Perfluorooctanoic Acid and Perfluorooctane Sulfonate in Michigan and New York Waters

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Introduction

Perfluorooctane sulfonate (PFOS), a perfluorinated organic contaminant, has become the subject of many recent investigations. PFOS and its precursor compounds have been used in a wide variety of consumer and industrial products. Other related perfluorinated compounds have also been reported to occur in the environment. For example, perfluorohexane sulfonate (PFHxS) is an impurity associated with PFOS. Perfluorooctanoic acid (PFOA) has found widespread use as an emulsifier for polymerization of fluoropolymers. These perfluorinated alkylated substances (PASs) are known to be resistant to degradation[1].

PFOS and PFOA have been detected in the blood of occupationally exposed workers at a few mg/L concentrations (mean 1.32 mg/L and 1.78 mg/L, respectively), and in the general population at µg/L concentrations (mean 28.4 µg/L PFOS) [2,3]. PFOS and PFOA have been detected in biota globally [4]. There is strong evidence to suggest that these PASs can bioaccumulate in the trophic levels of a food chain. Higher concentrations of PFOS are generally detected in fish eating predators than in the fish. The production of certain PASs, particularly those that are PFOS-related, has been phased out because of this concern of bioaccumulation, their detection in human serum and sparse knowledge of their toxicology[5]. Due to their persistence, these compounds will continue to be of concern for years. This highlights a need for accurate analysis of environmental samples for effective risk assessment[5].

Water analysis of PFOS and PFOA has been carried out with several methods. The most commonly used methods involve solid phase extraction (SPE) followed by HPLC-MS-MS. Method detection limits for PFOS and PFOA varied between 5 and 17 ng/L and 9 and 25 ng/L respectively[6,7]. Generally PFOS and PFOA concentrations in ambient waters, with no point source of pollution, are less than 5 ng/L [5]. We have developed a method using the Oasis HLB solid phase cartridge to achieve the required method detection limits. We have measured PFOS and PFOA concentration in surface waters collected from Michigan and New York.

PFOS and PFOA have been detected in the blood and liver of fish at µg/L concentrations both in Japan and the USA[5,6]. The current ion-pairing, liquid/liquid extraction method is suitable for these concentrations and we have measured PFOS and PFOA in the livers of fish from Michigan and New York waters. We have compared the data for fish and water concentrations and calculated bioaccumulation factors.

Methods and Materials

A total of 51 water samples, 56 fish liver samples, 24 fish egg samples and 31 fish muscle tissue samples, from Michigan waters were analyzed in this study. All samples were frozen until analysis. Whole fish were collected from Michigan waters of the Great Lakes and in inland water bodies in New York. Fish from Michigan were collected in 1999 and 2000. Water samples from Michigan were collected in 2001. Fish and water from New York were collected in 2003 and 2004. Water samples were thawed and allowed to settle. Aliquots (200 mL) were decanted slowly from each sample into polypropylene bottles. These samples were then spiked with PFBS recovery standard (10 ng) and extracted with Oasis HLB SPE cartridges (60 mg). Cartridges were preconditioned with methanol (4 mL) and then water (4 mL). Cartridges were washed with 40% methanol (4 mL) and then completely dried. The cartridges were then eluted with methanol (4 mL), and the eluent was concentrated to 1mL for analysis by HPLC-MS/MS.
Fish liver (1 g) was homogenized in milli-Q water (5 mL). Tetrabutylammonium hydrogen sulfate, 0.5M, (1 mL, pH10) and 0.25M Na_2CO_3/$NaHCO_3$ buffer (2 mL) were then added along with MTBE (5 mL). Samples were shaken for 20 min then centrifuged for 20 min to separate layers. An aliquot of the organic layer (4 mL) was transferred to a 15 mL polypropylene tube. This was concentrated with nitrogen gas to dryness and resuspended by vortexing in methanol (1 mL). This extract was filtered through 0.2 µm nylon mesh filter into an autosampler vial. Extracts were stored at -4 °C until analysis by HPLC-MS/MS.

Analytes were separated with a Hewlett-Packard® Series 1100 Liquid Chromatograph system with a Keystone® Betasil™ C_{18} 2x50 mm (5 µm) column**.** The mobile phase was held at 90% 2mM ammonium acetate, 10% methanol, then ramped to 90% methanol at 6 min. This was increased to 100% methanol at 11 min before being ramped back down to 10% methanol at 13 min. Flow rate was kept at 200 µL/min. Analytes were detected by a Micromass® API/mass spectrometer Quattro II™ Triple Quadrupole system. Optimal parameters were; cone voltage: 30–60 V, collision gas energy: 25–45 eV, mode: electrospray negative, source temperature: 150ºC ±10ºC. The following ion transitions were monitored; PFOS 499>99,80; FOSA 498>78, PFOA 413>169; PFHS 399>99; THPFOS 427>80.

Results and Discussion

Michigan Fish

PFOS was detected in the livers of chinook salmon, lake whitefish, and various other fish (see Table 1). Brown trout livers had significantly lower PFOS concentrations. Brown trout feed mainly on zooplankton, and less on small fish and invertebrates, than chinook salmon or lake whitefish. This explains the lower bioaccumulation of PFOS in brown trout liver tissue. Further, brown trout was collected from Lake Superior, which is relatively less polluted than other great lakes. PFOA, PFHS and FOSA were not detected in any fish liver samples at the detection limit of 19 ng/g (wet weight), for FOSA and PFHS, and 72 ng/g for PFOA.
These results are consistent with concentrations reported for the livers of fish from Tokyo Bay (62 – 198 ng/g)[5]. PFOS concentrations reported for fish liver from Lake Biwa, Japan, ranged from 3 to 310 ng/g. The data shows species specific concentration ranges and are likely determined by the diet of each species.

PFOS was detected in the muscle tissue of chinook salmon, lake whitefish, and various other fish (see Table 1). These concentrations are comparable or slightly higher than those detected in the liver of the same fish species. PFOA, PFHS and FOSA were not detected in any fish muscle samples. PFOS was detected in the eggs of chinook salmon, lake whitefish, and various other fish (see Table 1). These concentrations are approximately twice as high as concentrations found in the livers of the same fish species. This suggests that PFOS is actively transferred from adult female fish to their eggs. Occurrence of PFOS in eggs has implications for early life stage effects. In addition, these results suggest that PFOS can bind to specific proteins found in eggs, which could be the reason for high levels in eggs than in muscle or liver.

Table 1 – Concentrations of PFOS (ng/g, wet weight) detected in fish from Michigan, USA

Species	**Tissue**	**Location**	**PFOS**
Chinook salmon (n=6)	Liver	Webber Dam, Grand River, Michigan	32-173 (**100**)
Lake whitefish (n=5)	Liver	Great Lakes/Thunder Bay, Lake Huron	33-81 (**67**)
Brown trout (n=10)	Liver	Great Lakes/Lake Superior/Marquette	<17-26*
Various species (n=35)**	Liver	Inland Lakes, Michigan	<7.7-120 (**43**)
Carp (n=10)	Muscle	Saginaw Bay, Michigan	59-297 (**124**)
Chinook salmon (n=6)	Muscle	Webber Dam, Grand River, Michigan	<7-189 (**107**)
Lake whitefish (n=5)	Muscle	Great Lakes/Thunder Bay, Lake Huron	97-168 (**132**)
Brown trout (n=10)	Muscle	Great Lakes/Lake Superior/Marquette	<7-46*
Lake whitefish (n=2)	Eggs	Great Lakes/Thunder Bay, Lake Huron	145-381 (**263**)
Brown trout (n=3)	Eggs	Great Lakes/Lake Superior/Marquette	49-75 (**64**)
Various species** (n=19)	Eggs	Inland Lakes, Michigan	<7.7-222 (**69**)

*Only one or two samples above the limit of quantification – mean not calculated; Values below LOQ are denoted by '<'
Values below the detection limit were not included in the estimation of mean (in parentheses)
** Various species include: Coho salmon, lake trout, white sucker, carp, redhorse sucker, and largemouth bass from several Michigan lakes and rivers

Michigan Waters

PFOS was detected in 89% of Michigan water samples. The maximum concentration measured was 29 ng/L. PFOA was detected up to 36 ng/L. Background concentrations were found to be between 2 and 5 ng/L for PFOS and between <8 and 16 ng/L for PFOA. The highest concentrations were detected in the waters of south western Michigan (see Table 2). There are several paper mills located in this area which may provide a source for these high concentrations. Elevated concentrations of PFOS and PFOA were detected in and around Flint, and in Saginaw Bay waters.
The highest concentration of PFOS detected in Michigan waters was between 2.5 and 4.8 times lower than those detected downstream of a fluorochemical manufacturing facility on the Tennessee River[7] (75 – 144 ng/L). The range of PFOS concentrations detected in Michigan waters was similar to those found in Japanese surface waters[5].
The highest concentration of PFOA detected in Michigan waters was 3.8 – 14 times lower than those detected downstream of a fluorochemical manufacturing facility on the Tennessee River[7] (140 – 498 ng/L). PFOA concentrations measured in upstream of the fluorochemical manufacturing facility were reported as < 25 ng/L.

Fig 1 - Sampling Locations of Water in Michigan

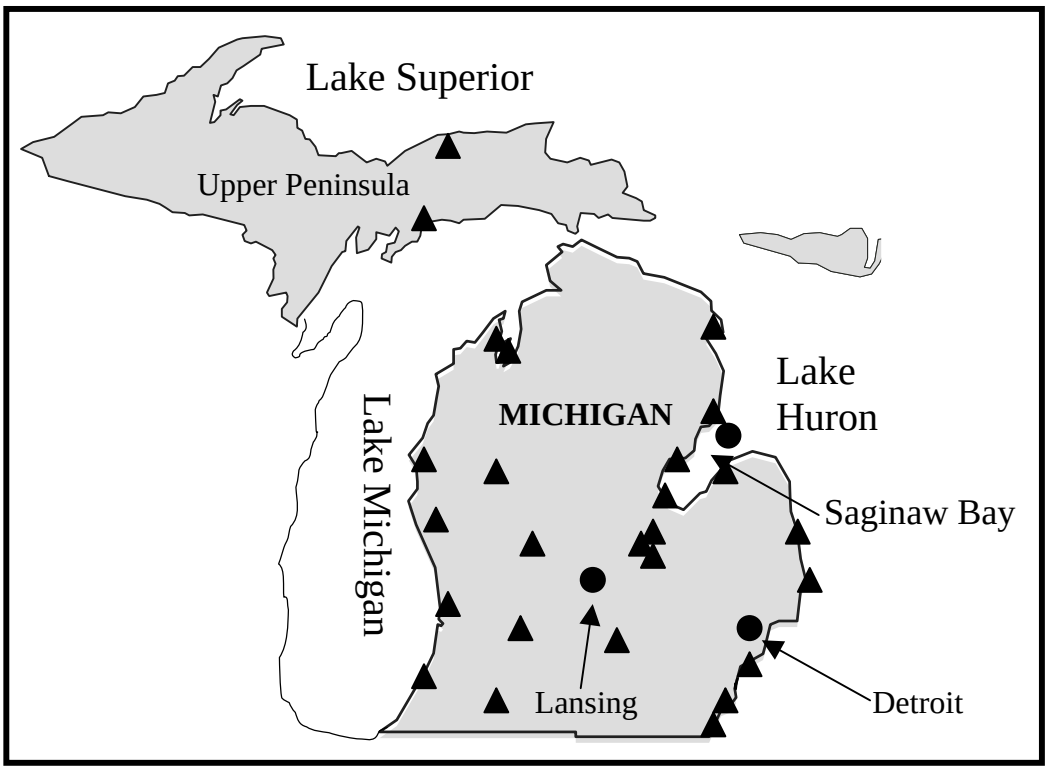

Table 2 – Concentrations of perfluorinated alkylated substances (ng/L, wet wgt) detected in Michigan waters

Location	[PFOS] ng/L	[PFOA] ng/L
Detroit Region (n=10)	<0.8 - 6.13 (**3.48**)	<8 - 16.14 (**9.16**)
Flint Region (n=4)	1.50 - 12.31 (**4.90**)	<8 - 23.01 (**14.13**)
Saginaw Bay Region (n=5)	3.10 - 12.69 (**7.52**)	<8 - 24.08 (**14.12**)
North Eastern Michigan (n=2)	0.87 - 6.34 (**3.60**)	<8
Upper Peninsula (n=7)	<0.8 - 3.09 (**1.84**)	<8 - 13.77 (**5.63**)
North Western Michigan (n=2)	<0.8 - 4.48 (**2.24**)	11.96 - 13.06 (**12.51**)
Western Michigan (n=6)	<0.8 - 5.32 (**1.79**)	<8 - 15.17 (**8.34**)
South Western Michigan (n=5)	7.22 - 29.26 (**16.10**)	8.74 - 35.86 (**21.64**)
Lansing Region (n=3)	1.04 - 4.96 (**2.68**)	<8 - 13.37 (**9.87**)

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