THE FIRST ENVIRONMETAL SURVEY OF PERFLUOROOCTANE SULFONATE (PFOS) AND RELATED COMPOUNDS IN JAPAN

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Introduction

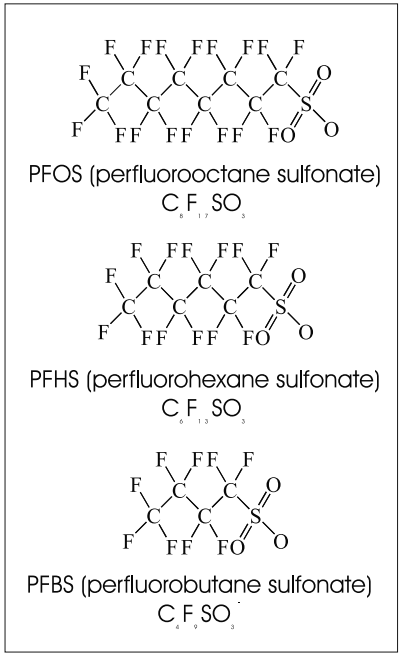
Perfluorooctane sulfonate (PFOS) and related perfluorinated compounds (*e.g.* PFHS, PFBS, PFOA) have received world wide attention during the last three years. This class of chemicals is also being referred to as "PCBs of the twenty first century". These compounds are globally distributed, environmentally persistent, bioaccumulative, and are potentially harmful. Toxicity of these chemicals needs further investigation. Compared with chlorinated and brominated organic compounds, the environmental distribution of perfluorinated compounds (PFCs) is poorly understood. Sulfonyl - based fluorochemicals have been produced and used for over 40 years (1). The products containing PFOS and related compounds have been used wide variety of applications such as coatings for textiles, papers, packaging, fire-fighting foams, herbicides and pesticides. PFOS has been found to accumulate in birds and mammals through a non-lipid related mechanism of accumulation. Perfluorinated compounds have been shown to concentrate in the blood and liver of humans and wildlife (1). But, until recently, the extent and magnitude of environmental distribution of PFCs was unknown.

Concern over environmental pollution by PFCs has been growing and is a subject of current interest. While earlier surveys have made measurement of PFCs in tissues from selected global locations, extensive location-specific investigations are needed to understand the dynamics and fate of these new class of compounds. Japan is one of the major industrialized nations in the world and prior to this investigation occurrence of PFCs in environmental media in Japan was not known. In 2000, the first national project on PFOS and related compounds was started at AIST under the support of New Energy and Industrial Technology Development Organization (NEDO). An international study between AIST, Japan and Michigan State University, USA was established in 2001, and a survey was made to estimate PFOS in the blood of Japanese humans, which showed the presence of measurable level (few ten parts-per-billion) (2). In this study, we report results of the first environmental survey of PFOS and related compounds in some environmental samples (human, fish and sea water) collected from Japan.

Materials and Methods

Sample collection

Several fish and coastal sea water samples were collected from Tokyo Bay in March, 2002. Live fishes collected by fisherman were dissected and liver and blood were taken into polypropylene tubes. Surface sea water was collected using a stainless steel sampler and one L of water were transferred into a polypropylene bottle. To reduce a residual chlorine, 200 µL of sodium thiosulfate solution (250 mg/mL) was added into each bottle. Fish and sea water samples were placed in dry ice and kept in dark from the time of collection until transport to the laboratory, and then stored at –30 °C for fish samples and 4 °C for sea water samples until analysis.



Extraction procedure

One mL of (0.5M) tetrabutylammonium hydrogensulfate solution, and 2mL of sodium carbonate buffer (0.25 M, pH 10) were added to one mL of blood samples in a polypropylene tube and thoroughly mixed for extraction. After that, five mL of methyl-*tert*-butyl ether (MTBE) was added, and the mixture was shaken for 20 min. After centrifugation, MTBE layers were transferred into another polypropylene tube. The solvent was evaporated under nitrogen and replaced with 0.5mL of methanol. This extract was passed through a nylon mesh filter (0.2 μm) into HPLC vial. For the extraction of liver samples, one g of liver was homogenized with 5mL of distilled water. One mL of this homogenate was transferred into a polypropylene tube, and extracted according to the same procedure described above.

For sea water samples, 500 mL of water samples was passed through C18 SPE cartridge (10 g, 35 mL; tC18 cartridges, Waters) which was conditioned with 100 mL of methanol followed 50 mL of distilled water. The cartridge was then washed with 50mL of 40% methanol in water. The target fraction was eluted with exactly 50mL of methanol and collected into a polypropylene tube. This eluant was evaporated under nitrogen gas to 0.4mL and transferred into a HPLC vial.

Analysis

HPLC-MS/MS measurement was performed using an Agilent HP1100 liquid chromatograph equipped with LCQ (TermoQuest; Finnigan). Twenty μL of final solution was injected onto a CAPCELL PAK C18 column (2.0mm i.d.×50mm length, 3μm, SHISEIDO FINE CHEMICALS) with a 2mM ammonium acetate/methanol as mobile phase starting at 30 % methanol. MS/MS parameter were optimized to transmit the $[M\text{-}K]^-$ (m/z : 499) ion for PFOS using atmospheric pressure ionization operated in the electrospray negative ion mode. Ions were monitored using selected ion monitoring for ions 499 and 99 for quantitative determination of PFOS, m/z 399 for PFHS, and m/z 299 for PFBS.

Results and Discussion

Concentrations of PFOS, PFH and PFBS in fishes are shown in Table 1. For comparison, PCBs and PCDD/DF concentrations in fish samples are also shown. PFOS was found in every fish samples from the Tokyo Bay, ranging in concentrations from 30 to 558 ng/g, wet wt, in liver and from 2 to 448 ng/mL in blood. PFHS was also detected in some fish and the maximum concentration was founded 19 ng/g in the liver of Flat Fish and 558 ng/mL in the blood of Conger Eel. However, no PFBS was found in any fish. Concentrations of PFOS in Japanese fish were relatively higher than those in some fish samples from the Great Lakes region of the USA (1). Concentrations of PFOS were comparable to those of PCBs and 10,000 times higher than those of PCDDs and PCDFs (3, 4).

Some Japanese human blood were also analyzed for PFOS and the concentrations were greater than 20 ng/ml in some samples. The values are similar to or less than those in the USA, where average concentration of PFOS was 28 ng/mL in human sera (5). In general, PFOS concentrations in fish blood was approximately 10 times higher than those in Japanese human blood.

PFOS was also found in surface sea water around the Tokyo Bay (Table 2). Concentrations of PFOS in surface sea water ranged from 16 to 87 ng/L. These concentrations were comparable to those of PAH and much more higher than PCBs and PCDDs/PCDFs in sea water from Tokyo Bay. Based on the concentrations in fish liver and sea water (mean: 42 ng/L), bioconcentration factors (BCF) of PFOS in fish were estimated; Common sea bass (883 – 3,147); Conger eel (13,214); Flat fish (3,736 – 4,698);

Table 1. Concentrations [#] of perfluoroalkane sulfonates, PCBs and PCDD/DFs in fish samples.

Location	species	tissue	n	PFOS	PFHS	PFBS	PCBs	PCDDs	PCDFs	ref.
Tokyo Bay, Japan	Common sea bass	liver	3	37-144	N.D.-10	N.D.	-	-	-	
		blood	3	30-146	N.D.-4	N.D.	-	-	-	
	Conger eel	liver	1	558	18	N.D.	-	-	-	
		blood	1	357	N.D.	N.D.	-	-	-	
	Flat fish	liver	2	158-198	7-19	N.D.	-	-	-	
		blood	2	74-194	28-38	N.D.	-	-	-	
	Japanese stingfish	liver	2	30-192	N.D.	N.D.	-	-	-	
		blood	2	2-488	N.D.-4	N.D.	-	-	-	
	Rockfish	liver	3	60-78	N.D.-9	N.D.	-	-	-	
		blood	3	63-176	N.D.-5	N.D.	-	-	-	
Michigan waters, USA	Chinool salmon	liver	6	33-170	-	-	-	-	-	(1)
	Lake whitefish		5	33-81	-	-	-	-	-	(1)
	Brown trout		10	<17-26	-	-	-	-	-	(1)
Northern Pacfic Ocean	Yellow-fin tuna		12	<7	-	-	-	-	-	(1)
Mediterranean Sea	Blue-fin tuna		8	21-87	-	-	-	-	-	(1)
Tokyo Bay, Japan	Common sea bass	edible tissue	5	-	-	-	120-200	-	-	(3)
	Black rockfish	whole body	1	-	-	-	-	1.1	4.7	(4)
	Olive flounder		1	-	-	-	-	0.73	1.9	(4)
	Bartailed flathead		1	-	-	-	-	0.76	1.3	(4)
	Stingray		1	-	-	-	-	8.8	6.8	(4)
	Sea bass		1	-	-	-	-	2.4	10	(4)
	Gray mullet		1	-	-	-	-	0.82	3.9	(4)

 # Consentrations of perfluoroalkane sulfonates in liver and blood are shown as ng/g (wet wt.) and ng/ml, respectively. PCBs and PCDDs/PCDFs are expressed as ng/g(wet wt.) and pg/g(wet wt.), respectively.

Table 2. Concentrations of perfluoroalkane sulfonates, PCBs, pyrene, acenaphthene, linear alkylbenzen sulfonate(LAS) and PCDDs/PCDFs in surface water samples [#]

Location	n	PFOS	PFHS	PFBS	PCBs	pyrene	acenaphthene	LAS	PCDDs	PCDFs	ref.
Tokyo Bay, Japan	4	17 - 87	N.D.	-	-	-	-	-	-	-	
Tennessee River- Upstream	22	17 - 54	-	-	-	-	-	-	-	-	(7)
Tennessee River, Downstream	18	75 - 144	-	-	-	-	-	-	-	-	(7)
Tokyo Bay, Japan	3	-	-	-	0.35 - 0.70	-	-	-	2.6 - 3.1	1.3 - 2.2	(6)
Coastal area, Japan	4	-	-	-	-	6 - 12	-	-	-	-	(3)
	1	-	-	-	-	-	12	-	-	-	(3)
Tama River, Japan	18	-	-	-	-	-	- 3,740 - 79,800		-	-	(8)

Concentration of perfluoroalkane sulfonates, PCBs, pyrene, acenaphthene and LAS (total LAS) are expressed as ng/L. PCDD/DFs concentrations are expressed as fg/L.

Japanese stingfish (713 – 4,551); Rockfish (1,425 – 1,860). This is the first report about BCF of PFOS in fish in field conditions and these are similar to the estimation from laboratory test (9). These results provide the first evidence of occurrence of PFOS in sea water and fishes from Tokyo Bay and that the concentrations are comparable to those in the U.S.A. The environmental concentrations of PFOS may be similar to those of PCBs in Tokyo Bay and a comparative survey is underway. Bioaccumulation of PFOS in fish from sea water is significant in Tokyo Bay. It is necessary to perform comprehensive survey of PFOS and related compounds in Japan and to understand the mechanisms of transport and chemodynamics of PFOS in the environment.

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