

# **Report for 2002MN8B: 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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## **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  $^{19}\text{F}$  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 fluorosilica gel column for the removal of chromatographic interference. This method has been validated for fish tissue samples by quadrupole time of flight mass spectrometry to insure that no other ions coelute with our PFCs and that all ion suppression/matrix effects have been removed. This clean-up method will enable users of HPLC coupled to any type of mass spectrometer to routinely analyze environmental samples for PFCs. Furthermore it will allow for the quantitation of ion suppression/matrix effects by manufacturing blanks that contain compounds from the matrix, but not PFCs. In developing this method, analyses indicate the presence of perfluorooctane sulfonate (PFOS), in livers from northern pike from three remote lakes, supporting our hypothesis that atmospheric deposition is responsible for transport of perfluorochemicals to the environment.

## **Introduction**

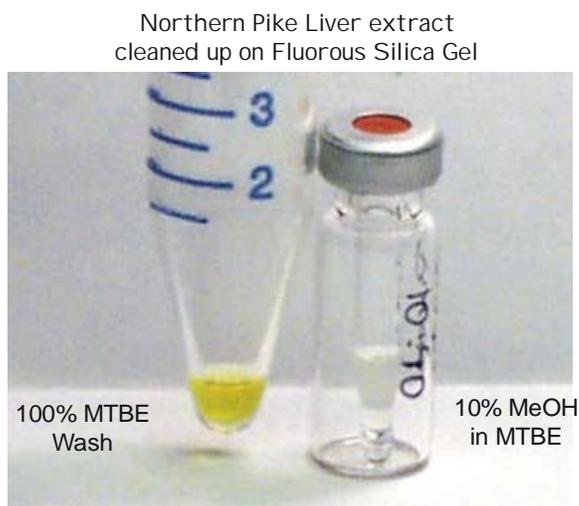
Perfluorochemicals (PFCs) represent an emerging issue of environmental concern due to their global distribution, persistence and bioaccumulation. It is the hypothesis of this project that their global distribution is a result of atmospheric transport. However, there are analytical barriers to testing this or any other hypothesis regarding the environmental fate and transport of perfluorochemicals. Unlike most of the well-studied hydrophobic organic contaminants (HOCs), perfluorochemicals are not lipophilic, but lipophobic and therefore do not accumulate in the fat stores of organisms. Rather they bind to proteins in the blood, liver and bile. The PFCs must first be liberated from the proteins using ion pair extraction in an established method. Once liberated, the PFCs must be detected. Contrary to most other HOCs, most PFCs are rather nonvolatile and cannot be determined by gas chromatography. The advent of liquid chromatography coupled with electrospray mass spectrometry has allowed for the analysis of PFCs. However, there are compounds that interfere with the determination of PFCs. To date this problem has been solved using LC/MS/MS where the transition from parent to daughter ion is monitored. LC/MS/MS is much more expensive than single quadrupole LC/MS, and not as available to most environmental chemistry researchers. Furthermore, other compounds present in the sample matrix can affect the initial ionization of analyte through what is often called ion

suppression or matrix effects. Other researchers have found these matrix effects/ion suppression by standard addition to environmental samples. This is time consuming and must be done to every sample if ion suppression/matrix effects are to be quantified, and knowledge of the presence of these effects still does not allow for the quantitation of the effect. Therefore what is needed is a robust clean-up technique for the analysis of a variety of environmental matrices for routine analysis of samples for PFCs. Once established, the clean-up technique will allow analysis by single quadrupole or triple quadrupole mass spectrometry for the investigation of environmental fate and transport of PFCs.

## Results

Our inspiration for separating the interferences 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. Initial tests proved fruitful using a combination of methanol and water. Subsequent batches of fluorous silica gel and recleaned fluorous silica gel from the first batch did not behave the same. Therefore more extensive method development was performed on new and re-used fluorous silica gel from two different suppliers. The resulting method involves a glass column and either Fluoroflash (Hologent Technologies, Inc. Baldwin Park, CA) or Fluorochrom (Silicycle, Quebec Canada) fluorous silica gel as follows.

A slurry of methanol and approximately 10 g of FluoroFlash or Fluorochrom was added to a 1 cm diameter glass column to pack a 1 cm by 16 cm column. No less than 200 mL of methanol was eluted through the column to clean the fluorous silica gel. The column was then conditioned with 50 mL of MTBE. The fish tissue extract was loaded onto the column followed by three 50  $\mu$ L rinses of MTBE to quantitatively transfer the entire sample onto the column. The column was wash with 20 mL of MTBE and 20 mL of 5:95 methanol:MTBE. The column was eluted with 10:90 methanol MTBE to remove PFOS. The column was finally rinsed with 50 mL of methanol to remove any remaining extract components from the column. The 10:90 eluent was then reduced under a gentle stream of ultra-pure nitrogen to approximately 100  $\mu$ L. An internal standard (PFDoA) was added to the sample and sample delivered into an autovial for analysis. A depiction of the MTBE fraction and 10:90 fraction is given in Figure 1.



During standard tests, the PFCs were retained on the column until the final 100% methanol rinse, but it appears that the lipid components of the fish extracts act as a mobile phase to remove PFOS from the fluorosilica gel column.

Extracts of fish liver and whole fish homogenate were analyzed by single quadrupole LC/MS and PFOS was determined quantitatively without chromatographic interference. The extracts were then sent to Doug Kuehl of the US EPA's Mid-Continent Ecological Division in Duluth Minnesota for analysis by quadrupole time of flight mass spectrometry (LC/Q-TOF). Chromatograms run on the Q-TOF showed only PFOS in the extract, concluding that the fluorosilica gel clean-up method adequately removes all interfering compounds, eliminating ion suppression/matrix effects (Figure 2).

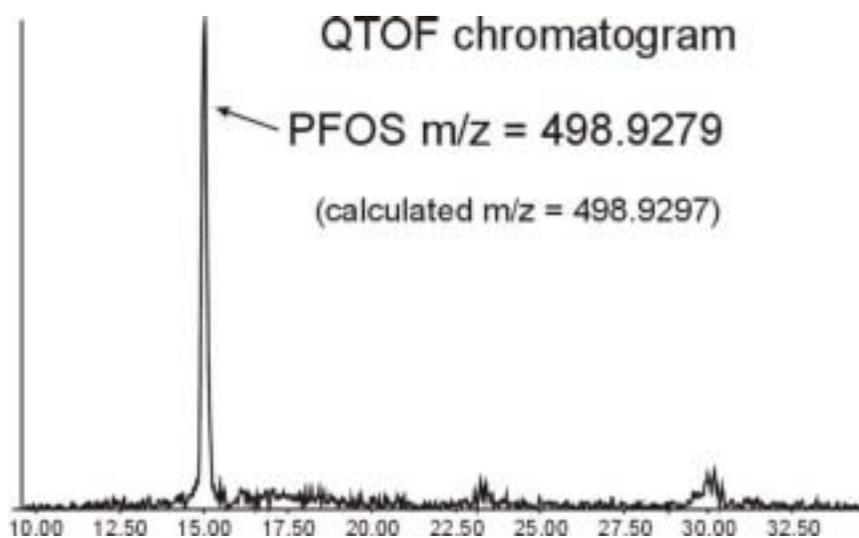


Figure 2. QTOF chromatogram showing PFOS in fish extract cleaned up by fluorosilica gel.

Another advantage to the fluorosilica gel clean-up method that we have developed comes about in the study of ion suppression/matrix effects. The traditional way of quantifying ion suppression/matrix effects is to add your analyte of interest between the HPLC and MS as a baseline, and then inject a blank into the HPLC and observe changes in the baseline at the retention time of your analyte. The reason that PFCs have become such an environmental concern is the detection of PFOS in humans and wildlife around the globe. As such there are no available blanks for analysis. Our fluorosilica gel clean-up method has the potential to manufacture blanks as seen by the MTBE fraction in Figure 1.

Samples used for the development of the fluorosilica gel clean-up method included livers from northern pike taken from three remote lakes in Voyageurs National Park on the northern border of Minnesota with Canada. The three lakes are Agnes, Locator and Little Trout. These lakes have no inlet, outlet or industry. The only access is by foot, therefore, it is felt that any PFCs present in these fish will represent atmospheric transport to these remote sites. Results of the fish liver samples are summarized in Table 2.

Table 2.

Lake	Tissue	PFOS Concentration (ng/g wet weight)
Locator	Liver	ND
Locator	Liver	12.2
Little Trout	Liver	0.81
Little Trout	Liver	ND
Little Trout	Liver	18.5
Little Trout	Liver	3.63
Agnes	Liver	0.57
Agnes	Muscle	0.08
Agnes	Liver	0.46
Agnes	Muscle	ND
Agnes	Liver	1.1
Agnes	Muscle	ND

### Future work

The clean-up method is being prepared for publication and will make up the majority of Kelly J. Dorweiler's Masters Thesis. The method will also be tested for efficacy on water samples, and those samples collected by this study will eventually be cleaned and analyzed. These samples include:

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
Lake Harriet	Hennepin	urban	water	6/24/02
Minnesota River	Scott	suburban/agricultural	water	6/24/02
White Bear Lake	Washington	suburban	water	7/11/02

### 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. It will also remove ion suppression/matrix effects for those investigators using LC/MS/MS and can be used to manufacture blanks for ion suppression/matrix effects experiments.

**List of Publications and Presentations:**

Kelly J. Dorweiler and Matt F. Simcik, "Detection and Quantitation of Perfluorinated Chemicals in Fish Samples Using Single Quadrupole LC/MS" submitted to *Environmental Science & Technology* **in review**

Matt F. Simcik, "Use of single quadropole LC/MS in perfluorochemical analysis." Presented at the Approaches to the analysis of PFOA and its salts in environmental matrices – problems and pitfalls Workshop in Hamburg, Germany. Sponsored by the Association of Polymer Manufacturers Europe May 1-2, 2003.

Matt F. Simcik and Kelly J. Dorweiler, "Detection and Quantification of Perfluorochemicals in Environmental Samples," Society of Environmental Toxicology and Chemistry 23<sup>rd</sup> Annual Meeting, Salt Lake City, UT, November 16-20, 2002

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

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

**Student Training:**

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

Alison Wagner, Chemistry, undergraduate.