Report for 2001MN3441B: Fluorochemicals in Minnesota Waters: An Emerging Environmental Issue

There are no reported publications resulting from this project.

Report Follows:

Fluorochemicals in Minnesota waters: An emerging environmental issue

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Project duration: January 31, 2001 to January 30, 2003

Summary

Perfluorochemicals are an emerging class of global concern. To date the only established methods for their determination in environmental samples have been LC/MS/MS and ^{19}F NMR, requiring expensive equipment. In order to open the field of investigation to a broader range of environmental laboratories, we developed a single quadrupole LC/MS method for the determination of perfluorochemicals in environmental samples employing a fluorous silica gel column for the removal of chromatographic intereference. This method has been validated for fish tissue and surface water samples. In addition to method development we have collected water, sediment and fish tissue samples to test several hypotheses. Our overall hypothesis is that the global distribution of perfluorochemicals is due to atmospheric transport. We therefore sampled a group of small lakes that are expected to only be subject to atmospheric sources. Preliminary results indicate the presence of one perfluorochemical, perfluorooctane sulfonate (PFOS), in livers from northern pike from Agnes Lake, supporting our hypothesis that atmospheric deposition is responsible for transport of perfluorochemicals to the environment. We have also collected water samples from several lakes, rivers and waste water treatment plants to determine spatial distributions in Minnesota waters and identify specific sources such as waste water treatment plants and/or urban areas.

Introduction

Fluorochemicals represent an emerging issue of environmental concern due to their global distribution, persistence and bioaccumulation. It is the hypothesis of this project that their global distribution is a result of atmospheric transport. The objectives of this project are to establish baseline data on the concentrations of these chemicals in surface waters and sewage treatment effluent around the state of Minnesota, and use spatial heterogeneity to infer source areas and transport mechanisms. A group of lakes under study are located in Voyageurs National Park with no industry or surface water inflow from industrial areas. By detecting fluorochemicals of interest in these lakes, where the only possible source is atmospheric deposition, we will directly test our hypothesis.

Table 1.

Lake	County	Geographic Region	Media	Date Sampled
Locator	St. Louis	remote	water & fish	5/24/01
Loiten	St. Louis	remote	water	5/24/01
Shoepack	St. Louis	remote	water	5/23/01
Jorgens	St. Louis	remote	water	5/23/01
Agnes	St. Louis	remote	water & fish	5/23/01
Little Trout	St. Louis	remote	water & fish	5/24/01
Fish Trap	Morrison	agricultural	water	8/18/01
Itasca	Clearwater	remote	water	8/22/01
Minnetonka	Hennepin	suburban	water	6/3/01
			water	7/12/01
			water	8/16/01
			water	5/19/02
Mississippi River	Hennepin	urban	water	6/24/02
Lake Calhoun	Hennepin	urban	water	6/24/02
Lake of the Isles	Hennepin	urban	water	6/24/02

Results to date

To date, we have sampled several surface waters in Minnesota (Table 1), and sampled the remaining lakes, rivers and sewage treatment plants from our original list in the fall of 2002. At this time we have analyzed water from Lake Minnetonka, and fish from Lake Erie and Agnes Lake in Voyageurs National Park. We have detected both perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) in the water sample and PFOS in most of the fish samples.

Significant chromatographic interferences from dissolved organic carbon in the water samples and biological molecules from the fish samples occurred without prior liquid-solid chromatography. These interferences are a problem only with single quadrapole LC/MS because we are unable to monitor the transition from parent to daughter ions, as is possible with more expensive instrumentation used for LC/MS/MS. Therefore we have developed an analytical chemistry method to clean-up environmental samples and make them amenable to single quadrapole LC/MS.

Our inspiration for separating the intereferences from the fluorochemicals comes from synthetic organic chemistry where fluorinated compounds are removed from nonfluorinated compounds using fluorous silica gel. The theory is that the fluorous silica gel will selectively retain fluorinated compounds, but release them with the appropriate solvent. We have been successful in our attempts to separate perfluorochemicals from environmental matrices using this technique and have recently submitted for publication the results from the fish samples. Figures 1 and 2 illustrate the efficiency of fluorous silica gel to separate fluorochemicals from environmental interferences. Results of the

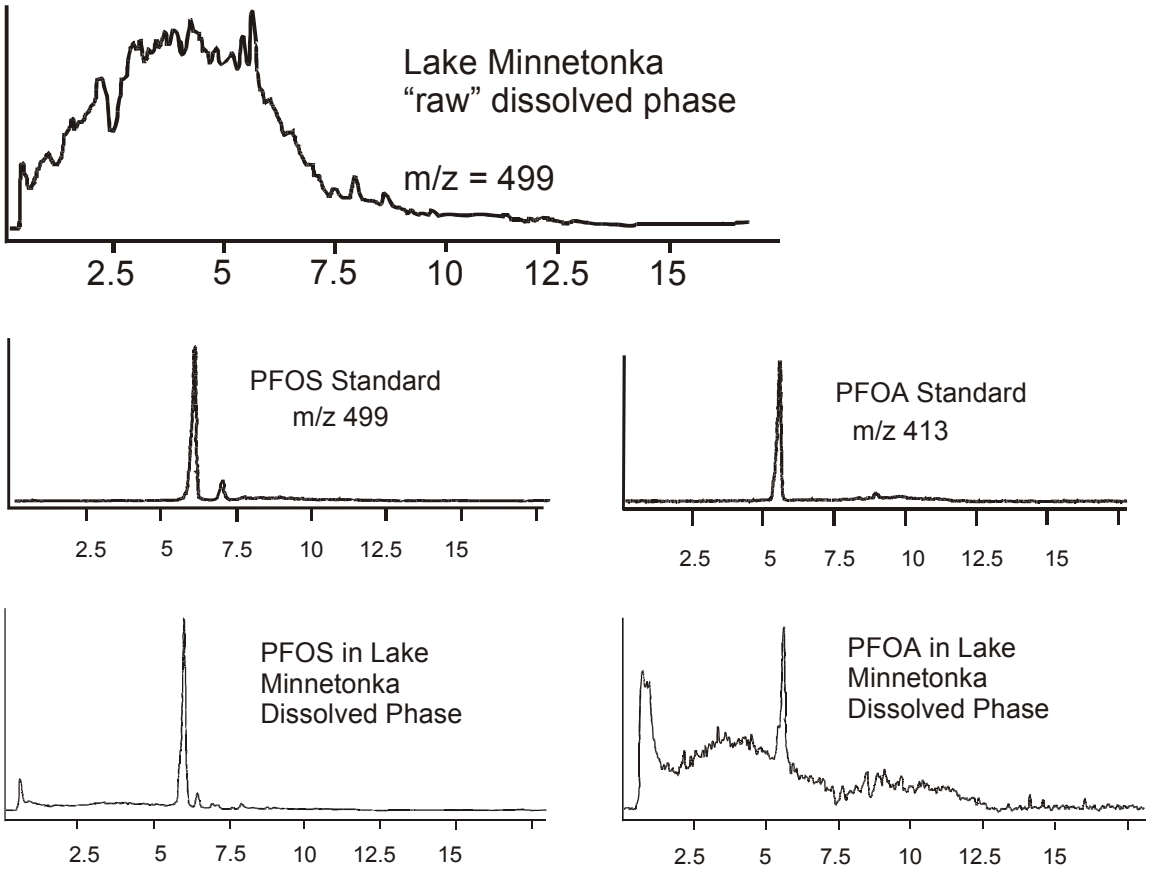

Figure 1. LC/MS chromatograms comparing "raw" water extracts and "cleaned-up" water extracts from Lake Minnetonka.

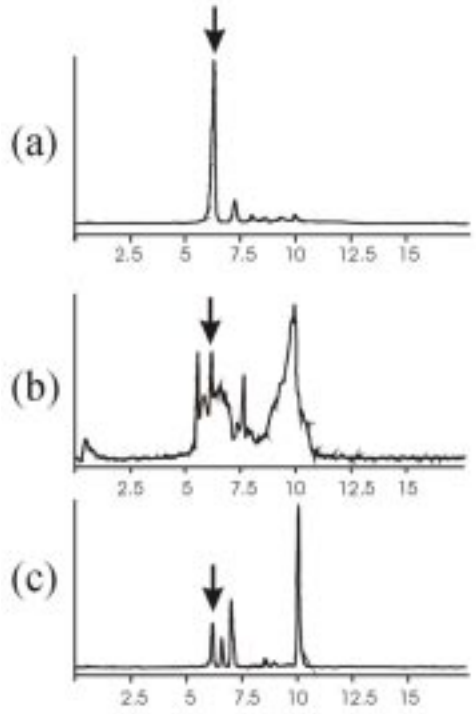

Figure 2. Lake Erie walleye extracts analyzed by HPLC-ES/MS: (a) extracted ion chromatogram of PFOS standard with parent ion 499; (b) extracted ion chromatogram of uncleaned fish extract with m/z of 499; (c) extracted ion chromatogram of cleaned fish extract by fluorour silica gel. Arrows indicate PFOS peaks. From: Dorweiler and Simcik, in review.

samples analyzed to date are summarized in Table 2.

Ongoing work

Our next step is to continue collecting surface water samples from around the state of Minnesota. During fall and winter we will analyze these samples, as well as the associated filters and sediment samples, to determine the partitioning of perfluorochemicals.

Summary of important findings

The successful development of a method conducive to single quadrupole liquid chromatography mass spectrometry (LC/MS) will enable many more investigators to study the environmental chemistry of the emerging contaminant class of perfluorochemicals.

List of publications and presentations

Dorweiler, K.J. and M.F. Simcik. 2002. Detection and Quantitation of Perfluorinated Chemicals in Fish Samples Using Single Quadrupole LC/MS *Environmental Science & Technology* (submitted)

Dorweiler, K.J. and M.F. Simcik. 2002. Detection and Quantification of Perfluorinated Chemicals in Surface Waters, International Association for Great Lakes Research 45th Conference on Great Lakes Research, Winnipeg, MB June 2-6, 2002

Dorweiler, K.J. and M.F. Simcik. 2002. Analysis of Minnesota Surface Water Samples for Fluorinated Surfactants, Minnesota Water 2002 Conference, St. Cloud, MN. April 18, 2002.

Table 2.

Sample	PFOS	PFOA
Lake Minnetonka	3.5 ng/L	3.5 ± .3 ng/L (n=3)
Lake Erie Walleye 1	28 ng/g wet weight	ND
Lake Erie Walleye 2	7.1 ng/g wet weight	ND
Agnes Lake Northern Pike 1	1.1 ng/g wet weight	ND
Agnes Lake Northern Pike 2	0.91 ng/g wet weight	ND
Agnes Lake Northern Pike 3	ND	ND

Related submitted grants

Project Title: Perfluorinated Surfactants in Great Lakes Fish
Current/Pending: Pending
Source of Support: Minnesota Sea Grant
Total Award Amount: $63,297
Total Award Period Covered: 02/01/03 – 1/31/05

Student training

Kelly J. Dorweiler, Environmental Health, M.S. expected Spring 2003.