

# Identification of a Major Source of Perfluorooctane Sulfonate (PFOS) at a Wastewater Treatment Plant in Brainerd, Minnesota

James Kelly, Minnesota Department of Health, St. Paul, Minnesota  
 Laura Solem, Minnesota Pollution Control Agency, St. Paul, Minnesota



## BACKGROUND

Perfluorooctane sulfonate (PFOS) is a globally distributed persistent contaminant in environmental and biological media. Due to the history of perfluorochemical (PFC) manufacture and waste disposal in the state, Minnesota has been evaluating the presence of PFCs in groundwater, surface water and fish. PFOS has been shown to bioaccumulate in fish tissue, and the detection of elevated concentrations of PFOS in fish in a number of lakes and rivers in Minnesota has resulted in the issuance of PFOS-based fish consumption advice in some instances. While PFC waste disposal sites have been identified as one potential source, currently, little is known about other source(s) of PFOS in lakes and rivers in Minnesota.

In 2007, the Minnesota Pollution Control Agency (MPCA) conducted a study of PFCs in influent, effluent, and sludge at 28 public and private wastewater treatment plants (WWTPs) throughout Minnesota. Samples of influent (n=32), effluent (n=28), and sludge (n=23) were analyzed for 13 PFCs by Axys Analytical Services, British Columbia, Canada.

Minnesota WWTPs, mainly in urban areas, had elevated levels of several PFCs that could reasonably be attributed to local sources, including known PFC contamination from waste disposal sites or the use of PFC containing products at an industrial facility or airport. A notable exception was PFOS in the influent, effluent, and sludge from the City of Brainerd WWTP, operated by Brainerd Public Utilities (BPU). The plant is located approximately 135 miles northwest of St. Paul, and discharges to the Mississippi River. This plant had the highest detections of PFOS in all three media of any of the wastewater treatment plants tested, with an effluent PFOS level of 1,510 nanograms per liter (ng/L). No PFCs were detected in the wells supplying drinking water to the city of Brainerd.

BPU conducted an investigation of the wastewater collection system to identify the source(s) of the PFOS contamination. The main source (~95%) of the PFOS was identified as a large chrome plating operation in the city who reported using a surfactant product to control hexavalent chromium emissions.

Samples collected within the plating facility by BPU staff identified the specific points where PFOS remains in the plating solution tanks. An alternate surfactant product that does not contain PFOS is currently being used by the facility. Levels of PFOS in the chrome plating tank at the facility have declined, and PFOS levels at the BPU WWTP are expected to decline over time.

## MPCA 2007 STUDY

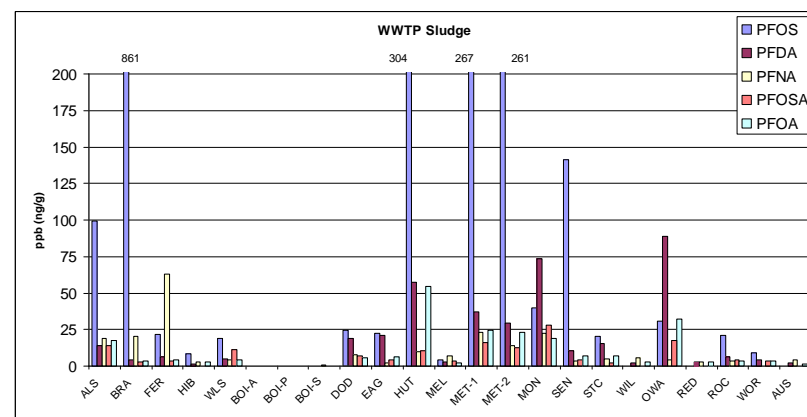
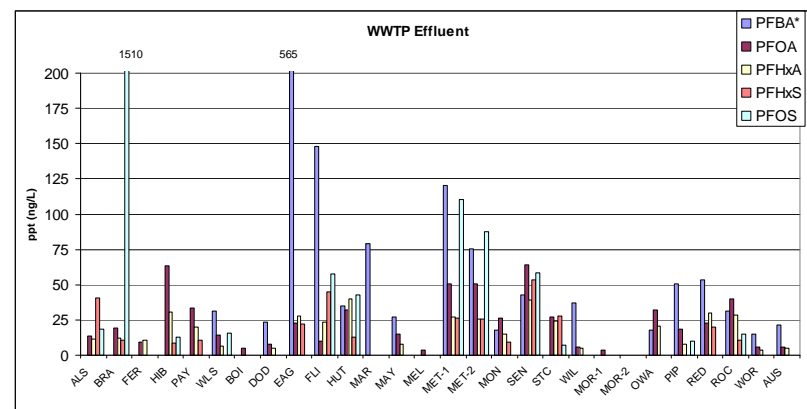
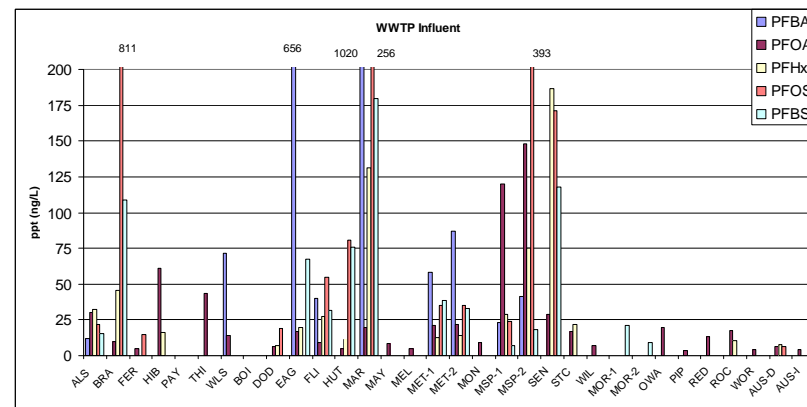
The MPCA study was conducted to determine if WWTPs are a source of PFCs to Minnesota waters. PFCs have been reported in waste streams of WWTPs in other parts of the country<sup>1,2,3</sup>. The plants in Minnesota were selected to represent 1) a wide geographic distribution, 2) receipt of a variety of wastes (municipal, commercial, industrial), and 3) a variety of treatment processes. The survey was designed to provide as broad a range of data as possible across Minnesota.

The MPCA is also conducting other investigations to assess the presence and to identify potential sources of PFCs in the ambient environment, including storm water outfalls, land disposal facilities, ambient surface and ground water, and ambient air.



MPCA 2007 WWTP Sample Locations

## MPCA 2007 STUDY RESULTS



## CITY OF BRAINERD INVESTIGATION

The initial BPU investigation (implemented by Barr Engineering Company, Minneapolis, MN) involved the collection of 35 samples of wastewater from the Brainerd WWTP and numerous locations throughout the city. The samples were collected using new polyethylene bailers lowered into the waste stream (typically through an open manhole), filled, and then decanted into sample containers provided by the laboratory. The samples were analyzed by MPI Research (formerly Exygen Research) of State College, PA for the presence of 13 PFCs, including PFOS. The results from samples collected at the WWTP itself were generally consistent with the MPCA results for PFOS. Analysis of samples taken in the wastewater collection system detected PFOS in five samples, four at low concentrations ranging from 80 to 1,180 ng/L. The fifth sample, collected in an industrial park in the SE corner of the city, had a PFOS concentration of 49,800 ng/L. This sample was collected from a manhole in front of a large chrome plating operation that specializes in vintage automobile parts.



Hexavalent Chromium Plating Bath

Representatives from the chrome plating operation contacted BPU staff to inform them that the company used a surfactant product that reportedly contained "organic fluorosulfonate" between 1% and 7% by weight. Approximately 16 fluid ounces of the product, Fumetrol™ 140 Mist Suppressant (Atotech USA, Rock Hill, SC), was added to the chrome plating bath per day. The surfactant product is designed to reduce surface tension, which in turn reduces emissions of hexavalent chromium from the plating solution. Hexavalent chromium can be released into the air with the bursting of bubbles formed below the surface of the tank solution during electroplating. This is important from a worker safety and environmental standpoint, as hexavalent chromium is toxic through inhalation and dermal contact, and is considered a human carcinogen<sup>4</sup>. As a result, the use of this PFOS-containing mist suppressant was exempted from the most recent (2007) U.S. Environmental Protection Agency (EPA) Significant New Use Rule regarding perfluoroalkyl sulfonates. EPA estimates that up to eight metric tons of PFOS-containing mist suppressants are used per year in the U.S.

## REFERENCES

- Loganathan, et al. 2007. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. *Water Research* 41: 4611-4620.
- Sinclair, E., and Kannan, K. 2006. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. *Environmental Science and Technology* 40: 1408-1414.
- Schultz, M.M., et al 2006. Fluorochemical mass flows in a municipal wastewater treatment plant. *Environmental Science and Technology* 40: 7350-7357.
- ATSDR 2000. Toxicological Profile for Chromium. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, GA. September 2000.

The facility has switched to a new product, MSP-28™ (Atotech USA, Rock Hill, SC) that analysis showed contains a much lower amount of PFOS, 460 ng/L. With some adjustment, the facility has been able to meet its hexavalent chromium emission limits using the replacement product.

Analysis of samples of other plating solutions in the facility (which also does copper and nickel plating) have confirmed that the chrome plating solution is the primary source of PFOS, and that since the switch was made to the replacement product PFOS levels in the chrome plating solution have declined, as shown in the table below.

## PFOS DATA, CHROME PLATING FACILITY

	Date	PFOS, ng/L*
Copper Plating Solution	11/14/2007	1,250
Nickel Plating Solution #1	12/12/2007	476**
Nickel Plating Solution #4	3/3/2008	212
Chrome Plating Solution	8/13/2007	7,414,000
	10/25/2007	1,650,000
	11/14/2007	823,000
	12/12/2007	1,635,000**
	3/3/2008	98,300

\*Analyses done by MPI Research, Inc, State College, PA  
 \*\*Analysis done by MDH Public Health Laboratory, St. Paul, MN

Levels of one other PFC, perfluorobutane sulfonate (PFBS) were also found to be exceptionally high in the chrome plating solution, up to 176,000,000 ng/L, or 176 parts per million.

In August 2007, the MPCA collected samples of four species of fish from the Mississippi River in Brainerd for analysis of PFCs by Axys Analytical Services. Relatively low levels of PFOS were detected in the fish fillet tissue samples, much lower than the threshold used by MDH for the issuance of fish consumption advice.

The findings of the Brainerd investigation represent the first comprehensive look at PFOS inputs to a WWTP, and the first documentation of the importance of chrome plating as a possible source of PFOS to a WWTP. Little is currently known about levels of PFOS in agricultural fields where PFOS-containing sludge from WWTP facilities is land applied, and further research is needed on the uptake of PFOS by crops or grazing animals.

## For more information:

- <http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/index.html>
- <http://www.pca.state.mn.us/cleanup/pfc/index.html>

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