

Atmospheric Deposition of Perfluorochemicals to Surface Waters

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INTRODUCTION

Perfluorochemicals (PFCs) are industrially produced compounds that contain a perfluorinated alkyl moiety of varying chain length and varying functional groups attached to that moiety. PFCs such as perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been found in fish, birds and mammals from mid-latitudes to the poles¹. These findings were initially surprising given the low volatility and relatively high aqueous solubility of these two compounds. Therefore, a major question regarding the global distribution of PFCs is one of transport.

Some have suggested that degradation of more volatile precursors such as the perfluorinated sulfonamides could degrade to PFOS². Recent work suggests that volatile PFCs including the fluorotelomer alcohols can be transported to remote regions via the atmosphere where they can react to form non-volatile perfluorocarboxylates such as perfluoroheptanoic acid (PFHpA), PFOA and perfluorononanoic acid (PFNA)³. The 8:2 fluorotelomer alcohol has also been shown to biodegrade aerobically to PFOA⁴. Therefore, there are two expected pathways of environmental contamination of PFCs, atmospheric transport of precursor chemicals with subsequent atmospheric or biodegradation and direct discharge of contaminated water. Because PFOA has both atmospheric and non-atmospheric sources, it is expected to dominate the perfluorocarboxylate distribution in surface waters near sources such as urban areas and wastewater treatment plants. However, in remote areas such as the arctic and land-locked lakes with little to no human interaction, where atmospheric deposition is thought to be the dominant pathway, other perfluorocarboxylates are expected to be present at equal or higher levels.

METHODS

Twelve surface water samples were taken from the Midwestern United States. Four waters were in the urban area of Minneapolis, MN including three connected lakes (Lake of the Isles, Lake Calhoun and Lake Harriet) and the Minnesota River. These waters are expected to have non-atmospheric sources of PFCs given their urban location and the presence of runoff and wastewater discharge. Four waters were from remote portions of Minnesota. Two are located along the north shore of Lake Superior in Tettegouche State Park (Tettegouche and Nipisiquit) approximately 6 km north of the town of Silver Bay, MN and 90 km northeast of Duluth, MN. The other two are from Voyageurs National Park along the U.S.-Canadian border (Loiten, Little Trout). The remote lakes are all hike-in lakes (no roads) and have no surface inflow. Therefore, any PFCs found in these lakes are expected to be from atmospheric deposition. Eight liter samples were taken at these eight sites by canoe at arms-length depth using 4L HDPE bottles (Nalgene, Rochester, NY). The final four samples are from two sites in Lake Michigan, one in the northern basin (site 47M) and one in the southern basin (site 18M). Water at these two sites was sampled at mid-epilimnetic and mid-hypolimnetic depths aboard the *RV Lake Guardian* using the rosette sampler, which is equipped with 8L polyethylene canisters that can be closed at varying depths. Water was transferred from the rosette canisters to 4L HPDE bottles totaling 4L from each site/depth.

Minnesota surface waters were filtered through 0.4 μm nylon filters prior to extraction. All samples were then extracted using 10g C_{18} solid phase extraction (SPE) cartridges (Supelco, Bellefonte, PA). The SPE cartridges were pre-conditioned with 25 mL each of methanol and HPLC water. The surface water was pulled through the SPE cartridge with a vacuum at a rate of 50 mL/min. The SPE cartridges were then centrifuged and pre-purified nitrogen passed through them to remove residual water. They were then eluted with 25 mL of methanol, taken to dryness under pre-purified nitrogen and reconstituted with approximately 1 mL of MTBE.

Once in MTBE the samples were cleaned up according to a liquid solid chromatography column method employing fluorous silica gel developed in our laboratory. Cleaned extracts were analyzed by single-quadrupole LC/MS. Quantitation of all PFCs is based on the parent ion relative to a four point external calibration standard series.

RESULTS AND DISCUSSION

PFOS was detected in all but two surface waters and the concentration ranged from ND to 47 ng/L. In the four remote lakes the concentration ranged from ND to 1.2 ng/L which is consistent with some of the lowest values reported in the literature, and reflects that lack of sources of PFCs to the region. The PFOS concentrations from urban surface waters ranged 2.4 to 47 ng/L. This range is similar for other urban waters from around the world such as Japan where Taniyasu *et al*⁵ reported values of ND to 59 ng/L and Saito *et al*⁶ reported values of 0.4 to 37 ng/L for urban waters not associated with any major source of PFOS. It is also similar to values reported by Hansen *et al*⁷ of 18 to 53 ng/L in the Tennessee River upstream of manufacturing plant. The range in PFOS concentration from Lake Michigan was from 0.93 to 3.1 ng/L with similar values for all samples except the epilimnion at site 47M in the northern basin (0.93 ng/L vs. 2.7 ± 0.4). These values are much smaller than those reported by Boulanger *et al*⁸ for Lake Erie (11 to 39 ng/L) and Lake Ontario (15 to 121 ng/L). It is not certain why Lake Michigan would have much lower concentrations of PFOS than Lakes Erie or Ontario.

PFOA was detected in all samples, and therefore in greater frequency than PFOS. The PFOA concentration in remote lakes ranged from 0.14 to 0.66 ng/L remote, which is among the lowest values reported for surface waters, similar to the lower concentrations found in the coastal waters of Hong Kong, South China and Korea⁹ and in surface waters of Japan⁶. The urban surface water PFOA concentration ranged from 0.45 to 19 ng/L, which is similar to the range reported for coastal Hong Kong and South China⁹ and Japan⁶, but lower than range reported for the coastal waters of Korea⁹ and the Tennessee River downstream of a production plant⁷. The Lake Michigan PFOA concentrations ranged from 0.28 to 3.4 ng/L, and was similar between the hypolimnion and epilimnion at a given site, but concentrations were lower at site 47M (0.34 and 0.28 ng/L for hypolimnion and epilimnion, respectively) than 18M (3.1 and 3.4 for hypolimnion and epilimnion, respectively). As for PFOS, these concentrations are much lower than those reported by Boulanger *et al*⁸ for Lake Erie (21 to 47 ng/L) and Lake Michigan (15 to 70 ng/L). Again, it is not clear why Lake Erie and Lake Ontario would have much higher PFOA concentrations, however, Boulanger *et al*⁸ also reported quite high field blanks (~10ng/L).

One other PFC was detected in all surface water samples, perfluoroheptanoic acid (PFHpA). In some cases PFHpA was dominant PFC in water. PFHpA concentrations ranged from 0.25 for LM47 Hypolimnion to 10.2 for Lake Calhoun, but remote lakes had relatively high concentrations ranging from 0.85 ng/L for Nipisiquit to 9.7 for Loiten.

This PFC has not been reported by other investigators for surface waters, so comparisons to background or source regions is not possible. However, given the relatively high concentrations found in remote lakes of Minnesota, it stands to reason that atmospheric deposition is a major source of PFHpA to surface waters. Therefore, the ratio of PFHpA to PFOA can be used as an effective tracer of atmospheric deposition. This ratio varies among regions of surface water in the Midwestern United States. For urban waters the ratio is less than unity indicating that PFOA concentrations exceed the PFHpA concentrations. This is expected since there are non-atmospheric sources of PFOA to these surface waters. As the surface waters increase in distance from urban areas the ratio increases. For the remote areas of Tettegouche State Park the ratio is around 6-7 (Table 1.) and for the more remote lakes of VNP the ratios are even higher (13 and 16 for Little Trout and Loiten Lakes, respectively). Therefore, the PFHpA to PFOA ratio seems to indicate the importance of urban areas to perfluorocarboxylates in surface water and hence the relative importance of atmospheric deposition.

REFERENCES

1. Giesy, J.P. and K. Kannan, *Global distribution of perfluorooctanesulfonate in wildlife*. Environmental Science and Technology, 2001. **35**(7): p. 1339-1342.
2. Martin, J.W., et al., *Collection of Airborne Fluorinated Organics and Analysis by Gas Chromatography/Chemical Ionization Mass Spectrometry*. Analytical Chemistry, 2002. **74**(3): p. 584-590.
3. Ellis, D.A., et al., *Degradation of Fluorotelomer Alcohols: A Likely Atmospheric Source of Perfluorinated Carboxylic Acids*. Environmental Science and Technology, 2004. **38**(12): p. 3316-3321.
4. Dinglasan, M.J.A., et al., *Fluorotelomer Alcohol Biodegradation Yields Poly- and Perfluorinated*

Acids. Environmental Science and Technology, 2004. **38**(10): p. 2857-2864.

5. Taniyasu, S., et al., *A Survey of Perfluorooctane Sulfonate and Related Perfluorinated Organic Compounds in Water, Fish, Birds, and Humans from Japan*. Environmental Science and Technology, 2003. **37**(12): p. 2634-2639.

6. Saito, N., et al., *Perfluorooctanoate and perfluorooctanesulfonate concentrations in surface water in Japan*. Journal of Occupational Health, 2004. **46**(1): p. 49-59.

7. Hansen, K.J., et al., *Quantitative Characterization of Trace Levels of PFOS and PFOA in the Tennessee River*. Environmental Science and Technology, 2002. **36**(8): p. 1681-1685.

8. Boulanger, B., et al., *Detection of Perfluorooctane Surfactants in Great Lakes Water*. Environmental Science and Technology, 2004. **38**(15): p. 4064-4070.

9. So, M.K., et al., *Perfluorinated Compounds in Coastal Waters of Hong Kong, South China, and Korea*. Environmental Science and Technology, 2004. **38**(15): p. 4056-4063.

Table 1. Ratios of PFHpA to PFOA in Surface Water Samples from the Midwestern United States

Site	Region	PFHpA/PFOA
Loiten	Remote – Voyageurs NP	16
Little Trout	Remote – Voyageurs NP	13
Nipisiquit	Remote – Tettegouche SP	6.0
Tettegouche	Remote – Tettegouche SP	6.8
Calhoun	Urban	0.53
Lake Harriet	Urban	0.76
Lake of the Isles	Urban	0.90
Minnesota River	Urban	0.61
47M Epilimnion	Lake Michigan	1.2
47M Hypolimnion	Lake Michigan	0.74
18M Epilimnion	Lake Michigan	1.2
18M Hypolimnion	Lake Michigan	0.26

Figure 1. Concentrations of PFCs in Surface Waters from the Midwestern United States.

