Endocrine Active Chemicals and Other Contaminants of Emerging Concern in Minnesota's Groundwater, 2009-2010

CLEAN WATER LAND & LEGACY AMENDMENT

Minnesota Pollution Control Agency

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Author

Sharon Kroening

Contributors / acknowledgements

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Minnesota Pollution Control Agency

520 Lafayette Road North | Saint Paul, MN 55155-4194 | www.pca.State.mn.us | 651-296-6300
Toll free 800-657-3864 | TTY 651-282-5332

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Contents

Executive Summary

The Minnesota Pollution Control Agency (MPCA) received an appropriation from the Clean Water Fund to expand the monitoring of endocrine active chemicals (EACs) and other contaminants of emerging concern in the State's groundwater. This report summarizes results from the first round of sampling, which was from November 2009 to June 2010. During this period, the agency tested 40 wells primarily in urban settings to determine the extent of any contamination from EACs and other contaminants of emerging concern in Minnesota's groundwater. Most of the sampled wells represented general groundwater quality conditions and tapped the shallow sand and gravel aquifers. Five wells tapped the deeper Prairie du Chien-Jordan aquifer.

The sampled wells purposely were selected because the well water contained increased boron concentrations, which suggested the water may contain EACs and other contaminants of emerging concern. Boron has many sources in the environment but may be associated with wastewater contamination, in which EACs and other contaminants of emerging concern often are present.

MPCA staff collected water samples from all the wells. The U.S. Geological Survey laboratories tested the samples for almost 100 different chemicals. These included prescription and non-prescription medicines, hormones, fragrances, detergent breakdown products, and fire retardants. Two antibiotics were included in the set of analyzed chemicals.

The results indicated EACs and other contaminants of emerging concern were detected less frequently in Minnesota's groundwater compared to the State's surface water resources. This likely is due to the physical properties and/or the degradation potential of the chemicals.

Twenty EACs and other contaminants of emerging concern were detected in about one-third of the 40 sampled wells. The number of chemicals detected in a single well ranged from one to ten. The most frequently detected chemicals were the fire retardant tris (dichloroisopropyl) phosphate, the antibiotic sulfamethoxazole, and the plasticizers bisphenol A and tributyl phosphate.

The EACs and other contaminants of emerging concern, when present in the groundwater, were detected at low concentrations. Over 80 percent of the detected chemicals were measured at concentrations of less than one microgram per liter. No concentrations exceeded any applicable health guidance set by the Minnesota Department of Health; however, health guidance values were available for only about 15 percent of the analyzed chemicals.

The EACs were detected in three of the 40 (eight percent) sampled wells. The detected EACs were bisphenol A, *trans*-diethylstilbestrol, and 4-cumylphenol. Two of the wells with EAC detections intersected a landfill-leachate plume. Bisphenol A is used to manufacture polycarbonate plastics and epoxy resins. Epoxy resins are used in food and drink packaging, compact discs, and medical devices and to coat products such as food cans, bottle tops, and water-supply pipes. Trans-diethylstilbestrol is a synthetic non-steroidal estrogen used to treat cold sores. 4-cumylphenol is a breakdown product of alkylphenol detergents.

The water from two wells affected by landfill leachate had the greatest number of detections of contaminants of emerging concern and the highest total sum of concentrations. These results suggested the State's continued efforts to properly close, monitor, and maintain landfills likely will help minimize the migration of the EACs and other contaminants of emerging concern to the groundwater.

Further data collection will refine this assessment of EACs and other contaminants of emerging concern. A limited number of shallow wells were available for sampling in areas using subsurface sewage treatment systems for wastewater disposal during this round of sampling; additional wells were installed in these aquifers as part of MPCA groundwater monitoring network enhancements since June 2010. The collection of additional data from these wells will refine this assessment, especially since there likely will be differences in the detected chemicals and concentrations due to variations in medication and household chemical usage among the State's population.

Introduction

Contaminants of emerging concern are synthetic or naturally-occurring chemicals that are not commonly monitored or regulated in the environment. Common classes of these chemicals include antibiotics, detergents, fire retardants, hormones, personal care products, and pharmaceuticals. Contaminants of emerging concern are not necessarily newly-manufactured chemicals. In some cases, the release of these chemicals into the environment has occurred for a long time, but laboratory techniques sensitive enough to detect them in the environment only were developed within the last decade.

The release of contaminants of emerging concern into the environment is of a particular concern because they may affect ecological or human health. The effect of chronic exposure to low levels of these chemicals to human or aquatic life generally is not known. In addition, some of these chemicals function as EACs. EACs are natural or synthetic chemicals that mimic or block the function of the natural hormone systems in humans and animals. EACs also are referred to as endocrine disrupting chemicals or EDCs in the scientific literature; however, scientists are increasingly adopting the usage of EAC as a more accurate description for contaminants that affect the endocrine system.

In Minnesota, scientists have measured contaminants of emerging concern in the State's water resources and unnatural endocrine activity in the State's aquatic life. Several studies conducted over the past decade have detected contaminants of emerging concern in the State's feedlot lagoons, groundwater, lakes, landfill leachate, municipal wastewater, and streams (Lee et al. 2004; Writer et al. 2010). Indicators of endocrine activity, such as the presence of vitellogenin in male fish, have been measured at more than 40 percent of the surface-water sites sampled in Minnesota (Lee et al. 2010). In Minnesota, unnatural endocrine activity was observed in fish exposed to wastewater treatment plant effluent as well as fish in diverse environmental settings, which suggests there are other sources of EACs to streams besides wastewater effluent, such as runoff from agricultural or urban lands, atmospheric deposition, or groundwater inflow.

The Minnesota Pollution Control Agency (MPCA) received appropriations from the Clean Water Fund from State fiscal years 2010-2013 to expand the monitoring of EACs and other contaminants of emerging concern in the State's groundwater. On November 4, 2008, Minnesota voters approved the Clean Water, Land, and Legacy Amendment to the State constitution to protect drinking water sources; enhance and restore wetlands, prairies, forests, and fish, game, and wildlife habitat; preserve the arts and cultural heritage; support parks and trails; and enhance and restore lakes, rivers, streams, and groundwater (State of Minnesota 2008). This amendment increased the sales and use tax by three-eighths of one percent on taxable sales starting July 1, 2009, and continuing through 2034. Approximately 33 percent of the funds were dedicated to a Clean Water Fund to protect, enhance, and restore water quality in lakes, rivers, streams, and groundwater. At least five percent of the Clean Water Fund was targeted to activities that protect drinking water sources. The MPCA used funds from this appropriation to test approximately 40 wells each year for EACs and other contaminants of emerging concern as part of the agency's ambient groundwater monitoring. The MPCA's Ambient Groundwater Monitoring Network primarily targets the groundwater unaffected by localized point sources of contamination, such as leaking petroleum product storage tanks, Superfund sites, or landfills. The network typically monitors parts of the sand and gravel and Prairie du Chien-Jordan aquifers with recently-recharged water. Contamination caused by humans likely reaches these parts of the aquifers more rapidly compared to the deeper aquifers present in the State.

Objective and scope

The primary objective of the first year of monitoring in State fiscal year 2010 (July 1, 2009-June 30, 2010) was to define the magnitude of contamination by EACs and other contaminants of emerging concern within the urbanized parts of Minnesota. The secondary objective was to determine the effects of common urban land uses on the occurrence and distribution of these chemicals in the groundwater.

The scope of this report is limited to data collected from 40 wells sampled from November 2009 to June 2010. This report primarily contains data on prescription and non-prescription medications, hormones, personal care products, fire retardants, detergent metabolites, fragrances, and other organic contaminants often found in a variety of household products. The antibiotics data is limited to two constituents. The data from selected pesticides (carbaryl, chlorpyrifos, diazinon, metalaxyl, and metolachlor) and volatile organic compounds (bromoform, isopropylbenzene, and tetrachloroethylene) that were included in one of the laboratory analytical methods will not be discussed in this report. The presence and distribution of pesticides in the State's groundwater is characterized by the Minnesota Department of Agriculture, and assessments of volatile organic compounds in the groundwater are reported in MPCA groundwater condition reports (O'Dell 2007).

Environmental setting

The State of Minnesota encompasses approximately 218,000 km^2 in the north-central part of the United States. Most of the State is covered by forested and agricultural lands. Thirty-two percent of the State is covered by forests, which are concentrated in the north. Agricultural land encompasses 44 percent of the State and is concentrated in the southern and western parts. Corn and soybeans are the primary crops grown. Cattle, hogs, and poultry are the main livestock raised. Urban land use comprises approximately six percent of the State and is concentrated within the Twin Cities Metropolitan Area (TCMA), although small localized urban areas also occur throughout the State. In 2011, 2.8 million of the State's 5.3 million human population resided in the TCMA (U.S. Census Bureau 2011). In the central part of the TCMA, wastewater is collected using sewerage systems and delivered to regional wastewater plants for treatment. The outlying parts of the TCMA generally rely on subsurface sewage treatment systems (SSTS) for wastewater treatment.

Sand and gravel aquifers primarily of glacial origin are exposed near the land surface over approximately one-fifth of the State (Figure 1). The aquifers are most extensive in the central part of the State and have a considerably smaller areal extent elsewhere. The sand and gravel aquifer thickness generally is less than 30 m but may extend to 100 m thick in the central and northwestern parts of the State. A series of Paleozoic-age bedrock aquifers underlie the sand and gravel aquifers in the southeastern part of the State. In most other parts of the State, Cretaceous-age sandstones or Precambrian-age crystalline rocks underlie the sand and gravel aquifers.

Buried sand and gravel aquifers are most prevalent in the west-central part of the State where glacial deposits are thick. These generally are confined aquifers with variable yields. The buried sand and gravel aquifers typically are difficult to locate since they have no surface expression.

Water supplies in the southeastern part of the State generally use the Prairie du Chien-Jordan aquifer. This aquifer is composed of bedrock-- the dolomitic Prairie du Chien Group and the underlying Jordan sandstone. Groundwater in the Prairie du Chien-Jordan aquifer primarily moves through fractures, joints, and solution channels in the Prairie du Chien Group (Delin and Woodward 1984). Flow through the Jordan aquifer primarily is intergranular with some fracture flow. The Prairie du Chien-Jordan aquifer generally is close to the land surface in the eastern and southeastern part of its extent. Elsewhere, it usually is buried by glacial deposits of varying thickness.

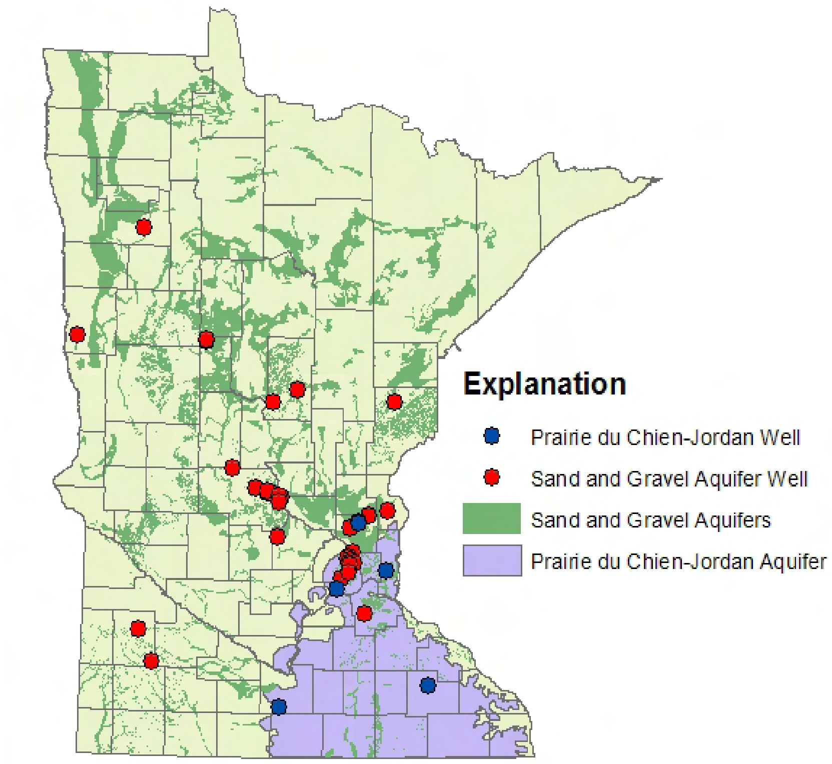

Figure 1. Location of sand and gravel and Prairie du Chien-Jordan aquifers in Minnesota and groundwater sampling points.
[The aquifer extents in this figure are generalized and parts of the Prairie du Chien-Jordan aquifer are not shown. Nearby sampling points may appear as one well due to the scale of the figure]

Approach

This study purposely sampled wells that may be affected by wastewater to determine the magnitude of any groundwater contamination by EACs and other contaminants of emerging concern. The sampled wells generally were located in urban areas and had increased boron concentrations compared to the other wells in the monitoring network. The majority of these wells also had detectable nitrate concentrations. Boron and nitrate have numerous sources in the environment but may be associated with wastewater contamination, in which EACs and other contaminants of emerging concern often are present (Ferrey 2011; Lee et al. 2004; Jackson and Sutton 2008; Conn et al. 2006; Swartz et al. 2006; Rudel et al. 1998). Boron is a whitening agent in detergents, and its presence in the groundwater can indicate wastewater contamination (Repert et al. 2006; LeBlanc 1984). Nitrate is the primary chemical of concern from a human health perspective in wastewater plumes (LeBlanc 1984; Robertson, Cherry, and Sudicky 1991). A study in Minnesota (Trojan et al. 2003) suggested nitrate concentrations are significantly greater in the groundwater underlying residential areas using SSTS compared to those that are sewered.

The MPCA sampled 40 wells to determine the concentrations of contaminants of emerging concern from November 2009 to June 2010. All of the sampled wells were monitoring or domestic wells with low flow rates. Most (37) represented ambient conditions and were from the MPCA's Ambient Groundwater Monitoring Network. The remaining three wells were part of networks maintained by the MPCA's Closed Landfill Program. The wells primarily represented contamination in the upper part of the sand and gravel aquifers. Seventy percent of the sampled wells were located near the water table in these aquifers and were less than 10 m deep. Approximately 20 percent of the wells tapped deeper parts of the sand and gravel aquifers and ranged from 12.2 to 34.1 m deep. One well tapped a buried sand and gravel aquifer in east-Central Minnesota. Approximately 10 percent of the sampled wells tapped the Prairie du Chien-Jordan aquifer. These were deepest wells sampled in the study and ranged from 33.2 to 44.2 m deep.

The effect of urban land use on the presence and distribution of EACs and other contaminants of emerging concern was determined by analyzing the data from a subset of 24 shallow wells (less than 10 m deep) located in residential and undeveloped areas. These wells represented three land use settings: 1) sewered residential, 2) residential areas relying on SSTS for wastewater treatment, and 3) undeveloped. Fifteen of the wells were located in sewered residential areas. Six of the wells were located in residential areas using SSTS. Three wells represented undeveloped areas and were located in forests in the northern part of the State. All sampled wells were located at least 50 feet away from a septic tank, which is the required isolation distance for water-supply wells installed in the State of Minnesota.

The extent of any contamination emanating from landfills was characterized by collecting data from three wells. These wells were located within the landfill's contaminant plume and were selected in consultation with hydrogeologists from the MPCA's Closed Landfill Program. All three landfills were unlined and located in the northwestern part of the TCMA. Two of the landfills primarily accepted municipal waste, and the other landfill primarily accepted demolition debris. None of the landfills were in operation at the time of sampling. All of them ceased accepting waste 15 to 27 years prior to sample collection.

Methods

Sampling

MPCA staff collected all of the water samples according to the standard United States Geological Survey (USGS) ultra-clean trace organics sampling procedures (USGS variously dated). At least three volumes of water were purged from the well and field measurements of temperature, specific conductance, pH, and dissolved oxygen were allowed to stabilize prior to withdrawing the water samples to ensure the samples represented fresh aquifer water. All water samples were collected from monitoring wells using a peristaltic or submersible pump outfitted with pre-cleaned Teflon tubing. Water samples were obtained from domestic wells prior to any treatment using an outside spigot outfitted with pre-cleaned Teflon tubing. All samples were filtered with a pre-cleaned 0.7-micron glass fiber filter into pre-cleaned amber glass bottles. All water samples were stored at four degrees Celsius until laboratory analysis. To minimize any sample contamination, the use of personal care items, such as insect repellents, colognes, perfumes, pharmaceuticals, caffeinated products, and tobacco was discouraged during sample collection and processing, and the water samples were not stored in proximity to these products.

MPCA staff also prepared all field blank samples submitted to the laboratories for this study. The staff prepared these samples in the field using water certified by the USGS to be free of all the chemicals listed in Tables 1-3. The field blank samples were in contact with all the equipment used to collect the environmental samples and subjected to the same sample processing and handling procedures.

Laboratory analytical

The laboratories analyzed the water samples by three analytical methods. A total of 92 contaminants of emerging concern were measured, including hormones, alkylphenol detergent degradates, plasticizers, fire retardants, pharmaceuticals, and personal care products (Tables 1-3). Some of these chemicals, such as bisphenol A, are known or suspected EACs. The USGS laboratories in Denver, Colorado performed all the laboratory analyses. The concentrations of 58 anthropogenic organic chemicals were determined using USGS method O-1433-01 (Zaugg et al. 2002) (Table 1). In this method, the chemicals were extracted using solid-phase extraction (SPE) and analyzed by capillary-column gas chromatography/mass spectrometry. The concentrations of 14 human prescription and nonprescription medications and selected degradates were determined using USGS method O-2080-08 (Furlong et al. 2008) (Table 2). This method included two antibiotics, sulfamethoxazole and trimethoprim. In this method, the laboratory staff extracted the chemicals by SPE and analyzed them using liquid chromatography/mass spectrometry with a polar reverse-phase octylsilane high-performance liquid chromatography column. An analytical method currently in development, USGS research method 2434, was used to determine the concentrations of 16 hormones plus four other chemicals (Table 3). These chemicals were analyzed by gas chromatography with tandem mass spectrometry following a derivatization process described in detail in by Erickson (2012).

Table 1. Anthropogenic organic chemicals analyzed in water samples, method reporting levels, and possible sources or uses of compounds.
[Concentrations are listed in micrograms per liter]

Compound	**Method reporting level**	**Possible sources or uses of compound**
Acetophenone	0.4	Fragrance in detergent, tobacco
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	0.028	Musk fragrance
3-*tert*-Butyl-4-hydroxyanisole (BHA)	8	Antioxidant, general preservative
Anthracene	0.028	Wood preservative, component of tar, diesel, crude oil
9,10-Anthraquinone	0.2	Used in manufacture of dye/textiles, seed treatment, bird repellant
Benzo[*a*]pyrene	0.1	Regulated polycyclic aromatic hydrocarbon, used in cancer research
Benzophenone	0.1	Fixative for perfumes and soaps
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)	0.1	Musk fragrance
5-Methyl-1H-benzotriazole	1	Antioxidant in antifreeze and deicers
1,4-Dichlorobenzene	0.040	Moth repellant, fumigate, deodorant
Bromoform	0.1	Wastewater ozination by-product, military explosives
Caffeine	0.1	Beverages, diuretic
Camphor	0.044	Flavor, odorant, ointments
Carbaryl	0.38	Insecticide, crop and garden uses
Carbazole	0.030	Insecticide, manufacture of dyes, explosives, lubricants
Chlorpyrifos	0.2	Insecticide, domestic pest and termite control
Cholesterol	2	Fecal indicator, plant sterol
Triethyl citrate (ethyl citrate)	0.4	Cosmetics, pharmaceuticals
Cotinine	0.038	Primary nicotine metabolite
3 *beta*-Coprostanol	2	Carnivore fecal indicator
para-Cresol	0.08-0.40	Wood preservative
Diazinon	0.2	Insecticide, nonagricultural uses, ants, flies
Fluoranthene	0.024	Component of coal tar and asphalt
Indole	0.1	Pesticide inert ingredient, fragrance in coffee

Table 1. Anthropogenic organic chemicals analyzed in water samples, method reporting levels, and possible sources or uses of compounds (continued).
[Concentrations are listed in micrograms per liter]

Compound	Method reporting level	Possible sources or uses of compound
3-Methyl-1H-indole (skatol)	0.036	Fragrance, stench in feces, coal tar
Isoborneol	0.2	Fragrance in perfumes, disinfectants
Isophorone	0.1	Solvent
Isopropylbenzene (cumene)	0.3	Manufacture of phenol/acetone, fuels, and paint thinner
Isoquinoline	0.046	Flavors and fragrances
d-Limonene	0.1	Fungicide, antmicrobial, antiviral, fragrance in aerosols
Menthol	0.3	Cigarettes, cough drops, liniment, mouthwash
Metalaxyl	0.1	Herbicide, fungicide, mildew, blight, pathogens, golf/turf
Methyl salicylate	0.044	Liniment, food, beverage, ultraviolet-absorbing lotion
Metolachlor	0.1	Herbicide, indicator of agricultural drainage
Naphthalene	0.040	Fumigant, moth repellent
2,6-Dimethylnaphthalene	0.1	Present in diesel fuel, kerosene
1-Methylnaphthalene	0.022	Gasoline, diesel fuel, crude oil
2-Methylnaphthalene	0.036	Gasoline, diesel fuel, crude oil
4-Cumylphenol	0.06	Nonionic detergent degradate
para-Nonylphenol (total)	2	Nonionic detergent degradate
4-Nonylphenol diethoxylate, sum of all isomers (NP2EO)	5	Nonionic detergent degradate
4-*n*-Octylphenol	0.16	Nonionic detergent degradate
4-*tert*-Octylphenol	0.14	Nonionic detergent degradate
4-*tert*-Octylphenol diethoxylate (OP2EO)	1	Nonionic detergent degradate
4-tert-octylphenol monoethoxylate (OP1EO)	1	Nonionic detergent degradate
Phenanthrene	0.032	Explosives, tar, diesel fuel, crude oil
Phenol	0.2	Disinfectant
Tributyl phosphate	0.2	Plasticizer, resin, wax, finish, roofing paper
Triphenyl phosphate	0.1	Plasticizer, resin, wax, finish, roofing paper
Tris(2-butoxyethyl) phosphate	0.8	Flame retardant
Tris(2-chloroethyl) phosphate	0.1	Plasticizer, flame retardant
Tris (dichloroisopropyl) phosphate	0.2	Flame retardant
Pyrene	0.042	Component of coal tar and asphalt
beta-Sitosterol	4	Plant sterol
beta-Stigmastanol	3	Plant sterol
N,N-Diethyl-*meta*-toluamide (DEET)	0.14	Mosquito repellent
Tetrachloroethylene	0.1	Solvent, degreaser, veterinary anthelminthic
Triclosan	0.20	Disinfectant, antimicrobial

Table 2. Prescription and non-prescription pharmaceuticals analyzed in water samples and method reporting limits.
[Concentrations are listed in micrograms per liter]

Compound	Method reporting level	Sources of use
1,7-dimethylxanthine	0.100	Caffeine degradate
Codeine	0.046	Analgesic
Caffeine	0.1	Stimulant
Thiabendazole	0.060	Fungicide, parasticide
Albuterol (Salbutamol)	0.080	Anti-asthmatic
Acetaminophen	0.120	Analgesic
Cotinine	0.038	Nicotine degradate
Dehydronifedipine	0.080	Nifedipine degradate; Nifedipine is a medication used to treat chest pain, hypertension, and other heart conditions (antihypertensive)
Carbamazepine	0.060	Anti-convulsant, ADHD
Trimethoprim	0.034	Antibiotic
Warfarin	0.080	Anticoagulant
Diphenhydramine	0.036	Antihistamine
Sulfamethoxazole	0.160	Veterinary and human antibiotic
Diltiazem	0.060	Medication used to treat angina, hypertension, and other heart conditions (antihypertensive)

Table 3. Hormones and other chemicals analyzed in water samples, class, and chemical source.
[ng/L, nanograms per liter]

Compound	Method reporting limit	Class	Sources or use
cis-Androsterone	0.8 ng/L	Natural androgen	Testosterone metabolite, used in deer repellent
4-Androsten-3,17-dione	0.8 ng/L	Natural androgen	Testosterone precursor, illicit steroid
Cholesterol	2000 ng/L	Natural sterol	Ubiquitous, produced by animals and plants
3-beta-Coprostenol	2000 ng/L	Natural sterol	Carnivore fecal indicator, useful sewage tracer
trans-Diethylstilbestrol	0.8 ng/L	Synthetic estrogen	Pharmaceutical
Epitestosterone	4 ng/L	Natural androgen	Human androgen
Equilenin	2 ng/L	Natural estrogen	Equine estrogen, hormone replacement therapy
Equilin	4 ng/L	Natural estrogen	Equine estrogen, hormone replacement therapy
17-*alpha*-Estradiol	0.8 ng/L	Natural estrogen	Low occurrence in humans, common in other species
17-*beta*-Estradiol	0.8 ng/L	Natural estrogen	Principal estrogen in humans, strong estrogen
Estriol	2 ng/L	Natural estrogen	Metabolite of 17-*beta*-Estradiol
Estrone	0.8 ng/L	Natural estrogen	Metabolite of 17-*beta*-Estradiol
17-*alpha*-Ethynylestradiol	0.8 ng/L	Synthetic estrogen	Used in oral contraceptives, very strong estrogen
11-Ketotestosterone	2 ng/L	Natural androgen	Very strong androgen
Mestranol	0.8 ng/L	Synthetic estrogen	Used in oral contraceptives, metabolized to ethynylestradiol prior to excretion

Table 3. Hormones and other chemicals analyzed in water samples, class, and chemical source (continued)
[ng/L, nanograms per liter]

Compound	Method reporting limit	Class	Sources or use
Norethindrone (19-Noresthisterone)	0.8 ng/L	Synthetic progestin	Used in oral contraceptives
Progesterone	8 ng/L	Natural progestin	Principal human progestational hormone
Dihydrotestosterone	4 ng/L	Natural androgen	Testosterone metabolite, very strong androgen
Testosterone	0.8 ng/L	Natural androgen	Principal human androgen, very strong androgen
Bisphenol A	100 ng/L		Plasticizer

Reporting of qualitatively identified compounds

The laboratories reported concentrations below the method reporting limit (MRL) for all of the analytical methods. The laboratory reported concentrations below the MRL because the analytical methods were classified by the USGS as “information rich” (Childress et al. 1999). The qualitative chemical identification in “information rich” methods was done using the relative retention time and the mass spectral fit. Chemical concentrations below the MRL or the lowest calibration standard were qualified to indicate it was estimated. Chemical concentrations also were qualified if there was a matrix interference or the analysis did not meet the quality-assurance criteria. Qualitatively identified chemicals whose concentrations were too low to quantify were qualified with a “M” code.

Quality assurance and quality control

An assessment of the analytical method performance and the amount of any sample contamination was essential to interpret the data collected in this study. The performance of all three analytical methods was affected by interferents in the sample matrix. These interferences often resulted from the coextraction of non-target compounds during sample preparation and analysis which caused a suppressed or enhanced response of the some of the analyzed chemicals. These matrix effects were described in detail by Furlong et al. (2008). The determination of the amount of any sample contamination also was critical in this study since EACs and other contaminants of emerging concern commonly are used by field and laboratory staff. This combined with the typically low concentrations measured in the environment (Barnes et al. 2008; Kolpin et al. 2002) makes the samples very prone to contamination.

The performance of each analytical method was measured using surrogate compound and matrix spike sample results. Surrogate compounds normally are not found in the environment but have similar physical and chemical properties as the analyzed chemicals. Surrogate compound recoveries provided information on the overall method performance. A matrix spike sample is a groundwater sample to which the target analytes were added. Matrix spike sample results, combined with those from the corresponding environmental sample, quantified any loss or gain of analytes due to the water-matrix characteristics. Two matrix spike samples were submitted for laboratory analysis. One of the matrix spike samples was prepared using ambient groundwater, and the other was prepared using groundwater collected downgradient of a closed landfill. The laboratories, unfortunately, did not spike all the samples as requested. This resulted in only one matrix spike sample associated with USGS method O-1433-01 (Table 2), and no matrix spike samples associated with USGS research method 2434 (Table 3).

Two types of quality-control samples were used to evaluate sample contamination. Laboratory blank samples were used to evaluate the contamination resulting from laboratory sample handling, extraction, and analysis. A limited number of field blank samples (four) also were collected to evaluate any contamination resulting from sample collection, processing, and analysis in both the field and laboratory.

Analytical method performance

The surrogate compound data indicated the analytical methods generally performed well. A 60- to 130-percent surrogate recovery was considered acceptable. The average surrogate recovery for all chemicals was 70 percent and ranged from approximately 40 to 90 percent for each individual chemical (Table 4). The large relative standard deviation associated with the carbamazepine-d_{10} and ethyl nicotinate-d_4 recoveries was due to low surrogate recoveries from groundwater samples directly affected by landfill-leachate plumes.

Table 4 shows the results from two sets of surrogate compounds that were analyzed as part of USGS research method 2434. Thirteen surrogate compounds were analyzed with the two groundwater samples collected in November 2009. Six of these surrogate compounds were determined to be susceptible to deuterium loss over the course of this study (Erickson 2012). The deuterium loss resulted in a positive bias in the concentrations of some of the chemicals analyzed. None of the chemicals detected in this study, however, were affected. To remedy this problem, the surrogate compounds susceptible to deuterium loss were replaced with new compounds. Five of the original surrogate compounds were retained, and five new surrogate compounds were added. The replacement compounds contained either carbon-13 or were non-direct analogs of the chemicals that had deuterium in positions not susceptible to deuterium loss.

Table 4. Summary of the Surrogate Compound Recoveries
[a, surrogate compound only used for USGS research method 2434 samples collected in 2009; b, surrogate compound only used for USGS research method 2434 samples collected in 2010]

Compound	Analytical Method	Mean % Recovery	% Relative Standard Deviation
Caffeine-^{13}c	USGS O-1433-01	85.9	10.7
Decafluorobiphenyl	USGS O-1433-01	43.7	20.2
Fluoranthene-d_{10}	USGS O-1433-01	84.6	12.0
Carbamazepine-d_{10}	USGS O-2080-08	61.1	46.9
Ethyl nicotinate-d_4	USGS O-2080-08	74.8	27.0
16-Epiestriol-d_2[b]	USGS 2434	52.4	50.4
Ethynylestradiol-d_4	USGS 2434	83.5	10.5
17-*beta*-Estradiol-$^{13}c_6$[b]	USGS 2434	85.7	12.7
17-*beta*-Estradiol-d_4[a]	USGS 2434	77.3	2.3
4-Androstenedione-d_7[a]	USGS 2434	58.6	8.8
Bisphenol A-d_{16}	USGS 2434	77.9	26.7
Cholesterol-d_7	USGS 2434	72.1	17.9
Dihydrotestosterone-d_4[a]	USGS 2434	85.0	11.2
Estriol-d_3[a]	USGS 2434	60.6	5.3
Estrone-$^{13}c_6$[b]	USGS 2434	83.4	20.7
Estrone-d_4	USGS 2434	58.6	4.1
Medroxyprogesterone-d_3[b]	USGS 2434	67.5	32.4
Mestranol-d_4	USGS 2434	81.2	9.8
Nandrolone-d_3[b]	USGS 2434	73.5	27.5

Table 4. Summary of the Surrogate Compound Recoveries (continued)
[a, surrogate compound only used for USGS research method 2434 samples collected in 2009; b, surrogate compound only used for USGS research method 2434 samples collected in 2010]

Compound	Analytical Method	Mean % Recovery	% Relative Standard Deviation
Norethindrone-d_6[a]	USGS 2434	65.9	10.7
Progesterone-d_9[a]	USGS 2434	42.9	8.6
Testosterone-d_5[a]	USGS 2434	69.2	7.4
Diethylstilbestrol-d_8	USGS 2434	73.4	14.7

The matrix spike sample results suggested that USGS methods O-1433-01 and O-2080-08 generally performed well for an ambient groundwater matrix. The average matrix spike percent recovery was 102 percent for the sample prepared using ambient groundwater. The recoveries of only 13 of the 58 chemicals in USGS method O-1433-01, however, were in the acceptable range (Appendix A). The recoveries of *beta*-sitosterol, cholesterol, menthol, tris(2-butoxyethyl) phosphate, tris(2-chloroethyl phosphate), and tris (dichloroisopropyl phosphate) were high and ranged from approximately 170-650 percent. These results suggested the measured concentrations of these chemicals were exaggerated. Numerous chemicals had low recoveries. Most of these were detergent metabolites, polycyclic aromatic hydrocarbons, and aromatic heterocyclic compounds.

The surrogate and matrix spike recoveries suggested USGS method O-2080-08 did not perform well for groundwater affected by landfill leachate. Both the surrogate and matrix spike recoveries were substantially outside of the acceptable range for this matrix. The average recoveries of the surrogate compounds carbamazepine-d_{10} and ethyl nicotine-d_4 were 7.6 and 33.4 percent. The average matrix spike recovery was 12.4 percent, and the recoveries for each individual compound in the matrix spike sample ranged from less than zero to 39.4 percent (Appendix B). The less than zero recovery for acetaminophen in Appendix B resulted from measuring a lower concentration in the matrix spike sample than in the associated environmental sample. These low recoveries suggested USGS method O-2080-08 may not be able to detect pharmaceuticals and personal care products at low concentrations in groundwater affected by landfill leachate.

Sample contamination

The laboratory blank samples generally showed small amounts of contamination. The number of laboratory blank samples collected varied with the analytical method. There were 18 laboratory blank samples associated with the samples analyzed using USGS method O-1433-01, and there were 19 laboratory blank samples associated with USGS method O-2080-08. Thirty-seven chemicals were detected in the laboratory blank samples. The measured concentrations generally were at least an order of magnitude lower than the method reporting limit (MRL). A small number of chemicals had concentrations that were within an order of magnitude of the MRL. These chemicals were camphor (0.0057 μg/L), *para*-cresol (0.012 μg/L), all isomers of *para*-nonylphenol (0.1 μg/L), cholesterol (0.3 μg/L), cotinine (0.01 μg/L), *d*-limonene (0.012 μg/L), methyl salicylate (0.0072 μg/L), triclosan (0.034 μg/L), and tris(2-butoxyethyl) phosphate (0.36 μg/L).

Eighteen chemicals were detected in four field blank samples. Most measured concentrations were within the range of those in the laboratory blank samples (Table 5). Four chemicals were detected at concentrations substantially greater than the MRL and the laboratory blank samples: *N,N*-diethyl-*meta*-toluamide, acetophenone, naphthalene, and phenol.

Table 5. Contaminants of emerging concern detected in laboratory and field blank samples [μg/L, microgram per liter; M, constituent presence verified but not quantified; ND, not detected].

Constituent	Reporting Limit	Range of concentrations detected in laboratory blank samples	Range of concentrations detected in field blank samples	Percent detection in field blank samples
Camphor	0.044 μg/L	0.0057 μg/L	M	25%
Carbazole	0.2 μg/L	ND	M	25%
N,N-Diethyl-*meta*-toluamide (DEET)	0.1 μg/L	ND	0.5-1.8 μg/L	50%
para-Cresol	0.08-0.40 μg/L	0.012 μg/L	E0.04-E0.06 μg/L	50%
1-Methylnaphthalene	0.022 μg/L	0.0014 μg/L	M	50%
2,6-Dimethylnaphthalene	0.1 μg/L	ND	M	
2-Methylnaphthalene	0.036 μg/L	0.0019 μg/L	M	50%
3-*beta*-Coprostanol	2 μg/L	0.15 μg/L	ND	0%
para-nonylphenol (total)	0.16 μg/L	0.1 μg/L	ND	0%
4-Nonylphenol diethoxylate, sum of all isomers (NP2EO)	5 μg/L	0.62 μg/L	ND	0%
4-*tert*-Octylphenol diethoxylate (OP2EO)	1 μg/L	0.04 μg/L	ND	0%
4-*tert*-Octylphenol monoethoxylate (OP1EO)	1 μg/L	0.07 μg/L	ND	0%
4-*tert*-Octylphenol	0.14 μg/L	0.004 μg/L	ND	0%
9,10-Anthraquinone	0.4 μg/L	0.029 μg/L	M	25%
Acetophenone	0.4 μg/L	0.09 μg/L	0.8 μg/L	25%
Anthracene	0.028 μg/L	ND	M	25%
Benzophenone	0.1 μg/L	0.009 μg/L	ND	0%
beta-Sitosterol	4 μg/L	0.4 μg/L	ND	0%
beta-Stigmastanol	3 μg/L	0.13 μg/L	ND	0%
Caffeine	0.1 μg/L	0.007 μg/L	ND	0%
Cholesterol	2 μg/L	0.3 μg/L	ND	0%
Cotinine	0.038 μg/L	0.01 μg/L	ND	0%
d-Limonene	0.1 μg/L	0.012 μg/L	ND	0%
Fluoranthene	0.024 μg/L	0.0009 μg/L	ND	0%
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	0.1 μg/L	0.003 μg/L	ND	0%
Isopropylbenzene (cumene)	0.3 μg/L	0.002 μg/L	ND	0%
Isophorone	0.1 μg/L	ND	M	25%
Isoquinoline	0.046 ug/L	ND	0.1 μg/L	25%
Menthol	0.3 μg/L	ND	M	25%

Table 5. Contaminants of emerging concern detected in laboratory and field blank samples (continued)
[µg/L, microgram per liter; M, constituent presence verified but not quantified; ND, not detected].

Constituent	Reporting Limit	Range of concentrations detected in laboratory blank samples	Range of concentrations detected in field blank samples	Percent detection in field blank samples
Methyl salicylate	0.044 µg/L	0.0072 µg/L	M	25%
Naphthalene	0.04 µg/L	0.0037 µg/L	0.1-0.2 µg/L	50%
Phenanthrene	0.032 µg/L	0.0014 µg/L	M	50%
Phenol	0.2 µg/L	0.054 µg/L	0.7-1.1 µg/L	50%
Pyrene	0.042 µg/L	0.0012 µg/L	ND	0%
Triclosan	0.20 µg/L	0.034 µg/L	ND	0%
Triethyl citrate (ethyl citrate)	0.40 µg/L	0.002 µg/L	ND	0%
Triphenyl phosphate	0.10 µg/L	0.003 µg/L	ND	0%
Tris(2-butoxyethyl) phosphate	0.8 µg/L	0.36 µg/L	ND	0%
Tris (2-chloroethyl phosphate)	0.1 µg/L	0.016 µg/L	E0.1 µg/L	25%
1,7-dimethylxanthine	0.10 µg/L	0.02 µg/L	ND	0%
Acetaminophen	0.12 µg/L	0.087 µg/L	ND	0%
Caffeine	0.10 µg/L	0.021 µg/L	ND	0%
Carbamazepine	0.06 µg/L	0.0009 µg/L	ND	0%
Dehydronifedipine	0.08 µg/L	0.0005 µg/L	ND	0%

Data analysis

The data were censored prior to statistical analysis to minimize the likelihood that any detections were the artifact of sample contamination. This data censoring was especially important since the laboratory reported concentrations below the MRL. In this study, environmental concentrations within 10 times of the highest value measured in the laboratory blank samples (Table 5) were reported as less than the MRL. Environmental concentrations similar to those in field-blank samples also were considered to be an artifact of sample contamination; these values were censored as less than the MRL. The environmental results were not adjusted for any contamination measured in the laboratory or field-blank samples.

The data for the USGS methods O-1433-01 and O-2080-08 (Tables 1-2) were not adjusted for surrogate or matrix spike recoveries. The method used to analyze hormone concentrations (Table 4) used an isotope-dilution procedure that automatically accounted for procedural losses in analysis.

Results

Detections

Twenty of the 92 EACs and other contaminants of emerging concern were detected in about one-third of the 40 sampled wells (Figures 2, 3). The detected chemicals represented a wide variety of uses or sources, including plastics manufacturing, prescription and non-prescription medications, fire retardants, insect repellants, and nonionic detergent degradates. The most-frequently detected chemicals were the fire retardant tris (dichloroisopropyl) phosphate (17.5 percent), the antibiotic sulfamethoxazole (10 percent), and the plasticizers biphenol A (7.5 percent) and tributyl phosphate (7.5 percent). The median number of chemicals detected in a single well was one, and the maximum number of chemicals detected in any one well was 10.

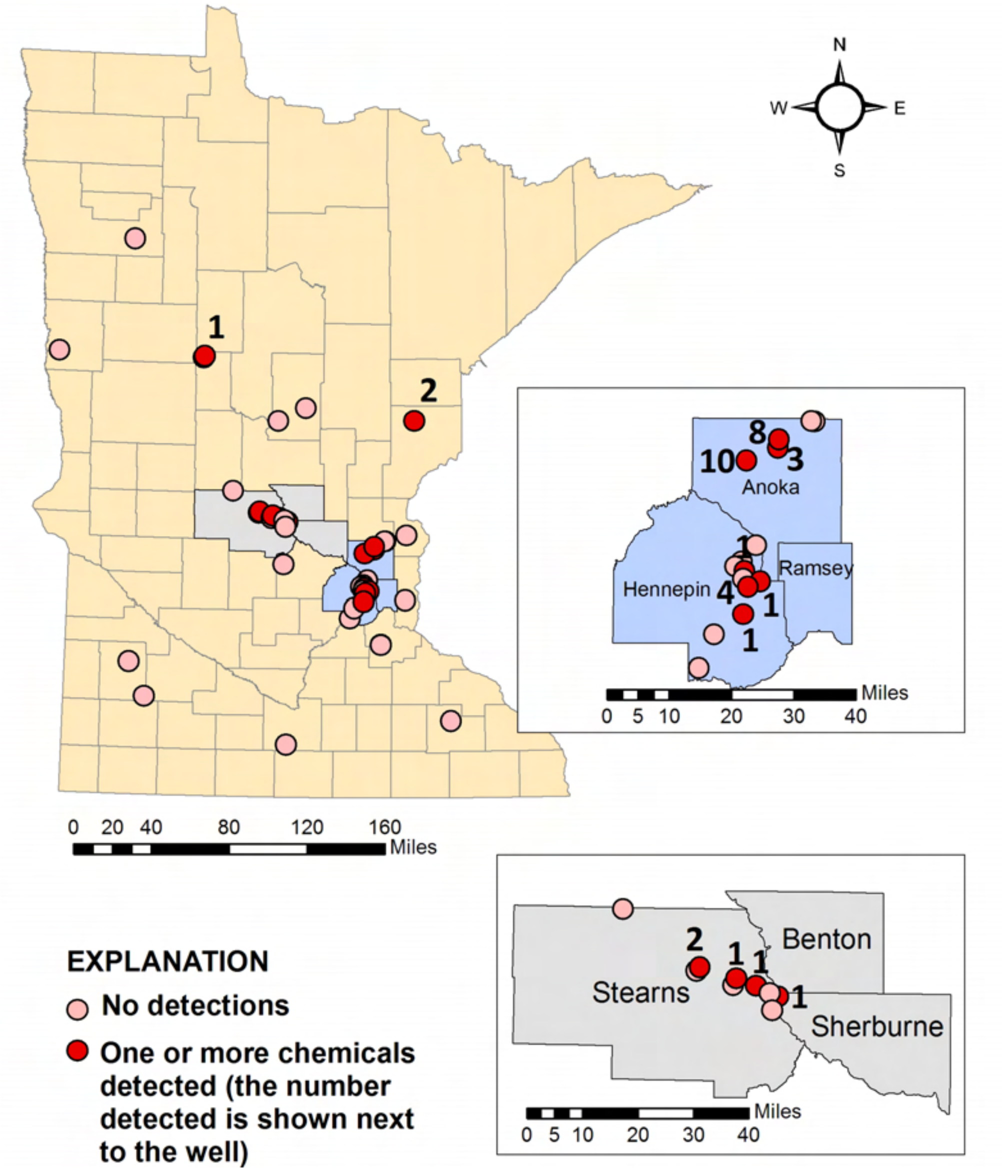

Figure 2. Wells with detections of endocrine active compounds and other contaminants of emerging concern in Minnesota's groundwater, 2009-2010. Wells located in the vicinity of Anoka, Benton, Hennepin, Ramsey,Sherburne, and Stearns Counties are shown on the inset maps.

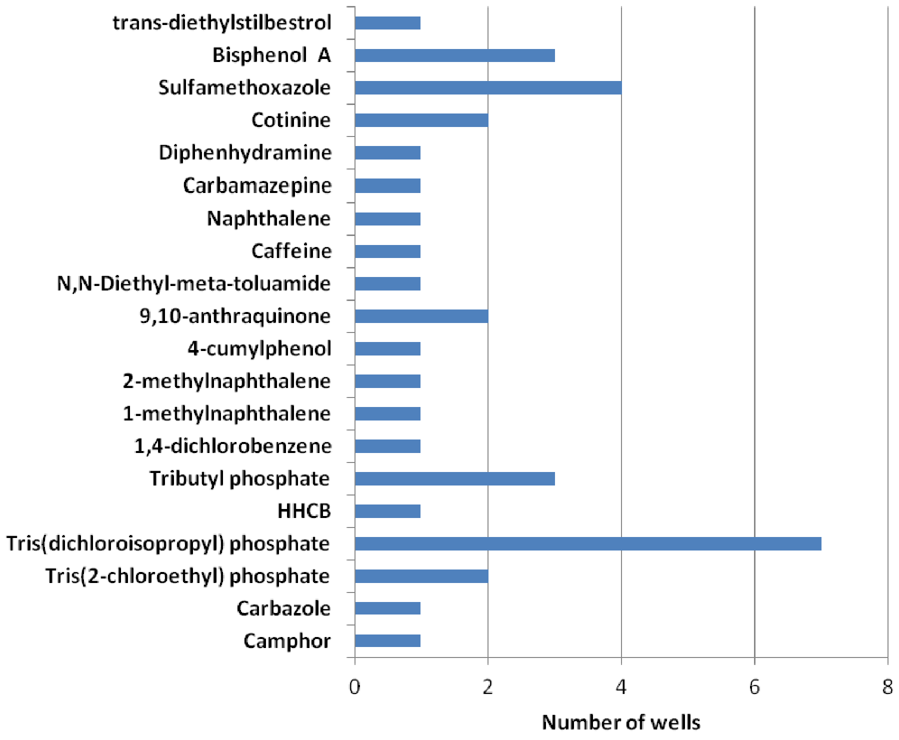

Figure 3. Detection frequency of contaminants of emerging concern in groundwater in Minnesota, November 2009- June 2010 [HHCB, Hexahydrohexamethylcyclopentabenzopyran].

Most detections of contaminants of emerging concern were from wells tapping the surficial sand and gravel aquifers. Twelve of the 13 wells with detections were located in these aquifers, and about 85 percent of the detections (32) were from wells located near the water table.

The available data suggested contaminants of emerging concern were detected more frequently in the vicinity of landfills compared to the other assessed settings. Contaminants of emerging concern were detected in two of the three wells tapping groundwater affected by landfill leachate. The median number of chemicals detected in wells installed to monitor contamination from the landfills was eight. In contrast, only one to four contaminants of emerging concern were detected in water from the other sampled wells.

Contaminants of emerging concern were detected more frequently in wells located within residential areas using SSTS compared to sewered residential and undeveloped areas (Figure 4). These chemicals were detected fifty percent of the wells in residential areas using SSTS and in about 30 percent of the wells in sewered residential and undeveloped areas. Several researchers (Conn et al. 2006; Rudel et al. 1998; Swartz et al. 2006) detected contaminants of emerging concern in the water discharged from and downgradient from SSTS; this is a likely source of these chemicals to the groundwater underlying unsewered residential areas. Leaking sanitary sewer lines are one source that may have contributed contaminants of emerging concern to the groundwater underlying sewered residential areas.

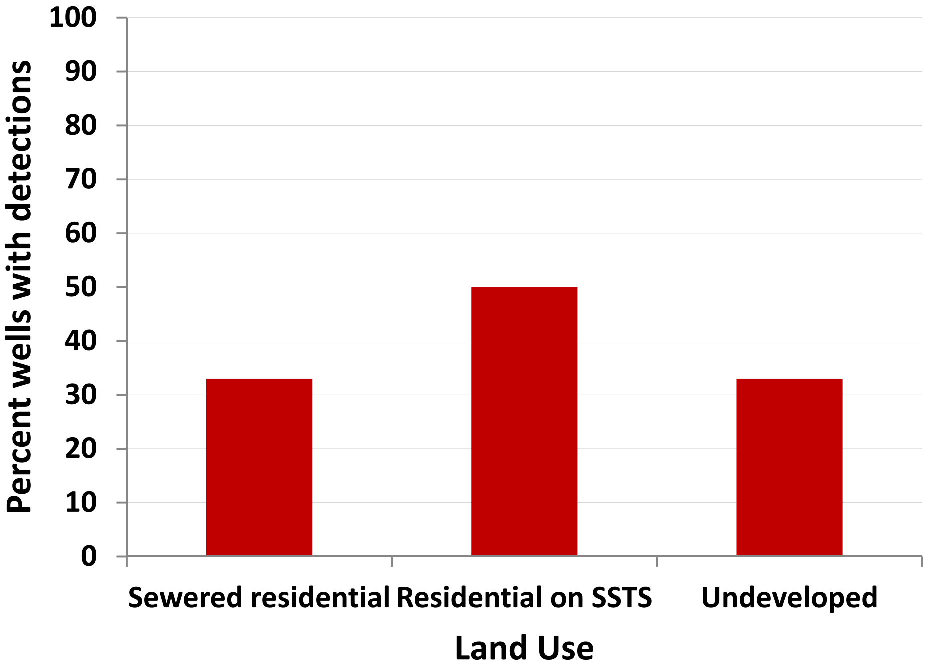

Figure 4. Percent of wells with detections of contaminants of emerging concern by land use setting.

Three of the 20 detected chemicals were EACs. The detected EACs were: 1) bisphenol A, 2) *trans*-diethylstilbestrol, and 3) 4-cumylphenol. Bisphenol A is used to manufacture polycarbonate plastics and epoxy resins. Polycarbonate plastics are used in food and drink packaging, compact discs, and medical devices. Epoxy resins commonly are used to coat metal products such as food cans, bottle tops, and water-supply pipes. Trans-diethylstilbestrol is a synthetic non-steroidal estrogen used to treat cold sores. 4-cumylphenol is a breakdown product of alkylphenol detergents.

EACs were detected in only eight percent of the sampled wells. Two of the wells with EAC detections tapped a landfill leachate plume. The other was a shallow well (9.4 m deep) that provided the water supply to a residence. Bisphenol A was the only EAC detected in this well. A mixture of bisphenol A, trans-diethylstilbestrol, and 4-cumylphenol was detected in the water from one of the wells located downgradient from a landfill.

Concentrations

Most contaminants of emerging concern were measured at low concentrations. Over 80 percent of the detected chemicals were measured at concentrations of less than one microgram per liter (µg/L), and approximately 50 percent of the detected chemical concentrations were measured at or below the MRL.

No concentrations exceeded any applicable health guidance values established by the Minnesota Department of Health. Health guidance values were available for approximately 15 percent of the chemicals analyzed (Table 6) and included health-risk limits (HRLs) and health-based-values (HBVs). HRLs and HBVs both are the concentration of a chemical in drinking water that poses little or no threat to humans; however, HRLs are promulgated by the State of Minnesota through a formal rulemaking process whereas HBVs are not. HBVs are developed when there is a need for health-based guidance for chemicals that do not have a HRL. HBVs also may be developed to update an existing HRL if there is new scientific information for the chemical or to apply new risk assessment methods. The method for calculating health-based guidance was revised in 2008 (Minnesota Department of Health 2008). The new method determined guidance values for several durations of exposure; such as acute, subchronic, and chronic, and took sensitive or high-exposed populations into account, such as infants and children.

Table 6. Human health-based guidance values from exposure to EACs and other contaminants of emerging concern in groundwater developed by the State of Minnesota and maximum concentrations measured in the groundwater, 2009-2010.
[µg/L, micrograms per liter; ng/L, nanograms per liter; ND, not determined; NA, not applicable; HBV, health- based value; HRL, health-risk limit; E, estimated concentration; M, presence verified but not quantified]

Constituent	Exposure Duration	Health guidance value	Maximum concentration in groundwater measured in this study	Type of health-based guidance	Publication year
Acetaminophen	Acute	200 µg/L	<0.12 µg/L	HBV	2011
	Short-term	200 µg/L			
	Subchronic	200 µg/L			
	Chronic	200 µg/L			
	Cancer	NA			
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	Acute	ND	<0.028 µg/L	HBV	2011
	Short-term	200 µg/L			
	Subchronic	40 µg/L			
	Chronic	20 µg/L			
	Cancer	NA			
Anthracene	Chronic	2000 µg/L	<0.028 µg/L	HRL	1993/1994
9,10-Anthraquinone	ND	ND	E0.1 µg/L	NA	NA
Bisphenol A[1]	Chronic	300 µg/L	4.41 µg/L	HBV	1998
Caffeine	ND	ND	0.1 µg/L	NA	NA
Camphor	ND	ND	0.9 µg/L	NA	NA
Carbazole	Cancer	20 µg/L	2.9 µg/L	HBV	2001
Carbamazepine	Acute Short-term Subchronic Chronic Cancer	40 µg/L 40 µg/L 40 µg/L 40 µg/L NA	0.092 µg/L	HBV	2011
Cotinine	ND	ND	E0.03 µg/L	NA	NA
4-Cumylphenol	ND	ND	M	NA	NA
1,4-Dichlorobenzene	ND	ND	0.1 µg/L	NA	NA
Diphenhydramine	ND	ND	E0.003 µg/L	NA	NA
Fluoranthene	Chronic	300 µg/L	<0.024 µg/L	HRL	1993
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	ND	ND	0.1 µg/L	NA	NA
Isophorone	Chronic	100 µg/L	<0.1 µg/L	HRL	1993
d-Limonene	Chronic	17,500 µg/L	<0.1 µg/L	HBV	1997
1-Methylnaphthalene	ND	ND	0.1 µg/L	NA	NA
2-Methylnaphthalene	ND	ND	0.1 µg/L	NA	NA
Naphthalene	Chronic	300 µg/L	0.8 µg/L	HRL	1994
	Acute	70 µg/L		HBV	2011
	Short-term	70 µg/L			
	Subchronic	70 µg/L			
	Chronic	70 µg/L			
	Cancer	NA			
Phenol	Chronic	4,000 µg/L	<0.2 µg/L	HRL	1993
Tributyl phosphate	ND	ND	E1 µg/L	NA	NA

Table 6. Human health-based guidance values from exposure to EACs and other contaminants of emerging concern in groundwater developed by the State of Minnesota and maximum concentrations measured in the groundwater, 2009-2010 (continued)

[µg/L, micrograms per liter; ng/L, nanograms per liter; ND, not determined; NA, not applicable; HBV, health based value; HRL, health-risk limit; E, estimated concentration; M, presence verified but not quantified]

Constituent	Exposure Duration	Health guidance value	Maximum concentration in groundwater measured in this study	Type of health-based guidance	Publication year
Tris(2-chloroethyl) phosphate	Acute	ND	1.4 µg/L	HBV	2011
	Short-term	300 µg/L			
	Subchronic	200 µg/L			
	Chronic	200 µg/L			
	Cancer	5 µg/L			
Tris(dichloroisopropyl) phosphate	ND	ND	0.3 µg/L	NA	NA
Pyrene	Chronic	200 µg/L	<0.042 µg/L	HRL	1993
Sulfamethoxazole	ND	ND	E0.11 µg/L	NA	NA
N,*N*-diethyl-*meta*-toluamide (DEET)	Acute	ND	E5.4 µg/L	HBV	2011
	Short-term	200 µg/L			
	Subchronic	200 µg/L			
	Chronic	200 µg/L			
	Cancer	NA			
trans-Diethylstilbestrol	ND	ND	0.49 ng/L	NA	NA
Triclosan	Acute	200 µg/L	<0.20 µg/L	HBV	2010
	Short-term	50 µg/L			
	Subchronic	50 µg/L			
	Chronic	50 µg/L			
	Cancer	NA			

[1] The Minnesota Department of Health is currently (2012) reevaluating this HBV.

The most frequently detected chemicals, tris (dichloroisopropyl) phosphate and sulfamethoxazole, were measured at low concentrations in the groundwater. The concentrations of the fire retardant tris (dichloroisopropyl) phosphate were measured at concentrations of 0.3 µg/L or lower, and the high matrix spike recoveries of this chemical suggested these low concentrations may have been exaggerated. All measured concentrations of the antibiotic sulfamethoxazole were estimated at 0.11 µg/L or lower.

N,N-diethyl-*meta*-toluamide, bisphenol A, carbazole, tris(2-chloroethyl) phosphate, and tributyl phosphate were measured at the highest concentrations (Table 6). *N,N*-diethyl-*meta*-toluamide and carbazole were detected in one well. Tris(2-chloroethyl) phosphate was detected in two wells. Bisphenol A and tributyl phosphate were detected in three wells. Most of the high concentrations were associated with well water that was affected by landfill leachate.

The highest total sum of concentrations was from two wells affected by landfill-leachate plumes. The total sum of concentrations in these two wells was 14.31 and 4.79 ug/L, respectively. In the other wells with detections, the number of chemicals detected and the total sum of concentrations was substantially lower compared to these. The number of chemicals detected in the other wells ranged from one to four, and the total sum of concentrations ranged from near zero to 2.92 ug/L.

Discussion

The EACs and other contaminants of emerging concern were detected less frequently in Minnesota's groundwater compared to the State's surface water resources. The fewer detections in the groundwater were consistent with results from national-scale groundwater monitoring (Barnes et al. 2008). Twenty chemicals were detected in Minnesota's groundwater from November 2009 to June 2010. In contrast, over twice as many chemicals (56) were detected in stream samples collected during a Statewide reconnaissance of contaminants of emerging concern (Lee et al. 2004). Similarly, EACs and other contaminants of emerging concern were detected at about 30 percent of the wells sampled in this study but were detected in most of the assessed streams (Lee et al. 2004). EACs and other contaminants of emerging concern also were detected less frequently in the groundwater compared to streams located in urban areas in Minnesota. Lee et al. (2004) sampled two streams located within the TCMA. EACs and other contaminants of emerging concern were detected in all stream sampling events, and the median number of detections was 6.5. In contrast, the median number of detections in this groundwater investigation was one.

The physical properties and/or the degradation potential of the chemicals likely resulted in the differences among the detection frequencies between this study of Minnesota's groundwater and the previous Statewide reconnaissance (Lee et al. 2004). Some chemicals frequently detected in the State's surface waters are not very soluble in water. The octanol-water partition coefficient (K_{ow}) is a ratio representing the solubility of a chemical in octanol (a non-polar solvent) to its solubility in water. A chemical with a high K_{ow} has a strong tendency to sorb to soil. The logarithm of the K_{ow} values of cholesterol, *beta*-sitosterol, and acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), which were frequently detected in the State's surface waters, ranged from 6.4-9.7. In contrast, the logarithm of the K_{ow} values of the constituents detected in Minnesota's groundwater were substantially lower than these values, ranging from approximately 1.2-3.8. These values suggested that cholesterol, *beta*-sitosterol, and AHTN have a high potential to sorb to soil or the aquifer matrix, and the transport of these chemicals may be retarded in the groundwater. Some EACs and other contaminants of emerging concern detected in the State's surface waters, such as caffeine or acetaminophen, likely rapidly degrade (Snyder et al. 2004). This may result in the quick attenuation of these chemicals in the groundwater.

The types of EACs and other contaminants of emerging concern most frequently detected in Minnesota's groundwater varied from those most frequently detected in the State's surface water resources and a national reconnaissance of groundwater quality (Barnes et al. 2008) and untreated groundwater used for human consumption (Focazio et al. 2008). A survey of the State's surface water resources from 2000-02 (Lee et al. 2004) determined the most-frequently detected contaminants of emerging concern were caffeine, cholesterol, *N,N*-diethyl-*meta*-toluamide, *beta*-sitosterol, AHTN, and acetaminophen. A national reconnaissance of the groundwater (Barnes et al. 2008) determined the most-frequently detected chemicals were *N,N*-diethyl-*meta*-toluamide, bisphenol A, tris(2-chloroethyl) phosphate, sulfamethoxazole, and 4-octylphenol monoethoxylate. A national reconnaissance of untreated groundwater used as a drinking water source (Focazio et al. 2008) determined the most frequently-detected chemicals were carbamazepine, bisphenol A, 1,7-dimethylxanthine, and tris(2-chlorethyl) phosphate.

Differences in the design of this study compared to the national reconnaissance of the groundwater (Barnes et al. 2008) and untreated groundwater used as a drinking water source (Focazio et al. 2008) may have influenced the detection frequencies of the EACs and other contaminants of emerging concern. Barnes et al. (2008) targeted wells near known or suspected contaminant sources, and about two-thirds of the sampled wells were located in agricultural areas. In contrast, most of the wells sampled in this study were located in urban areas. Both national reconnaissance studies sampled wells that generally were deeper compared to those in this study. Barnes et al. (2008) and Focazio et al.

(2008) sampled wells with median depths of 19.2 m and 51 m, respectively. In contrast, the wells sampled in this study generally were substantially shallower, with a median depth of 8 m.

The results from this study underscore the importance of landfills as a potential source of EACs and other contaminants of emerging concern to the groundwater. Similar to a previous assessment of these chemicals in Minnesota's groundwater (Lee et al. 2004) and elsewhere (Barnes et al. 2004; Holm et al. 1995), the greatest number of EAC and other contaminants of emerging concern detections were in groundwater downgradient from landfills. The high and frequent detections in the groundwater downgradient from the closed landfills, which did not accept any new waste for at least 15 years prior to sampling, also indicated some EACs and other contaminants of emerging concern may persist for decades in the groundwater system under the appropriate conditions. This result also suggests the State's efforts to properly close, monitor, and maintain landfills likely are important factors in minimizing EAC and other contaminants of emerging concern from migrating to other parts of the aquifers.

The results from this study likely provided a conservative estimate of the number of EACs and other contaminants of emerging concern detected in groundwater affected by landfill leachate. The low matrix spike and surrogate recoveries suggested the analytical methods may not have been able to detect pharmaceuticals and personal care products at low concentrations in groundwater affected by landfill leachate.

Data limitations

This study did not describe conditions throughout the sand and gravel and Prairie du Chien aquifers and cannot be extrapolated to all of Minnesota's principal aquifers. This study purposely sampled wells affected by boron and nitrate contamination. These results likely do not represent conditions throughout all of Minnesota's sand and gravel aquifers since water-quality conditions in these aquifers are highly variable over short distances and change with depth (Warner and Arnold 2010; O'Dell 2007) and also vary with land use (Fong 2000). The sensitivity of the Prairie du Chien-Jordan aquifer to contamination largely varies with the permeability of the geologic materials overlying the aquifer. The aquifer has a low sensitivity to contamination in areas where it is covered by shale (Berg 2003). In contrast, the aquifer has a high sensitivity to contamination in areas where: 1) there are little to no glacial sediments overlying the aquifer; and 2) the shale is absent or eroded and the aquifer is overlain by high permeability deposits such as glacial outwash.

Further data collection will refine the assessment of the effects of land use on the presence and distribution of EACs and other contaminants of emerging concern in the groundwater. A limited number of wells in residential areas using SSTS were available for sampling from November 2009 to June 2010. The MPCA's Ambient Groundwater Monitoring Network was enhanced after June 2010 to provide a better characterization of the effects of land use on groundwater quality. Additional wells in residential areas using SSTS were installed for this monitoring network enhancement during the course of this study. Future water samples from these wells likely will be analyzed for EACs and other contaminants of emerging concern and will refine this assessment. This study did not monitor some settings susceptible to contamination from EACs and other contaminants of emerging concern, such as feedlots (Meyer et al. 2000) or agricultural lands amended with biosolids from wastewater treatment facilities (Kinny et al. 2006).

A better understanding of the amount of contamination in the water samples is essential to assess the occurrence of EACs and other contaminants of emerging concern in the groundwater since these chemicals frequently were detected at concentrations at or below the MRL. A limited number of field blank samples (4) were collected from November 2009 to June 2010 to determine whether the detected concentrations were an artifact of contamination. The collection of additional field blank samples during subsequent sampling events would provide a better assessment of the magnitude of contamination in the data and may result in a refined assessment of the occurrence of these chemicals in Minnesota's groundwater.

Summary and Conclusions

This study suggested EACs and other contaminants of emerging concern were present at low concentrations in the ambient groundwater underlying urban areas in Minnesota that may be affected by wastewater contamination. Over 80 percent of the detected chemicals were measured at concentrations of less than one microgram per liter (μg/L). No concentrations exceeded any applicable health guidance values established by the Minnesota Department of Health. The most-frequently detected chemicals were the fire retardant tris (dichloroisopropyl) phosphate, the antibiotic sulfamethoxazole, and the plasticizers bisphenol A and tributyl phosphate, which were detected in approximately 20 percent or less of the sampled wells.

EACs were detected in three of the sampled wells. The detected EACs were bisphenol A, trans-diethylstilbestrol, and 4-cumylphenol. Two of the wells with detections of these chemicals tapped a landfill-leachate plume, and the remaining well was shallow and supplied water to a residence.

Groundwater affected by landfill leachate had the largest number of detections of EACs and other contaminants of emerging concern and the highest total sum of concentrations of these chemicals. The State's continued efforts to properly close, monitor, and maintain landfills likely will help minimize the migration of these contaminants to other parts of the aquifers.

Further data collection will refine this assessment of EACs and other contaminants of emerging concern in Minnesota's groundwater. A limited number of wells in residential areas on SSTS were available for sampling from November 2009 to June 2010. The MPCA's Ambient Groundwater Monitoring Network currently (2012) is being enhanced to provide a better assessment of the effects of land use on groundwater quality. Additional wells in unsewered residential areas were installed for this monitoring network enhancement during the course of this study. These wells likely will be targeted for sampling as part of future monitoring. This study did not assess other settings susceptible to contamination from EACs and other contaminants of emerging concern, such as feedlots (Meyer et al. 2000) or agricultural lands amended with biosolids from wastewater treatment facilities (Kinny et al. 2006).

Additional data on the amount of contamination in the water samples is needed for subsequent assessments of EACs and other contaminants of emerging concern in the groundwater since these chemicals frequently were detected at concentrations at or below the method reporting limit. The collection of more field blank samples during future sampling events will provide a better assessment of the magnitude of contamination and will refine the characterization of the occurrence of these chemicals in Minnesota's groundwater.

Appendix A. Matrix spike recoveries for an ambient groundwater sample analyzed using USGS method O-1433-01[Table does not include volatile organic compounds or pesticides listed in Table 1].

Compound	Matrix spike recovery, in percent
1,4-dichlorobenzene	77.7
Camphor	77.7
Carbazole	22.2
N-N-Diethyl-*meta*-toluamide (DEET)	44.4
para-Cresol	81.0
1-Methylnaphthalene	33.3
2,6-Dimethylnaphthalene	33.3
2-Methylnaphthalene	33.3
3-*beta*-Coprostanol	83.3
3-Methyl-1H-indole (skatol)	Near zero
3-*tert*-Butyl-4-hydroxyanisole (BHA)	Near zero
4-Cumylphenol	Near zero
4-*n*-Octylphenol	Near zero
para-Nonylphenol (total)	27.8
4-Nonylphenol diethoxylate, sum of all isomers (NP2EO)	41.0
4-*tert*-Octylphenol diethoxylate (OP2EO)	Near zero
4-*tert*-Octylphenol monoethoxylate (OP1EO)	68.3
4-*tert*-Octylphenol	Near zero
5-Methyl-1H-benzotriazole	27.8
9,10-Anthraquinone	44.4
Acetophenone	99.9
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	44.4
Anthracene	22.2
Benzo[a]pyrene	22.2
Benzophenone	88.8
beta-sitosterol	166.5
beta-stigmastanol	55.5
Caffeine	88.8
Carbazole	22.2
Cholesterol	333
Cotinine	75.5
d-Limonene	133.2
Fluoranthene	22.2
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	44.4
Indole	11.1

Compound	Matrix spike recovery, in percent
Isoborneol	77.7
Isophorone	33.3
Isoquinoline	Near zero
Menthol	299.7
Methyl salicylate	88.8
Naphthalene	22.2
Phenanthrene	22.2
Phenol	99.9
Pyrene	22.2
Tributyl phosphate	44.4
Triclosan	222
Triethyl citrate (ethyl citrate)	44.4
Triphenyl phosphate	66.6
Tris(2-butoxyethyl) phosphate	654.6
Tris(2-chloroethyl) phosphate	177.6
Tris (dichloroisopropyl) phosphate	366.3

Appendix B. Matrix spike recoveries for samples analyzed using USGS method O-2080-08.

Compound	Matrix spike recovery, in percent	
	Ambient groundwater	Groundwater affected by landfill leachate
Thiabendazole	65.7	0
1,7-dimethylxanthine	117.6	39.4
Acetaminophen	115.8	-12.9
Albuterol (Salbutamol)	98.0	22.3
Caffeine	98.3	34.1
Carbamazepine	77.6	5.0
Codeine	85.4	26.3
Cotinine	85.8	23.4
Dehydronifedipine	118.9	19.5
Diltiazem	65.7	Near zero
Diphenhydramine	67.8	3.2
Sulfamethoxazole	35.8	2.5
Trimethoprim	82.4	3.9
Warfarin	118.6	7.1

REFERENCES

Barnes, K.K., **S.C. Christenson**, **D.W. Kolpin**, **M.J. Focazio**, **E.T. Furlong**, **S.D. Zaugg**, **M.T. Meyer**, and **L.B Barber**. 2004. Pharmaceuticals and other organic waste water contaminants within a leachate plume downgradient of a municipal landfill. Ground Water Monitoring and Remediation *Ground Water Monitoring and Remediation* **24**:8.

Barnes, K.K., **D.W. Kolpin**, **E.T. Furlong**, **S.D. Zaugg**, **M.T. Meyer**, and **L.B. Barber**. 2008. A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States - I) Groundwater. *Science of the Total Environment* **402**:9.

Berg, J.A. 2003. Goodhue County Hydrogeologic Atlas-- Sensitivity to pollution of the uppermost bedrock aquifers. St. Paul: Minnesota Department of Natural Resources.

Childress, C.J.O., **W.T. Foreman**, **B.F. Connor**, and **T.J. Maloney**. 1999. New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory. U.S. Geological Survey.

Conn, K.E., **L.B. Barber**, **G.K. Brown**, and **R.L. Siegrist**. 2006. Occurrence and fate of organic contaminants during onsite wastewater treatment. Environmental Science and Technology. *Environmental Science and Technology* 40:9.

Delin, G.N., and **D.G. Woodward**. 1984. Hydrogeologic setting and the potentiometric surfaces of the regional aquifers in the Hollandale Embayment, Southeastern Minnesota, 1970-80. U.S. Geological Survey.

Erickson, M.L. 2012. Steroidal hormones and other endocrine active compounds in shallow groundwater in non-agricultural areas of Minnesota-Study design, methods, and data, 2009-10. Mounds View: U.S. Geological Survey.

Ferrey, M. 2011. Wastewater treatment plant endocrine disrupting chemical monitoring study. St. Paul: Minnesota Pollution Control Agency.

Focazio, M.J., **D.W. Kolpin**, **K.K. Barnes**, **E.T. Furlong**, **M.T. Meyer**, **S.D. Zaugg**, **L.B. Barber**, and **E.M. Thurman**. 2008. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States-- II) Untreated drinking water sources. *Science of the Total Environment* 402:16.

Fong, A.L. 2000. Water-quality assessment of part of the Upper Mississippi River Basin, Minnesota and Wisconsin-Ground-water quality in three different land-use areas, 1996-98. Mounds View: U.S. Geological Survey.

Furlong, E.T., **S.L. Werner**, **B.D. Anderson**, and **J.D. Cahill**. 2008. Determination of human-health pharmaceuticals in filtered water by chemically modified styrene-divinylbenzene resin-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry. In *Techniques and Methods Book 5, Chapter B5*: U.S. Geological Survey.

Holm, J.V., **K. Rugge**, **P.L. Bjerg**, and **T.H. Christenson**. 1995. Occurrence and distribution of pharmaceutical organic compounds in the groundwater downgradient of a landfill (Grindsted, Denmark). *Environmental Science and Technology* 29 (5):6.

Jackson, J., and **R. Sutton**. 2008. Sources of endocrine-disrupting chemicals in urban wastewater, Oakland, CA. *Science of the Total Environment* **405**:8.

Kinny, C.A., **E.T. Furlong**, **S.D. Zaugg**, **M.R. Burkhardt**, **S.L. Werner**, **J.D. Cahill**, and **G.R. Jorgensen**. 2006. Survey of organic wastewater contaminants in biosolids destined for land application. Environmental Science and Technology *Environmental Science and Technology* 40:10.

Kolpin, D.W., **E.T. Furlong**, **M.T. Meyer**, **E.M. Thurman**, **S.D. Zaugg**, **L.B Barber**, and **H.T. Buxton**. 2002. Pharmaceuticals, Hormones, and other organic wastewater contaminants in U.S. Streams, 1999-2000: A National Reconnaissance. *Environmental Science and Technology* 36:12.

LeBlanc, D.R. 1984. plume in a sand and gravel aquifer, Cape Cod, Massachusetts. U.S. Geological Survey.

Lee, K.E., **L.B Barber**, **E.T. Furlong**, **J.D. Cahill**, **D.W. Kolpin**, **M.T. Meyer**, and **S.D. Zaugg**. 2004. Presence and distribution of organic wastewater compounds in wastewater, surface, ground, and drinking waters, Minnesota, 2000-02. U.S. Geological Survey.

Lee, K.E., **H.L. Schoenfuss**, **L.B. Barber**, **J.H. Writer**, **V.S. Blazer**, **R.L. Kiesling**, and **M.L. Ferrey**. 2010. Endocrine active chemicals and endocrine disruption in Minnesota streams and lakes-- implications for aquatic resources, 1994-2008. U.S. Geological Survey.

Meyer, M.T., **J.E. Bumgarner**, **J.L. Varns**, **J.V. Daughtridge**, **E.M. Thurman**, and **K.A. Hostetler**. 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* 248:8.

Minnesota Department of Health. 2008. Statement of Need and Reasonableness in the Matter or Proposed Rules of the Minnesota Department of Health Relating to Health Risk Limits for Groundwater. St. Paul: Minnesota Department of Health.

O'Dell, C. 2007. Minnesota's Groundwater Condition: A Statewide View. St. Paul: Minnesota Pollution Control Agency.

Repert, D.A., **L.B Barber**, **K.M. Hess**, **S.H. Keefe**, **D.B. Kent**, **D.R LeBlanc**, and **R.L. Smith**. 2006. Long-term natural attenuation of carbon and nitrogen within a groundwater plume after removal of the treated wastewater source. *Environmental Science and Technology* 40:9.

Robertson, W.D., **J.A. Cherry**, and **E.A. Sudicky**. 1991. Ground-water contamination from two small septic systems on sand aquifers. *Ground Water* 29:11.

Rudel, R.A., **S.J. Melly**, **P.W. Geno**, **G. Sun**, and **J.G. Brody**. 1998. Identification of alkylphenols and other estrogenic phenolic compounds in wastewater, septage, and groundwater on Cape Cod, Massachusetts. *Environmental Science and Technology* 32:9.

Snyder, D.A., **J. Leising**, **P. Westerhoff**, **Y. Yoon**, **H. Mash**, and **B. Vanderford**. 2004. Biological and physical attenuation of endocrine disruptors and pharmaceuticals-- Implications for water reuse. *Ground Water Monitoring and Remediation* 24 (2):11.

Constitution of the State of Minnesota. November 4, 2008.

Swartz, C.H., **S. Reddy**, **M.J. Benotti**, **H. Yin**, **L.B Barber**, **B.J. Brownawell**, and **R.A. Rudell**. 2006. Steroid estrogens, nonylphenol ethoxylate metabolites, and other wastewater contaminants in a groundwater affected by a residential septic system on Cape Cod, MA. *Environmental Science and Technology* 40:9.

Trojan, M.D., **J.S. Maloney**, **J.M. Stockinger**, and **E.P.**

Lahtinen Eid, M.J. 2003. Effects of land use on ground water quality in the Anoka Sand Plain aquifer of Minnesota. *Ground Water* 41:11.

U.S. Census Bureau. 2011. *2010 Census Results-Minnesota* 2011 [cited Nov. 1, 2011 2011]. Available from <http://2010.census.gov>.

U.S. Geological Survey. variously dated. National field manual for the collection of water-quality data. U.S. Geological Sruvey.

Warner, K.L., and **T.L. Arnold**. 2010. Relations that affect the probability and prediction of nitrate concentrations in private wells in the glacial aquifer system in the United States. U.S. Geological Survey.

Writer, J.H., **L.B Barber**, **G.K. Brown**, **H.E. Taylor**, **R.L. Kiesling**, **M.**L. **Ferrey**, **N.D. Jahns**, **S.E. Bartell**, and **H.L. Schoenfuss**. 2010. Anthropogenic tracers, endocrine-disrupting chemicals, and endocrine disruption in Minnesota lakes. *Science of the Total Environment* 409:12.

Zaugg, S.D., **S.G Smith**, **M.P. Schroeder**, **L.B Barber**, and **M.R. Burkhardt**. 2002. Method 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.