Wastewater Treatment Plant Endocrine Disrupting Compound Monitoring Study

Preliminary progress report to the Legislature

Minnesota Pollution Control Agency

April 15, 2010

This report was printed in limited quantities. The electronic version of this report can be found on the MPCA Website at: http://www.pca.state.mn.us/hot/legislature/reports/index.html

Authors

Mark Ferrey, MPCA

Contributors

Jeffrey Writer, USGS
Kathy Lee, USGS
Larry Barber, USGS
Paul Hoff, MPCA

Estimated cost of preparing this report *(as required by Minn. Stat. § 3.197)*

Total staff time: 10 hrs.

Salary Fringe and Indirect	$543.00
Production/duplication	$30.00
Total	$573.00

The MPCA is reducing printing and mailing costs by using the Internet to distribute reports and information to wider audience. Visit our web site for more information.

MPCA reports are printed on 100% post-consumer recycled content paper manufactured without chlorine or chlorine derivatives.

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

This report is available in alternative formats upon request, and online at www.pca.state.mn.us

Document number: lrp-ei-3sy10

Summary and Introduction

The 2010-2011 Biennial Budget, enacted in 2009, directed and funded the Minnesota Pollution Control Agency (MPCA) to study the effluent from at least 20 wastewater treatment plants (WWTPs) to obtain a more complete picture of the types and amounts of endocrine disrupting compounds (EDCs) released into the state's surface water. (See Appendix A for statutory language).

This report summarizes progress for this work on samples collected from 25 wastewater treatment plants in Minnesota. WWTPs that were sampled differed in capacity and treatment type. Preliminary results show that pharmaceuticals, triclosan, nonylphenol, nonylphenol ethoxylates, octylphenol, octylphenol ethoxylates, bisphenol A, and hormones were detected in the water samples, mostly in effluent from the plants. Complete analytical results for this portion of the study will be available by June 1, 2010. Data on sediment, estrogenicity measurements, and fish analysis will be provided in the final report due to the Minnesota Legislature January 15, 2011.

Background

More than 500 wastewater treatment plants (WWTP) discharge effluent to surface waters throughout Minnesota. WWTP effluent contains chemicals used in homes, industry, and agriculture including endocrine-active chemicals and pharmaceuticals. (Scientists are increasingly adopting the term "endocrine active chemicals" (EACs) over the term "endocrine disrupting chemicals" as a more accurate description for chemicals affecting the endocrine system) EACs affect the regulation of the endocrine system and may mimic or block the function of natural hormones.

Several previous research and monitoring studies have identified EACs and pharmaceuticals in WWTP effluent and receiving streams. These investigations have also shown evidence of endocrine disruption in fish downstream of WWTP effluents. Available data suggest that concentrations of EACs and pharmaceuticals in Minnesota WWTPs and receiving streams greatly vary, and that some WWTPs are discharging biologically significant levels of these chemicals. However, the number of WWTPs sampled among the various studies represents a small fraction (less than five percent) of the WWTPs in Minnesota and thus may not be representative of all WWTPs in Minnesota.

The US Geological Survey (USGS) and the Minnesota Pollution Control Agency (MPCA), together with St. Cloud State University (SCSU) and the University of St. Thomas (UST), are collaborating on this project.

The objectives of the study are:

- To measure the concentrations of EACs and pharmaceuticals in water samples collected from the effluents from WWTPs and at sites upstream and downstream of WWTP effluent discharge.
- To measure the concentrations of EACs in bottom sediments collected upstream and downstream of effluent discharges at a subset of sites.
- To estimate estrogencity of water samples using an *in vitro* assay.
- To study the effect of the WWTP effluents on fish through on-site exposure experiments.

Site selection

During this study, 48 stream locations and 25 wastewater treatment plants (Figure 1, Table 1) were sampled to determine the occurrence of a broad suite of organic chemicals including endocrine active chemicals and pharmaceuticals in water and bottom sediments. Sampling occurred between September 2, 2009, and November 23, 2009.

Streams that were selected for study ranged in drainage area from less than 5 to 48,000 square miles. Land use varies upstream of the sampling sites, ranging from forested land in the northern parts of Minnesota to those with dominantly agricultural land in the southern areas of the state.

A diversity of wastewater treatment plants were selected to include those of differing treatment types (continuous flow vs. periodic releases), differing processing steps (activated sludge vs. trickling filters), and plant design flows ranged from 0.04 to 251 million gallons per day (Table 2).

Figure 1. Map showing the sampling locations during 2009. Each triangle represents three sites (one upstream, one downstream, and one wastewater effluent sample).

Table 1. List of sampling sites and sampling dates

City	Position	Site Name	Date Sampled
Austin	Upstream	Cedar River above Treatment Plant at Austin, MN	9/8/2009
Austin	WWTP	Austin WWTP Outflow at Austin, MN	9/8/2009
Austin	Downstream	Cedar River below Treatment Plant at Austin, MN	9/8/2009
Duluth	Upstream	St. Louis River at Hwy 23 above Fond Du Lac, MN	10/1/2009
Duluth	WWTP	Western Lake Superior Sanitary District - WWTP at Duluth, MN	10/1/2009
Duluth	Downstream	Lake Superior in St. Louis Bay at Duluth, MN	10/1/2009
East Grand Forks	Upstream	Red River of the North above WWTP at East Grand Forks, MN	10/21/2009
East Grand Forks	WWTP	Wastewater Lift Station Outflow at East Grand Forks, MN	10/21/2009
East Grand Forks	Downstream	Red river of the North Below WWTP at East Grand Forks, MN	10/21/2009
Ely	Upstream	Shagawa Lake at Mouth of Burntside River near Ely, MN	9/28/2009
Ely	WWTP	Ely WWTP Outflow at Ely, MN	9/28/2009
Ely	Downstream	Shagawa Lake near Ely WWTP Outflow at Ely, MN	9/28/2009
Eveleth	Upstream	Elbow Creek above Eveleth WWTP at Eveleth, MN	9/29/2009
Eveleth	WWTP	Eveleth WWTP Outflow at Eveleth, MN	9/29/2009
Eveleth	Downstream	Elbow Creek below Eveleth WWTP at Eveleth, MN	9/29/2009
Fairmont	Upstream	Center Creek on Co. Rd. 143, at Fairmont, MN	9/9/2009
Fairmont	WWTP	Fairmont WWTP Outflow at Fairmont, MN	9/9/2009
Fairmont	Downstream	Center Creek below WWTP at Fairmont, MN	9/9/2009
Grand Rapids	Upstream	Mississippi River above WWTP at Grand Rapids, MN	9/30/2009
Grand Rapids	WWTP	Grand Rapids WWTP Outflow at Grand Rapids, MN	9/30/2009
Grand Rapids	Downstream	Mississippi River below WWTP at Grand Rapids, MN	9/30/2009
Hinckley	Upstream	Grindstone River above WWTP near Hinckley, MN	9/2/2009
Hinckley	WWTP	Hinckley WWTP near Hinckley, MN	9/2/2009
Hinckley	Downstream	Grindstone River below Hinckley, MN	9/2/2009
Hutchinson	Upstream	South Fork of the Crow River above WWTP at Hutchinson, MN	9/14/2009
Hutchinson	WWTP	Hutchinson WWTP Outflow at Hutchinson, MN	9/14/2009
Hutchinson	Downstream	South Fork of the Crow River below Hutchinson, MN	9/14/2009
Lake City	Upstream	Mississippi River (Lake Pepin) above Lake City, MN	9/23/2009
Lake City	WWTP	Lake City WWTP Outflow at Lake City, MN	9/23/2009
Lake City	Downstream	Mississippi River (Lake Pepin) at Mile 771 near Lake City, MN	9/23/2009
Lester Prairie	Upstream	South Fork Crow River above WWTP at Lester Prairie, MN	9/15/2009
Lester Prairie	WWTP	Lester Prairie WWTP Outflow at Lester Prairie, MN	9/15/2009
Lester Prairie	Downstream	South Fork Crow River below WWTP at Lester Prairie, MN	9/15/2009
Litchfield	Upstream	Jewitts Creek at U.S. HWY. 12 in Litchfield, MN	10/8/2009
Litchfield	WWTP	Litchfield WWTP Outflow near Litchfield, MN	10/8/2009

City	Position	Site Name	Date Sampled
Litchfield	Downstream	*Jewitts Creek near Litchfield, MN*	10/8/2009
Luverne	Upstream	Rock River above WWTP near Luverne, MN	10/6/2009
Luverne	WWTP	Luverne WWTP Outflow near Luverne, MN	10/6/2009
Luverne	Downstream	Rock River below WWTP near Luverne, MN	10/6/2009
Lynd	Upstream	Redwood River above Lynd WWTP near Lynd, MN	11/23/2009
Lynd	WWTP	Lynd WWTP Outflow near Lynd, MN	11/23/2009
Lynd	Downstream	Redwood River below Lynd WWTP near Lynd, MN	11/23/2009
Marshall	Upstream	Redwood River above WWTP below Marshall, MN	10/7/2009
Marshall	WWTP	Marshall WWTP outfall at Marshall, MN	10/7/2009
Marshall	Downstream	Redwood River below WWTP near Marshall, MN	10/7/2009
Melrose	Upstream	Sauk River above Melrose WWTP at Melrose, MN	9/17/2009
Melrose	WWTP	Melrose WWTP Outflow at Melrose, MN	9/17/2009
Melrose	Downstream	Sauk River below Melrose WWTP at Melrose, MN	9/17/2009
Pelican Rapids	Upstream	Pelican River above WWTP at Pelican Rapids, MN	10/19/2009
Pelican Rapids	WWTP	Pelican Rapids WWTP Outflow at Pelican Rapids, MN	10/19/2009
Pelican Rapids	Downstream	Pelican River below WWTP at Pelican Rapids, MN	10/19/2009
Rochester	Upstream	South Fork Zumbro River at Rochester, MN	9/22/2009
Rochester	WWTP	Rochester WWTP Outflow at Rochester, MN	9/22/2009
Rochester	Downstream	South Fork Zumbro R. below WWTP near Rochester, MN	9/22/2009
Sauk Centre	Upstream	Sauk River above Sauk Centre WWTP at Sauk Centre, MN	9/16/2009
Sauk Centre	WWTP	Sauk Centre WWTP Outflow at Sauk Centre, MN	9/16/2009
Sauk Centre	Downstream	Sauk River below Sauk Centre WWTP at Sauk Centre, MN	9/16/2009
Spring Valley	Upstream	Spring Valley Creek above Spring Valley WWTP Outflow at Spring Valley, MN	9/21/2009
Spring Valley	WWTP	Spring Valley WWTP Outflow at Spring Valley, MN	9/21/2009
Spring Valley	Downstream	Spring Valley Creek below Spring Valley WWTP Outflow at Spring Valley, MN	9/21/2009
St. Paul	Upstream	Mississippi River at Industrial Molasses St. Paul, MN	9/24/2009
St. Paul	WWTP	Metro Plant (WWTP) Outflow in St. Paul, MN	9/24/2009
St. Paul	Downstream	Mississippi River at South St. Paul, MN	9/24/2009
Williams	Upstream	Williams Creek above WWTP at Williams, MN	10/20/2009
Williams	WWTP	Williams WWTP Outflow at Williams, MN	10/20/2009
Williams	Downstream	Williams Creek below WWTP at Williams, MN	10/20/2009
Worthington	Upstream	Okabena Creek above WWTP Outflow at Worthington, MN	9/9/2009
Worthington	WWTP-Domestic	Worthington WWTP Outflow at Worthington, MN	9/9/2009
Worthington	WWTP-Industrial	Industrial WWTP Outflow near Worthington, MN	9/9/2009
Worthington	Downstream	Okabena Creek below WWTP Outflow at Worthington, MN	9/9/2009
Zimmerman	Upstream	Tibbets Brook above WWTP outflow at Zimmerman, MN	9/3/2009
Zimmerman	WWTP	Zimmerman WWTP outflow at Zimmerman, MN	9/3/2009
Zimmerman	Downstream	Tibbets Brook below WWTP outflow at Zimmerman, MN	9/3/2009

Table 2. Characteristics of wastewater treatment plants sampled during 2009 (MGD, million gallons per day) [preliminary and subject to revision].

Minnesota Identification Number (NPDES)	US Geological Survey Station Number	Site Name	Design Flow (MGD)	Disinfection Description	Principal Treatment Components
MN0022683	433913092581601	Austin WWTP Outflow at Austin, MN	8.5	Chlorination	Trickling Filter
MN0020508	475435091522601	Ely WWTP Outflow at Ely, MN	1.5	Chlorination	Activated Sludge - extended aeration
MN0023337	472737092324501	Eveleth WWTP Outflow at Eveleth, MN	1	Chlorination	Activated Sludge - extended aeration
Fff1	434018094273301	Fairmont WWTP Outflow at Fairmont, MN	3.9	Ultraviolet Light	Activated Sludge - contact stabilization, conventional, step feed
MN0022080	471336093301801	Grand Rapids WWTP Outflow at Grand Rapids, MN	15.2	Chlorination	Activated Sludge - contact stabilization, conventional, step feed
MN0023701	460107092543101	Hinckley WWTP near Hinckley, MN	0.5	Ultraviolet Light	Activated Sludge - extended aeration
MN0055832	445220094212201	Hutchinson WWTP Outflow at Hutchinson, MN	5.4	Ultraviolet Light, Chlorination, Dechlorination	Activated Sludge - extended aeration, oxidation ditch
MN0031178	433847095330001	Industrial WWTP Outflow near Worthington, MN	2	Chlorination	Activated Sludge
MN0020664	442626092152201	Lake City WWTP Outflow at Lake City, MN	1.52	Ultraviolet Light	Activated Sludge - contact stabilization, conventional, step feed
MN0023957	445243094020301	Lester Prairie WWTP Outflow at Lester Prairie, MN	0.36	Ultraviolet Light	Activated Sludge - extended aeration, oxidation ditch
MN0023973	450833094311001	Litchfield WWTP Outflow near Litchfield, MN	2.4	Chlorination, Dechlorination	Trickling Filter
MN0020141	433856096115801	Luverne WWTP Outflow near Luverne, MN	1.5	Chlorination, Dechlorination	Trickling Filter

Minnesota Identification Number (NPDES)	US Geological Survey Station Number	Site Name	Design Flow (MGD)	Disinfection Description	Principal Treatment Components
MNG580030	442415095523001	Lynd WWTP Outflow near Lynd, MN	0.045	None	Secondary Stabilization Pond
MN0022179	442846095463201	Marshall WWTP outfall at Marshall, MN	4.5	Ultraviolet Light	Activated Sludge - contact stabilization, conventional, step feed
MN0020290	454040094480701	Melrose WWTP Outflow at Melrose, MN	3	Chlorination, Dechlorination	Activated Sludge - contact stabilization, conventional, step feed
MN0029815	445509093024301	Metro Plant (WWTP) Outflow in St. Paul, MN	251	Chlorination, Dechlorination	Activated Sludge - contact stabilization, conventional, step feed
MN0022225	463408096052401	Pelican Rapids WWTP Outflow at Pelican Rapids, MN	0.91	Chlorination, Dechlorination	Trickling Filter
MN0024619	440350092275501	Rochester WWTP Outflow at Rochester, MN	19.1	Chlorination, Dechlorination	Activated Sludge - contact stabilization, conventional, step feed
MN0024821	454308094562601	Sauk Centre WWTP Outflow at Sauk Centre, MN	0.88	Chlorination, Dechlorination	Activated Sludge - contact stabilization, conventional, step feed
MN0051934	434122092225001	Spring Valley WWTP Outflow at Spring Valley, MN	0.94	Chlorination, Dechlorination	Activated Sludge - extended aeration, oxidation ditch
MN0021814	475834097032002	Wastewater Lift Sta. Outflow at East Grand Forks, MN	1.4	None	Secondary Stabilization Pond
MN0049786	464538092072601	Western Lake Superior Sanitary District - WWTP at Duluth, MN	48.4	Chlorination, Dechlorination	Activated Sludge - pure oxygen, Bar Screen - mechanical
MN0021679	484627094570801	Williams WWTP Outflow at Williams, MN	0.08	Ultraviolet Light	Preaeration - less than two hours detention time
MNG640105	433838095344201	Worthington WWTP Outflow at Worthington, MN	4	Chlorination	Trickling Filter
MN0042331	452559093345601	Zimmerman WWTP outflow at Zimmerman, MN	0.45	Ultraviolet Light	Activated Sludge - conventional, sequencing batch reactors

Preliminary results

Preliminary analyses show that pharmaceuticals are present in Minnesota wastewaters (Figure 2) and streams (Figure 3). Pharmaceuticals detected include carbamazepine (anticonvulsant), diphenhydramine (antihistamine), trimethoprim and sulfamethoxazole (antibiotics), diltiazem (heart arrhythmia medication), caffeine (stimulant), codeine, cotinine (nicotine metabolite), and 1,7-dimethylxanthine (caffeine metabolite). The concentrations were generally low (less than 1 microgram per liter) and most were below laboratory reporting levels. Concentrations for each chemical will be available in June, 2010, pending completion of quality assurance/quality control review.

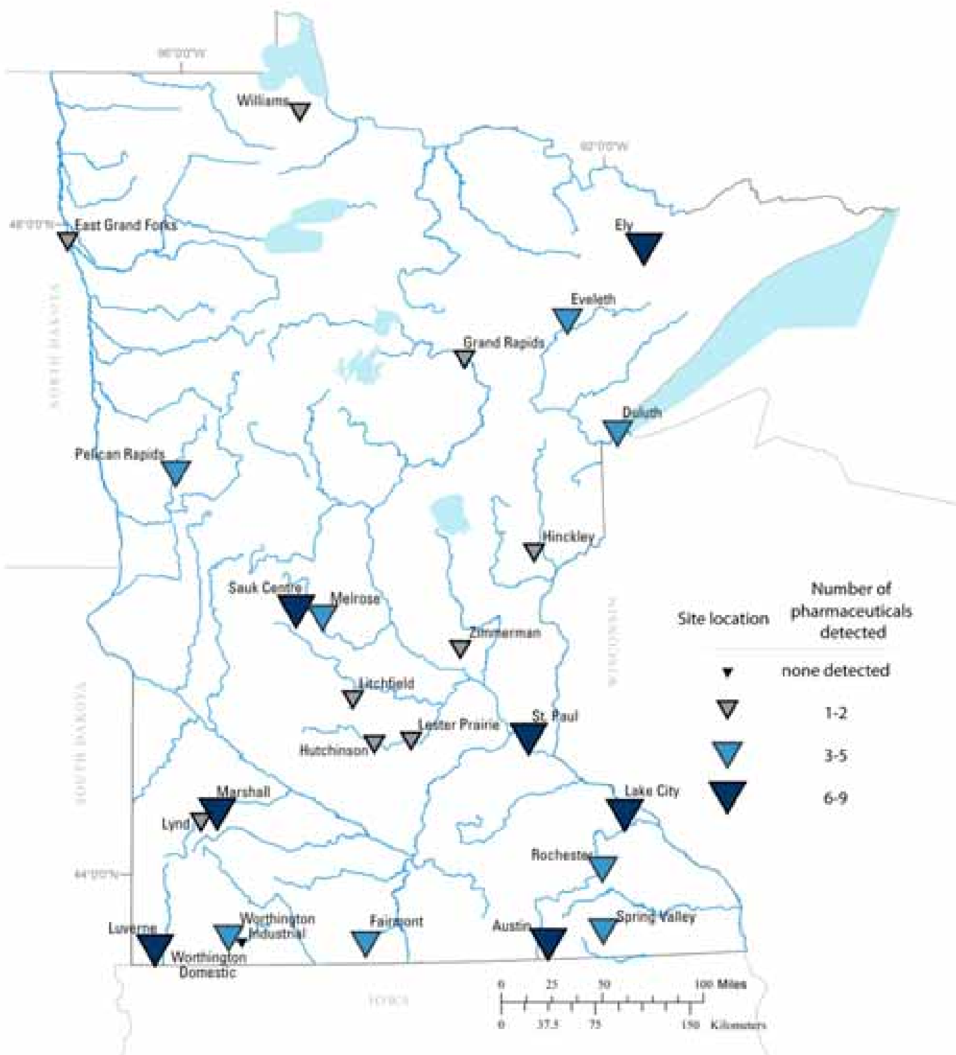

Figure 2. Map showing the number of pharmaceuticals detected in wastewater treatment plant effluent samples collecting during 2009. Preliminary Results Subject to Revision.

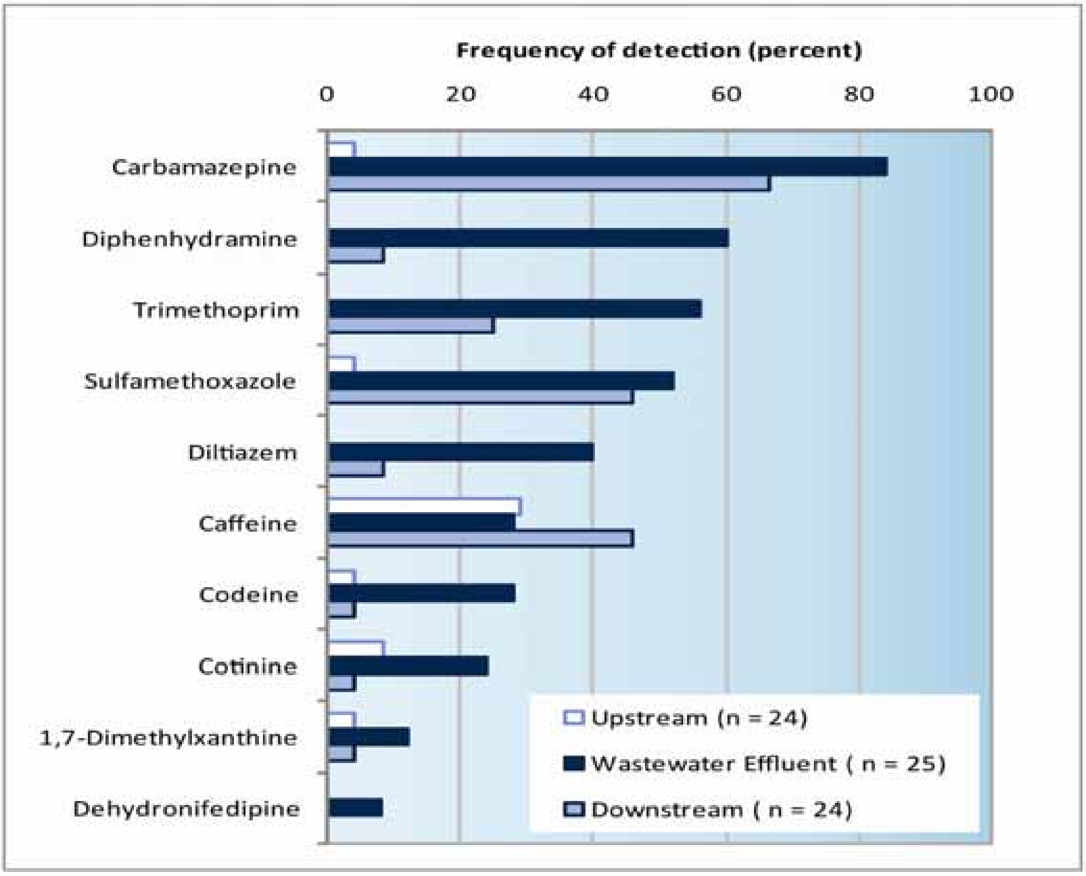

Figure 3. Graph showing the frequency of detection of pharmaceuticals measured in water samples collected from wastewater effluent and from stream sites located upstream and downstream of effluent discharge during 2009. Preliminary Results Subject to Revision.

Pharmaceuticals generally occurred as mixtures with the number detected ranging from zero to nine among all samples. There were more pharmaceuticals detected in WWTP effluent samples (average of four pharmaceuticals) than in samples collected downstream of effluent (average of two pharmaceuticals) and stream samples collected upstream of effluent (average of one pharmaceutical). Some of the pharmaceuticals such as caffeine were present both upstream and downstream of wastewater discharges while other pharmaceuticals such as carbamazepine were found primarily downstream from wastewater treatment plant discharge (Figure 3). The behavior of these chemicals seems appropriate given their solubilities and degradation rates. Two of the pharmaceuticals had low percent laboratory recoveries (sulfamethoxazole and diltiazem).

Nonylphenol, octylphenol, nonylphenol ethoxylates, and octylphenol ethoxylates were detected in the effluent from several of the WWTPs sampled. These compounds were also detected at many upstream and downstream sampling locations. The antibacterial compound triclosan was detected in most of the samples of WWTP effluent, with fewer detections at downstream locations. The hormones estrone, 17-β-estradiol, and the synthetic steroid hormone, ethinylestradiol, were detected at upstream and downstream sampling locations as well as in the WWTP effluent. Concentrations for each chemical will be available in June, 2010, pending completion of quality assurance/quality control review.

Study progress highlights

- Project start dates: planning in July-August 2009, monitoring began September 2009.
- Project planning: consulted representatives from the University of Minnesota, St. Cloud State University, Metropolitan Council Environmental Services, Minnesota Department of Natural Resources, Minnesota Department of Health, USGS, and MPCA. Also consulted with WWTP operators concerning the study.
- Measured stream discharge and sampled water at all sites (25 WWTPs and 48 stream sites).
- Analyses for nutrients, chloride, sulfate, and pharmaceuticals are complete and are in the quality assurance phase.
- Completed a rhodamine dye study at all small streams for use in time of travel estimates.
- The time of travel data are in the processing phase with approximately 75 percent of the work complete.
- Collected bottom sediment at all stream sites. The workplan specifies analyses of a subset of those sediments. The remaining samples are archived for future interest. Seventy percent of bottom sediment samples have been analyzed for wastewater indicator chemicals and 60 percent have been analyzed for hormones.
- Completed GIS analyses including drainage area, basin land use, count of the upstream wastewater treatment plants and feedlots where possible, stream slope, and distances between sampling sites. Prepared basin maps for each site.
- Created a USGS website with project information for public review-- http://mn.water.usgs.gov/projects/EACWWTP/index.html
- Worked with the Freshwater Society to publish an article about the WWTP study: http://www.freshwater.org/index.php/facets-of-freshwater-september-2009/172-ednocrine-disrupting-chemicals-major-minnesota-research-under-way
- All samples for estrogenicity analysis at UST are in progress.
- Fish studies led by SCSU will commence in Spring 2010 at several WWTP sites using a Mobile Exposure Laboratory Trailer.
- Final report due date January 15, 2011.

In conclusion, the study of endocrine disrupting compounds near wastewater treatment plants, commissioned in the 2010-2011 budget is underway and on schedule. The water sample analysis phase is nearly complete and additional work on sediment, estrogenicity analysis, and fish testing will be completed in the remainder of the study. A final report is due to the Legislature on January 15, 2011.

Appendix A: 2009 Statutory Language for Endocrine Disruptor Monitoring

From 2009 Session Law Chapter 172, Article 2, Sec. 4 (f) and Sec. 29

(f) $896,000 the first year is to establish a network of water monitoring sites, to include at least 20 additional sites, in public waters adjacent to wastewater treatment facilities across the state to assess levels of endocrine-disrupting compounds, antibiotic compounds, and pharmaceuticals as required in this article. The data must be placed on the agency's Web site.

Sec. 29. **ENDOCRINE-DISRUPTOR MONITORING.**
(a) The commissioner of the Pollution Control Agency shall establish a network of water monitoring sites in public waters adjacent to wastewater treatment facilities across the state to assess levels of endocrine disrupting compounds, antibiotic compounds, and pharmaceuticals.
(b) Each of the monitoring sites must provide enhanced monitoring of the effluent at the discharge point of the wastewater treatment facility and monitoring of the public waters above and below the discharge point.
(c) The monitoring sites must be located throughout the state, represent a variety of wastewater treatment facility sizes based on the number of gallons of water discharged per day, and represent a variety of waste treatment systems used for primary, secondary, and tertiary disinfecting treatment and management of biosolids.
(d) In establishing the monitoring network, the commissioner of the Pollution Control Agency must consult with the commissioners of health and natural resources, the United States Geological Survey, the Metropolitan Council, local wastewater treatment facility operators, and the Water Resources Center at the University of Minnesota. Consideration may be given to monitoring sites at facilities identified as part of a total maximum daily load study and facilities located on a water body identified for enhanced protection. The initial monitoring network must include at least ten sites.
(e) Monitoring must include, but is not limited to, endocrine-disrupting compounds from natural and synthetic hormones, pharmaceuticals, personal care products, and a range of industrial products and by-products. At a minimum, concentrations of estrone, nonylphenol, bisphenol-A, 17-beta-estradiol, 17-alpha-ethynylestradiol, estriol, and antibacterial triclosan must be monitored. Additional compounds, antibacterial compounds, and pharmaceuticals potentially impacting human health and aquatic communities may be considered for identification and monitoring including, but not limited to, nonylphenol ethoxylates, octylphenol, and octylphenol ethoxylates; the hormones androstenedione, trenbelone, and diethylphthalate; antidepressant medications, including fluoxetine and fluvoxamine; carbamazepine; and triclocarban.
(f) The commissioner of the Pollution Control Agency shall begin the monitoring and testing required under this section no later than November 1, 2009. Information about requirements under this section and the results from the monitoring and testing must be available on the agency's Web site by June 1, 2010. The commissioner shall submit a preliminary report on the results of the monitoring and testing to the chairs of the legislative committees with jurisdiction over environment and natural resources policy and finance by April 15, 2010, and a final report no later than January 15, 2011.