of use. Samples generally comprised a mixture of compounds (average of 6 OWCs) and 90 percent of the samples had at least one OWC detected. Concentrations for detected OWCs generally were less than 3 micrograms per liter. The ten most frequently detected OWCs were metolachlor (agricultural-use herbicide); cholesterol (sterol primarily associated with animal waste); caffeine (stimulant), N,N-diethyl-*meta*-toluamide (DEET) (topical insect repellent); bromoform (disinfection by product); tri(2-chloroethyl)phosphate (flame-retardant and plastic component); *beta*-sitosterol (plant sterol that is a known endocrine disruptor); acetyl-hexamethyl-tetrahydro-naphthalene (AHTN) (synthetic musk widely used in personal care products, and a known endocrine disruptor); bisphenol-A (plastic component and a known endocrine disruptor); and cotinine (metabolite of nicotine).

Wastewater treatment plant influent and effluent, landfill leachate, and ground water underlying a waste

dump had the greatest number of OWCs detected. OWC detections in ground-water were low except underlying the one waste dump studied and feedlots. There generally were more OWCs detected in surface water than ground water, and there were twice as many OWCs detected in the surface water sites downstream from wastewater treatment plant (WWTP) effluent than at sites not directly downstream from effluent. Comparisons among site classifications apply only to sites sampled during the study.

Results of this study indicate ubiquitous distribution of measured OWCs in the environment that originate from numerous sources and pathways. During this reconnaissance of OWCs in Minnesota it was not possible to determine the specific sources of OWCs to surface, ground, or drinking waters. The data indicate WWTP effluent is a major pathway of OWCs to surface waters and that landfill leachate at selected facilities is a potential source of OWCs to WWTPs. Aquatic organism or human exposure to some OWCs is likely based on OWC distribution. Few aquatic or human health standards or criteria exist for the OWCs analyzed, and the risks to humans or aquatic wildlife are not known. Some OWCs detected in this study are endocrine disruptors and have been found to disrupt or influence endocrine function in fish. Thirteen endocrine disruptors, 3-*tert*-butyl-4-hydroxyanisole (BHA), 4-cumylphenol, 4-*normal*-octylphenol, 4-*tert*-octylphenol, acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), benzo[*a*]pyrene, *beta*-sitosterol, bisphenol-A, diazinon, nonylphenol diethoxylate (NP2EO), octylphenol diethoxylate (OP2EO), octylphenol monoethoxylate (OP1EO), and total *para*-nonylphenol (NP) were detected. Results of reconnaissance studies may help regulators who set water-quality standards begin to prioritize which OWCs to focus upon for given categories of water use.

INTRODUCTION

Household, industrial, and agricultural-use compounds (HIAs), pharmaceuticals, antibiotics, sterols, and hormones are newly recognized classes of organic compounds that are often associated with wastewater. These organic wastewater compounds (OWCs) are characterized by high usage rates, potential health effects, and continuous release into the environment through human activities (Halling-Sorensen and others, 1998; Daughton and Ternes, 1999). OWCs can enter the environment through a variety of sources and may not be completely removed in wastewater treatment systems (Richardson and Bowron, 1985; Stumpf and others, 1996; Ternes, 1998) resulting in potentially continuous sources of OWCs to surface, ground, and drinking waters. OWCs have been detected in surface and ground waters throughout the world (Stumpf and others, 1996; Heberer and others, 1997; Buser and others, 1998; Ternes, 1998; Heberer and others, 1998; Daughton and Ternes, 1999). Kolpin and others (2002) reported that 80 percent of 139 streams sampled across the United States contained at least one OWC.

The continual introduction of OWCs into the environment may have undesirable effects on humans and animals (Daughton and Ternes, 1999). Much of the concern has focused on the potential for endocrine disruption (change in normal processes in the endocrine system) in fish. Field investigations in Europe and the United States suggest that selected OWCs (nonionic-detergent metabolites, plasticizers, pesticides, and natural or synthetic sterols and hormones) have caused changes in the endocrine systems of fish (Purdom and others, 1994; Jobling and Sumpter, 1993; Folmar and others, 1996; Folmar and others, 2001; Goodbred and others, 1997). In Minnesota, male common carp (*Cyprinus carpio*) collected in the effluent channel from the St. Paul/Minneapolis Metropolitan Wastewater Treatment Plant showed signs of endocrine disruption (Folmar and others, 1996; Lee and others, 2000).

An additional concern is the introduction of antibiotics and other pharmaceuticals into the environment. Antibiotics and other pharmaceuticals administered to humans and animals are not always completely metabolized and are excreted in urine or feces as the original product or as metabolites (Daughton and Ternes, 1999). The introduction of antibiotics into the environment may result in strains of bacteria that become resistant to antibiotic treatment (Daughton and Ternes, 1999).

It is important to determine the presence and distribution of OWCs in Minnesota's wastewater, surface, ground, and drinking waters because of potential human and ecosystem health concerns. The U.S. Geological Survey (USGS), in cooperation with the Minnesota Department of Health (MDH), and the Minnesota Pollution Control Agency (MPCA) conducted a reconnaissance study to determine the presence and distribution of OWCs in wastewater, surface, ground, and drinking waters in Minnesota during October 2000 through November 2002. The purpose of this report is to describe the results of this study and to document the quality-assurance procedures used to evaluate data quality.

STUDY DESIGN AND METHODS

Sites were selected to determine the presence and distribution of selected OWCs in potential wastewater, ground, surface, and drinking water sources in Minnesota. A total of 65 sites were selected, which included classifications as wastewater, surface-, ground-, and drinking-water sites (figs. 1 and 2; table 1).

The wastewater site classification included wastewater treatment plant influent and effluent, leachate from landfills, and water underlying feedlot lagoons. Wastewater treatment plants (WWTPs) were selected based on major influent composition, processing techniques, and accessibility. WWTPs sampled during this study differed in design flows, treatment techniques, and composition of influent (table 2). Effluent was sampled from four WWTPs (Sites 2, 3, 4, 5). Both the influent (Site 1) and effluent (Site 2) were sampled from one WWTP (East Grand Forks).

Three landfills were selected for leachate sampling. Landfill leachate (water that had passed through waste and collected in perimeter drains) was expected to have high concentrations of OWCs and would provide an estimate of the greatest expected concentrations. Landfill leachate was included in the wastewater classification (as opposed to the ground-water classification) because leachate at the facilities sampled is collected and transported to WWTPs for treatment. Landfills were selected based on type of waste received and accessibility. Landfills varied with respect to total capacity, type of waste, and leachate amount generated (table 3). Two of the landfill locations (Sites 6 and 7) were sanitary landfills and one (Site 8) was an industrial landfill.

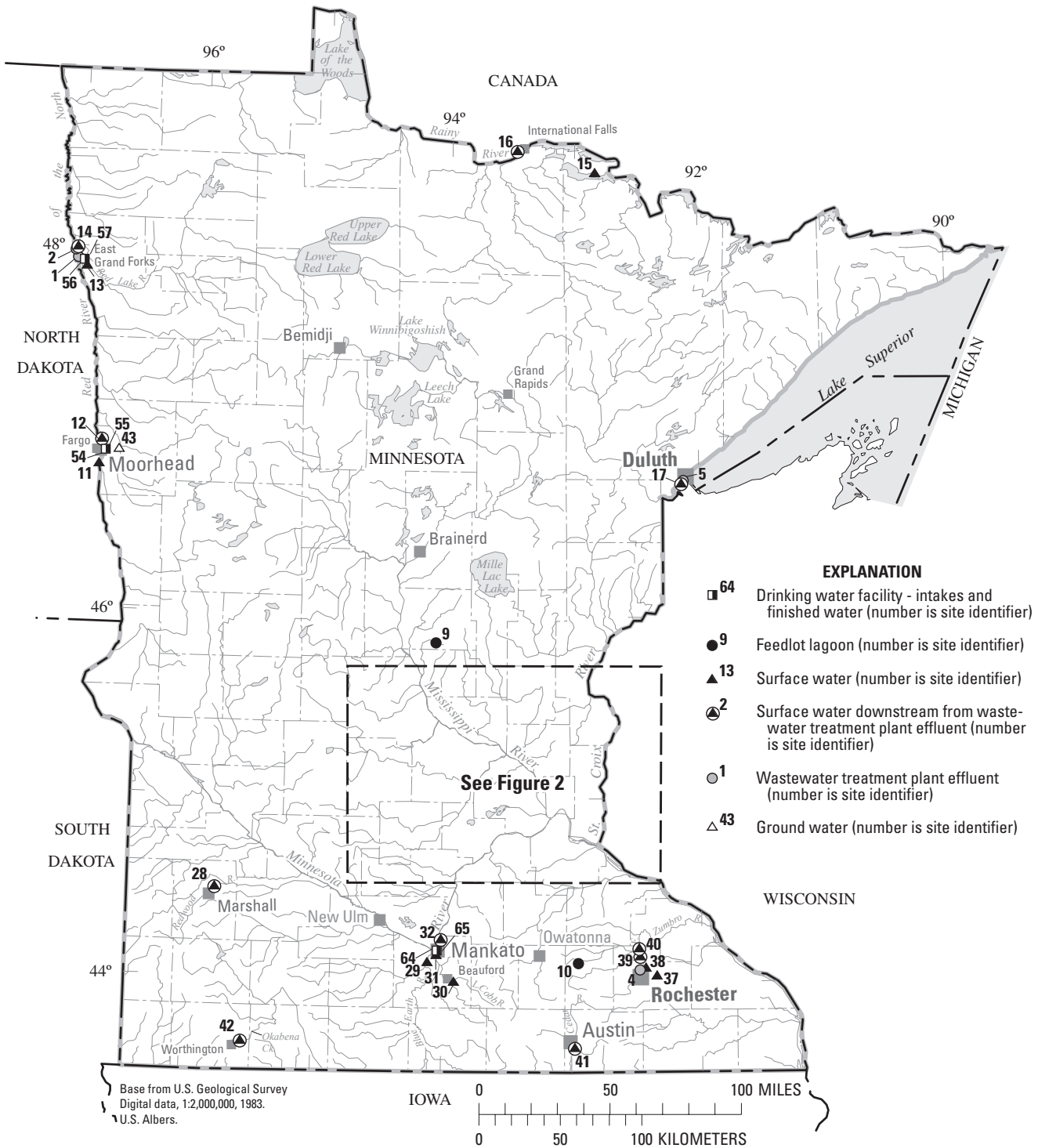


Figure 1. Location of study area and sampling sites (see table 1).

Two feedlot lagoons (Sites 9 and 10) used for livestock waste were selected to determine if OWCs in livestock waste pass through the compacted clay layer surrounding the lagoon basin. The two selected lagoons have systems to monitor the quantity and quality of seepage through compacted clay liners that underlie

the sidewalls and bottoms of the lagoons. The systems consist of polyvinyl chloride (PVC) sheets that route seepage to a sump. Site 9 is located at a large hog farm, and holds a manure-water mixture from a nearby swine gestation barn (Ruhl, 1999). Site 10 holds waste from a small dairy farm (Wall and others, 1998). Selected

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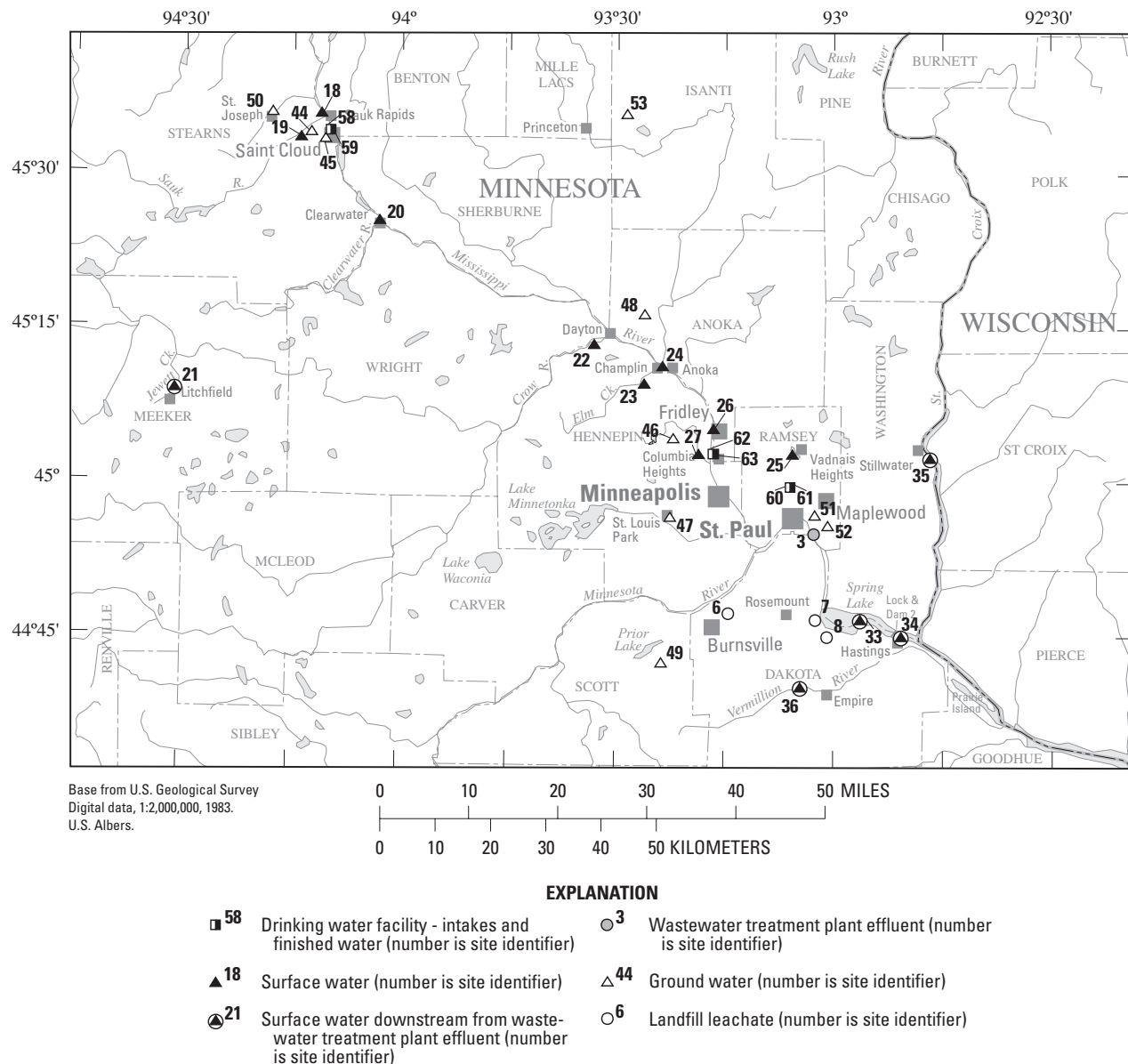


Figure 2. Location of sampling sites in east-central Minnesota, (see table 1).

feedlot lagoons were considered representative of other lagoons in the state of Minnesota.

There were 32 surface-water sites selected for this study (table 4). Surface-water sites were selected because of proximity to WWTP effluent discharge points and drinking-water-facility intakes, or basin land use. A remote lake in Voyageurs National Park with little human influence was selected as a reference location (Site 15). There were 11 sites selected on streams or lakes upstream from, and in close proximity to, drinking water-facility-intake pipes to determine potential sources of OWCs. There were 15 stream or lake sites (Sites 12, 14, 16, 17, 21, 28, 32, 33, 34, 35, 36, 39, 40, 41, and 42) selected downstream from WWTP effluent discharges

(most within 1 mile of the discharge location) to determine if WWTP effluent is a potential source of OWCs to these streams.

This reconnaissance study included additional cooperative research. Three sites (Sites 38, 39, and 40) were sampled to determine the longitudinal change in OWCs upstream and downstream from WWTP effluent as part of a nationwide study by the U.S. Environmental Protection Agency and USGS Toxics Substances Hydrology Program. Site 38 is located upstream from WWTP effluent (Site 4), Site 39 is 250 ft downstream from the effluent discharge, and Site 40 is 1 mile downstream from effluent discharge. In addition, three sites (Sites 23,

Table 1. Selected sampling sites, and site classifications, Minnesota, 2000-02

[WWIF, wastewater treatment plant influent; WWEF, wastewater treatment plant effluent; WWTP, wastewater treatment plant; LFLCH, landfill leachate; FLLAG, feedlot lagoon; SW, surface water; SDW, surface water downstream from wastewater treatment plant effluent discharge; GWDW, ground water used for municipal drinking water supply; GWUI, ground water underlying mixed urban/residential/commercial/industrial land use that is seweraged; GWUNSW, ground water underlying urban residential area that is unseweraged; GWD, ground water underlying a waste dump; GWFLT, ground water underlying a feedlot; DWI, drinking water intakes; DWO, finished drinking water; HN, Hennepin County; MW, monitoring well].

Site identifier (fig.1 or 2)	Site name	Site classification
Wastewater sites		
1	WWTP Lift Station Inflow at East Grand Forks	WWIF
2	WWTP Outflow at East Grand Forks	WWEF
3	Metropolitan Council Environmental Services WWTP Outflow in St. Paul	WWEF
4	WWTP outflow at Rochester	WWEF
5	Western Lake Superior Sanitary District WWTP outflow at Duluth	WWEF
6	Sanitary Landfill-1	LFLCH
7	Sanitary Landfill-2	LFLCH
8	Industrial Landfill-1	LFLCH
9	Morrison County feedlot lagoon	FLLAG
10	Dodge County feedlot lagoon	FLLAG
Surface-water sites		
11	Red River of the North above Fargo, N.Dak.	SW
12	Red River of the North below Fargo, N.Dak.	SDW
13	Red Lake River at State Hwy 220 above East Grand Forks	SW
14	Red River of the North below WWTP at East Grand Forks	SDW
15	Ek Lake near International Falls	SW
16	Rainy River below International Falls	SDW
17	Lake Superior in St. Louis Bay at Duluth	SDW
18	Mississippi River above Sauk River near Sauk Rapids	SW
19	Sauk River near St. Cloud	SW
20	Mississippi River above Clearwater River near Clearwater	SW
21	Jewitt's Creek near Litchfield	SDW
22	Crow River below State Hwy 101 at Dayton	SW
23	Elm Creek near Champlin	SW
24	Mississippi River near Anoka	SW
25	Vadnais Lake at Pumping Station in Vadnais Heights	SW
26	Rice Creek at County Road 1 in Fridley	SW
27	Shingle Creek at Queen Ave. in Minneapolis	SW
28	Redwood River below WWTP near Marshall	SDW
29	Blue Earth River near Rapidan	SW
30	Little Cobb River near Beauford	SW
31	Blue Earth River at County Road 90 near Mankato	SW
32	Minnesota River at Mankato	SDW
33	Mississippi River at Ninninger	SDW
34	Mississippi River below Lock and Dam 2 at Hastings	SDW
35	St. Croix River below Stillwater	SDW
36	Vermillion River below Empire WWTP near Empire	SDW
37	Bear Creek Tributary near Chester	SW
38	South Fork Zumbro River at Rochester	SW
39	South Fork Zumbro River near Rochester	SDW
40	South Fork Zumbro River below WWTP near Rochester	SDW
41	Cedar River below WWTP at Austin	SDW
42	Okabena Creek near Worthington	SDW
Ground-water sites		
43	Moorhead City well number 9	GWDW
44	Burlington Northern well near St. Cloud	GWUI
45	St. Cloud Rail Authority well	GWUI
46	HN-K well	GWUI
47	St. Louis Park well	GWUI
48	Anoka County observation well	GWUNSW
49	Prior Lake observation well	GWUNSW
50	St. Joseph observation well	GWUNSW
51	MW-6 at Pigs Eye Dump	GWD
52	MW-14 at Pigs Eye Dump	GWD
53	Isanti County Observation well near Princeton	GWFLT
Drinking-water sites		
54	Moorhead Drinking Water Facility intake water at Moorhead	DWI
55	Moorhead Drinking Water Facility finished water at Moorhead	DWO
56	East Grand Forks Drinking Water Facility intake water at East Grand Forks	DWI
57	East Grand Forks Drinking Water Facility finished water at East Grand Forks	DWO
58	St. Cloud Drinking Water Facility intake water at St. Cloud	DWI
59	St. Cloud Drinking Water Facility finished water at St. Cloud	DWO
60	St. Paul Drinking Water Facility intake water at Maplewood	DWI
61	St. Paul Drinking Water Facility finished water at Maplewood	DWO
62	Minneapolis Drinking Water Facility intake water at Columbia Heights	DWI
63	Minneapolis Drinking Water Facility finished water at Columbia Heights	DWO
64	Mankato Drinking Water Facility intake water at Mankato	DWI
65	Mankato Drinking Water Facility finished water at Mankato	DWO

Table 2. Characteristics of wastewater treatment plants sampled, Minnesota, 2000-02

[WWTP, wastewater treatment plant; NA, not available; NPDES, National Pollutant Discharge Elimination System; SP, stabilization pond; AS, activated sludge; M, mechanical screen bars; MGD, million gallons per day; CHL/DCHL, chlorination/dechlorination; (Patricia King and Angela Preimesberger, Minnesota Pollution Control Agency, written commun., 2003)].

Site identifier (fig. 1 or 2)	Facility name (NPDES number)	Receiving water	Annual average wet, and (dry) design flow (MGD)	Treatment technique	Disinfection method	Description of significant influent sources
1, 2	WWTP inflow and outflow at East Grand Forks (MN0021814)	Red River of the North	1.4 (NA)	2 cell -SP	NA	Domestic waste, potato processing
3	Metropolitan Council Environmental Services WWTP outflow in St. Paul (MN0029815)	Mississippi River	314 (250)	Step aeration, AS	CHL/DCHL	Domestic waste; battery, coil and can coating; electroplating, food and dairy processing; iron and steel; laundry; leather and tanning; livestock; medical facilities; metal finishing; organic chemicals; energy/power; pharmaceutical manufacturing; plastics; pulp and paper; railroads; solid waste landfill leachate
4	WWTP outflow at Rochester (MN0024619)	South Fork Zumbro River	19.1 (11.1)	AS	CHL/DCHL	Domestic waste; food and dairy processing; gas stations; incinerators; landfill leachate; laundry; medical facilities; metal finishing; power generator
5	Western Lake Superior Sanitary District WWTP outflow at Duluth (MN0049786)	Lake Superior	48.4 (35.3)	AS, M	CHL/DCHL	Domestic waste; electroplating; foundry; inorganic chemical; metal finishing; organic chemical; pulp and paper; pharmaceutical manufacturing; steam and electric power; timber products

Table 3. , written commun., 2003)

Site identifier (fig. 1 or 2)	Landfill	Capacity (cubic yards)	Capacity used (cubic yards)	Tons of municipal waste landfilled	Tons of demolition waste landfilled	Tons of industrial waste landfilled	Leachate generated (gallons)	Leachate disposal location
6	Sanitary Landfill-1	14,028,000	11,841,400	198,829	Separate area	111,251	1,750,235	Metropolitan Council Environmental Services WWTP in St. Paul, Minn. (Site 3)
7	Sanitary Landfill-2	24,000,000	20,207,320	277,130	205	222,853	8,533,596	Metropolitan Council Environmental Services WWTP in St. Paul, Minn. (Site 3)
8	Industrial Landfill-1	6,037,983	664,244	0	0	283,081	3,474,161	Metropolitan Council Environmental Services WWTP in St. Paul, Minn. (Site 3) when volume exceeds amount permitted at Rosemount WWTP

Table 4. Land use and land cover percentages, and drainage areas in the basin upstream from surface-water sampling locations, Minnesota, 2000-02[nd, not determined; the sum of land use/land cover percentages may not equal 100 due to absence of an 'other' category; mi², square miles; WWTP, wastewater treatment plant].

Site identifier (fig. 1 or 2)	Site name	Percent urban	Percent forest/shrub	Percent agriculture	Percent wetland	Basin Area (mi ²)
11	Red River of the North above Fargo, N.Dak.	0.6	7.5	79.0	7.8	6,621
12	Red River of the North below Fargo, N.Dak.	0.8	7.4	79.1	7.7	6,704
13	Red Lake River at St. Hwy 220 above East Grand Forks	0.5	14.5	41.5	33.6	5,710
14	Red River of the North below WWTP at East Grand Forks	0.7	7.6	76.0	11.6	25,713
15	Ek Lake near International Falls	0	80	0	20.0	1.21
16	Rainy River below International Falls	0.3	61.6	1.1	21.0	4,452
17	Lake Superior in St. Louis Bay at Duluth	1.5	46.9	7.5	37.6	3,719
18	Mississippi River above Sauk River near Sauk Rapids	0.9	38.8	25.5	24.7	12,582
19	Sauk River near St. Cloud	1.2	9.8	71.9	12.1	1,034
20	Mississippi River above Clearwater River near Clearwater	1.0	36.4	29.3	23.6	13,762
21	Jewitt's Creek near Litchfield	7.3	4.4	63.9	14.9	26.9
22	Crow River below State Hwy 101 at Dayton	1.5	6.7	73.9	12.4	2,750
23	Elm Creek near Champlin	8.7	1.6	84.0	2.8	85.8
24	Mississippi River near Anoka	1.2	30.1	37.8	21.6	19,092
25	Vadnais Lake at Pumping Station in Vadnais Heights	nd	nd	nd	nd	nd
26	Rice Creek at County Road 1 in Fridley	22.2	10.2	39.2	18.6	180.2
27	Shingle Creek at Queen Ave. in Minneapolis	71.0	0.9	20	0.7	28.2
28	Redwood River below WWTP near Marshall	1.8	2.8	87.8	4.8	268.9
29	Blue Earth River near Rapidan	1.7	3.2	91.0	2.6	2,430
30	Little Cobb River near Beauford	0.2	0.5	94.0	4.0	130
31	Blue Earth River at County Road 90 near Mankato	1.7	3.2	91.0	2.6	3,536
32	Minnesota River at Mankato	1.0	3.5	88.5	4.5	14,917
33	Mississippi River at Ninninger	2.5	19.0	66.0	7.1	37,000
34	Mississippi River at Lock and Dam 2 at Hastings	2.5	18.0	66.0	7.1	37,000
35	St. Croix River below Stillwater	0.6	49.0	28.8	17.0	7,025
36	Vermillion River below Empire WWTP near Empire	13.8	10.6	65.0	7.6	118.9
37	Bear Creek Tributary near Chester	nd	nd	nd	nd	nd
38	South Fork Zumbro River at Rochester	5.4	7.7	83.6	2.9	301.6
39	South Fork Zumbro River near Rochester	5.4	7.7	83.6	2.9	301.6
40	South Fork Zumbro River below WWTP near Rochester	5.4	7.7	83.6	2.9	301.6
41	Cedar River below WWTP at Austin	3.4	3.4	90.6	2.4	244.3
42	Okabena Creek near Worthington	28.1	0.9	68.0	0.8	8.2

27, and 30) were sampled cooperatively with the USGS National Water-Quality Assessment (NAWQA) Program. These sites have been sampled extensively by the NAWQA Program.

Ground-water sites (table 5) included 1 production well (Site 43), 8 monitoring wells (Sites 44-47, 50-53), and 2 temporary drive-point test wells (Sites 48 and 49). Ground-water sites were selected based on proximity to potential OWC sources and surrounding land-use characteristics, with the exception of Site 43 in the Quaternary aquifer near Moorhead, Minnesota that was sampled because it serves as a source of water for the Moorhead Drinking Water Facility (DWF).

The monitoring wells were less than 40 ft deep. There were four wells located in mixed urban residential/commercial/industrial land use in sewered areas, two wells located in the waste dump, and one well located in the feedlot. Two temporary drive-point test wells (Sites 48 and 49) and one monitoring well (Site 50) were selected in unsewered areas near individual sewage treatment system leach fields (septic systems).

Six drinking water facilities (DWFs) (Sites 54-65 shown in table 6) were selected for this study. Two DWFs were selected in the Red River of the North Basin (Moorhead, and East Grand Forks), and four DWFs were sampled in the Upper Mississippi River Basin (St. Cloud, St. Paul, Minneapolis, and Mankato). These facilities have different source waters and varying water-treatment techniques (table 6). Selected DWFs (except Mankato and Moorhead DWFs) utilize surface water as their source for drinking water production. Mankato DWF draws most of its water from Ranney collector wells adjacent to the Blue Earth and Minnesota Rivers. Ranney wells used by the Mankato DWF are approximately 60 ft below the land surface. Ground water at the Ranney wells could be influenced by recharge from the Blue Earth and Minnesota Rivers (George Rosati, City of Mankato Water Treatment Facility, oral commun., 2000). One water production well that serves as a source of intake water for Moorhead DWF also was sampled (Site 43). This well is used intermittently as a drinking water source in conjunction with surface water from the Red River of the North and was in production during two sampling periods (Fall of 2000, and Summer of 2001). Both intake and finished water from DWFs were sampled.

All samples were collected using protocols and procedures to obtain a representative sample and avoid sample contamination. Specific protocols and methods

are documented for the collection and processing of water-quality samples (U.S. Geological Survey, 2003), and streamflow computation (Rantz and others, 1982 a and b; Morlock and others, 2002). During collection or processing of samples, sample collectors did not use personal care items (such as insect repellent, colognes, aftershave, and topical antibiotics), and they did not consume caffeinated products (coffee, tea, carbonated beverages). All samples were collected with inert materials such as Teflon, glass, or stainless steel. A multi-parameter probe was used to measure field parameters (specific conductance, pH, water temperature, and dissolved oxygen) at each site (U.S. Geological Survey, 2004a).

Integrated width-and depth-sampling techniques were used to sample WWTP effluent from the effluent discharge channels outside of three plants (Sites 3, 4, and 5) and from the treated effluent at Site 2 in the outflow of the settling pond during release to the Red River of the North (U.S. Geological Survey, 2003). Both raw and treated sewage were collected from the East Grand Forks WWTP (Sites 1 and 2). Untreated sewage influent was collected from an interceptor line at Site 1 by filling a Teflon sample bottle from the incoming waste stream.

Landfill leachate samples were collected with a Teflon bailer from leachate storage tanks and composited in glass or Teflon containers. The leachate at Site 6 was collected from an underground storage tank that collected water from selected locations within the landfill. Leachate from Site 7 was collected from an above ground storage tank representative of selected locations within the landfill. Leachate from Site 8 was collected from an above ground storage tank that was representative of the entire landfill.

Wastewater samples from feedlot lagoons used for animal waste (Sites 9 and 10) were collected from the drainage system underlying the lagoon. A sump pump was used to collect water passing through the compacted clay layer that was intercepted by a plastic liner.

Stream samples were collected using established USGS techniques (U.S. Geological Survey, 2003). Samples were collected from boats, bridges, or by wading, depending on stream size and streamflow conditions. Stream samples were collected with a depth-integrating sampler from 5-10 verticals and composited in a Teflon or glass container prior to processing. Lake samples (Sites 15 and 17) were collected with a depth-integrating sampler from 5-10 locations in the lake.

Table 5. Characteristics of ground-water sites sampled, Minnesota 2000-02 (Angel Preimesberger, Minnesota Pollution Control Agency, written commun., 2003)
 [PVC, polyvinyl chloride; SS, stainless steel; ST, steel; HN, Hennepin County; MW, monitoring well; NA, not available]

Site identifier (fig. 1 or 2)	Local well number	Site name	Description	Screened interval (feet)	Well depth (feet)	Casing construction material
43	222050	Moorhead City well number 9	Water production well	78.0 - 111.3	114.0	ST
44	444225	Burlington Northern well near St. Cloud	Sewered, older residential and industrial	4.0 - 14.4	16.5	ST
45	594128	St. Cloud Rail Authority well	Sewered older residential, commercial, and industrial	16.5 - 21.5	23.2	PVC
46	560417	HN-K well	Sewered, older residential, commercial, and industrial	17.5 - 22.5	22.5	PVC
47	216031 (MW-2)	St. Louis Park well	Sewered industrial	31.0 - 36.0	36.0	SS
48	NA	Anoka County observation well	Temporary drive-point test well within 100 feet of a septic system	0 - 2.0	2.0	SS
49	NA	Prior Lake observation well	Temporary drive-point test well within 100 feet of a septic system	0 - 2.0	2.0	SS
50	540955	St. Joseph observation well	Observation well within 100 feet of a septic system	26.0 - 31.0	31.0	PVC
51	MW-6	MW-6 at Pigs Eye Dump	Closed dump	15.2 - 17.2	20.0	ST
52	MW-14	MW-14 at Pigs Eye Dump	Closed dump	22.3 - 27.6	27.6	ST
53	591791	Isanti County observation well near Princeton	Dairy feedlot with approximately 70 head of cattle	8.5 - 13.5	14.0	PVC

Table 6. Characteristics of drinking water facilities sampled, Minnesota, 2000-02

Site identifier (fig. 1 or 2)	Location	Source water	Approximate number of people served	Average daily water production (MGD)	Treatment objective	Treatment process or chemical
54-55	Moorhead Drinking Water Facility at Moorhead	80-90 percent is from the Red River of the North, and the remainder from Quaternary buried and water table aquifers.	36,200	4.1	Softening Coagulation pH control Disinfection and taste/odor control Filtration Corrosion control Prevent tooth decay Secondary disinfection	Lime-soda ash Ferric sulfate Carbon dioxide Ozone Dual media filters Sodium hexametaphosphate Fluoride Chloramines
56-57	East Grand Forks Drinking Water Facility at East Grand Forks	100 percent Red Lake River	7,500	1.5	Taste/odor control Coagulation Coagulation aid Softening Softening Corrosion control pH control Disinfection Prevent tooth decay Filtration Disinfection	Powdered activated carbon and/or potassium permanganate Alum Cationic polymer Lime-soda ash Sodium aluminate Polyphosphate Carbon dioxide Chlorine Fluoride Mixed media filters Chloramines
58-59	St. Cloud Drinking Water Facility at St. Cloud	100 percent Mississippi River	59,000	7	Taste/odor control Coagulation Softening pH control Disinfection Corrosion control Disinfection Prevent tooth decay Filtration	Powdered activated carbon and/or potassium permanganate Alum Lime-soda ash Carbon dioxide Chlorine Polyphosphate Chloramines Fluoride Filters
60-61	St. Paul Drinking Water Facility at Maplewood	70 percent is from Mississippi River water that is passed through a chain of lakes including Vadnaais Lake. The remaining 30 percent from the Prairie du Chien-Jordan aquifer and local watershed runoff	415,000	50	Taste/odor control Softening Coagulation Prevent tooth decay pH control Disinfection Disinfection Filtration Corrosion control	Powdered activated carbon and/or potassium permanganate Lime/Alum Ferric chloride Fluoride Carbon dioxide Chlorine Chloramines Anthracite/sand filters Sodium hydroxide and stannous chloride
62-63	Minneapolis Drinking Water Facility at Columbia Heights	100 percent from the Mississippi River	500,000	70	Softening Coagulation Taste/odor control pH control Disinfection Prevent tooth decay Coagulation Filtration Corrosion control	Lime Alum Powdered activated carbon and potassium permanganate Carbon dioxide Chloramines Fluoride Ferric chloride Sand/mixed media filters Poly/ortho phosphate
64-65	Mankato Drinking Water Facility at Mankato	70 percent from the Ranney collector wells underlying (60-foot depth) the Blue Earth and Minnesota Rivers. The remaining 30 percent from wells (700 feet) in the Mt.Simon/Hinckley aquifer.	33,000	4.5	Softening pH adjustment Filtration Prevent tooth decay Corrosion control Disinfection	Lime Carbon dioxide Sand filter Fluorides Phosphate Chlorine

Hydrographers measured streamflow concurrent with sample collection at most stream sites. Streamflow was measured using current meters (Rantz and others, 1982 a and b) where stream cross sections could be waded. A boat-mounted acoustic-Doppler measuring device aboard a boat traversing the river was used to measure streamflow where depths in stream cross sections precluded wading (Morlock and others, 2002). At selected sites with continuous recording gages, streamflow was obtained from the USGS National Water Information System (NWIS) (U.S. Geological Survey, 2004b).

Ground-water samples were collected from monitoring wells using USGS protocols (U.S. Geological Survey, 2003). Samples were collected after at least three well volumes had been pumped and field parameters had stabilized. A positive displacement pump with a stainless steel head, and Teflon tubing was used for sampling monitoring wells. The water production well (Site 43) was sampled from a faucet in the well house. Two drive-point temporary test holes (Sites 48 and 49) within 100 ft of an active septic system in unsewered urban areas were sampled with a peristaltic pump and polyethylene tubing inserted into a steel probe that had a stainless steel screen. Water samples were collected from the upper 2 ft of the water table.

Intake and finished water samples were collected inside DWFs. The samples were collected from an intake faucet and a finished-water faucet that also were used for internal DWF monitoring. Samples were collected from the faucets when field parameters had stabilized.

All sites were sampled at least once from October 2000 through November 2002. At 30 sites, 3-4 water samples were collected during: (1) fall baseflow, (2) winter baseflow, (3) spring-snowmelt runoff, and (4) summer-storm runoff.

Following collection, samples were composited into a glass container and chilled prior to processing. Chilled water samples were processed within 1-2 hours of collection. Each sample was filtered through a 0.7- μ m glass fiber filter that was baked at 450°C for 2 hours. Approximately 100 mL of filtrate was wasted before sample collection to flush the filtration system. Once the system was flushed, water was filtered into pre-cleaned amber glass bottles and refrigerated before shipping to selected laboratories (National Water-Quality Laboratory, Denver, Colorado; U.S. Geological Survey Laboratory, Ocala,

Florida; and U.S. Geological Survey Laboratory, Boulder, Colorado).

USGS research and official production methods were used to analyze for the 114 selected OWCs in this study (appendix 1). This list of OWCs was developed during previous and ongoing studies by the USGS Toxics Substances Hydrology Program. OWCs were selected based upon usage, toxicity, potential estrogenic activity, and persistence in the environment (Barnes and others, 2002; Kolpin and others, 2002). Research methods are experimental in contrast to official production methods, and are not conducted in a routine-production capacity. Research methods typically are in development and extensive quality-control information is often not available; therefore, there is uncertainty associated with compound concentrations.

There were five different analytical methods used in this study. The following descriptions of analytical Methods 1-5 are intended to provide an overview. Methods 1, 2, 4, and 5 are USGS research methods, and Method 3 is an official USGS production method. Analytical data summarized in this report, and can be accessed electronically on the world wide web (U.S. Geological Survey, 2004 a-f).

Analytical Method 1 analyzes for 16 human prescription and nonprescription pharmaceuticals and their select metabolites in filtered water samples (including two antibiotics that also are analyzed using Method 2; and 2 pharmaceuticals that also are analyzed using Methods 3 and 4). Pharmaceuticals were extracted from water samples using hydrophilic-lipophilic-balance (HLB) solid phase extraction (SPE) cartridges. Sample extracts were separated and measured by reversed phase high-performance liquid chromatography/electrospray ionization mass spectrometry (HPLC/[ESI]MS) using selected ion monitoring (SIM). Additional details on this method are provided elsewhere (Barnes and others, 2002; Kolpin and others, 2002; Cahill and others, 2004).

Analytical Method 2 analyzes for 21 veterinary and human antibiotics in filtered water samples. These analyses were completed at the U.S. Geological Survey Laboratory in Ocala, Florida. Antibiotics were extracted by tandem SPE and analyzed by HPLC/[ESI]MS using SIM. The tandem SPE included an Oasis HLB cartridge (60 mg) followed by a mixed mode, HLB-cation exchange (MCX) cartridge (60 mg) (Waters Inc., Milford, Mass.). Additional details on this method are provided elsewhere (Meyer and others, 2000; Barnes and others, 2002; Kolpin and others, 2002).

Analytical Methods 3 and 4 analyze for 63 OWCs in filtered water including 57 HIAs, 2 pharmaceuticals, and 4 sterols (including 2 sterols also analyzed by Method 5). These analyses were completed at the U.S. Geological Survey National Water-Quality Laboratory in Denver, Colorado. Method 3 is an official USGS production method (USGS laboratory schedule 1433). Samples were extracted by vacuum through disposable SPE cartridges that contain polystyrene-divinylbenzene resin. Sorbed compounds were eluted with dichloromethane-diethyl ether. Compounds were measured by capillary-column gas chromatography/mass spectrometry (GC/MS). Additional details on this method are provided by Zaugg and others (2002).

Analytical Method 4 (custom laboratory method 8033) analyzed for the same compounds as Analytical Method 3. Water samples were extracted using continuous liquid-liquid extraction (CLLE) with methylene chloride at pH 2.0, and analyzed by GC/MS. Additional details on this method are provided elsewhere (Brown and others, 1999; Barber and others, 2000; Barnes and others, 2002; Kolpin and others, 2002; Zaugg and others, 2004).

Analytical Method 5 analyzes for 20 sterols and hormones (Barber and others, 2000; Barnes and others, 2002; Kolpin and others, 2002). These analyses were completed at the U.S. Geological Survey Laboratory in Boulder, Colorado. Extracts from Methods 3 and 4 were derivatized to deactivate the hydroxyl and keto functional groups and reanalyzed. The technique used in this method is the formation of the trimethylsilyl ethers of the hydroxyl groups and the oximes of the keto groups. After derivatization, the samples were analyzed by GC/MS.

Analyte identification for all methods had to meet qualitative and quantitative criteria (Barnes and others, 2002; Kolpin and others, 2002). A positive identification was based on elution within the expected retention time. In addition, the sample spectra and ion abundance ratio was required to match that of the reference standard analytes. After identification criteria were attained, analyte concentrations were calculated using a 5–8-point calibration curve (concentrations generally from 0.01 to 10.0 µg/L) using internal standard quantitation. The base-peak ion was used for quantitation, and, if possible, as many as two fragment qualifier ions were used for ion abundance ratio confirmation. Calibration standards are processed throughout the extraction procedure for Method 2, which generally corrects concentrations for

method losses, but not for matrix effects. Methods 1, 3, 4 and 5 do not extract calibration standards; thus the reported concentrations are not corrected for method losses.

Method reporting levels (MRLs) were determined for each analyte by a previously published procedure (U.S. Environmental Protection Agency, 1992). Selected analyte concentrations were flagged with an “E” to indicate estimated values. These include all concentrations above or below the calibration curve, concentrations for analytes with average recoveries less than 60 percent, analytes routinely detected in laboratory blanks, and constituents with reference standards prepared from technical mixtures (Barnes and others, 2002; Kolpin and others, 2002).

QUALITY ASSURANCE

Because some research methods used in this study are newly developed and methods are not published, a description of the data quality (including properties of the measurement such as precision, bias, and detection limits) is included in this report. A quality-assurance plan was established to evaluate laboratory and field sampling techniques, to assess possible sources of contamination, and to assure representative samples. Laboratory quality-control samples were used to validate analytical data. Field quality-assurance samples were used to assess sample collection and processing.

Laboratory quality-control samples included laboratory blanks, reagent spikes, and surrogates. At least one fortified laboratory spike and at least one laboratory blank was analyzed with each set of 10–16 field samples. Laboratory reagent blanks were used to assess potential sample contamination. Recoveries for compounds spiked into reagent water, and surrogate compounds in field samples indicate the general proficiency of the laboratory methods. Most methods had surrogate compounds added to samples prior to extraction to monitor method performance. Surrogates are chemicals that have similar properties to the analytes of interest, but do not interfere with quantitation of the compounds of interest. A summary of the laboratory spikes, reagent blanks, and surrogates are included in this report (appendixes 2 and 3).

Among all the laboratory reagent blank samples processed and analyzed 50 OWCs were detected (appendix 2). There were few detections of OWCs in laboratory blank samples in Methods 1 and 2 except acetamino-

phen (detected in 10 percent of the blanks) and caffeine (detected in 20 percent of the blanks). There were 47 OWCs detected for Methods 3 and 4 combined. One or more of these compounds, including *d*-limonene, isophorone, naphthalene, nonylphenol diethoxylate (NP2EO), *para*-nonylphenol (NP), prometon, tetrachloroethylene (TCE), and tributyl phosphate, were detected in at least 30 percent of the laboratory reagent blanks. Many of these OWCs were detected in laboratory blanks at low concentrations that were below MRLs and below concentrations detected in most field samples with the exception of isophorone. In order to correct for laboratory blank contamination, environmental samples with an OWC concentration less than 10 times the concentration of an OWC in the corresponding set blank was reported as a nondetection.

The average percent recoveries for laboratory reagent spikes for Methods 1-4 were 72, 102, 75, and 82 percent, respectively. Acceptable recoveries for these methods at the USGS Laboratories range from 60 to 120 percent. Most OWC recoveries were in the range of 60–120 percent with the exception of diltiazem, diphenhydramine, ibuprofen, and ranitidine (analyzed by Method 1); ciprofloxacin and virginiamycin (analyzed by Method 2); and 1,4-dichlorobenzene, 3-*tert*-butyl-4-hydroxyanisole (BHA), cotinine, dichlorvos, *d*-limonene, isopropyl benzene, NP, and TCE (analyzed by either Method 3 or 4). Low laboratory spike recoveries for these OWCs could indicate that there are false negatives (error in not identifying an OWC that is actually present) in an environmental sample. False negatives are more likely than false positives (error in identifying a OWC that is not present in a sample) as each USGS laboratory (National-Water Quality, Ocala, and Boulder Laboratories) had stringent and conservative procedures for qualitative identification of the compound. Low laboratory recoveries for these OWCs may indicate that the frequency of detection is underestimated, and highlights the need to continue to refine the analytical procedures to obtain less variability, better recoveries, and lower detections limits.

Average surrogate recoveries ranged from 27 to 171 percent (appendix 3). High and low surrogate recoveries result from sample components that interfere with isolation, detection, and quantification of the surrogate. Field sample concentrations for those samples with low surrogate recoveries may be underestimated, while samples with high surrogate recoveries may be overestimated.

Potential contamination of samples because of collection and sample processing was assessed with field-blank samples. Two types of blank samples were collected: field blanks and office blanks. Field blanks were prepared at the selected site prior to, or following, a scheduled field sample. Office blanks were processed in the laboratory at the USGS Minnesota District field office. In both cases, blank samples were prepared by processing HPLC grade organic-free water (Baker Analyzed, J.T. Baker Co.) through the same equipment used to collect and process field samples. A total of 13 blanks were submitted for Method 1, 9 blanks for Method 2, 14 blanks for Method 3 and 4, and 7 blanks for Method 5, and generally analyzed for all OWCs (appendix 4).

Most OWCs were detected infrequently in field blank samples, were at estimated concentrations below the MRL, and were below field sample concentrations verifying the general effectiveness of sampling protocols used for this study. Nine of the 114 OWCs analyzed for in this study were detected in the field blank samples (appendix 4). Cholesterol (Method 5) was the most frequently detected OWC in field blank samples followed by phenol (Methods 3 and 4), and caffeine (Method 1). Phenol concentrations exceeded MRLs and some field sample concentrations. The frequency of detections and high concentrations at or exceeding the MRL for phenol may indicate a contamination source in field sampling procedures or demonstrates the ubiquitous nature of this compound. Environmental samples were not corrected for field blank contamination as there were no instances where the OWCs detected in field or office blanks coincided with the occurrence of the same OWC in an environmental sample during a similar time frame.

Field replicate samples were collected to determine variability of detections and concentrations resulting from sample and laboratory processing techniques (sample splitting, filtration, and transport). Replicate samples consist of a split of the field sample so the field and replicate samples should be nearly equal in composition. Samples were submitted for 5 replicates for Method 1, 7 replicates for Method 2, 9 replicates for Methods 3 and 4, and 4 replicates for Method 5 (appendix 4). Most were duplicate samples and one was a triplicate. Replicate samples were collected at locations where few OWC detections were expected (DWFs) and where OWC detections were expected (WWTP effluent, stream sites downstream of WWTP effluent, and feedlot lagoons). By collecting replicates at both ends of this spectrum the detection consistency and the variability in concentrations was evaluated. The detection consistency

was evaluated by determining the number of replicates that had consistent detections (and nondetections) of selected OWCs. Concentrations of detected compounds were compared by calculating a relative standard deviation (RSD) for each compound.

There was a wide range in RSDs (from 0 to 101.1 percent) among all OWCs and all replicates (appendix 4). The average RSD (11.2 percent) for all OWCs and all replicates is low considering the new research methods utilized in this study. Replicate samples from three DWFs were appropriate primarily for comparison of OWC detection consistency, but limited for concentration comparisons, as there were 12 OWC detections in the field and corresponding replicate samples, and a high percentage of the data were below the MRL. Detection and nondetection consistencies were confirmed for most OWCs in DWF samples.

Replicate samples for WWTP effluent, streams directly downstream from effluent, and feedlot lagoon samples had more OWC detections, and were useful for both determinations of detection consistency and concentration comparisons. Detection consistency was confirmed for most comparisons. The average RSD for OWCs in wastewater replicate samples was 11.3 percent, and RSDs were less than 20 percent for most OWCs. Cholesterol (Methods 3, 4, and 5), diazinon, 3-*beta*-coprostanol (Methods 3, 4, and 5), 3-methyl-1H-indole (skatol), and phenol had the greatest average RSDs. For most comparisons; however, field and replicate concentrations were within an order of magnitude, and were within the laboratory analytical error associated with these compounds. For example, 3-*beta*-coprostanol concentrations analyzed by Method 3 in field and replicate samples from Site 3 on March 28, 2001 (0.59 and 0.38 µg/L respectively) had a RSD of 30.1 percent. While this RSD is greater than the accepted standard of 10 percent, these two concentrations are low, and the difference in concentration is within laboratory analytical error.

OWCs measured by more than one analytical method described in this report also were used to evaluate the results for this study. Three types of comparisons were made. The first was a comparison of 34 samples using Methods 3 and 4. This was important as field samples were analyzed by a combination of these two methods. The second comparison was for six compounds analyzed for more than one of the methods listed in this report (3-*beta*-coprostanol, caffeine, cholesterol, cotinine, sulfamethoxazole, and trimethoprim). The third comparison was a limited investigation of bromoform

concentrations between Method 3 and a USGS production method (USGS laboratory schedule 1307) (Connor and others, 1998).

Methods 3 and 4 were used to analyze for HIAs in 34 samples. A comparison was made between these two methods to determine if data from the two methods could be combined. The two methods were compared graphically (fig. 3), and in terms of detection consistency. Concentrations of all compounds (except bromoform) from each method were plotted against each other and a linear regression line was prepared. Bromoform concentrations were not included because subsequent investigation indicated they may be overestimated by both methods. This line provides a representation of how the two methods compare, but does not provide information about specific OWCs as there generally were too few detections per OWC to prepare a regression line for each.

Among the 34 samples analyzed, 54 OWCs were detected. Detection and nondetection consistencies were confirmed for greater than 90 percent of the comparisons. Selected OWCs (*d*-limonene, isophorone, and phenol) were detected more frequently in Method 3 than Method 4. Concentrations of most OWCs were consistently greater for Method 3 than for Method 4 based on the visual inspection and regression analyses (fig. 3). The concentration differences; however, did not vary substantially between Methods 3 and 4, and generally were within one order of magnitude and within the laboratory analytical error for selected OWCs for most comparisons. This pattern holds true for WWTPs and landfill leachate samples with relatively greater concentrations, and for more dilute DWF samples.

There is reasonable agreement between Methods 3 and 4 indicating that data from both methods can be compared for this discussion of OWC presence and distribution. There were some inconsistencies that were biased to a certain method (*d*-limonene, isophorone, and phenol). *d*-Limonene, isophorone, and phenol are expected to have greater detection frequencies in Method 3 than Method 4; therefore, they were removed from further comparisons among sites and site classifications.

Caffeine, cotinine, trimethoprim, sulfamethoxazole, cholesterol, and 3-*beta*-coprostanol were analyzed by more than one method described in this report. Cotinine and caffeine were analyzed by Methods 1, 3, and 4; sulfamethoxazole and trimethoprim were analyzed by Methods 1 and 2; and cholesterol and 3-*beta*-coprostanol were analyzed by Methods 3, 4, and 5. There were

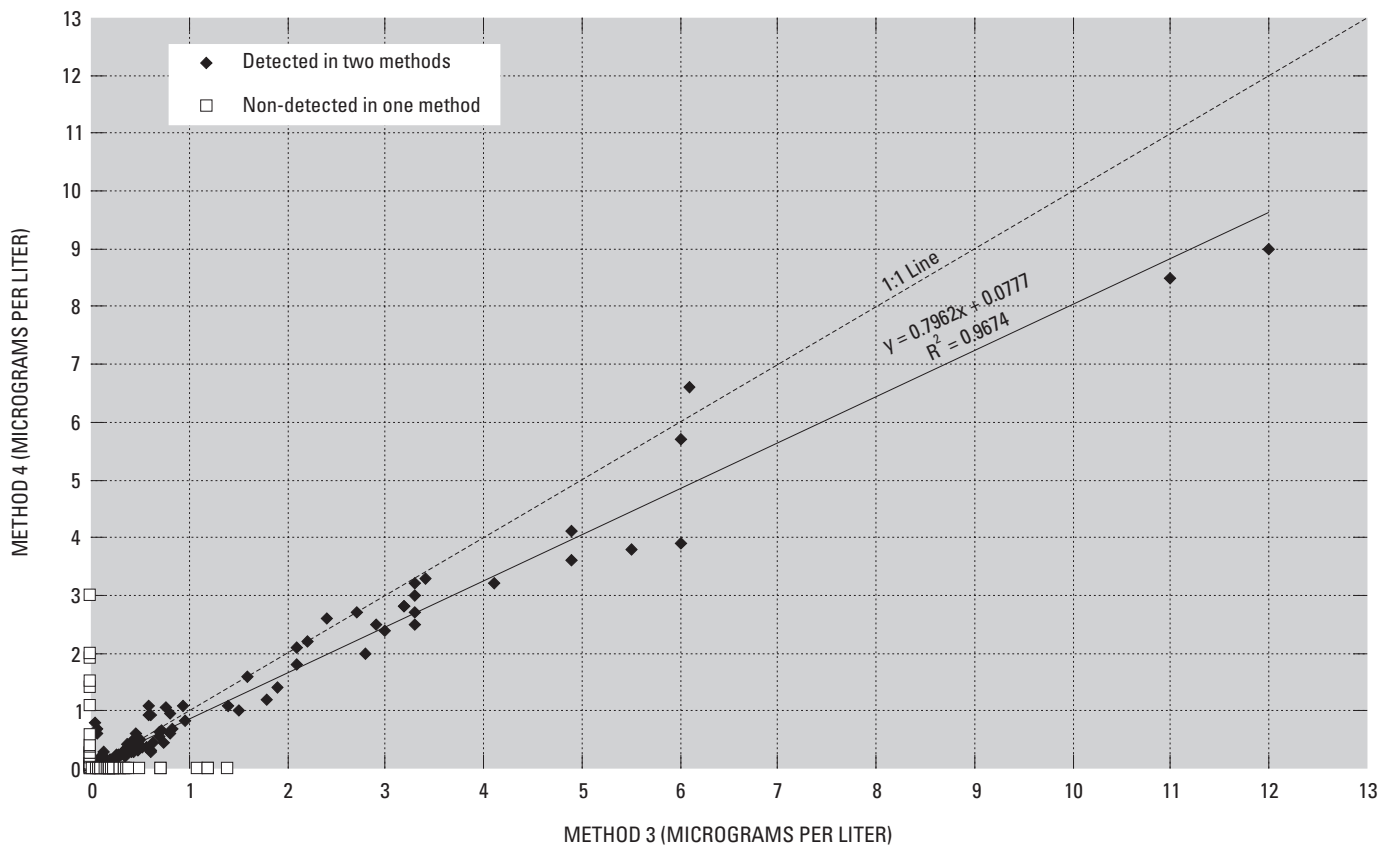


Figure 3. Comparison of results from U.S. Geological Survey analytical Methods 3 and 4 for selected organic wastewater compounds with the exception of bromoform. [Regression line (solid line) was prepared using detections only.]

different laboratory-method reporting limits (MRLs) among the methods. For example, the MRL for cotinine was 0.023 µg/L for Method 1, and 1.0 µg/L for Methods 3 and 4 (table 7). The detection frequency is not expected to be similar among methods with different MRLs. The frequency of detection was greater in those methods with lower detection limits as expected. For example, cotinine was detected in 23 samples analyzed by Method 1 and in 3 samples by methods 3 or 4 (table 7). Only 2 of the 23 samples analyzed by Method 1 had cotinine concentrations that were great enough to be detected in Methods 3 or 4, which equates to a detection consistency of 90 percent. The detection consistency of the remaining OWCs was confirmed in 99 percent of the determinations for cholesterol and 3-*beta*-coprostanol; 85 percent for trimethoprim; 80 percent for caffeine; and 50 percent for sulfamethoxazole.

Methods 3 and 4 target a wide variety of OWCs that serve as indicators of multiple types of wastewater. One of those OWCs, bromoform, is a regulated trihalomethane, and is a byproduct of drinking water or wastewater disinfection that is formed when chlorine reacts with organic matter and bromide. Methods 3 and 4 are appro-

priate for detection of bromoform based on spike recoveries (average of 71 percent) for 132 laboratory reagent spikes analyzed at the USGS NWQL for a separate study, and bromoform has a unique mass spectrum with little possibility of analytical interference (Steve Zaugg, U.S. Geological Survey, oral commun., 2004). The recoveries for spike samples analyzed with the environmental samples during this study also were in the same range (appendix 2). Sample processing for Methods 3 and 4, however, does not include a preservation step that is intended to stop the formation of bromoform in the sample bottle. It is possible; therefore, that bromoform could form in the sample bottle after sample collection and prior to sample analyses. This may result in an overestimation of bromoform concentrations in samples in comparison to a sampling methodology that includes preservation.

A limited sampling was completed to determine if bromoform concentrations from Methods 3 and 4 were similar to concentrations from sample processing and analytical techniques that include a preservation step (USGS laboratory schedule 1307 for volatile organic compounds) (Connor and others, 1998). One finished

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Table 7. Basic summary statistics for 91 organic wastewater compounds among all environmental samples analyzed, Minnesota, 2000-02

[*d*-limonene, isophorone, and phenol were removed from this table because the combination of methods 3 and 4 were not appropriate for these compounds. Carbamazepine, diphenhydramine, and the sterols and hormones analyzed by method 5 (with the exception of cholesterol, and 3-*beta*-coprostanol) are not included because they were not analyzed at all sites. Caffeine, cotinine, sulfamethoxazole, trimethoprim, 3-*beta*-coprostanol, and cholesterol were analyzed by more than one method. --, not applicable; µg/L, micrograms per liter].

Analytical method	Organic wastewater compounds	Method reporting limit (µg/L)	Minimum concentration (µg/L)	Maximum concentration (µg/L)	Number of detections	Frequency of detection (percent)
Pharmaceuticals						
1	1,7-dimethylxanthine	0.018	0.008	3.29	15	11.5
1	Acetaminophen	0.009	0.004	16	20	15.3
1	Caffeine	0.014	0.0003	14	33	25.2
3,4	Caffeine	0.5	0.041	0.47	19	13.9
1	Codeine	0.024	0.007	0.203	9	6.9
1	Cotinine	0.023	0.0025	1.2	23	17.6
3,4	Cotinine	1.0	0.14	0.22	3	2.2
1	Dehydronifedipine	0.01	0.001	0.012	6	4.6
1	Diltiazem	0.012	0.005	0.146	9	6.9
1	Gemfibrozil	0.015	--	--	0	0
1	Ibuprofen	0.018	0.12	0.71	4	3.1
1	Ranitidine	0.01	0.0082	0.446	5	3.8
1	Salbutamol	0.029	0.002	0.006	2	1.5
1	Warfarin	0.001	--	--	0	0
Antibiotics						
2	Carbadox	0.05-0.10	--	--	0	0
2	Chlorotetracycline	0.02-0.10	0.11	0.52	2	1.5
2	Ciprofloxacin	0.01	0.01	0.01	2	1.5
2	Doxycycline	0.05-0.1	--	--	0	0
2	Enrofloxacin	0.01-0.02	--	--	0	0
2	Erythromycin-H ₂ O	0.02-0.05	0.02	0.57	14	10.8
2	Lincomycin	0.01-0.05	0.01	0.37	3	2.3
2	Norfloxacin	0.01-0.02	--	--	0	0
2	Oxytetracycline	0.05	--	--	0	0
2	Roxithromycin	0.01-0.03	--	--	0	0
2	Sarafloxacin	0.01-0.02	--	--	0	0
2	Sulfadimethoxine	0.01-0.05	--	0.11	1	0.8
2	Sulfamerazine	0.02-0.05	--	--	0	0
2	Sulfamethazine	0.01-0.05	0.07	0.16	2	1.5
2	Sulfamethizole	0.05-0.1	--	0.07	1	0.8
1	Sulfamethoxazole	0.023	0.0039	0.342	14	10.7
2	Sulfamethoxazole	0.05-0.1	0.02	0.5	6	3.8
2	Sulfathiazole	0.05-0.1	--	0.05	1	0.8
2	Tetracycline	0.02-0.05	0.07	0.3	2	1.5
1	Trimethoprim	0.014	0.001	5.58	15	11.5
2	Trimethoprim	0.01-0.03	0.06	0.15	4	2.1
2	Tylosin	0.02-0.05	--	--	0	0
2	Virginiamycin	0.1	--	--	0	0
Household, industrial, and agricultural use-compounds						
3,4	1,4-dichlorobenzene	0.5	0.12	7.5	10	7.5
3,4	1-methylnaphthalene	0.5	0.076	1.9	7	5.2
3,4	2,6-dimethylnaphthalene	0.5	0.091	1.1	6	4.5
3,4	2-methylnaphthalene	0.5	0.077	2	8	6.0
3,4	3-methyl-1H-indole (skatol)	1.0	0.013	27	18	13.5
3,4	3-tert-butyl-4-hydroxyanisole (BHA)	5.0	2.1	5.1	2	1.5
3,4	4-cumylphenol	1.0	0.6	1.2	3	2.2
3,4	4-normal-octylphenol	1.0	0.12	1.6	3	2.2
3,4	4-tert-octylphenol	1.0	0.18	2.8	6	4.5
3,4	5-methyl-1H-benzotriazole	2.0	0.45	24	10	7.5
3,4	Acetophenone	0.5	0.21	29	7	5.2

Table 7. Basic summary statistics for 91 organic wastewater compounds among all environmental samples analyzed, Minnesota, 2000-02—Continued

[*d*-limonene, isophorone, and phenol were removed from this table because the combination of methods 3 and 4 were not appropriate for these compounds. Carbamazepine, diphenhydramine, and the sterols and hormones analyzed by method 5 (with the exception of cholesterol, and 3-*beta*-coprostanol) are not included because they were not analyzed at all sites. Caffeine, cotinine, sulfamethoxazole, trimethoprim, 3-*beta*-coprostanol, and cholesterol were analyzed by more than one method. --, not applicable; µg/L, micrograms per liter].

Analytical method	Organic wastewater compound	Method reporting limit (µg/L)	Minimum concentration (µg/L)	Maximum concentration (µg/L)	Number of detections	Frequency of detection (percent)
3,4	Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	0.5	0.059	5.3	25	18.7
3,4	Anthracene	0.5	0.044	0.33	4	3.0
3,4	Anthraquinone	0.5	0.056	0.81	15	11.2
3,4	Benzo[<i>a</i>]pyrene	0.5	--	0.051	1	0.7
3,4	Benzophenone	0.5	0.056	6.2	19	14.2
3,4	Bisphenol-A	1.0	0.084	26	24	17.9
3,4	Bromacil	0.5	0.02	1.4	6	4.5
3,4	Bromoform	0.5	0.13	74	31	22.4
3,4	Camphor	0.5	0.14	98	7	5.2
3,4	Carbaryl	1	--	--	0	0
3,4	Carbazole	0.5	0.031	0.72	6	4.5
3,4	Chlorpyrifos	0.5	--	--	0	0
3,4	Diazinon	0.5	0.025	0.083	5	3.7
3,4	Dichlorvos	1.0	--	--	0	0
3,4	Fluoranthene	0.5	0.057	0.32	9	6.6
3,4	Hexahydrohexamethyl-cyclopentabenzopyran (HHCb)	0.5	0.049	1.5	13	9.7
3,4	Indole	0.5	0.012	1.4	8	6.0
3,4	Isoborneol	0.5	1.2	44	2	1.5
3,4	Isopropylbenzene (cumene)	0.5	0.056	2.2	5	3.7
3,4	Isoquinoline	0.5	--	--	0	0
3,4	Menthol	0.5	0.071	96	9	6.7
3,4	Metalaxyl	0.5	--	--	0	0
3,4	Methyl salicylate	0.5	0.013	3.2	6	4.5
3,4	Metolachlor	0.5	0.008	1.3	49	35.8
3,4	N,N-diethyl- <i>meta</i> -toluamide (DEET)	0.5	0.027	47	32	23.9
3,4	Naphthalene	0.5	0.093	10	8	6.0
3,4	Nonylphenol diethoxylate (NP2EO)	5.0	0.52	42	12	9.0
3,4	Octylphenol diethoxylate (OP2EO)	1.0	0.81	8.4	2	1.5
3,4	Otylphenol monoethoxylate (OP1EO)	1.0	0.4	7	3	2.2
3,4	<i>para</i> -cresol	1.0	0.049	1000	13	9.7
3,4	<i>para</i> -nonylphenol (NP)	5.0	0.76	56	15	11.2
3,4	Pentachlorophenol	2.0	0.018	0.62	14	10.4
3,4	Phenanthrene	0.5	0.04	0.38	5	3.7
3,4	Prometon	0.5	0.26	2	2	1.5
3,4	Pyrene	0.5	0.04	0.082	7	5.2
3,4	Tetrachloroethylene	0.5	0.055	17	10	7.5
3,4	Tri(2-butoxyethyl)phosphate	0.5	0.11	5.3	20	17.2
3,4	Tri(2-chloroethyl)phosphate	0.5	0.053	9.2	27	20.1
3,4	Tri(dichlorisopropyl)phosphate	0.5	0.053	2.5	20	14.9
3,4	Tributyl phosphate	0.5	0.058	13	18	13.4
3,4	Triclosan	1.0	0.088	4.3	10	8.2
3,4	Triethyl citrate (ethyl-citrate)	0.5	0.076	2.9	16	11.9
3,4	Triphenyl phosphate	0.5	0.051	0.24	14	10.4
Sterols and Hormones						
3,4	3- <i>beta</i> -coprostanol	2.0	0.32	81	18	13.4
5	3- <i>beta</i> -coprostanol	0.005	0.001	2.607	18	13.4
3,4	<i>beta</i> -sitosterol	2.0	0.55	36	26	19.4
3,4	<i>beta</i> -stigmastanol	2.0	0.79	5.7	8	6.0
3,4	Cholesterol	2.0	0.48	130	35	26.1
5	Cholesterol	0.005	0.004	3.35	82	92.0

water sample from Site 65 was split into three samples. One sample was filtered and analyzed for Method 3 using the methodology described in this report, one sample was filtered, acidified with ascorbic acid, and analyzed using Method 3; and the remaining sample was not filtered, was acidified with ascorbic acid, and analyzed with the USGS laboratory schedule 1307 for volatile organic compounds. The results from this limited comparison show that bromoform concentrations reported for the filtered, unacidified, Method 3 samples, were approximately 100 times greater than those reported for either the acidified Method 3 sample or the schedule 1307 sample. Bromoform concentrations reported for Methods 3 and 4; therefore, may be overestimated in some samples (particularly wastewater effluent and finished drinking water samples) based on this limited comparison.

DATA EVALUATION

Evaluation of data includes several procedures to ensure consistent comparisons among samples. Although previously described, these procedures are consolidated and discussed in this section for clarity. Field sample concentrations for OWCs analyzed by Methods 1, 3, and 4 that were less than 10 times the concentrations in the corresponding laboratory reagent blanks were censored (reported as less than the MRL) to ensure that environmental concentrations did not reflect laboratory contamination. Data from Methods 2 and 5 were quality assured in the laboratory and censored prior to distribution. A large proportion of the OWC concentrations are reported as estimated values. Each laboratory had stringent and conservative procedures for qualitative identification of the compounds; therefore, all OWC detections (estimated and non estimated) were used in the analyses in this report. There is less certainty in the OWC concentrations generated by research methods because the analyses are in development and there are not enough quality-assurance data in some cases to determine concentrations within acceptable confidence limits.

Evaluation showed that detection consistency between Methods 3 and 4 generally were similar for most of the OWCs (with the exceptions of *d*-limonene, isophorone, and phenol); therefore, samples analyzed by both methods were combined for comparison. In the case where a sample was analyzed by both methods, Method 3 data were used. *d*-Limonene, isophorone, and phenol were not used for any comparisons because their

detection frequency differed between Methods 3 and 4, and; therefore, could produce inconsistent results among samples.

Carbamazepine and diphenhydramine (Method 1), and the sterols and hormones (Method 5) were not used for comparisons because they were not analyzed at all sites. One laboratory method was selected for OWCs analyzed for more than one method. Trimethoprim, sulfamethoxazole, caffeine, and cotinine analyzed by Method 1; and cholesterol and 3-*beta*-coprostanol analyzed by Methods 3 and 4 were used.

In summary, USGS laboratories analyzed 114 OWCs for this study. Three HIAs (*d*-limonene, isophorone, and phenol), 2 pharmaceuticals (carbamazepine and diphenhydramine), and 18 sterols and hormones analyzed using Method 5 were removed from comparisons among sites or site classifications. This results in a total of 91 OWCs that are used for comparisons among sites and site classifications in the remainder of this report.

HYDROLOGIC SETTING AND BASIC WATER-QUALITY PARAMETERS

Differences in the hydrologic conditions and basic water-quality parameters among sites may contribute to the presence of OWCs and their fate and transport. A more focused study would be required to determine how these factors would influence OWC detections and concentrations.

Sampling occurred during four periods representing a variety of hydrologic conditions. Two of the sampling periods were during fall and winter baseflow when ground water was the primary source of water to the streams sampled. The remaining two sampling periods were during spring snowmelt and summer storm runoff when surface runoff was the primary source of water to streams sampled. During this reconnaissance study, no attempt was made to collect samples at the same place on the streamflow hydrograph (rising limb, peak flow, declining limb), which may influence detections and concentrations.

Basic water-quality parameters of specific conductance, pH, water temperature, and dissolved oxygen varied by site and period sampled. These parameters vary diurnally and seasonally due to weather, ground-water interactions, and internal factors such as microbial

and algal production. Differences in basic water-quality parameters among sites provide useful information about factors that could contribute to differences in presence and distribution of OWCs. For example, differences in pH, temperature, and dissolved oxygen, may indicate differences in microbial or algal productivity, which may contribute to different rates of OWC metabolism.

PRESENCE AND DISTRIBUTION OF ORGANIC WASTEWATER COMPOUNDS AMONG ALL SITES

The 74 OWCs (49 HIAs, 10 pharmaceuticals, 11 antibiotics, and 4 sterols or hormones) detected during this study (table 7) represent a wide variety of uses. Samples generally included a mixture of compounds (average of 6 OWCs per sample) and 90 percent of the samples had at least one OWC detected. The 10 most frequently detected OWCs among all samples were metolachlor (agricultural use-herbicide); cholesterol (sterol primarily associated with animal fecal matter); caffeine (stimulant in coffee, soft-drinks, and nonprescription medications), N,N-diethyl-*meta*-toluamide (DEET) (topical insect repellent); bromoform (by-product of waste- and drinking-water disinfection); tri(2-chloroethyl)phosphate (flame-retardant and plasticizer); *beta*-sitosterol (plant sterol and a known endocrine disruptor); acetyl-hexamethyl-tetrahydro-naphthalene (AHTN) (synthetic musk fragrance widely used in personal care products); bisphenol-A (plastic component used in the manufacture of polycarbonate resins and a known endocrine disruptor); and cotinine (metabolite of nicotine). With respect to individual classes of OWCs, caffeine, cotinine, and acetaminophen, were the three most frequently detected pharmaceuticals. Trimethoprim, an erythromycin metabolite (erythromycin H₂O), and sulfamethoxazole were the most frequently detected antibiotics. Cholesterol, *beta*-sitosterol, and 3-*beta*-coprostanol were the most frequently detected sterols.

Concentrations of detected OWCs generally were less than 3 µg/L. Nearly 75 percent of the detections had estimated concentrations below MRLs. Concentrations of 3-*beta*-coprostanol, acetophenone, BHA, bromoform, caffeine, camphor, cholesterol, isoborneol, menthol, nonylphenol diethoxylate (NP2EO), octylphenol diethoxylate (OP2EO), *para*-cresol, and *para*-nonylphenol (NP) generally were above the MRL.

PRESENCE AND DISTRIBUTION OF ORGANIC WASTEWATER COMPOUNDS FOR SPECIFIC SITE CLASSIFICATIONS

WASTEWATER

Domestic WWTP influent and effluent, landfill leachate, and water underlying feedlot lagoons were selected as potential wastewater sources for this study. A total of 67 of the 91 OWCs were detected among wastewater samples. Wastewater influent and effluent, and landfill leachate had the greatest number of OWCs detected and water underlying feedlot lagoons had the least number detected. There were differences within site classifications and temporal variability among different sampling periods in terms of the number and the types of OWCs detected.

Wastewater Treatment Plants

WWTP samples were complex mixtures of OWCs likely due to the diversity of incoming domestic and industrial waste sources and treatment procedures. Most of the OWCs analyzed (63 of the 91 OWCs) were detected among all WWTP samples, averaging 27.1 OWCs per sample. Compounds detected included: 44 HIAs, 9 pharmaceuticals, 6 antibiotics, and 4 sterols. Among all WWTP samples, the untreated influent sample at Site 1 had the greatest number of OWCs detected, and the total number of OWCs detected in WWTP effluent was greatest at Site 5 (fig. 4). The most frequently detected OWCs in wastewater effluent samples included AHTN, benzophenone, cholesterol, erythromycin H₂O, hexahydrohexamethyl-cyclopentabenzopyran (HHCB), NP2EO, tri(2-chloroethyl)phosphate, tributyl phosphate, tri(dichloroisopropyl)phosphate, and triethyl citrate. The prevalence of these OWCs in WWTP effluent is expected because they are widely used in products such as fragrances, antibiotics, plasticizers, flame retardants, and detergents, or are plant or animal sterols. Similar types of OWCs in WWTP effluent have been reported by Daughton and Ternes (1999), Barber and others (2000), Kummerer (2001), Wilkison and others (2002), and Buerge and others (2003).

The types of HIAs detected varied among WWTPs. For example, the WWTP effluent sample from Site 5 had

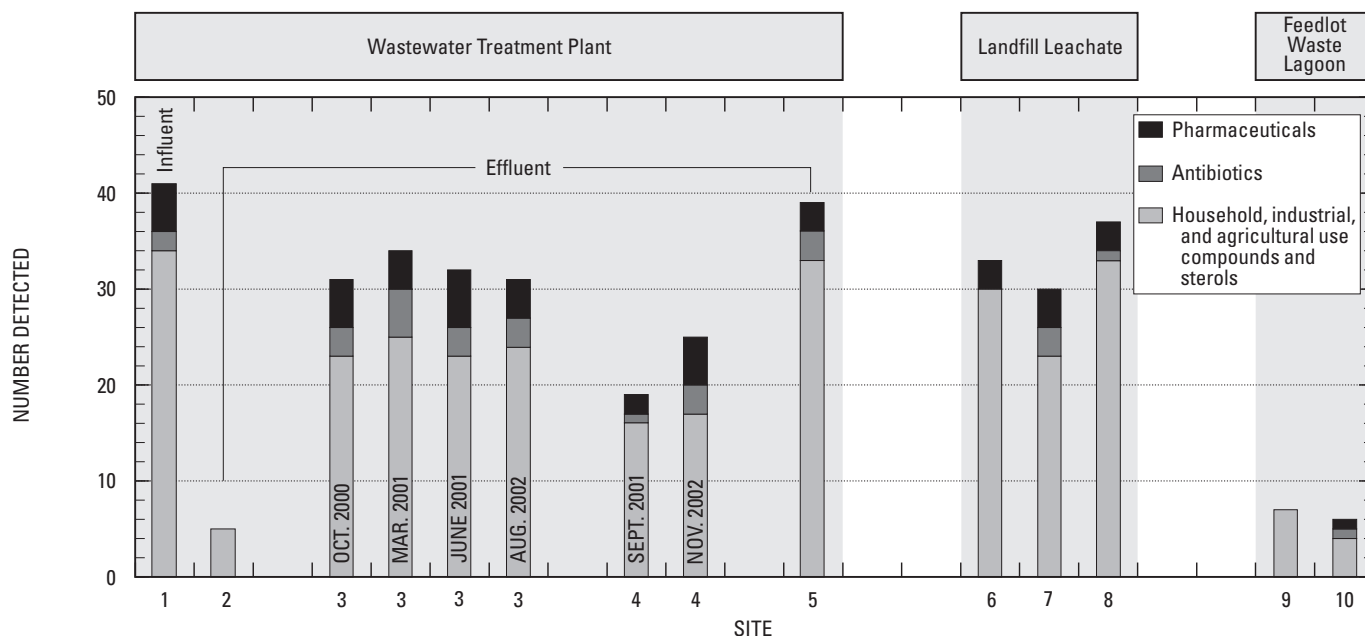


Figure 4. Organic wastewater compounds detected in wastewater treatment plant, landfill leachate, and feedlot waste lagoon samples, Minnesota, 2000-02. [Site identification numbers can be found in table 1 and figures 1 an 2.]

greater detections of polyaromatic hydrocarbons (PAHs) and nonionic detergent metabolites than other WWTPs. In contrast, the number of pharmaceuticals and antibiotics detected were similar among all WWTP samples with the exception of Site 2, where none were detected. With the exception of Site 2, there were 5 pharmaceuticals or antibiotics that were common to all WWTP effluent samples (caffeine, cotinine, diltiazem, erythromycin H₂O, and trimethoprim). Although acetaminophen, ibuprofen, and ranitidine are nonprescription pharmaceuticals and have high usage rates, they were not frequently detected in WWTP effluent, potentially due to degradation during treatment (Stumpf and others 1996; Ternes, 1998) or absence in the influent to the WWTP.

There was temporal variability in the number of OWCs detected in samples collected from Sites 3 and 4, with approximately 50 percent of the OWCs detected common to all sampling periods at any particular WWTP. For example, the number of OWCs ranged from 31-34 at Site 3 during four sampling events, and ranged from 19-25 at Site 4 during two sampling periods (fig. 4). Temporal changes in WWTP influent sources or treatment techniques may be the reason for this.

Difference in the types of compounds detected among WWTPs, and among multiple sampling periods at one WWTP may be due to differences in influent sources or treatment techniques. These spatial and temporal differences emphasize the importance of routine sampling to fully characterize the variability in chemical

composition of WWTP effluent. This variability was likely not captured during this reconnaissance study.

Both the influent (Site 1) and effluent (Site 2) were sampled from the East Grand Forks WWTP, allowing a cursory investigation of OWC removal. The untreated influent water at Site 1 had 41 OWCs. In contrast, the treated water at Site 2 in the settling pond outflow (after the 6-month settling/treatment period) had 5 OWC detections. It was not possible to fully determine if treatment techniques influenced the types and concentrations of OWCs detected because of the 6-month settling/treatment period. The difference between OWC detections in influent and effluent water could be because many OWCs likely degraded during processing, partitioned into the sediment and biota in the treatment pond, or volatilized.

There were 11 endocrine disrupting compounds (EDCs) detected among WWTP samples including 4-cumylphenol, 4-normal-octylphenol, 4-tert-octylphenol, AHTN, beta-sitosterol, bisphenol-A, diazinon, NP2EO, OP1EO, OP2EO, and NP. The number of EDCs detected in WWTP effluent among all sampling periods was greatest at Site 3 (9 EDCs) and Site 5 (9 EDCs).

Landfill Leachate

A total of 46 OWCs were detected among all three landfill leachate samples averaging 33.7 OWCs per

sample. OWCs detected included 35 HIAs, 4 pharmaceuticals (acetaminophen, caffeine, cotinine, ibuprofen), 3 antibiotics (chlorotetracycline, lincomycin, and trimethoprim), and 4 sterols (3-*beta*-coprostanol, *beta*-sitosterol, *beta*-stigmastanol, and cholesterol). The total number of OWC detections in leachate was greatest at Site 8, the industrial landfill (fig. 4).

A wide variety of OWCs were detected in landfill leachate including PAHs, fragrances, plastic components, flame retardants, and solvents. About one-half the OWCs detected among all landfill leachate samples were common among all three leachate samples, and 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, 4-*tert*-octylphenol, acetaminophen, acetophenone, benzophenone, bisphenol-A, caffeine, camphor, cotinine, isopropyl benzene, naphthalene, DEET, *para*-cresol, skatol, NP, tri(2-butoxyethyl)phosphate, tri(2-chloroethyl)phosphate, tributyl phosphate, tri(dichloro isopropyl)phosphate, and triethyl citrate were detected in all landfill leachate samples. The high number and variability in types of OWCs detected among landfill sites is likely due to diversity of waste that was landfilled and the spatial and temporal variability in waste types throughout a landfill. The composition of a leachate sample may depend on the day and the areas sampled. The presence of pharmaceuticals in the industrial landfill leachate was unexpected as domestic waste was not accepted at that location. Leachate from Sites 6, 7, and occasionally Site 8 is transferred to the Metropolitan WWTP (Site 3) for treatment. The removal efficiency of OWCs in WWTP is only documented for selected OWCs (Stumpf and others, 1996).

The number of OWCs detected per landfill leachate sample was similar to WWTP influent and effluent samples (fig. 4). Generally, there were more PAHs detected in landfill leachate than in other wastewater samples. PAHs are formed during incomplete combustion of organic materials such as coal, oil, and wood. PAHs are lipophilic (bind to organic matter) and may be prevalent in landfill leachate because there are relatively greater inputs of PAHs to landfills or slow degradation in the anaerobic conditions in landfills.

There were 7 EDCs found in landfill leachate samples: 4-cumylphenol, 4-*tert*-octylphenol, *beta*-sitosterol, BHA, bisphenol-A, OP1EO, and NP. The number of EDCs detected varied from 4-7 among landfills, and Site 8 (the industrial landfill) had the greatest number of EDCs detected.

Feedlot Lagoons

There were 11 OWCs (9 HIAs; 1 pharmaceutical (diltazem); and 1 antibiotic (lincomycin)) detected in the water underlying the two feedlot lagoons (Sites 9 and 10). The number of OWCs was similar between the two sites (fig. 4). Bisphenol-A, skatol and NP were detected at both sites. Camphor, indole, isopropyl benzene, *para*-cresol, and triphenyl phosphate were unique to Site 9, and diltiazem, lincomycin, and metolachlor were unique to Site 10.

While the sources of these OWCs are unknown, bisphenol-A, NP, and triphenyl phosphate could have leached from the polyvinyl chloride (PVC) pipes or liner in the feedlot lagoon drainage collection system. NP is a component in cleaning agents that may also be used in feedlot operations. Metolachlor (herbicide) could originate from surface runoff or atmospheric deposition into lagoons and subsequent leaching through the drainage collection system. The presence of lincomycin (antibiotic used for animal treatment), and indole and skatol (chemicals produced by bacteria in animal intestines) may be from the animal waste in the lagoon. The presence of diltazem (human antihypertensive medication), isopropyl benzene (solvent) and *para*-cresol (disinfectant) cannot be explained.

There were fewer OWCs and lower concentrations in feedlot lagoon samples than other identified wastewater sources. It was not possible to determine if the OWCs were removed as they passed through the compacted clay lining of the waste lagoon, or were not initially present in the lagoon. Each feedlot lagoon had two EDCs detected (bisphenol-A and NP).

SURFACE WATER

There were 56 OWCs detected among all surface-water samples (36 HIAs, 9 pharmaceuticals, 7 antibiotics, and 4 sterols), averaging 6 OWCs per sample. In descending order of detection frequency, the most frequently detected OWCs among all surface-water samples were metolachlor, caffeine, cholesterol, DEET, *beta*-sitosterol, AHTN, and acetaminophen. The total number of OWCs detected varied from 0 at the reference site at Ek Lake in Voyageurs National Park (Site 15) to 28 at Jewitt's Creek near Litchfield (Site 21), which is located downstream from a WWTP effluent discharge.

22 Presence and distribution of organic wastewater compounds in wastewater, surface, ground and drinking water

Table 8. Number of organic-wastewater compounds detected at surface-water sites, Minnesota 2000-02

[OWC, organic wastewater compound; HIA, household, industrial, and agricultural use compounds; --, not analyzed; WWTP, wastewater treatment plant; SW, sample taken from surface water site not directly influenced by WWTP discharge; SDW, sample taken from a surface water site directly downstream of a WWTP discharge. Sites 23, 27, and 30 were analyzed for USGS laboratory Methods 3 and 4 only].

Site identifier (fig. 1 or 2)	Site name	Site classification	Sample date (mm/dd/yy)	Pharmaceutical detections	Antibiotic detections	HIA detections	Total OWC detections
Red River of the North Basin							
11	Red River of the North above Fargo, N.Dak.	SW	10/19/00	1	0	0	1
11	Red River of the North above Fargo, N.Dak.	SW	04/11/01	1	0	7	8
11	Red River of the North above Fargo, N.Dak.	SW	07/12/01	0	0	7	7
12	Red River of the North below Fargo, N.Dak.	SDW	10/18/00	0	2	7	9
12	Red River of the North below Fargo, N.Dak.	SDW	04/11/01	1	0	1	2
12	Red River of the North below Fargo, N.Dak.	SDW	07/12/01	0	0	2	2
13	Red Lake River at State Hwy 2220 above East Grand Forks	SW	10/23/00	0	0	1	1
13	Red Lake River at State Hwy 220 above East Grand Forks	SW	04/12/01	0	0	1	1
13	Red Lake River at State Hwy 220 above East Grand Forks	SW	07/09/01	--	1	0	1
14	Red River of the North below WWTP at East Grand Forks	SDW	10/25/00	2	0	3	5
14	Red River of the North below WWTP at East Grand Forks	SDW	07/10/01	0	0	2	2
Rainy and Lake Superior Basins							
15	Ek Lake near International Falls	SW	09/20/01	0	0	0	0
16	Rainy River below International Falls	SDW	09/05/01	1	0	3	4
17	Lake Superior in St. Louis Bay at Duluth	SDW	09/05/01	4	0	9	13
Mississippi River Basin							
18	Mississippi River above Sauk River near Sauk Rapids	SW	10/17/00	0	0	2	2
18	Mississippi River above Sauk River near Sauk Rapids	SW	04/16/01	0	0	1	1
18	Mississippi River above Sauk River near Sauk Rapids	SW	06/27/01	0	0	0	0
19	Sauk River near St. Cloud	SW	10/16/00	2	0	5	7
19	Sauk River near St. Cloud	SW	04/10/01	0	0	4	4
19	Sauk River near St. Cloud	SW	04/27/01	--	--	3	3
19	Sauk River near St. Cloud	SW	06/26/01	0	0	1	1
20	Mississippi River above Clearwater River near Clearwater	SW	10/17/00	2	0	0	2
20	Mississippi River above Clearwater River near Clearwater	SW	04/17/01	0	0	2	2
20	Mississippi River above Clearwater River near Clearwater	SW	06/26/01	0	0	1	1
21	Jewitt's Creek near Litchfield	SDW	09/06/01	5	2	21	28
22	Crow River below State Hwy 101 at Dayton	SW	10/11/00	3	1	3	7
22	Crow River below State Hwy 101 at Dayton	SW	04/09/01	1	0	4	5
22	Crow River below State Hwy 101 at Dayton	SW	06/21/01	0	0	1	1
23	Elm Creek near Champlin	SW	04/27/01	--	--	6	6
24	Mississippi River near Anoka	SW	10/03/00	1	0	3	4
24	Mississippi River near Anoka	SW	04/19/01	0	0	1	1
24	Mississippi River near Anoka	SW	06/22/01	0	0	2	2
25	Vadnais Lake at Pumping Station in Vadnais Heights	SW	10/10/00	0	0	2	2

Table 8. Number of organic-wastewater compounds detected at surface-water sites, Minnesota 2000-02—Continued

[OWC, organic wastewater compound; HIA, household, industrial, and agricultural use compounds; --, not analyzed; WWTP, wastewater treatment plant; SW, sample taken from surface water site not directly influenced by WWTP discharge; SDW, sample taken from a surface water site directly downstream of a WWTP discharge. Sites 23, 27, and 30 were analyzed for USGS laboratory Methods 3 and 4 only].”

Site identifier (fig. 1 or 2)	Site name	Site classification	Sample date (mm/dd/yy)	Pharmaceutical detections	Antibiotic detections	HIA detections	Total OWC detections
25	Vadnais Lake at Pumping Station in Vadnais Heights	SW	04/20/01	1	0	0	1
25	Vadnais Lake at Pumping Station in Vadnais Heights	SW	06/19/01	0	0	0	0
26	Rice Creek at County Road 1 in Fridley	SW	10/04/00	0	0	6	6
26	Rice Creek at County Road 1 in Fridley	SW	04/06/01	3	0	2	5
26	Rice Creek at County Road 1 in Fridley	SW	06/15/01	2	0	5	7
27	Shingle Creek at Queen Ave. in Minneapolis	SW	05/02/01	--	--	11	11
28	Redwood River below WWTP near Marshall	SDW	09/10/01	2	2	2	6
29	Blue Earth River near Rapidan	SW	10/12/00	0	0	2	2
30	Little Cobb River near Beauford	SW	05/04/01	--	--	3	3
31	Blue Earth River at County Road 90 near Mankato	SW	04/03/01	1	0	2	3
31	Blue Earth River at County Road 90 near Mankato	SW	07/02/01	0	0	4	4
32	Minnesota River at Mankato	SDW	10/13/00	0	0	2	2
32	Minnesota River at Mankato	SDW	04/04/01	1	0	3	4
32	Minnesota River at Mankato	SDW	07/02/01	0	0	--	0
33	Mississippi River at Ninninger	SDW	08/28/02	1	1	2	4
34	Mississippi River below Lock and Dam 2 at Hastings	SDW	10/02/00	1	2	6	9
34	Mississippi River below Lock and Dam 2 at Hastings	SDW	04/19/01	1	0	1	2
34	Mississippi River below Lock and Dam 2 at Hastings	SDW	06/25/01	1	0	6	7
35	St. Croix River below Stillwater	SDW	09/18/01	1	0	0	1
36	Vermillion River below Empire WWTP near Empire	SDW	09/17/01	4	3	10	17
37	Bear Creek Tributary near Chester	SW	08/27/02	0	1	2	3
38	South Fork Zumbro River at Rochester	SW	11/05/02	6	2	11	19
39	South Fork Zumbro River near Rochester	SDW	09/20/01	1	1	10	12
39	South Fork Zumbro River near Rochester	SDW	11/04/02	9	3	12	24
40	South Fork Zumbro River below WWTP near Rochester	SDW	11/05/02	9	3	8	20
41	Cedar River below WWTP at Austin	SDW	09/19/01	4	1	9	14
		Des Moines River Basin					
42	Okabena Creek near Worthington	SDW	09/10/01	3	0	14	17

The number and types of OWCs detected varied among sites (table 8). The number of OWCs detected and concentrations generally were greater in small streams (average of 8.9 OWCs) located within 1 mile downstream from WWTP effluent discharges (Sites 21, 28, 36, and 39-42) than at other surface-water sites (average of 3.6 OWCs) indicating that WWTP effluent may be a source of OWCs to surface water. There also were a greater number of OWCs detected at Site 17 in St. Louis Bay of Lake Superior (similar number of detections to small streams that are effluent dominated) near the WWTP effluent discharge from Site 5. Large river sites located downstream from WWTP effluent discharges (Sites 12, 14, 16, and 32-35) generally had fewer OWCs detected than small stream sites located downstream from WWTP effluent discharges. The greater number of OWCs in the small streams may be because effluent comprised a greater proportion of stream flow than large rivers.

OWCs that were frequently detected in WWTP effluent such as the animal sterol (*3-beta*-coprostanol), fragrances (AHTN and HHCB), flame retardants and plastic components (tri(2-butoxyethyl)phosphate, tri(2-chloroethyl)phosphate, tributyl phosphate, and tri(dichloroisopropyl)phosphate), and the pharmaceuticals or antibiotics (caffeine, cotinine, erythromycin H₂O, sulfamethoxazole, and trimethoprim) also were detected more frequently in streams directly downstream than upstream from WWTP effluent discharge. Some OWCs, such as *beta*-sitosterol, cholesterol, metolachlor, DEET (topical insect repellent), and skatol, were detected in streams directly and not directly downstream from WWTP effluent discharge suggesting that these OWCs may persist in streams from upstream WWTP sources or there may be other sources of these OWCs in addition to WWTP effluent. Cholesterol and *beta*-sitosterol are animal and plant sterols whose sources could be aquatic or terrestrial biota. Metolachlor (agricultural herbicide) is likely from runoff or atmospheric deposition, and DEET may enter streams directly through removal from treated skin during swimming.

OWC types and number of detections varied temporally at sites that were sampled more than once. For example, there were 2, 7, and 9 OWCs detected at Site 34 over three sampling periods (table 8). These temporal differences likely are influenced by upstream discharges, surface runoff, streamflow, water temperature, chemical characteristics, degradation rates, and biological metabolism and uptake.

Selected OWCs were detected more frequently during specific seasonal and hydrologic conditions. For example, metolachlor was detected more frequently during the spring or summer runoff periods (Sites 11, 12, 14, 18, 19, 20, 22, 24, 26, and 34), likely from runoff from agricultural land use. DEET was detected more frequently in fall or summer (Sites 11, 19, 24, 26, 31, and 34) possibly indicating increased human use during that period. *beta*-Sitosterol was more prevalent in the fall (Sites 12, 22, 25, 26, 31, and 32), which may result from senescing plants and algae or changes in the input or discharges of sterols from WWTPs. While patterns in detections were observed, this study did not fully characterize the sources and variability in OWC detections and concentrations due to limited temporal and spatial sampling.

A longitudinal study of the Zumbro River near Rochester (Sites 38-40) was useful for understanding the presence and distribution of OWCs upstream and downstream from WWTP effluent discharges and their fate in surface water. A series of sites, including upstream from an incoming WWTP effluent discharge (Site 38), the WWTP effluent (Site 4), 250 ft downstream from the effluent discharge (Site 39), and one-mile downstream from the effluent discharge (Site 40) were sampled. The total number of OWCs detected was lowest at Site 38 (19 OWCs), greater at Site 39 (24 OWCs), and reduced at Site 40 (20 OWCs). The relatively large number of OWCs detected upstream from WWTP effluent discharge (Site 38) was unexpected and may indicate upstream sources of OWCs in addition to WWTP effluent. There were several OWCs not detected in the WWTP effluent that were detected at Sites 39 and 40 (1,7-dimethylxanthine, acetaminophen, menthol, metolachlor, and salbutamol), and indicating potential sources other than the WWTP effluent.

Small streams (Sites 23, 26, and 27) draining urban land in the Minneapolis and St. Paul metropolitan area had a relatively large number of OWC detections considering that no direct source of WWTP effluent enters these streams directly upstream from the sampling location. The number of OWCs detected was similar to some stream sites located downstream from WWTP effluent even though Sites 23 and 27 were only analyzed for Methods 3 and 4, and; therefore, the number of OWCs may have been greater if analyzed using all methods. Potential sources of these OWCs in urban streams may be from individual sewage treatment systems, accidental discharge from sewer lines, or direct inputs through runoff or atmospheric deposition.

OWC detection frequency from this study for sites downstream from WWTPs compared closely to results by Kolpin and others (2002) for 139 streams in the United States located primarily downstream from WWTPs. The frequency of detection for OWCs was similar between the two studies with a few exceptions: 5-methyl-1H-benzotriazole, bisphenol-A, cholesterol, DEET, diazinon, fluoranthene, naphthalene, NP2EO, NP, pyrene, TCE, and triclosan, were more frequently detected by Kolpin and others (2002). This comparison indicates that there are similarities in the Minnesota and National results for surface waters influenced by wastewaters. The site types sampled, and analytical procedures, however, heavily influenced OWC detection frequencies. A more thorough analysis; therefore, would be required to place Minnesota results in context with National studies.

There were from one to five EDCs detected per surface-water site. Among all sites seven EDCs (AHTN, beta-sitosterol, bisphenol-A, diazinon, 4-normal-octylphenol, NP, and NP2EO) were detected. Site 21 had the greatest number and concentrations of EDCs among all surface-water sites.

GROUND WATER

For all ground-water samples, 31 OWCs (28 HIAs, 1 pharmaceutical (caffeine), and 2 antibiotics (sulfa-

methoxazole, and sulfamethazine)) were detected with an average of 3 OWCs detected per sample. There were few OWCs detected in the individual wells (0-5 OWCs) except those wells (Sites 51 and 52) underlying a waste dump (8 and 21 OWCs, respectively) (fig. 5).

The types of OWCs detected differed among sites. Components in sunscreen or topical linement products, fragrances, plasticizers, and pesticides were detected in municipal supply well (Site 43) samples (table 9). A total of 5 OWCs were detected at Site 43 and OWCs were detected twice during four samplings. The relatively greater number of OWCs detected at Site 43 in the March 2001 is unusual compared to the other sampling periods where none or one OWC was detected.

Three OWCs were detected in the mixed urban industrial/residential/commercial wells (Sites 44-47). Among those detected were industrial compounds such as solvents (TCE), nonionic-detergent metabolites (NP2EO) and flame retardants (tri(2-chloroethyl)phosphate). TCE concentrations at Site 47 (17 µg/L) exceeded the MCL of 5 µg/L and the HAL of 10 µg/L. Only two compounds; the antibiotic (sulfa-methoxazole) and DEET, were detected in wells located in urban residential-unsewered areas (Sites 48-50).

A wide variety of OWCs were detected in ground-water samples underlying a waste dump (Sites 51 and 52). OWCs detected include: caffeine, insect repellants,

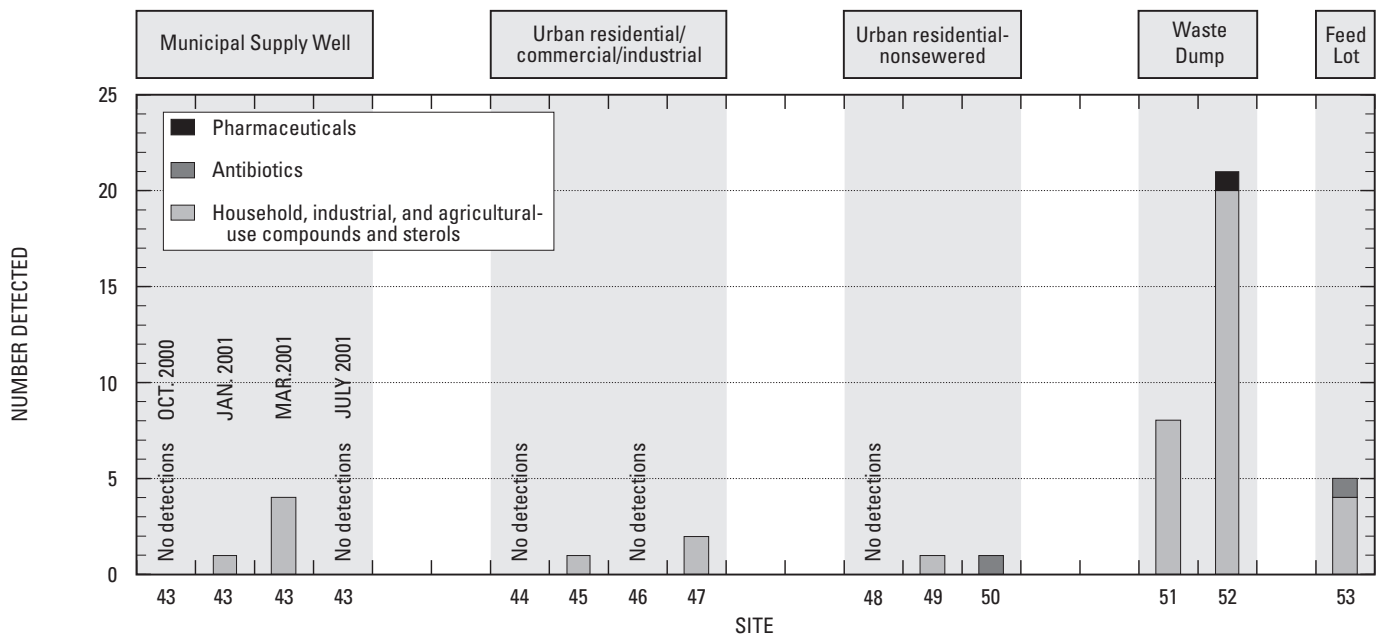


Figure 5. Organic wastewater compounds detected in ground-water samples, Minnesota, 2000-02. [Site identification numbers can be found in table 1 and figures 1 and 2.]

Table 9. Organic wastewater compounds detected at Moorhead Drinking Water Facility and surface- and ground-water sites used as sources of drinking water

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Source Waters		Moorhead Drinking Water Facility at Moorhead, Minn	
	Red River of the North above Fargo, N. Dak. (Site 11)	Moorhead City Well Number 9 (Site 43)	Intake Water (Site 54)	Finished Water (Site 55)
Compounds detected in fall 2000 baseflow	October 19, 2000 <u>1,7-dimethylxanthine</u>	October 18, 2000 none detected	October 18, 2000 none detected	October 18, 2000 bromoform
Compounds detected in winter 2001 baseflow	not sampled	January 23, 2001 ¹ benzophenone	January 23, 2001 benzophenone, bisphenol-A, cholesterol	January 23, 2001 bromoform, methyl salicylate
Compounds detected in spring 2001 runoff	April 11, 2001 Acetyl-hexamethyl-tetrahydro-naphthalene(AHTN), <i>beta</i> -sitosterol, <i>beta</i> -stig-mastanol, bisphenol-A, methyl salicylate, metolachlor, pentachlorophenol, <u>acetaminophen</u>	April 11, 2001 ¹ Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), bisphenol-A, methyl salicylate, metolachlor	April 11, 2001 <u>acetaminophen</u> , pentachlorophenol	April 11, 2001 bromoform
Compounds detected in summer 2001 storm runoff	July 12, 2001 Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), cholesterol, menthol, metolachlor, N,N-diethyl- <i>meta</i> -toluamide (DEET), <i>para</i> -nonylphenol (NP), triclosan	July 11, 2001 none detected	July 11, 2001 N,N-diethyl- <i>meta</i> -toluamide (DEET), metolachlor	July 11, 2001 Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), bromoform, <i>para</i> -nonylphenol (NP)

¹ Well not used as a source of drinking water on this date.

nonionic detergent metabolites, PAHs, and plastic components. Six of the eight compounds detected at Site 51 were detected at Site 52, but there were a greater number of OWCs and greater concentrations at Site 52 than Site 51. This may be explained by variability in the waste material and differences in locations and depths of the two wells. The dump is listed on the Minnesota Pollution Control Agency's State Superfund list of priorities, and various types of refuse were disposed at the site (Minnesota Pollution Control Agency, 2001; Minnesota Department of Health, 2003).

There were relatively greater number of OWCs detected from the well located in the feedlot (Site 53) than most other ground-water sites with the exception of Sites 51 and 52. An anticorrosive compound (5-methyl-1H-benzotriazole), an ingredient in liniments (camphor), a compound found in the intestines of animals (indole), a disinfectant (*para*-cresol), and an antibiotic used for

animals (sulfamethazine) were detected in ground water underlying the feedlot (Site 53).

While the types of OWCs generally reflected the land use overlying monitoring wells, this study sampled a small number of wells and therefore the variability of specific OWCs in Minnesota ground-water resources is unknown. There were four EDCs detected in ground-water samples: AHTN (Site 43), bisphenol-A (Sites 43, 51, and 52), OP1EO (Site 51), and NP2EO (Site 47).

DRINKING WATER

The intakes and finished water from six drinking water facilities were sampled for this study (tables 9-14). Within the Red River of the North Basin, Moorhead, and East Grand Forks DWFs were sampled. Within the Upper Mississippi River Basin, the St. Cloud, St. Paul,

Table 10. Organic wastewater compounds detected at East Grand Forks Drinking Water Facility and surface water sites used as sources of drinking water

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Selected Source Water	East Grand Forks Drinking Water Facility at East Grand Forks, Minn.	
	Red Lake River at County Rd. 220 above East Grand Forks, Minn. (Site 13)	Intake Water (Site 56)	Finished Water (Site 57)
Compounds detected in fall 2000 baseflow	October 23, 2000 triphenyl phosphate	October 24, 2000 none detected	October 24, 2000 bromoform
Compounds detected in winter 2001 baseflow	not sampled	January 24, 2001 tributyl phosphate, triphenyl phosphate	January 24, 2001 bromoform, benzophenone, methyl salicylate
Compounds detected in spring 2001 runoff	April 12, 2001 3-methyl-1H-indole (skatol)	April 12, 2001 bromacil, 3-methyl-1H-indole (skatol)	April 12, 2001 bromoform
Compounds detected in summer 2001 storm runoff	July 9, 2001 <u>sulfadimethoxine</u> ; sample not analyzed by method 1	no pharmaceuticals or antibiotics detected; sample not analyzed by methods 3 and 4	July 10, 2001 bromoform

Minneapolis, and Mankato DWFs were sampled. Surface and ground waters that serve as source waters for selected DWFs also were sampled to provide information regarding potential sources of OWCs that may be drawn into facility intakes. Among the source waters for the drinking water facilities, smaller streams tended to have greater numbers of OWCs detected than large rivers, lakes, or ground-water sources.

There were 26 OWCs detected in intake and 13 OWCs detected in finished-water samples (tables 9-14). In general, few OWCs (0-9 OWCs) were detected in each intake and finished DWF water sample, averaging 2 OWCs per sample. Differences in OWC detections among DWFs likely were due to differences in source waters, treatment processes, and sample timing. Minneapolis DWF had the greatest number of OWCs (12 OWCs) detected in intake samples while the Mankato DWF had the greatest number of OWCs detected in finished water samples (8 OWCs) during all sampling periods.

A wide variety of OWCs were detected in either intake or finished drinking water samples including: anthraquinone, *beta*-sitosterol, bisphenol-A, bromacil, caffeine, camphor, cholesterol, DEET, fluoranthene, metolachlor, and tri(2-chloroethyl)phosphate. The ten most frequently detected OWCs in drinking water facility intakes anthraquinone, *beta*-sitosterol, bisphenol-A, bromacil, caffeine, cholesterol, DEET, fluoranthene,

metolachlor, and tri(2-chloroethyl)phosphate. Bromoform was detected in all finished DWF samples, as it is a chlorination disinfectant byproduct. Other OWCs that were detected in finished drinking water include anthraquinone, carbazole, and metolachlor. Seven EDCs were detected in DWF samples (AHTN, benzo[*a*]pyrene, *beta*-sitosterol, bisphenol-A, diazinon, NP, and NP2EO). EDCs generally were detected in intake samples, with the exception of Mankato DWF where one EDC (*beta*-sitosterol) was detected in finished water.

Inconsistencies in OWC detections between drinking and source waters probably were the result of differences in sampling area, sampling timing, introduction or removal of selected OWCs during treatment procedures, or analytical imprecision. For example: (1) OWCs detected in surface or ground water that are source waters for DWFs were not always detected in DWF intake waters, (2) OWCs detected in intake or finished waters were not in the source waters, and (3) OWCs detected in the intakes were not detected in finished water.

Variability in OWC detections among intake and source water samples could be due to differences in sampling location. A width and depth integrated sample was collected at all stream sites. These integrated samples are representative of the entire stream, whereas the drinking water intake sample generally is withdrawn from one specific area of the stream. Therefore, OWCs located in water near one bank of the stream, but not near the

Table 11. Organic wastewater compounds detected at St. Cloud Drinking Water Facility and surface water sites used as sources of drinking water.

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Selected Source Waters		St. Cloud Drinking Water Facility at St. Cloud, Minn.	
	Mississippi River above Sauk River near Sauk Rapids, Minn (Site 18)	Sauk River near St. Cloud, Minn. (Site 19)	Intake Water (Site 58)	Finished Water (Site 59)
Compounds detected in fall 2000 baseflow	October 17, 2000- methylnaphthlene, naphthalene, <u>di-phenhydramine</u>	October 16, 20001 methylnaphthalene, 2-methylnaphthalene, cholesterol, naphthalene, N,N-diethyl- <i>meta</i> -toluamide (DEET), <u>caffeine</u> , <u>1,7-dimethylxanthine</u>	October 16, 2000 none detected	October 16, 2000 bromoform
Compounds detected in winter 2001 baseflow	not sampled	not sampled	January 22, 2001 3- <i>beta</i> -coprostanol, bisphenol-A, cholesterol, nonylphenol diethoxylate (NP2EO), triethylcitrate (ethyl citrate), <i>beta</i> -stigmastanol	January 22, 2001 bromoform
Compounds detected in spring 2001 runoff	April 16, 2001 metolachlor	April 10, 2001 <i>beta</i> -sitosterol, metolachlor, pentachlorophenol, 3-methyl-1H-indole (skatol) April 27, 2001 bisphenol-A, cholesterol, metolachlor; pharmaceuticals and antibiotics not analyzed	April 16, 2001 metolachlor	April 16, 2001 bromoform, metolachlor
Compounds detected in summer 2001 storm runoff	June 27, 2001 none detected	June 26, 2001 metolachlor	June 27, 2001 none detected	June 27, 2001 bromoform

other, would be detected in the stream sample, but not in the drinking water intake sample. Differences in OWC detections between the intake samples and ground water that served as source water may be due to differences in travel time of the ground water to the plant. Another potential factor contributing to these differences may be laboratory imprecision, as most OWCs were detected near their respective MRLs.

This study was designed to characterize the presence and distribution of OWCs in drinking and source waters. The time-of-travel from the sampling site to the drinking

water DWF would be necessary to quantify inputs from source waters or removal rates during treatment.

COMPARISON AMONG SITE CLASSIFICATIONS

Among all site classifications, few OWCs were detected in the intake or finished water samples from DWFs. WWTP influent and effluent, and landfill leachate had the greatest average number of OWCs

Table 12. Organic wastewater compounds detected at St. Paul Drinking Water Facility and surface water sites used as sources of drinking water

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydro-logic condition	Selected Source Waters			St. Paul Drinking Water Facility at Maplewood, Minn.	
	Crow River below State Hwy. 101 at Dayton, Minn. (Site 22)	Mississippi River near Anoka, Minn. (Site 24)	Vadnais Lake at Pumping Station in Vadnais Heights, Minn (Site 25)	Intake Water (Site 60)	Finished Water (Site 61)
Compounds detected in fall 2000 baseflow	October 11, 2000 <u>1,7-dimethylxanthine</u> , <u>acetaminophen</u> , <u>beta-sitosterol</u> , <u>caffeine</u> , <u>cholesterol</u> , <u>sulfamethoxazole</u> , tri(dichlorisopropyl) phosphate	October 3, 2000 tri(2-butoxyethyl) phosphate, fluoranthene, pyrene, <u>caffeine</u> .	October 10, 2000 <u>beta-sitosterol</u> , cholesterol	October 10, 2000 <u>beta-sitosterol</u>	October 10, 2000 bromoform
Compounds detected in winter 2001 baseflow	not sampled	not sampled	not sampled	January 17, 2001 anthraquinone, carbazole, N,N-diethyl- <i>meta</i> -toluamide (DEET)	January 17, 2001 anthraquinone, bromoform, carbazole, N,N-diethyl- <i>meta</i> -toluamide (DEET)
Compounds detected in spring 2001 runoff	April 9, 2001 <u>acetaminophen</u> , indole, pentachlorophenol, 3-methyl-1H-indole (skatol), metolachlor	April 19, 2001 metolachlor	April 20, 2001 <u>cotinine</u>	April 18, 2001 anthraquinone, <u>erythromycin-H₂O</u> , fluoranthene	April 19, 2001 bromoform
Compounds detected in summer 2001 storm runoff	June 21, 2001 metolachlor	June 22, 2001 metolachlor, N,N-diethyl- <i>meta</i> -toluamide (DEET)	June 19, 2001 none detected	June 19, 2001 none detected	June 19, 2001 bromoform

detected (table 15). This same pattern also was observed for selected general use categories (antibiotics, pharmaceuticals, fragrances and flavors, nonionic detergent metabolites, pesticides, and EDCs). The greater number and diversity of OWCs in these site classifications reflects the diversity of waste that is treated and/or stored at WWTP or landfill facilities. The average number of OWCs and the average number of OWCs in selected general use categories (except PAHs) were greater in surface water downstream than upstream from WWTP effluent discharge indicating that WWTP effluent may be a source of OWCs to streams.

More OWCs were detected in surface water than ground water, with the exceptions of ground water underlying the waste dump or underlying feedlots. This may be due to more potential sources of OWCs to surface water compared to ground water sampled in this study or more rapid loss of OWCs from ground

water through adsorption, degradation, or transport. The greater number of OWCs in ground water underlying the waste dump reflects the diversity of waste that was deposited at this particular site.

Selected OWCs were more prevalent in particular site classifications. Antibiotic and pharmaceutical detections were rare, but were greatest at WWTP influent and effluent, landfill leachate, and surface water downstream from WWTPs. Antibiotics also were detected in ground water underlying a feedlot. PAHs were prevalent in the WWTP influent, landfill leachate, and ground water underlying the waste dump. EDCs were most commonly detected in landfill leachate, and WWTP influent and effluent.

These comparisons among site classifications are an attempt to understand the potential sources and presence of OWCs in Minnesota surface and ground water.

Table 13. Organic wastewater compounds detected at Minneapolis Drinking Water Facility and surface water sites used as sources of drinking water.

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Selected Source Waters		Minneapolis Drinking Water Facility at Columbia Heights, Minn.	
	Mississippi River near Anoka, Minn(Site 24).	Rice Creek at County Road 1 in Fridley, Minn.(Site 26)	Intake Water(Site 62)	Finished Water(Site 63)
Compounds detected in fall 2000 baseflow	October 3, 2000 tri(2-butoxyethyl)phosphate, fluoranthene, pyrene, <u>caffeine</u>	October 4, 2000 Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), <u>beta</u> -sitosterol, cholesterol, fluoranthene, N,N-diethyl- <i>meta</i> -toluamide (DEET), pyrene	October 4, 2000 bisphenol-A, <u>beta</u> -sitosterol, cholesterol	October 4, 2000 bromoform
Compounds detected in winter 2001 baseflow	not sampled	not sampled	January 16, 2001 anthraquinone, tri(2-chloroethyl)phosphate	January 16, 2001 anthraquinone, bromoform, tri(2-chloroethyl)phosphate
Compounds detected in spring 2001 runoff	April 19, 2001 metolachlor	April 6, 2001 <u>acetaminophen</u> , <u>caffeine</u> , <u>cotinine</u> , pentachlorophenol, 3-methyl-1H-indole(skatol)	April 18, 2001 metolachlor	April 18, 2001 bromoform, metolachlor
Compounds detected in summer 2001 storm runoff	June 22, 2001 metolachlor, N,N-diethyl- <i>meta</i> -toluamide (DEET)	June 15, 2001 bromacil, <u>caffeine</u> , cholesterol, <u>cotinine</u> , diazinon, metolachlor, N,N-diethyl- <i>meta</i> -toluamide (DEET)	June 18, 2001 benzo[a]pyrene, beta-sitosterol, bromacil, cholesterol, <u>caffeine</u> , diazinon, fluoranthene, metolachlor, pyrene	June 18, 2001 bromoform

These results apply to this study only and are not meant to be extrapolated to all sites that fit into the selected site classifications. A random selection of a larger number of sites in each classification and increased sampling frequency may allow for confirmation of results from this study.

IMPLICATIONS FOR WATER QUALITY AND HUMAN AND AQUATIC HEALTH

This reconnaissance study indicates widespread presence of OWCs in wastewater, surface, ground, and drinking waters in Minnesota. The types of OWCs detected indicate a variety of sources and pathways to the environment including domestic and industrial disposal into WWTPs and landfills and subsequent discharge of treated effluent to surface waters, runoff from land surfaces, infiltration into ground water, direct

disposal into surface water, and atmospheric deposition. Results of this study indicate that WWTP effluent is a major pathway of OWCs to surface waters and that landfill leachate from selected facilities is a potential source of OWCs to some WWTPs. Numerous pathways for these chemicals to enter the environment exist; however, and it was not possible to determine the relative contributions of various sources during this reconnaissance study.

The comparisons among site classifications only apply to sites sampled in this study. Some OWCs are likely removed through WWTP treatment processes and degradation in landfills although the efficiency at which they do so varies considerably (Stumpf and others, 1996). The presence of OWCs in surface water indicates that some OWCs are not removed through treatment processes or have additional sources other than treated wastewater. In general, there was insufficient temporal sampling to thoroughly understand the variability in

Table 14. Organic wastewater compounds detected at Mankato Drinking Water Facility and surface water sites used as sources of drinking water

[Site identifiers can be found in table 1 and figures 1 and 2; compounds that are underlined are either pharmaceuticals or antibiotics; shaded columns are drinking-water facility intake or finished water.]

Seasonal and hydrologic condition	Selected Source Waters ¹		Mankato Water Drinking Water Facility at Mankato, Minn.	
	Blue Earth River near Rapidan, Minn. (Site 29)	Blue Earth River at Co. Road 90 near Mankato, Minn. (Site 31)	Intake Water (Site 64)	Finished Water (Site 65)
Compounds detected in fall 2000 baseflow	October 12, 2000 <i>beta</i> -sitosterol, metolachlor	not sampled	October 12, 2000 metolachlor	October 12, 2000 bromoform, metolachlor
Compounds detected in winter 2001 baseflow	not sampled	not sampled	January 18, 2001 metolachlor, tri(2-chloroethyl)phosphate	January 18, 2001 anthraquinone, bromoform, carbazole, fluoranthene, metolachlor, pyrene, tri(2-chloroethyl)phosphate
Compounds detected in spring 2001 runoff	not sampled	April 3, 2001 <i>acetaminophen</i> , metolachlor, 3-methyl-1H-indole (skatol)	April 4, 2001 metolachlor	April 4, 2001 <i>beta</i> -sitosterol, bromoform, metolachlor
Compounds detected in summer 2001 storm runoff	not sampled	July 2, 2001 cholesterol, triphenyl phosphate, metolachlor, N,N-diethyl- <i>meta</i> -toluamide (DEET)	June 28, 2001 bromacil, <i>caffeine</i> , tetrachloroethylene	June 28, 2001 bromoform, metolachlor

¹ Ranney wells adjacent to the Blue Earth and Minnesota Rivers are used for source water for the Mankato Drinking Water Facility. The two surface water sites (Sites 29 and 31) were sampled because there was evidence that the ground-water quality at the depth of the Ranney wells would be similar to the overlying surface water.

OWC presence and distribution particularly with respect to ground water. The limited temporal sampling that was completed indicates high variability in OWC occurrence in WWTP effluent, as well as surface and drinking waters. This variability suggests that exposure to aquatic organisms or humans of OWCs measured in this study would be constantly in flux depending upon OWC use, disposal methods, treatment methods, and physical, chemical and biological processes.

Little information is readily available concerning the toxicity of many of the OWCs because few aquatic or human health standards, or criteria exist for the OWCs analyzed. Only one U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) was exceeded for tetrachloroethylene at a shallow well located in mixed urban land use; however, the MCL is only applicable, in this case, as a point of reference as this well is not used for drinking water supply. The state of Minnesota has stream water-quality standards for a small number of the OWCs measured (anthracene,

bromoform, chlorpyrifos, fluoranthene, naphthalene, pentachlorophenol, phenanthrene, phenol, and tetrachloroethylene) and no sample concentrations exceeded those values. Results of this reconnaissance study may help regulators, who set water-quality health standards, begin to prioritize which OWCs to focus upon for given categories of water use.

While little toxicity information is available, selected OWCs detected in this study are known EDCs with respect to fish endocrine systems (Purdum and others, 1994; Jobling and Sumpter, 1993; Folmar and others, 1996; Goodbred and others, 1997; Lee and others, 2000). Thirteen EDCs were detected which include: BHA, 4-cumylphenol, 4-*normal*-octylphenol, 4-*tert*-octylphenol, AHTN, benzo[*a*]pyrene, *beta*-sitosterol, bisphenol-A, NP2EO, OP2EO, OP1EO, and NP.

Table 15. Summary statistics for selected general use categories among site classes, Minnesota, 2000-02

The number in parentheses indicates the number of organic wastewater compounds in a particular general use category that were summarized. The average number of compounds detected by site classification is not the sum of individual averages per general use categories (except GWUI and GWUNSW) because not all general use categories are shown (those categorized as 'other' in Appendix 1). The endocrine disrupting compound column is a subset of other categories. The number of compounds analyzed for this table do not include hormones or sterols analyzed by method 5; *d*-limonene, isophorone, or phenol analyzed by methods 3-4; or carbamazepine and diphenhydramine analyzed by method 1.

[WWIF, wastewater treatment plant influent; WWEF, wastewater treatment plant effluent; LFLCH, landfill leachate; FLLAG, water underlying a feedlot lagoon; SW, surface water; SDW, surface water downstream from wastewater treatment plant effluent discharge; GWDW, ground water used for municipal drinking water supply; GWUI, ground water underlying urban/residential/commercial/industrial land use; GWUNSW, ground water underlying urban residential area that is unsewered; GWD, ground water underlying a waste dump; GWFLT, ground water underlying a feedlot; DWI, drinking water intakes; DWO, finished drinking water].

Site classification	Number of samples analyzed	Average number of organic wastewater compounds detected per sample for selected general use categories ²										
		Average number of compounds detected per sample (87)	Antibiotics (21)	Pharmaceuticals (12)	Plastic component-sand flame retardants (7)	Fragrances and flavors (9)	Nonionic detergent metabolites (7)	Polyaromatic hydrocarbons (9)	Pesticides (12)	Sterols (4)	Disinfectants, solvents, and anti-oxidants (6)	Endocrine disrupting compounds (14)
WWIF	1	41.0	2.0	5.0	4.0	8.0	3.0	8.0	2.0	4.0	2.0	4.0
LFLCH	3	33.7	1.7	3.3	6.3	4.0	3.0	5.7	2.7	2.0	2.0	5.0
WWEF	8	27.1	2.6	3.6	5.5	2.9	2.1	0.8	2.5	2.4	2.8	3.8
GWD	2	14.5	0	0.5	4.5	1.5	0.5	3.0	1.5	0	0.5	1.5
SDW	23	8.9	0.9	2.3	1.8	1.0	0.3	0	1.1	1.2	0.3	1.0
FLLAG	2	6.5	0.5	0.5	1.5	2.0	1.0	0	0.5	0	0.5	2.0
GWFLT	1	5.0	1.0	0	0	2.0	0	0	0	0	1.0	0
SW	¹ 32-37	3.6	0.1	0.7	0.3	0.4	0.1	0.3	1.0	0.6	0.1	0.4
DWI	24	2.0	0	0.1	0.3	0	0	0.2	0.6	0.4	0	0.3
DWO	24	1.9	0	0	0.1	0	0	0.1	0.4	0	1.0	0.1
GWDW	4	1.3	0	0	0.3	0.3	0	0	0.3	0	0	0.5
GWUI	4	0.8	0	0	0.3	0	0.3	0	0	0	0.3	0.3
GWUNSW	3	0.7	0.3	0	0	0	0	0	0.3	0	0	0

¹ Number of samples analyzed slightly by laboratory method. There were 32, 33, and 37 SW samples analyzed by methods 1, 2, and 3-4 respectively.

² Organic wastewater compounds classified as general-use category "other" are listed in Appendix 1.

SUMMARY AND CONCLUSIONS

This report provides the results of a cooperative study of the Minnesota Department of Health, Minnesota Pollution Control Agency, and the U.S. Geological Survey to determine the presence and distribution of 91 organic wastewater compounds (OWCs) at 65 sites in Minnesota during October 2000 through November 2002. Sites included wastewater (wastewater treatment plant influent and effluent, leachate from landfills, and water underlying feedlot lagoons); surface water; ground water (sewered and unsewered mixed urban land use, a waste dump, and feedlots); and the intake and finished drinking water from drinking-water facilities. OWCs are newly recognized classes of compounds that include household, industrial, and agricultural-use compounds (HIAs), pharmaceuticals, antibiotics, and sterols and hormones, which are characterized by high usage rates, have potential health effects, and are continuously released into the environment through human activities.

Results of this study illustrate the ubiquitous distribution of these compounds in the environment. There were 74 OWCs (49 household, industrial, and agricultural use compounds, 10 pharmaceuticals, 11 antibiotics, and 4 sterols or hormones) detected that represent a wide variety of uses and sources. Samples generally were comprised of a mixture of compounds (average of 6 OWCs) and 90 percent of the samples had at least one OWC detected. Average concentrations for detected OWCs generally were less than 3 micrograms per liter. The most frequently detected OWCs among all samples were metolachlor, cholesterol, caffeine, N,N-diethyl-*meta*-toluamide, bromoform, tri(2-chloroethyl)phosphate, *beta*-sitosterol, acetyl-hexamethyl-tetrahydro-naphthalene, bisphenol-A, and cotinine.

The greatest number and diversity of OWCs was found in wastewater influent and effluent, and landfill leachate (averages of 41, 27.1, and 33.7 respectively) compared to other site classifications. The most common OWCs detected in wastewater effluent samples included widely used fragrances, plasticizers, flame retardants, nonionic detergent surfactants, and plant and animal sterols. The most commonly detected OWCs in landfill leachate samples were polyaromatic hydrocarbons, fragrances, plasticizers, flame retardants, and solvents.

Wastewater treatment plants (WWTPs) and landfills receive diverse waste sources from the communities

they serve. There is likely OWC removal through treatment processes in WWTPs and degradation in landfills although the efficiency at which this occurs is not well understood and likely varies. This study showed differences in the types and numbers of OWCs detected among WWTPs and among time periods within one WWTP. These differences may be the result of varying sources of influent and treatment techniques. There was variability in types of OWCs detected among landfill sites, which is likely due to diversity of waste that was landfilled, and the spatial and temporal variability in waste type throughout a landfill.

The variety and number of OWCs detected in streams and lakes in this study indicate that there are numerous pathways for OWCs to enter surface water. A wide variety of OWCs (56 OWCs) were detected among all surface-water samples with an average of 6 OWCs per sample. Metolachlor, caffeine, cholesterol, N,N-diethyl-*meta*-toluamide (DEET), *beta*-sitosterol, acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), and acetaminophen were the most frequently detected OWCs among all surface-water samples. The number of OWCs detected and concentrations generally were greater in small streams (average of 8.9 OWCs), located within 1 mile downstream of WWTP effluent discharges than at other surface-water sites (average of 3.6 OWCs) indicating that WWTP effluent is a likely source of OWCs to selected surface waters. Small streams draining urban land use in the Minneapolis and St. Paul metropolitan area had a relatively high number of OWC detections considering that no direct source of WWTP effluent enters these streams directly upstream of the sampling location. Potential sources of these OWCs in urban streams may be individual sewage treatment systems, accidental discharge from sewer lines, or direct inputs through runoff or atmospheric deposition.

The types of OWCs detected at stream sites indicate diverse sources to streams. The animal sterol (3-*beta*-coprostanol), fragrances (AHTN and HHCB), flame retardants and plastic components (tri(2-butoxyethyl)phosphate, tri(2-chloroethyl)phosphate, tributyl phosphate, and tri(dichloroisopropyl)phosphate)), and the pharmaceuticals (caffeine, cotinine, erythromycin H₂O, and trimethoprim) also were detected more frequently in streams directly downstream than upstream from WWTP effluent discharge. In contrast, *beta*-sitosterol, metolachlor, N,N-diethyl-*meta*-toluamide, and 3-methyl-1H-indole were detected in streams both directly and not directly downstream from WWTP effluent

discharge suggesting there may be other sources of these OWCs in addition to WWTP effluent.

In general, more OWCs were detected in surface water than in ground water. Among all ground-water samples, 31 OWCs were detected, and an average of 3 OWCs were detected per sample. There were few OWCs detected in the individual wells (0-4 OWCs) except those wells located in the waste dump site (8-21 OWCs), and a well located in a feedlot (5 OWCs).

Few OWCs were detected (0-9 detected per sample with an average of 2 per sample) at the six drinking water facilities sampled during this study. Among all facilities, 26 OWCs were detected in intake and 13 OWCs were detected in finished-water samples. The most frequently detected OWCs in drinking water facility intakes were anthraquinone, *beta*-sitosterol, bisphenol-A, bromacil, caffeine, cholesterol, DEET, fluoranthene, metolachlor, and tri(2-chloroethyl)phosphate. Bromoform was detected in all finished drinking water samples, as it is a disinfectant byproduct. Other OWCs that were detected in finished drinking water include anthraquinone, carbazole, and metolachlor.

OWCs in the source waters for each drinking-water facility may be taken in for processing and may be present in the intake or finished water samples. A variety of OWCs including fragrances, plasticizers, pharmaceuticals, pesticides, nonionic detergent metabolites, sterols, and disinfectants were detected in the source waters. Among the source waters for the drinking-water facilities, smaller streams tended to have greater numbers of OWCs detected than large rivers, lakes, or ground-water sources. The greater number of OWCs detected in small streams may be due to greater potential sources or relatively less dilution than larger rivers.

Inconsistencies exist between the OWCs detected in drinking and source waters. For example: (1) OWCs detected in surface or ground water that are source waters for drinking-water facilities were not always detected in the intake waters, (2) OWCs detected in intake or finished waters were not in the source waters, and (3) OWCs detected in the intakes were not detected in finished water. These inconsistencies probably are a result of differences in sampling area, timing of sampling, introduction or removal of selected OWCs during treatment procedures, or analytical imprecision.

This reconnaissance study indicates widespread presence of OWCs in wastewater, surface, ground, and drinking waters in Minnesota. Aquatic organism or

human exposure to the OWCs would likely be in constant flux depending upon OWC use, disposal methods, treatment methods, and physical, chemical, and biological processes. Although exposure to OWCs is possible, concentrations generally are low and few aquatic or human health standards, or aquatic criteria exist for the OWCs analyzed. The risks of OWCs to humans or wildlife are not known, with the exception of selected OWCs detected in this study, that are known endocrine disruptors, and have been found to disrupt or influence endocrine function in fish. Results of this reconnaissance study, may help regulators who set water quality health standards, begin to prioritize which OWCs to focus upon for given categories of water use.

REFERENCES

- Barber, L.B., Brown, G.K., and Zaugg, S.D., 2000, Potential endocrine disrupting organic chemicals in treated municipal wastewater and river water, *in* Keith, L.H., Jones-Lepp, T.L., and Needham, L.L., eds., *Analysis of Environmental Endocrine Disruptors*: Washington D.C., American Chemical Society Symposium Series 747, p. 97-123.
- Barnes, K.K., Meyer, M.T., Thurman, M.T., Furlong, E.T., Zaugg, S.D., and Barber, L.B., 2002, Water-quality data for pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: U.S. Geological Survey Open File Report 02-94, <http://toxics.usgs.gov/pubs/OFR-02-94/>
- Brown, G.K., Zaugg, S.D., and Barber, L.B., 1999, Wastewater analysis by gas chromatography/mass spectrometry: *in* Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999. Volume 2 of 3. Contamination of Hydrologic Systems and Related Ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018B, p. 431-435.
- Buchanan, T.J., and Somers, W.P., 1969, Discharge measurements at gaging stations: U.S. Geological Survey Techniques for Water Resources Investigations, book 3, chap. A8, 65 p.
- Buerge, I.J., Polger, T., Muller, M.D., and Buser, H.R., 2003, Caffeine—An anthropogenic marker for wastewater contamination of surface waters: *Environmental Science and Technology*, v. 37, no. 4, p. 691-700.
- Buser, H.R., Muller, M.D., and Theobald, N., 1998, Occurrence and fate of the pharmaceutical drug clofibrate and the herbicide mecoprop in various Swiss lakes and in the North Sea: *Environmental Science and Technology*, v. 32, no. 1, p. 188- 192.

- Buser, H.R., Poiger, T., and Muller, M.D., 1999, Occurrence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface waters and in wastewater: *Environmental Science and Technology*, v. 33, no. 15, p. 2529-2535.
- Cahill, J.D., Furlong, E.T., Burkhardt, M.R., Kolpin, D.W., and Anderson, L.R., 2004, Determination of pharmaceutical compounds in surface- and ground-water samples by solid-phase extraction and high-performance liquid chromatography electrospray-ionization mass spectrometry: *Journal of Chromatography A*, v. 1041, no. 1-2, p. 171-180.
- Connor, B.F., Rose, D.L., Noriega, M.C., Murtagh, L.K., and Abney, S.R., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of 86 volatile organic compounds in water by gas chromatography/mass spectrometry, including detections less than reporting limits: U.S. Geological Survey Open-File Report 97-829, 78 p.
- Daughton, C.G., and Ternes, T.A., 1999, Pharmaceuticals and personal care products in the environment—Agents of subtle change: *Environmental Health Perspectives*, v. 107 (supplement 6), p. 907-938.
- Davidian, Jacob, and Carter, R.W., 1968, General procedure for gaging streams: U.S. Geological Survey Techniques for Water-Resources Investigations, book 3, chap. A6, 13 p.
- Extension Toxicology Network, 2003, EXTTOXNET InfoBase: World Wide Web accessed September 19, 2003 at URL <http://ace.orst.edu/info/exttoxnet>
- Folmar, L.C., Denslow, N.D., Kroll, K., Orlando, E.F., Enblom, J., Marcino, J., Metcalfe, C., and Guillet, L.J., 2001, Altered sex steroids and vitellogenin induction in walleye (*Stizostedion vitreum*) collected near a metropolitan sewage treatment plant: *Archives of Environmental Contamination and Toxicology*, v. 40 p. 392-398.
- Folmar, L.C., Denslow, N.D., Rao, V., Chow, M., Crain, P.A., Enblom, J., Marcino, J., and Guillet, L.J., Jr., 1996, Vitellogenin induction and reduced serum testosterone concentrations in feral male carp (*Cyprinus carpio*) captured near a modern metropolitan sewage treatment plant: *Environmental Health Perspectives*, v. 104, p. 1096-1101.
- Goodbred, S.G., Gilliom, R.J., Gross, T.S., Denslow, N.D., Bryant, W.L., and Schoeb, T.R., 1997, Reconnaissance of 17-estradiol, 11-ketotestosterone, vitellogenin, and gonad histopathology in common carp of United States streams—Potential for contaminant-induced endocrine disruption: U.S. Geological Survey Open-File Report 96-627, 47 p.
- Halling-Sorensen, B., Nielsen, S.N., Lanzky, P.F., Ingerslev, F., Lutzhoft, H.C.H., and Jorgensen, S.E., 1998, Occurrence, fate, and effects of pharmaceutical substances in the environment—A review: *Chemosphere*, v. 36, no. 2, p. 357-394.
- HealthCentral.com, 2003, RxList, the internet drug index: World Wide Web accessed September 19, 2003 at URL <http://www.rxlist.com>
- Heberer, T., and Stan, H.J., 1996, Occurrence of polar organic contaminants in Berlin drinking water: *Vom Wasser*, v. 86, p. 19-31.
- Heberer, T., Dunnbier, U., Reilich, C., and Stan, H.J., 1997, Detection of drugs and drug metabolites in ground-water samples of a drinking water treatment plant: *Fresenius Environmental Bulletin*, v. 6, p. 438-443.
- Heberer, T., Schimide-Baumier, K., and Stan, H.J., 1998, Occurrence and distribution of organic contaminants in the aquatic system in Berlin, Part I. Drug residues and other polar contaminants in Berlin surface and groundwater: *Acta Hydrochemica Hydrobiologica*, v. 26, p. 272-278.
- Hirsch, R., Ternes, T., Haberer, K., and Kratz, K.L., 1999, Occurrence of antibiotics in the aquatic environment: *Science of the Total Environment*, v. 225, p. 109-118.
- Hirsch, R., Ternes, T.A., Haberer, K., Mehlich, A., Ballwanz, F., and Kratz, K.L., 1998, Determination of antibiotics in different water compartments via liquid chromatography-electrospray tandem mass spectrometry: *Journal of Chromatography A*, v. 518, p. 213-223.
- Jobling, S., Nolan, M., Tyler, C.R., Brighty, G., and Sumpter, J.P., 1998, Widespread sexual disruption in wild fish: *Environmental Science and Toxicology*, v. 32, p. 2498-2506.
- Jobling, S., Sheahan, D., Osborne, J.A., Matthiessen, P., and Sumpter, J.P., 1996, Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*), exposed to estrogenic alkylphenolic chemicals: *Environmental Toxicology and Chemistry*, v. 15, p. 194-202.
- Jobling, S., and Sumpter, J.P., 1993, Detergent components in sewage effluent are weakly oestrogenic to fish—An in vitro study using rainbow trout (*Oncorhynchus mykiss*) hepatocytes: *Aquatic Toxicology*, v. 27, p. 361-372.
- Jorgensen, S.E., and Halling-Sorensen, B., 2000, Drugs in the environment: *Chemosphere*, v. 40, p. 691-699.
- Kennedy, E.J., 1983, Computation of continuous records of streamflow: U.S. Geological Survey Techniques for Water-Resources Investigations, book 3, chap. A13, 53 p.
- Kime, D.E., 1998, Endocrine disruption in fish: Boston, Mass., Kluwer Academic Publishers, 396 p.
- Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., and Buxton, H.T., 2002, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000—A national reconnaissance: *Environmental Science and Technology*, v. 36, p. 1202-1211.
- Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water-data-collection protocols and procedures for the National Water-Quality Assessment Program—Collection and documentation of water quality samples and related data: U.S. Geological Survey Open File Report 95-399, 113 p.

- Kummerer, K., ed., 2001, Pharmaceuticals in the environment—Sources, fate, effects, and risks: New York, Springer-Verlag, 265 p.
- Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Selection and installation of wells, and supporting documentation: U.S. Geological Survey Water-Resources Investigations Report 96-4233, 69 p.
- Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data collection procedures for the National Water-Quality Assessment Program—Selection, installation, and documentation of wells, and collection of related data: U.S. Geological Survey Open-File Report 95-398, 69 p.
- Lee, K.E., Blazer, V.S., Denslow, N.D., Goldstein, R.M., and Talmage, P.J., 2000, Use of biological characteristics of common carp (*Cyprinus carpio*) to indicate exposure to hormonally active agents in selected Minnesota streams, 1999: U.S. Geological Survey Water-Resources Investigations Report 00-4202, 47 p.
- Lindholst, C., Pedersen, K.L., and Pedersen, S.N., 2000, Estrogenic response of bisphenol-A in rainbow trout (*Oncorhynchus mykiss*): Aquatic Toxicology, v. 48, p. 87-94.
- Lindsey, M.E., Meyer, M.T., and Thurman, E.M., 2001, Analysis of trace levels of sulfonamide and tetracycline antimicrobials in ground water and surface water using solid-phase extraction and liquid chromatography/mass spectrometry: Analytical Chemistry, v. 73, p. 4640-4646.
- Meyer, M.T., Bumgarner, J.E., Varns, J.L., Daughtridge, J.V., Thurman, E.M., and Hostetler, K.A., 2000, Use of radioimmunoassay as a screen for antibiotics in confined animal feeding operations and confirmation by liquid chromatography/mass spectrometry: Science of the Total Environment, v. 248, p. 181-187.
- Minnesota Department of Health, 2003, Description of Pig's Eye Landfill: World Wide Web accessed September 2003, at URL www.health.state.mn.us/divs/eh/hazardous/pigseye.html
- Minnesota Pollution Control Agency, 2001, Progress on Pig's Eye Dump cleanup activities: Minnesota Pollution Control Agency Legislative Fact Sheet, 2 p.
- Morlock, S.E., Nguyen, H.T., and Ross, J.H., 2002, Feasibility of acoustic doppler velocity meters for the production of discharge records from U.S. Geological Survey streamflow-gaging stations: U.S. Geological Survey Water-Resources Investigations Report 01-4157, 59 p.
- Muller, S.R., Singer, H.P., and Canonica, S., 2000, Fate and behavior of the biocide triclosan in the aquatic environment [abs.]: National Meeting of the American Chemistry Society, Division of Environmental Chemistry, v. 40, no. 1, p. 166-167.
- National Institute of Standards and Technology, 2003, NIST WebBook: World Wide Web accessed September 19, 2003 at URL <http://webbook.nist.gov>.
- National Research Council, 1999, Hormonally active agents in the environment: Washington, DC, National Academy Press, 429 p.
- National Toxicology Program, 2003, Chemical health and safety data: World Wide Web accessed September 2003, at URL http://ntp-server.niehs.nih.gov/Main_Pages/ChemHS.html.
- Pawlowski, S., Islinger, M., Völkl, A., Braunbeck, T., 2000, Temperature-dependent vitellogenin-mRNA expression in primary cultures of rainbow trout (*Oncorhynchus mykiss*) hepatocytes at 14 and 18°C: Toxicology in Vitro, v. 14, no. 6, p. 531-540.
- Purdum, C.E., Hardman, P.A., Bye, V.J., Eno, N.C., Tyler, C.R., and Sumpter, J.P., 1994, Estrogenic effects of effluents from sewage treatment works: Chemistry and Ecology, v. 8, p. 275-285.
- Rantz, S.E., and others, 1982a, Measurement and computation of streamflow—1. Measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, p. 1-284.
- Rantz, S.E., and others, 1982b, Measurement and computation of streamflow—2. Computation of discharge: U.S. Geological Survey Water-Supply Paper 2175, p. 285-631.
- Richardson, M.L., and Bowron, J.M., 1985, The fate of pharmaceutical chemicals in the aquatic environment: Journal of Pharmacy and Pharmacology, v. 37, p. 1-12.
- Ruhl, J. F., 1999, Quantity and quality of seepage from two earthen basins used to store livestock waste in southern Minnesota during the first year of operation, 1997-98: U.S. Geological Survey Water-Resources Investigations Report 99-4206, 35 p.
- Sacher, F., Lochow, E., Bethmann, D., and Brauch, H.J., 1998, Occurrence of drugs in surface waters: Vom Wasser, v. 90, p. 233-243.
- Sedlak, D.L., Gray, J.L., and Pinkston, K.E., 2000, Understanding microcontaminants in recycled water: Environmental Science and Technology, v. 34, p. 509A-515A.
- Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 42 p.
- Spectrum Laboratories, Inc., 2003, Compound list: World Wide Web accessed September 2003, at URL <http://www.speclab.com/compound/chemabc.htm>.
- Stan, H.J., Heberer, T., and Linkerhagner, M., 1994, Occurrence of clofibric acid in the aquatic system—Is the use in human medical care the source of the contamination of surface, ground and drinking water?: Vom Wasser, v. 83, p. 57-68.

- Stumpf, M., Ternes, T.A., Heberer, K., Seel, P., and Baumann, W., 1996, Determination of pharmaceuticals in sewage plants and river water: *Vom Wasser*, v. 86, p. 291-303.
- Stumpf, M., Ternes, T.A., Wilken, R.D., Rodriques, S.V., and Baumann, W., 1999, Polar drug residues in sewage and natural waters in the state of Rio de Janeiro, Brazil: *Science of the Total Environment*, v. 225, p. 135-141.
- Ternes, T.A., 1998, Occurrence of drugs in German sewage treatment plants and rivers: *Water Resources Research*, v. 32, no. 11, p. 1245-1260.
- Ternes, T.A., Stumpf, M., Schuppert, B., and Heberer, K., 1998, Simultaneous determination of antiseptics and acidic drugs in sewage and river water: *Vom Wasser*, v. 90, p. 295-309.
- U.S. Environmental Protection Agency, 1992, Guidelines establishing test procedures for the analysis of pollutants (Appendix B to part 136, Definition and procedure for the determination of the method detection limit) U.S. code of Federal regulations, Title 40, revised as of July 1, 1992.
- U.S. Environmental Protection Agency, 2002, 2002 Edition of the Drinking Water Standards and Health Advisories: U.S. Environmental Protection Agency, Office of Water, Washington, DC, EPA Report Number: 822-R-02-038, 12 p.
- U.S. Geological Survey, 2003, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A1: <http://water.usgs.gov/owq/FieldManual/> variously paged.
- U.S. Geological Survey, 2004a, Basic water quality field parameters for sites sampled: U. S. Geological Survey at <http://water.usgs.gov/pubs/sir/2004/5138/parameters.html>
- U.S. Geological Survey, 2004b, National Water Information System (NWIS): last accessed March 30, 2004, at <http://waterdata.usgs.gov/mn/nwis>
- U.S. Geological Survey, 2004c, Pharmaceutical field data: U.S. Geological Survey at <http://water.usgs.gov/pubs/sir/2004/5138/pharmaceuticals.html>
- U.S. Geological Survey, 2004d, Antibiotics field data: U.S. Geological Survey at <http://water.usgs.gov/pubs/sir/2004/5138/antibiotics.html>
- U.S. Geological Survey, 2004e, Household, industrial, agricultural use compounds field data: U.S. Geological Survey at <http://water.usgs.gov/pubs/sir/2004/5138/household.html>
- U.S. Geological Survey, 2004f, Sterols and hormones field data: U.S. Geological Survey at <http://water.usgs.gov/pubs/sir/2004/5138/sterols.html>
- Wall, D.B., Trapp, P., and Ellingboe, R., 1998, Effects of clay-lined manure storage systems on ground-water quality in Minnesota—A summary: Extended Abstracts of Papers and Posters Presented at the February 10–12, 1998 Soil and Water Conservation Society Meeting in Ames, Iowa, on Manure Management—In Harmony with the Environment, p. 363.
- Wilde, F.D., Iwatsubo, R.T., Gibs, Jacob, and Radtke, D.B., eds., 1997, National field manual for the collection of water-quality data—Collection of water samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, variously paged.
- Wilde, F.D., Radtke, D.B., Iwatsubo, R.T., and Gibs, Jacob, 1997, National field manual for the collection of water-quality data—Preparations for water sampling: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A1, variously paged.
- Wilde, F.D., Radtke, D.B., Iwatsubo, R.T., Gibs, Jacob, and Sandstrom, M.W., eds., 1997, National field manual for the collection of water-quality data—Selection of equipment for water sampling: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A2, variously paged.
- Wilkison, D.H., Armstrong, D.J., Blevins, D.W., 2002, Effects of wastewater and combined sewer overflows on water quality in the Blue River Basin, Kansas City, Missouri and Kansas, July 1998–October 2000: U.S. Geological Survey Water-Resources Investigations Report 02-4107, 162 p.
- Zaugg, S.D., Smith, S.G., Schroeder, M.P., Barber, L.B., and Burkhardt, M.R., 2002, Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory—Determination of wastewater compounds by polystyrene-divinylbenzene solid-phase extraction and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01-4186, 37 p.

Appendix 1. Potential uses of organic wastewater compounds analyzed in water samples, Minnesota 2000-02

[Analytical methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; nd, not determined; HA, health advisory; MCL, maximum contaminant level; µg/L, micrograms per liter].

Analytical method	Organic wastewater compound	General use category ¹	HA (MCL) µg/L ²	CASRN ³	Potential uses ⁴
Pharmaceuticals					
1	1,7-dimethylxanthine	PHARM	nd	611-59-6	Metabolite of caffeine
1	Acetaminophen	PHARM	nd	103-90-2	Nonprescription analgesic; anti-inflammatory
1,3,4	Caffeine	PHARM	nd	58-08-2	Stimulant or diuretic
1	Carbamazepine	PHARM	nd	298-46-4	Anticonvulsant; antiepileptic; antineuralgia treatment; bipolar disorders
1	Codeine	PHARM	nd	76-57-3	Narcotic analgesic
1,3,4	Cotinine	PHARM	nd	486-56-6	Primary metabolite of nicotine
1	Dehydronifedipine	PHARM	nd	67035-22-7	Metabolite of Procardia: a vasodilator
1	Diltiazem	PHARM	nd	33286-22-5	Antihypertensive; calcium channel blocker
1	Diphenhydramine	PHARM	nd	147-24-0	Antihistamine
1	Gemfibrozil	PHARM	nd	25812-30-0	Cholesterol regulator
1	Ibuprofen	PHARM	nd	15687-27-1	Nonprescription anti-inflammatory analgesic
1	Ranitidine	PHARM	nd	66357-35-5	Nonprescription antacid
1	Salbutamol	PHARM	nd	18559-94-9	Antiasthmatic bronchodilator
1	Warfarin	PHARM	nd	81-81-2	Anticoagulant
Antibiotics					
2	Carbadox	ANTIB	nd	6804-07-5	Antibiotic to prevent and treat dysentery in swine and to maintain weight gain
2	Chlortetracycline	ANTIB	nd	57-62-5	Tetracycline antibiotic used for swine, poultry, cattle, and sheep
2	Ciprofloxacin	ANTIB	nd	85721-33-1	Fluoroquinolone antibiotic used for canine and swine
2	Doxycycline	ANTIB	nd	564-25-0	Tetracycline antibiotic used for humans and canines
2	Enrofloxacin	ANTIB	nd	93106-60-6	Fluoroquinolone antibiotic used for canine and swine
2	Erythromycin-H ₂ O	ANTIB	nd	114-07-8	Metabolite of erythromycin (a macrolide antibiotic) used for humans, poultry, and swine
2	Lincomycin	ANTIB	nd	154-21-2	Antibiotic used for poultry and swine
2	Norfloxacin	ANTIB	nd	70458-96-7	Fluoroquinolone antibiotic used for humans
2	Oxytetracycline	ANTIB	nd	6153-64-6	Tetracycline antibiotic used for poultry, fish, swine, cattle, sheep, bees, and lobster
2	Roxithromycin	ANTIB	nd	80214-83-1	Macrolide antibiotic
2	Sarafloxacin	ANTIB	nd	98105-99-8	Fluoroquinolone antibiotic used for poultry
2	Sulfadimethoxine	ANTIB	nd	122-11-2	Sulfonamide antibiotic used for fish and poultry
2	Sulfamerazine	ANTIB	nd	127-79-7	Sulfonamide antibiotic used for fish
2	Sulfamethazine	ANTIB	nd	57-68-1	Sulfonamide antibiotic used for swine and cattle
2	Sulfamethizole	ANTIB	nd	144-82-1	Sulfonamide antibiotic used for swine
1,2	Sulfamethoxazole	ANTIB	nd	723-46-6	Sulfonamide antibiotic used for humans
2	Sulfathiazole	ANTIB	nd	72-14-0	Sulfonamide antibiotic used for swine
2	Tetracycline	ANTIB	nd	60-54-8	Tetracycline antibiotic used for humans, canine, and cattle
1,2	Trimethoprim	ANTIB	nd	738-70-5	Antibiotic used for humans and canines
2	Tylosin	ANTIB	nd	1401-69-0	Antibiotic used for humans and canines
2	Virginiamycin	ANTIB	nd	11006-76-1	Antibiotic used for poultry, swine, and cattle
Household, industrial, and agricultural use compounds					
3,4	1,4-dichlorobenzene	PEST	(75)	106-46-7	Deodorizer for restrooms; fumigant to control moths, molds, and mildew; suspected endocrine disruptor
3,4	1-methylnaphthalene	PAH	nd	90-12-0	Comprises 2-5 percent of gasoline, diesel, and crude
3,4	2,6-dimethylnaphthalene	PAH	nd	581-42-0	Indicator of diesel and kerosene, but not a significant component in gasoline

Appendix 1. Potential uses of organic wastewater compounds analyzed in water samples, Minnesota 2000-02—Continued

[Analytical methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; nd, not determined; HA, health advisory; MCL, maximum contaminant level; µg/L, micrograms per liter].

Analytical method	Organic wastewater compound	General use category ¹	HA (MCL) µg/L ²	CASRN ³	Potential uses ⁴
3,4	2-methylnaphthalene	PAH	nd	91-57-6	Comprises 2-5 percent of gasoline, diesel, and crude
3,4	3-methyl-1H-indole (skatol)	FRAG	nd	83-34-1	Fragrance of the stench in feces and coal tar
3,4	3- <i>tert</i> -butyl-4-hydroxyanisole (BHA)	ANTIOX/EDC	nd	25013-16-5	Antioxidant and preservative; known endocrine disruptor
3,4	4-cumylphenol	NID/EDC	nd	599-64-4	Known endocrine disruptor
3,4	4- <i>normal</i> -octylphenol	NID/EDC	nd	1806-26-4	Known endocrine disruptor
3,4	4- <i>tert</i> -octylphenol	NID/EDC	nd	140-66-9	Known endocrine disruptor
3,4	5-methyl-1H-benzotriazole	ANTIOX	nd	136-85-6	Antioxidant in antifreeze and deicers; also an anti-corrosive agent
3,4	Acetophenone	FRAG	nd	98-86-2	Fragrance in soap and detergent; flavor in beverages and tobacco; solvent for cellulose ethers
3,4	Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	FRAG/EDC	nd	21145-77-7	Synthetic musk fragrance with widespread usage; known endocrine disruptor
3,4	Anthracene	PAH	nd	120-12-7	Wood preservative; also found in coal tar, diesel, and crude, but not gasoline
3,4	Anthraquinone	OTHER	nd	84-65-1	Manufacture of dye for textiles; seed treatments; bird repellent
3,4	Benzo(a)pyrene	PAH/EDC	(0.2)	50-32-8	Regulated polycyclic aromatic hydrocarbon; known endocrine disruptor
3,4	Benzophenone	OTHER	nd	119-61-9	Fixative for perfumes and soaps; a photoinitiator in the curing of inks with ultra-violet light; suspected endocrine disruptor
3,4	Bisphenol-A	PLASTIC/EDC	nd	80-05-7	Manufacture of polycarbonate resins; used in PVC resins; antioxidant; known endocrine disruptor
3,4	Bromacil	PEST	nd	314-40-9	Herbicide used primarily for non-crop grass and brush control
3,4	Bromoform	DISINF	(80)	75-25-2	Trihalomethane; byproduct of water disinfection
3,4	Camphor	FLAV	nd	76-22-2	Flavor or odorant in ointments
3,4	Carbaryl	PEST/EDC	700	63-25-2	Insecticide for crop and garden uses; known endocrine disruptor
3,4	Carbazole	PEST	nd	86-74-8	Manufacture of dyes, explosives, and lubricants; also an insecticide
3,4	Chlorpyrifos	PEST/EDC	20	2921-88-2	Domestic pest/termiticide control; highly restricted; known endocrine disruptor
3,4	Diazinon	PEST/EDC	0.6	333-41-5	Insecticide for control of ants, flies, and grubs; known endocrine disruptor
3,4	Dichlorvos	PEST	nd	62-73-7	Insecticide in pet collars for control of fleas; suspected endocrine disruptor
3,4	<i>d</i> -Limonene	FRAG	nd	5989-27-5	Antimicrobial; antiviral; a fragrance in aerosols
3,4	Fluoranthene	PAH	nd	206-44-0	Common in coal tar and asphalt, but not gasoline and diesel
3,4	Hexahydrohexamethylcyclopentabenzopyran (HHCB)	FRAG	nd	1222-05-5	Musk fragrance with widespread usage
3,4	Indole	FRAG	nd	120-72-9	Produced by bacteria in swine intestines; coffee fragrance; inert ingredient in pesticides
3,4	Isoborneol	FRAG	nd	124-76-5	Fragrance and disinfectant
3,4	Isophorone	SOLV	100	78-59-1	Solvent for lacquers, plastics, oils, silicon, and resins
3,4	Isopropylbenzene (cumene)	SOLV	nd	98-82-8	Paint thinner in octane aviation fuel; used in styrene, acetone and phenol production
3,4	Isoquinoline	FLAV	nd	119-65-3	Flavor and fragrance
3,4	Menthol	FLAV	nd	89-78-1	Flavor or odorant in cigarettes, cough drops, liniment, and mouthwash
3,4	Metaxyl	PEST	nd	57837-19-1	Fungicide for soil pathogens, mildew, and blight
3,4	Methyl salicylate	OTHER	nd	119-36-8	Used in liniments, food, beverages, and UV-adsorbing lotions
3,4	Metolachlor	PEST	(100)	51218-45-2	Herbicide used on corn
3,4	Naphthalene	PAH	(100)	91-20-3	Moth repellent; component in gasoline; found naturally in fossil fuels, burning tobacco or wood; used in dyes, resins, leather tanning agents, and in the insecticide carbaryl

Appendix 1. Potential uses of organic wastewater compounds analyzed in water samples, Minnesota 2000-02—Continued

[Analytical methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; nd, not determined; HA, health advisory; MCL, maximum contaminant level; µg/L, micrograms per liter].

Analytical method	Organic wastewater compound	General use category ¹	HA (MCL) µg/L ²	CASRN ³	Potential uses ⁴
3,4	N,N-diethyl- <i>meta</i> -toluamide (DEET)	PEST	nd	134-62-3	Insecticide used for mosquito control
3,4	Nonylphenol diethoxylate (NP2EO)	NID/EDC	nd	26027-38-2	Nonionic detergent metabolite; known endocrine disruptor
3,4	Octylphenol diethoxylate (OP2EO)	NID/EDC	nd	26636-32-8	Nonionic detergent metabolite; known endocrine disruptor
3,4	Octylphenol monoethoxylate (OP1EO)	NID/EDC	nd	26636-32-8	Nonionic detergent metabolite; known endocrine disruptor
3,4	<i>para</i> -cresol	OTHER	nd	106-44-5	Intermediate for dyes, pigments, drugs, disinfectant, ultra violet absorbers and pesticides; suspected endocrine disruptor
3,4	<i>para</i> -nonylphenol (NP)	NID/EDC	nd	84852-15-3	Nonionic detergent metabolite; known endocrine disruptor
3,4	Pentachlorophenol	PEST	(1)	87-86-5	Restricted-use pesticide for termite control; wood preservative for utility poles, railroad ties, and wharf pilings; suspected endocrine disruptor
3,4	Phenanthrene	PAH	nd	85-01-8	Manufacture of explosives; used in coal tar, diesel, or crude, but not gasoline
3,4	Phenol	DISINF	4000	108-95-2	Disinfectant; raw material in the production of phenolic resins; raw material for bisphenol-A and aniline.
3,4	Prometon	PEST	100	1610-18-0	Herbicide used as a soil sterilant
3,4	Pyrene	PAH	nd	129-00-0	In coal tar and asphalt, but not gasoline or diesel; used to make dyes, plastics, pesticides, and benzol[a]pyrene
3,4	Tetrachloroethylene (TCE)	SOLV	10 (5)	127-18-4	Solvent and degreaser; used in dry-cleaning products
3,4	Tri(2-butoxyethyl)phosphate	FIRE	nd	78-51-3	Flame retardant and plastic component
3,4	Tri(2-chloroethyl)phosphate	FIRE	nd	115-96-8	Flame retardant and plasticizer; suspected endocrine disruptor
3,4	Tri(dichlorisopropyl)phosphate	FIRE	nd	13674-87-8	Flame retardant used in rigid and flexible polyurethane foams; suspected endocrine disruptor
3,4	Tributyl phosphate	FIRE	nd	126-73-8	Flame retardant and antifoaming agent
3,4	Triclosan	DISINF	nd	3380-34-5	Antimicrobial disinfectant
3,4	Triethyl citrate (ethyl-citrate)	PLASTIC	nd	77-93-0	Used in cosmetics and pharmaceuticals; produced from citric acid; used to plasticize vinyl resins
3,4	Triphenyl phosphate	PLASTIC	nd	115-86-6	Plasticizer used in resins, waxes, finishes, roofing paper
Sterols and Hormones					
5	11-ketotestosterone	HORMONE	nd	nd	Reproductive hormone
5	17- <i>alpha</i> -estradiol	HORMONE/EDC	nd	57-91-0	Reproductive hormone; known endocrine disruptor
5	17- <i>alpha</i> -ethynyl estradiol	HORMONE/EDC	nd	57-63-6	Ovulation inhibitor; known endocrine disruptor
5	17- <i>beta</i> -estradiol	HORMONE/EDC	nd	50-28-2	Reproductive hormone; known endocrine disruptor
5	19-norethisterone	HORMONE/EDC	nd	68-22-4	Ovulation inhibitor; known endocrine disruptor
3,4,5	3- <i>beta</i> -coprostano	STER	nd	360-68-9	Usually a carnivore fecal indicator
5	4-androstene-3,17-dione	HORMONE	nd	63-05-8	Androgenic hormone
3,4	<i>beta</i> -sitosterol	STER/EDC	nd	83-46-5	A sterol in plant oils, legumes, and wood; known endocrine disruptor
3,4	<i>beta</i> -stigmastanol	STER	nd	19466-47-8	Generally a plant sterol
3,4,5	Cholesterol	STER	nd	57-88-5	Often a fecal indicator; also a plant sterol
5	cis-androsterone	HORMONE	nd	53-41-8	Urinary steroid; known endocrine disruptor
5	Diethylstilbestrol (DES)	HORMONE/EDC	nd	56-53-1	Synthetic estrogen; known endocrine disruptor
5	Epitestosterone	HORMONE	nd	481-30-1	Reproductive hormone

Appendix 1. Potential uses of organic wastewater compounds analyzed in water samples, Minnesota 2000-02—Continued

[Analytical methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; nd, not determined; HA, health advisory; MCL, maximum contaminant level; µg/L, micrograms per liter].

Analytical method	Organic wastewater compound	General use category ¹	HA (MCL) µg/L ²	CASRN ³	Potential uses ⁴
5	Equilenin	HORMONE/EDC	nd	517-09-9	Estrogen replacement therapy; known endocrine disruptor
5	Equilin	HORMONE/EDC	nd	474-86-2	Estrogen replacement therapy; known endocrine disruptor
5	Estrone	HORMONE	nd	53-16-7	Reproductive hormone
5	Estrilol	HORMONE/EDC	nd	50-27-1	Reproductive hormone; known endocrine disruptor
5	Mestranol	HORMONE/EDC	nd	72-33-3	Ovulation inhibitor; known endocrine disruptor
5	Progesterone	HORMONE/EDC	nd	57-83-0	Reproductive hormone; known endocrine disruptor
5	Stanolone	HORMONE	nd	10418-03-8	Synthetic anabolic steroid
5	Testosterone	HORMONE	nd	58-22-0	Reproductive hormone; known endocrine disruptor
5	Trenbolone	HORMONE	nd	10161-33-8	Synthetic anabolic steroid

¹PLASTIC, plastic component; FIRE, fire retardant; EDC, endocrine disrupting compound for selected fish species; FRAG, fragrance; FLAV, flavor; NID, nonionic detergent metabolite; SOLV, solvent; PEST, pesticide; DISINF, disinfectants; ANTIOX, antioxidants; ANTIB, antibiotic; PHARM, pharmaceutical; PAH, polyaromatic hydrocarbons; STER, plant or animal sterols; HORMONE, natural and synthetic hormones. Compounds generally have multiple uses and sources. For purposes of this report compounds are characterized by the most common uses.

² Health advisories (HA) and maximum contaminant levels (MCL) are human health related advisories or standards (U.S. Environmental Protection Agency, 2002). HA are shown in italics and MCLs are in parentheses. The HA is an estimate of acceptable drinking water levels for a chemical substance based on health effects information. It is not a legally enforceable Federal standard, but serves as technical guidance to assist Federal, state, and local officials. The lifetime HA is the concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for a lifetime of exposure. The MCL is the highest level of a contaminant that is allowed in drinking water. MCLs are enforceable standards for community drinking water.

³The chemical abstracts registry number gistry database. A CASRN

is a numeric identifier that can contain up to 9 digits, divided by hyphens into 3 parts. For example, 58-08-2 is the CASRN for caffeine. The online database provides a source for the latest registry number information: <http://www.cas.org/Support/lookup.html>

⁴ Sour

nology, 2003; HealthCentral.com, 2003; Extension Toxicology Network, 2003).

oxicology Program, 2003; National Institute of Standards and Tech-

Appendix 2: Quality-control data summary for laboratory reagent spike and blank samples for all analytes, Minnesota 2000-02.

[Analytical Methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; RSD, relative standard deviation; µg/L; micrograms per liter; na, not available; nd, not detected; --not applicable; parentheses show results for method 4].

Analytical method	Organic wastewater compound	Reagent spike samples				Reagent blank samples			
		Average percent recovery	RSD	Number of samples	Minimum µg/L	Average µg/L	Maximum µg/L	Number of samples with detections ¹	
Pharmaceuticals									
1	1,7-dimethylxanthine	104	42	40	0.001	0.002	0.003	2	
1	Acetaminophen	87	37	40	0.0017	0.009	0.0139	4	
1	Caffeine	81	30	40	0.001	0.004	0.008	8	
3,4	Caffeine	73 (80)	31 (14)	21 (9)	0.0099 (nd)	0.010 (nd)	0.011 (nd)	3 (0)	
1	Carbamazepine	73	42	30	--	--	--	0	
1	Codeine	80	3	40	--	--	--	0	
1	Cotinine	74	38	40	--	--	--	0	
3,4	Cotinine	53 (66)	61 (39)	21 (11)	--	--	--	0	
1	Dehydromifedipine	81	27	40	--	--	0.0056	1	
1	Diltiazem	47	39	40	--	--	--	0	
1	Diphenhydramine	56	33	36	--	--	--	0	
1	Gemfibrozil	100	210	39	--	--	--	0	
1	Ibuprofen	59	54	40	--	--	--	0	
1	Ranitidine	34	53	40	--	--	--	0	
1	Salbutamol	76	32	40	--	--	--	0	
1	Warfarin	65	36	40	--	--	--	0	
Antibiotics									
2	Carbadox	100	9.4	10	--	--	--	0	
2	Chlortetracycline	114	17	10	--	--	--	0	
2	Ciprofloxacin	125	6.5	10	--	--	--	0	
2	Doxycycline	86	13	10	--	--	--	0	
2	Enrofloxacin	135	17	10	--	--	--	0	
2	Erythromycin-H ₂ O	103	11	10	--	--	0.01	1	
2	Lincomycin	110	15	10	--	--	--	0	
2	Norfloxacin	130	8	10	--	--	--	0	
2	Oxytetracycline	74	4	10	--	--	--	0	
2	Roxithromycin	115	13	10	--	--	--	0	
2	Sarafloxacin	120	8	10	--	--	--	0	
2	Sulfadimethoxine	91	5	10	--	--	--	0	
2	Sulfamerazine	110		10	--	--	--	0	
2	Sulfamethazine	86	5	10	--	--	--	0	
2	Sulfamethizole	na	na	10	--	--	--	0	
1	Sulfamethoxazole	61	48	40	--	--	--	0	
2	Sulfamethoxazole	102	6	10	--	--	--	0	
2	Sulfathiazole	95	7	10	--	--	--	0	
2	Tetracycline	97	10	10	--	--	--	0	
1	Trimethoprim	69	30	40	--	--	--	0	
2	Trimethoprim	87	9	10	--	--	--	0	
2	Tylosin	116	13	10	--	--	--	0	
2	Virginiamycin	52	8	10	--	--	--	0	

Appendix 2: Quality-control data summary for laboratory reagent spike and blank samples for all analytes, Minnesota 2000-02—Continued

[Analytical Methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; RSD, relative standard deviation; µg/L, micrograms per liter; na, not available; nd, not detected; --not applicable; parentheses show results for method 4].

Analytical method	Organic wastewater compound	Reagent spike samples				Reagent blank samples			
		Average percent recovery	RSD	Number of samples	Minimum µg/L	Average (µg/L)	Maximum (µg/L)	Number of samples with detections ¹	
Household, industrial, and agricultural use-compounds									
3,4	1,4-dichlorobenzene	75 (46)	19 (31)	21 (11)	0.006 (nd)	0.018 (nd)	0.019 (nd)	5 (0)	
3,4	1-methylnaphthalene	85 (70)	20 (22)	21 (7)	0.005 (nd)	0.011 (nd)	0.008 (nd)	3 (0)	
3,4	2, 6-dimethylnaphthalene	83 (67)	21 (25)	21 (7)	0.014 (nd)	0.016 (nd)	0.018 (nd)	2 (0)	
3,4	2-methylnaphthalene	76 (80)	19 (13)	21 (7)	0.01 (nd)	0.018 (nd)	0.014 (nd)	3 (0)	
3,4	3-methyl-1H-indole (skatol)	64 (79)	26 (16)	21 (7)	--	--	0.009 (nd)	1 (0)	
3,4	3- <i>tert</i> -butyl-4-hydroxyanisole (BHA)	46 (33)	53 (42)	21 (10)	--	--	--	0	
3,4	4-cumylphenol	83 (88)	23 (15)	21 (7)	--	--	(1.2)	0(1)	
3,4	4-normal-octylphenol	64 (79)	31 (18)	21 (11)	--	--	--	0	
3,4	4- <i>tert</i> -octylphenol	72 (63)	25 (27)	21 (7)	0.002 (nd)	0.014 (nd)	0.032 (nd)	6 (0)	
3,4	5-methyl-1H-benzotriazole	86 (83)	25 (20)	21 (11)	--	--	--	0	
3,4	Acetophenone	93 (81)	15 (21)	21 (11)	--	--	0.055 (nd)	1 (0)	
3,4	Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	81 (80)	19 (14)	20 (7)	0.004 (nd)	0.008 (nd)	0.019 (nd)	4 (0)	
3,4	Anthracene	82 (79)	21 (23)	21 (11)	--	--	--	0	
3,4	Anthraquinone	78 (72)	21 (38)	21 (11)	--	--	--	0	
3,4	Benzoflpyrene	68 (84)	27 (13)	21 (9)	--	--	0.009 (nd)	1 (0)	
3,4	Benzophenone	90 (88)	20 (15)	21 (7)	--	--	0.0047 (nd)	1 (0)	
3,4	Bisphenol-A	90 (77)	43 (27)	21 (9)	0.0091 (nd)	0.025 (nd)	0.041 (nd)	2 (0)	
3,4	Bromacil	87 (86)	18 (12)	21 (7)	--	--	0.033 (nd)	1 (0)	
3,4	Bromoforn	73 (67)	21 (18)	21 (7)	--	--	--	0	
3,4	Camphor	90 (88)	19 (16)	21 (7)	0.005 (nd)	0.006 (nd)	0.006 (nd)	3 (0)	
3,4	Carbaryl	64 (66)	40 (24)	21 (7)	--	--	--	0	
3,4	Carbazole	67 (86)	39 (15)	20 (7)	0.002 (nd)	0.002 (nd)	0.002 (nd)	1 (0)	
3,4	Chlorpyrifos	82 (76)	19 (25)	21 (11)	nd (nd)	nd (nd)	nd (nd)	0	
3,4	Diazinon	76 (82)	20 (15)	21 (11)	--	--	--	0	
3,4	Dichlorvos	2 (84)	129 (10)	21 (7)	--	--	--	0	
3,4	<i>d</i> -Limonene	60 (36)	35 (27)	21 (7)	0.026 (nd)	0.058 (nd)	0.16 (nd)	7 (0)	
3,4	Fluoranthene	80 (79)	21 (26)	21 (10)	0.0037 (nd)	0.01 (nd)	0.017- (nd)	3 (0)	
3,4	Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	88 (90)	34 (18)	21 (7)	0.0012 (nd)	0.0017 (nd)	0.0023 (nd)	3 (0)	
3,4	Indole	82 (69)	22 (25)	21 (7)	--	--	(0.075)	0 (1)	
3,4	Isoborneol	90 (84)	19 (18)	21 (7)	--	--	--	0	
3,4	Isophorone	96 (88)	17 (15)	21 (7)	0.05 (nd)	0.452 (nd)	4.4 (nd)	13 (0)	
3,4	Isopropylbenzene (cumene)	65 (38)	31 (26)	21 (7)	0.002 (nd)	0.008 (nd)	0.019 (nd)	5 (0)	
3,4	Isoquinoline	68 (80)	30 (14)	21 (7)	--	--	--	0	
3,4	Menthol	82 (84)	21 (19)	21 (7)	0.026 (nd)	0.026 (nd)	0.026 (nd)	1 (0)	
3,4	Metalaxyl	90 (89)	19 (17)	21 (7)	--	--	0.013 (0.012)	1 (1)	
3,4	Methyl salicylate	89 (84)	16 (15)	21 (7)	0.007 (nd)	0.01 (nd)	0.01 (nd)	3 (0)	
3,4	Metolachlor	88 (83)	20 (21)	21 (11)	0.003 (nd)	0.004 (nd)	0.005 (nd)	3 (0)	
3,4	Naphthalene	86 (68)	19 (25)	21 (11)	0.006 (nd)	0.031 (nd)	0.08 (nd)	8 (0)	
3,4	N,N-diethyl-meta-toluamide (DEET)	81 (81)	26 (27)	21 (9)	--	--	0.012 (nd)	1 (0)	
3,4	Nonylphenol diethoxylate (NP2EO)	75 (76)	24 (28)	21 (9)	0.24 (nd)	0.717 (nd)	2.3 (nd)	16 (0)	

Appendix 2: Quality-control data summary for laboratory reagent spike and blank samples for all analytes, Minnesota 2000-02—Continued

[Analytical Methods 1, 2, 4, and 5 are U.S. Geological Survey research methods, and Method 3 is an official U.S. Geological Survey production method; RSD, relative standard deviation; µg/L, micrograms per liter; na, not available; nd, not detected; --not applicable; parentheses show results for method 4.]

Analytical method	Organic wastewater compound	Reagent spike samples				Reagent blank samples			
		Average percent recovery	RSD	Number of samples	Minimum µg/L	Average (µg/L)	Maximum (µg/L)	Number of samples with detections ¹	
3,4	Octylphenol diethoxylate (OP2EO)	68 (76)	31 (19)	21 (11)	0.02 (nd)	0.144 (nd)	0.26 (nd)	5 (0)	
3,4	Octylphenol monoethoxylate (OP1EO)	81 (87)	25 (19)	21 (7)	0.014 (0.13)	0.31 (0.18)	1.1 (0.2)	4 (4)	
3,4	<i>para</i> -cresol	82 (72)	31 (24)	21 (11)	--	--	--	0	
3,4	<i>para</i> -nonylphenol (NP)	46 (57)	53 (33)	21 (7)	0.012 (nd)	0.815 (nd)	2.5 (nd)	8 (0)	
3,4	Pentachlorophenol	63 (61)	36 (48)	21 (11)	--	--	--	0	
3,4	Phenanthrene	88 (80)	25 (21)	21 (8)	0.001 (nd)	0.003 (nd)	0.003 (nd)	5 (0)	
3,4	Phenol	96 (71)	28 (22)	21 (11)	0.048 (nd)	0.171 (nd)	0.4 (nd)	5 (0)	
3,4	Prometon	89 (78)	18 (23)	21 (11)	0.005 (nd)	0.015 (nd)	0.028 (nd)	7 (0)	
3,4	Pyrene	78 (75)	21 (32)	21 (11)	0.0034 (nd)	0.008 (nd)	0.017 (nd)	3 (0)	
3,4	Tetrachloroethylene (TCE)	46 (27)	37 (33)	21 (11)	0.017 (nd)	0.065 (nd)	0.12 (nd)	9 (0)	
3,4	Tri(2-butoxyethyl)phosphate	83 (82)	27 (19)	21 (7)	0.087 (nd)	0.088 (nd)	0.09 (nd)	2 (0)	
3,4	Tri(2-chloroethyl)phosphate	86 (85)	23 (13)	21 (7)	--	--	0.12 (nd)	1 (0)	
3,4	Tri(dichlorisopropyl)phosphate	85 (79)	19 (24)	21 (11)	--	--	--	0	
3,4	Tributyl phosphate	90 (89)	20 (18)	21 (7)	0.007 (nd)	0.035 (nd)	0.063 (nd)	7 (0)	
3,4	Triclosan	73 (81)	23 (14)	21 (8)	--	--	--	0	
3,4	Triethyl citrate (ethyl-citrate)	93 (76)	20 (24)	21 (11)	0.003 (nd)	0.008 (nd)	0.018 (nd)	3 (0)	
3,4	Triphenyl phosphate	80 (82)	24 (28)	21 (10)	0.0029 (nd)	0.03 (nd)	0.053 (nd)	3 (0)	
Sterols and hormones									
5	11-ketotestosterone	na	na	na	na	na	na	na	
5	17- <i>alpha</i> -estradiol	na	na	na	na	na	na	na	
5	17- <i>alpha</i> -ethynyl estradiol	na	na	na	na	na	na	na	
5	17- <i>beta</i> -estradiol	na	na	na	na	na	na	na	
5	19-norethisterone	na	na	na	na	na	na	na	
3,4	3- <i>beta</i> -coprostanol	85 (88)	25 (23)	21 (7)	0.2 (nd)	0.338 (nd)	0.73 (nd)	6 (0)	
5	3- <i>beta</i> -coprostanol	na	na	na	na	na	na	na	
5	4-androstene-3,17-dione	na	na	na	na	na	na	na	
3,4	<i>beta</i> -sitosterol	65 (89)	35 (41)	21 (7)	0.59 (nd)	0.895 (nd)	1.2 (nd)	2 (0)	
3,4	<i>beta</i> -stigmastanol	72 (77)	35 (24)	21 (7)	0.46 (nd)	0.726 (nd)	1.2 (nd)	2 (0)	
3,4	Cholesterol	77 (81)	26 (39)	21 (9)	0.31 (nd)	0.74 (nd)	1.9 (nd)	6 (0)	
5	Cholesterol	na	na	na	na	na	na	na	
5	<i>cis</i> -androsterone	na	na	na	na	na	na	na	
5	diethylstilbestrol	na	na	na	na	na	na	na	
5	Epitestosterone	na	na	na	na	na	na	na	
5	Equilenin	na	na	na	na	na	na	na	
5	Equilin	na	na	na	na	na	na	na	
5	Estril	na	na	na	na	na	na	na	
5	Estrone	na	na	na	na	na	na	na	
5	Mestranol	na	na	na	na	na	na	na	
5	Progesterone	na	na	na	na	na	na	na	
5	Stanolone	na	na	na	na	na	na	na	
5	Testosterone	na	na	na	na	na	na	na	
5	Trenbolone	na	na	na	na	na	na	na	

¹there were 39, 108, 23, and 11 laboratory blank samples analyzed for methods 1-4 respectively.

Appendix 3. Quality assurance summary for laboratory surrogate compounds in samples analyzed with field samples, Minnesota, 2000-02

[value in parentheses is for method 4]

Method	Surrogate compound	Average percent recovery	Relative standard deviation
Method 1	Caffeine $^{13}\text{C}_3$	100	14
	Ethyl nicotinate d_4	73	33
Methods 3 and 4	Decafluorobiphenyl	84 (27)	48 (48)
	Caffeine $^{13}\text{C}_3$	93 (40)	77 (28)
	Flouoranthene - d_{10}	92 (32)	77 (31)
	Bisphenol-A - d_3	73 (56)	71 (57)
Method 5	17-beta-estradiol d_4	134	64
	Testosterone d_3	141	37
	Cholesterol d_7	171	51

Appendix 4. Quality assurance summary of field replicates and blanks, Minnesota, 2000-02[Only those O₂ research methods,

and Method 3 is an official U.S. Geological Survey production method. There were 5 replicates and 13 blanks analyzed by USGS method 1; 7 replicates and 9 blanks analyzed by USGS

µg/L, micrograms per liter; -- not applicable; Relative Standard Deviation calculated using replicates with detections in both samples].

Analytical Method	Organic wastewater compound	Field replicate sample summary						Field blank sample summary	
		Relative standard deviations			Number of replicate pairs with:			Number of blanks with a detection	Concentration range in blanks (µg/L)
		Minimum	Average	Maximum	Detections in both samples	Non-detections in both samples	Inconsistent detections between samples		
Pharmaceuticals									
1	1,7-dimethylxanthine	5.2	8.8	12.5	2	2	1		
1	Caffeine	3.0	11.1	24.7	3	2	0	4	0.0023-0.0084
3, 4	Caffeine	2.3	7.1	17.1	4	5	0		
1	Carbamazepine	0.9	6.8	16.5	3	2	0		
1	Codeine	--	--	10.1	1	3	1		
1	Cotinine	5.2	10.9	20.8	3	1	1		
3, 4	Cotinine	19.4	19.8	20.2	3	6	0		
1	Diltiazem	5.2	12.0	22.3	3	2	0		
1	Diphenhydramine	8.4	14.7	24.7	4	1	0		
1	Ranitidine	--	--	2.3	1	4	0		
1	Trimethoprim	1.7	4.2	6.1	3	2	0		
Antibiotics									
2	Ciprofloxacin	--	--	--	0	6	1		
2	Erythromycin-H ₂ O	2.5	14.3	43.5	5	2	0		
2	Sulfadimethoxine	--	--	--	0	6	1		
2	Sulfamethizole	--	--	9.4	1	6	0		
1	Sulfamethoxazole	4.2	10.7	17.1	2	3	0		
2	Tetracycline	--	--	--	0	5	2		
1	Trimethoprim	1.7	4.2	6.1	3	2	0		
2	Trimethoprim	0.0	10.1	20.2	3	4	0		
Household, industrial, and agricultural-use compounds									
3, 4	1,4-dichlorobenzene	0.0	6.0	10.9	5	4	0		
3, 4	3-methyl-1H-indole (skatol)	2.5	28.0	53.5	2	7	0	1	0.024
3, 4	4-tert-octylphenol	--	--	7.4	1	7	1		
3, 4	5-methyl-1H-benzotriazole	2.2	6.3	12.4	5	4	0		
3, 4	Acetophenone	--	--	6.4	1	8	0		
3, 4	Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	3.5	8.6	18.0	6	3	0	1	0.24
3, 4	Anthraquinone	0.0	8.5	16.6	4	4	1		
3, 4	Benzo[a]pyrene	--	--	--	0	8	1		
3, 4	Benzophenone	0.0	4.8	8.8	5	4	0		
3, 4	Bisphenol-A	4.3	10.5	18.6	4	4	1		
3, 4	Bromacil	--	--	0.0	1	8	0		
3, 4	Bromoform	0.0	6.0	21.8	7	2	0		
3, 4	Diazinon	--	--	8.0	1	6	2		
3, 4	Fluoranthene	--	--	--	0	8	1		
3, 4	Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	0.0	4.5	11.5	6	3	0		
3, 4	Indole	--	--	20.2	1	8	0		
3, 4	Isophorone	--	--	--	0	7	2	1	0.11
3, 4	Metolachlor	1.4	7.5	15.7	3	5	1		
3, 4	N,N-diethyl-meta-toluamide (DEET)	4.6	5.1	5.7	3	5	1		
3, 4	Nonylphenol diethoxylate (NP2EO)	4.0	7.7	18.4	5	4	0		
3, 4	Octylphenol, diethoxylate (OP2EO)	8.3	9.8	11.2	2	6	1		
3, 4	<i>para</i> -cresol total	0.0	6.2	19.2	4	5	0		
3, 4	<i>para</i> -nonylphenol (NP)	6.0	8.6	11.2	2	7	0		

Appendix 4. Quality assurance summary of field replicates and blanks, Minnesota, 2000-02—Continued

[Only those O₂ research methods, and Method 3 is an official U.S. Geological Survey production method. There were 5 replicates and 13 blanks analyzed by USGS method 1; 7 replicates and 9 blanks analyzed by USGS µg/L, micrograms per liter; -- not applicable; Relative Standard Deviation calculated using replicates with detections in both samples].

Analytical Method	Organic wastewater compound	Field replicate sample summary						Field blank sample summary	
		Relative standard deviations			Number of replicate pairs with:			Number of blanks with a detection	Concentration range in blanks (µg/L)
		Minimum	Average	Maximum	Detections in both samples	Non-detections in both samples	Inconsistent detections between samples		
3, 4	Pentachlorophenol	1.5	13.4	27.5	4	5	0		
3, 4	Phenol	1.1	26.2	61.2	6	3	0	5	0.36-1.9
3, 4	Pyrene	--	--	--	0	8	1		
3, 4	Tetrachloroethylene (TCE)	2.6	8.8	12.3	3	6	0		
3, 4	Tri(2-butoxyethyl)phosphate	5.3	5.9	7.1	4	5	0		
3, 4	Tri(2-chloroethyl)phosphate	1.2	3.3	6.1	6	3	0		
3, 4	Tributyl phosphate	4.8	7.0	9.4	5	4	0	1	0.093
3, 4	Triclosan	4.5	8.6	19.0	4	5	0		
3, 4	Tri(dichlorisopropyl)phosphate	2.2	6.4	10.8	6	3	0		
3, 4	Triethyl citrate (ethyl citrate)	3.9	9.0	15.1	5	3	1		
3, 4	Triphenyl phosphate	0.8	4.7	8.5	2	6	1		
Hormones and sterols									
3, 4	3- <i>beta</i> -coprostanol	15.7	40.6	99.8	3	4	2		
5	3- <i>beta</i> -coprostanol	29.6	30.9	32.2	2	1	1	2	0.004-0.069
3, 4	<i>beta</i> -sitosterol	2.5	9.1	15.7	2	4	3		
3, 4	<i>beta</i> -stigmastanol	--	--	--	0	8	1		
3, 4	Cholesterol	5.4	37.0	101.1	3	0	6		
5	Cholesterol	9.0	41.5	86.2	3	0	1	7	0.001-0.036
5	<i>cis</i> -androsterone	--	--	--	0	4	0	1	0.003
5	Stanolone	--	--	11.1	0	1	3		

