PERFLUOROOCTANE SULFONATE AND RELATED COMPOUNDS IN THE SOUTH CHINA SEA, SULU SEA AND JAPANESE ENVIRONMENTAL SAMPLES

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Introduction

Perfluorooctane sulfonate (PFOS) and its salts are fully fluorinated organic compounds that can be produced synthetically or through the degradation or metabolism of other fluorochemical products. Recent studies have shown that PFOS is a persistent and a bioaccumulative global contaminant. Sulfonyl - based fluorochemicals have been produced and used for over 40 years (1) for soil/stain resistance and surfactant applications and are used in certain textiles, upholstery, carpeting and specialty papers including food contact materials and fire fighting foams. Perfluorohexane sulfonate (PFHS), and Perfluorooctanoate (PFOA) are impurities in certain fluorochemical formulations including aqueous film fire-fighting foams. 3M Company, a major manufacturer of sulfonyl-based perfluorochemicals, announced the phase out of production of PFOS-based chemicals from December 2000 because of concerns about its persistence in the environment and the potential for long-term environmental effects. From July 2000, the Organization of Economic Cooperation and Development (OECD) has been leading an international collaboration on the scientific assessment of PFOS-based chemicals. Therefore, data on the occurrence and distribution of perfluorochemicals in the environment are needed for accurate risk assessment in all countries. Concern over environmental pollution by these chemicals has been growing and is a subject of current interest. While earlier surveys have made measurement in wild animal tissues from selected global locations (2), extensive local investigations are needed to understand the dynamics and fate of these new class of compounds. Because of industrial value of PFOS related compounds (PFCs), Japan, a major industrialized nation in the world, has persumably produced and used such compounds. Investigations on the occurrence of perfluorochemicals in environmental media in Japan are urgently needed. The AIST started the initial survey of PFCs related compounds in the domestic environment in 2000 (NEDO project). Preliminary results revealed pollution in coastal sea water, lake water, fish, domestic animals and humans (3, 4, 5). After discussions with the consortium formed by major manufactures and users in Japan, some national projects about PFOS-related compounds (development of reliable analytical method, environmental survey, exposure evaluation and waste materials treatment) were started by the AIST in 2003. As a part of this comprehensive project, we report results of the survey of sea water pollution in the South China Sea and Sulu Sea, in addition to up-dated environmental data in Japan.

Materials and Methods

Several fish and coastal sea water samples were collected from Tokyo Bay in 2002. Live fishes collected by fishermen 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 was transferred into a polypropylene bottle. To reduce residual chlorine content, 200µL 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. Blood samples from domestic animals, wild birds, and humans were collected and kept in polypropylene tube until analysis. Open ocean water samples were collected from the South China Sea and the Sulu Sea during the R/V Hakuho-Maru KH-02-4 cruise (Ocean Research Institute, the University of Tokyo) from 7 November to 18 December in 2002. A CTD Carousel system equipped with 36 Niskin-X bottles was used for water sampling from appropriate depths. Sampling locations in the South China Sea and the Sulu Sea are 3500 m and 1500 m in depth, respectively. For the purpose of understanding vertical profiles of PFCs concentrations, discrete water samples from surface to bottom were collected. Analysis of PFCs in these samples were carried out by using same methods used for coastal sea waters. Blood samples were subjected to ion-pair extraction method. Solid phase extraction method was used for water samples. HPLC-MS/MS measurement was performed using an Agilent HP1100 liquid chromatograph equipped with MS/MS (MICROMASS Co., Quatro Ultima Pt.). 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. MS/MS parameters were optimized to transmit the [M-K]- (m/z : 498.8) ion for PFOS using atmospheric pressure ionization operated in the electrospray negative ion mode. Ions were monitored using selected ion monitoring for ions 498.8 and 98.8 for quantitative determination of PFOS, m/z 398.8 and 79.9 for PFHS, m/z 298.8 and 79.9 for PFBS and m/z 413.0 and 168.7 for PFOA. THPFOS (1H, 1H, 2H, 2H- per-fluorooctane sulfonate) was used as procedual recovery standard. Details of collection of fish, domestic animals, humans and coastal sea water and analytical procedure are described previously (4,5)

Results and Discussion

Japanese environmental samples;

PFOS was found in blood and liver of all the 78 fish samples analyzed. Among various sampling locations, fishes collected from Tokyo Bay, Osaka Bay, and Lake Biwa contained greater concentrations of PFOS than those from Hiroshima Bay. Concentrations of PFOS in blood and liver of fishes ranged from 1 to 834 ng/mL, and from 3 to 7900 ng/g, wet wt, respectively. Concentrations of PFOS varied more than 100-fold depending on the species and location. For instance, concentrations of PFOS in the blood of Japanese stingfish collected from Tokyo Bay varied between 2 and 488 ng/mL. The highest concentrations of 834 ng/ml in blood and 7900 ng/g in liver were found in bluegill from Lake Biwa and ornate jobfish from Kin Bay, respectively. PFHS was detected in approximately 33% of the fish blood. Fishes from Tokyo Bay and Osaka Bay contained measurable concentrations of PFHS. The maximum concentration of PFHS found in blood and liver, respectively, were 121 ng/ml and 19 ng/g, wet wt. However, no PFBS was found in any of the fishes analyzed. Concentrations of PFOS in fishes from Tokyo Bay were relatively higher than those in some fish samples from the Great Lakes region (<17-380 ng/g, wet wt, in livers) of the USA (1).

PFOS was also found in the blood of Japanese population at concentrations ranging from 2.4 to14 ng/mL. Mean PFOS concentration in two female blood samples was 10 ng/mL, whereas that in males was 8 ng/mL. There was no significant correlation between PFOS concentrations in blood and age of the donor. Concentrations of PFOS were measured in the serum of three individuals. Concentrations in serum were 1.4 to 4-fold (mean: 2.5) greater than those found in the corresponding whole blood samples. PFHS was also found at concentrations ranging from <1 to 3.8 ng/mL. These results provide baseline data on the extent of PFOS exposures by Japanese citizens.

Birds such as carrion crow, mallard and pintail and pets such as rabbit and domestic duck contained detectable concentrations of PFOS in blood. Perfluorinated compounds have been reported to be used in folding cartoons used for pet food supplies. Low concentrations found in rabbit sera suggest sources arising from food contact papers that are impregnated with PFOS. Carrion crow, which are omnivorous birds, feeding on worms, insects, fruits, seeds and kitchen scarp contained PFOS concentrations ranging from 11 to 150 ng/mL (mean: 56 ng/mL) in the blood. Concentrations of PFOS in the blood of carrion crow were (11-150 ng/mL) less than those reported in the livers of several fish-eating water birds (<19-650 ng/g) collected from around Tokyo Bay (2).

Sea water samples from South China Sea, Sulu Sea and coastal area of Japan (Fig. 1);

PFOS was found in nine of the 25 surface water samples collected from coastal Japan. Among the sampling locations, PFOS was detected in all the surface seawater samples collected from Tokyo Bay and Osaka Bay at concentrations ranging from 8 to 59 ng/L and 4 ot 21 ng/L, respectively. PFBS were not detected in any of the water samples analyzed. The measured concentrations of PFOS in Tokyo Bay waters were similar to those reported for waters collected upstream (17-54 ng/L) of a fluorochemical manufacturing facility in the Tennessee River in the U.S., but less than those found downstream (75-144 ng/L) of the fluorochemical manufacturing facility (6, 7). The highest concentration of 144 ng PFOS/L measured in the Tennessee River was 2.4-fold greater than the highest concentration found in Tokyo Bay. Similarly, concentrations of PFOS in seawater samples were 3 to 4-orders of magnitude lower than those reported for water samples (<0.1-2210 mg/L) collected after a spill of PFOS-containing aqueous film fire fighting foam in Etobicoke Creek near Toronto, Canada (8). The highest concentration of PFOS found in Tokyo Bay water was approximately 20-fold less than the drinking water health advisory of 1 mg/L.

Concentration of PFOS in surface sea water from the South China Sea and Sulu Sea ranged from 0.01 to 0.11 ng/L. Concentrations of PFOA were 4 to 7 times higher than those of PFOS. Midoro Strait, a coastal area of Philippines contained no significant concentration of PFOS. It is worth to mention that PFHS was found in coastal waters but not in open ocean waters. Kin Bay (Okinawa prefecture) samples showed specific pattern of contamination with lower concentration of PFOS than PFHS possibly, suggesting the presence of local sources of PFHS.

Overall, concentration of PFOS in open ocean waters were 60 to 600 times lower than coastal sea waters of Japan. However, significant concentration of PFOS and PFOA were found in the South Sea and Sulu Sea and possible sources should be investigated in future.

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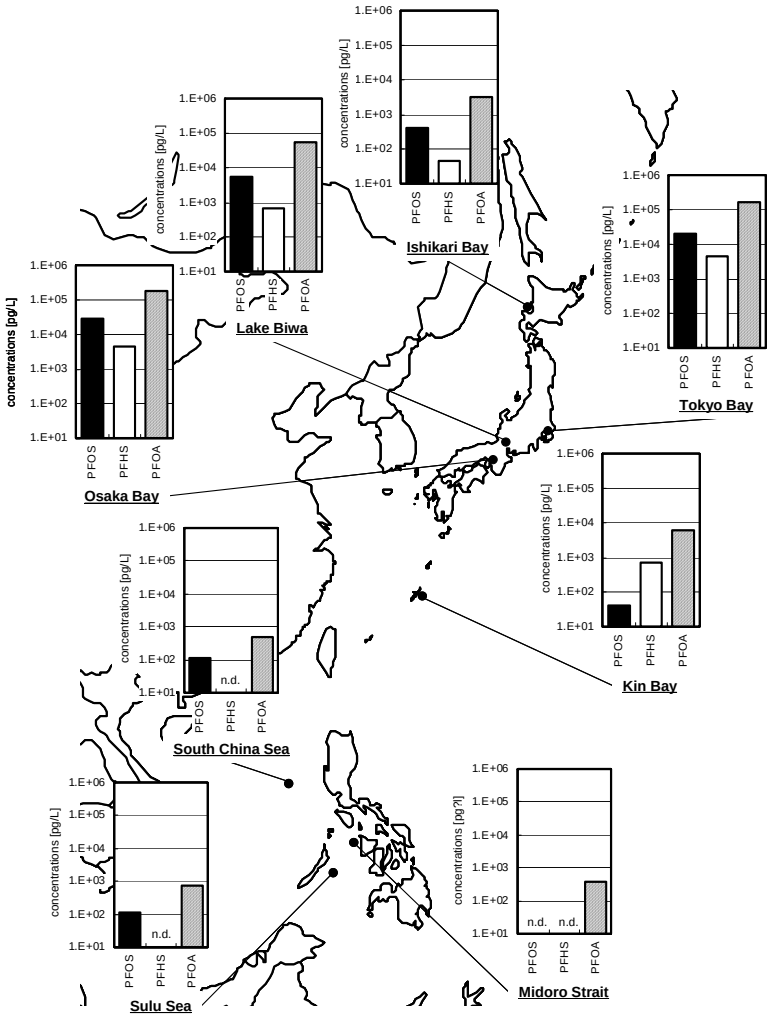

Fig. 1. Concentration of PFOS, PFHS and PFOA in surface sea water from the South China Sea, Sulu Sea and coastal Japan.

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