

# OTHER HALOGENATED POPs OF CONCERN

## GLOBAL DISTRIBUTION AND BIOACCUMULATION OF PERFLUORINATED HYDROCARBONS

Kurunthachalam Kannan and John P. Giesy

National Food Safety and Toxicology Center, Department of Zoology, Michigan State University, East Lansing, MI 48824, USA

### Introduction

The environmental distribution of fluorinated organic compounds (FOCs) has been less well described than the other halogenated hydrocarbons such as chlorinated and brominated compounds. This is despite the fact that FOCs, in particular, perfluorinated alkanes have been used in a wide variety of products and applications for more than 50 years. Perfluorinated compounds (PFCs) are resistant to hydrolysis, photolysis, microbial degradation or metabolism by vertebrates due to the high energy of carbon-fluorine bond and therefore, have the potential to persist in the environment. But, until recently, the extent and magnitude of environmental distribution of PFCs was unknown. Recent development of an analytical technique for PFCs using high performance liquid chromatography-negative ion electrospray tandem mass spectrometry (HPLC-ESMSMS) <sup>1</sup> permitted the survey of PFCs in livers and blood plasma of wildlife on a global scale <sup>2</sup>.

Evidence for the presence of organic forms of fluorine in human blood was presented as early as 1968 <sup>3</sup>. It was speculated that perfluorooctanoic acid (PFOA) and other synthetic fluorochemicals were the sources of PFCs found in the sera of general population. Only in the 1990s, using HPLC-ESMSMS analysis, were perfluorooctane sulfonate (PFOS) and PFOA identified in the blood sera of employees in the fluorochemical manufacturing industry at concentrations of up to 12.8 and 114 mg/mL, respectively <sup>4</sup>. The HPLC-ESMSMS analysis also detected perfluorooctanesulfonamide (FOSA), PFOA and perfluorohexane sulfonate (PFHS) in human blood <sup>1</sup>. These studies raised questions regarding the magnitude and extent of wildlife exposures to PFCs since, prior to this study, neither it was known if exposures were regional or global nor if wildlife were exposed to PFCs. To address these questions, archived tissues of marine mammals, birds, fishes, reptiles and amphibians from various parts of the world including Arctic and the Antarctic Oceans were analyzed for PFCs.

### Materials and Methods

Tissues of various species of aquatic mammals, birds, fish and amphibians were collected as part of earlier monitoring studies conducted by Michigan State University, East Lansing, Michigan, and archived tissues from federal and state agencies. Samples were collected under permits from state and federal agencies. Tissues of most individuals of aquatic mammals were obtained from stranded dead animals. Samples collected in the 1990s were used. Samples were obtained to represent various geographical locations including the Arctic and the Antarctic Oceans. About one thousand seven hundred samples have been analyzed since April 1999 to investigate the extent and magnitude of the distribution of PFCs in the global environment. Concentrations of PFOS, FOSA, PFHS and PFOA and other FOCs in liver, egg yolk, muscle or blood plasma were determined by use of high performance liquid chromatography (HPLC) with electrospray tandem mass spectrometry (ESMSMS) <sup>1</sup>.

## OTHER HALOGENATED POPs OF CONCERN

**Table 1.** Frequency (parentheses) and maximum concentrations (ng/g, wet wt) of PFOS and other fluorochemicals in animal tissues (detection limits varied from 1 to 35 ppb, wet wt).

Species	PFOS	FOSA	PFHS	PFOA
Marine mammals	1520 (77 %)	880 (15 %)	86 (10 %)	41 (4 %)
Mink & Otter	4900 (100 %)	680 (11 %)	85 (10 %)	110( 11 %)
Birds	2570 (60 %)	530 (10 %)	185 (11 %)	440 (3 %)
Fishes	1000 (38 %)	120 (9 %)	20 (3 %)	46 (2 %)

### Results and Discussion

#### Concentrations

Among the four PFCs monitored, only PFOS was commonly present in the tissues of wildlife (Table 1). FOSA, PFOA, PFHS were detected in the tissues of a few species (<20% of the samples analyzed), generally at concentrations (approximately 10- fold) less than those of PFOS.

While PFOS is a metabolic product of various sulfonated perfluorochemicals, FOSA, PFOA and PFHS are intermediates in the production of several perfluorinated compounds. FOSA and PFOA are also products used in various applications. PFOS was detectable in most samples including those from remote marine regions at concentrations greater than 1 ng/g<sup>2,5,6</sup>. Concentrations of PFOS in the blood of ringed and grey seals from the Canadian and Norwegian Arctic ranged from 3 to 50 ng/mL. PFOS concentrations were 2 to10-fold greater (14-230 ng/mL) in seals from relatively more contaminated locations such as the Baltic Sea. Similarly, blood plasma and serum of Laysan and black-footed albatrosses collected from remote oceanic locations such as the Midway Atoll in the North Pacific Ocean contained PFOS at concentrations ranging from 3 to 26 ng/mL. PFOS concentrations in the blood of cormorants and herring gulls from the North American Great Lakes were approximately 10-fold greater than those in albatrosses from Midway Atoll. While the liver of yellow-fin tuna from the northern North Pacific contained no detectable PFOS (<7 ng/g), blue-fin tuna from the Mediterranean Sea contained up to 87 ng/g PFOS in the liver. Similarly, livers of polar bear from Alaska contained concentrations of PFOS ranging from 180 to 680 ng/g, wet wt while PFOS concentrations in weddell seals from the Antarctic were less than the limit of quantification (35 ng/g). These results suggest that PFOS is distributed in remote areas including polar regions but that concentrations in wildlife from these areas were several fold less than those from more industrialized and urbanized areas such as the Baltic Sea and the North American Great Lakes. Blood plasma of bald eagle fledglings collected from the midwestern United States contained PFOS concentrations up to 2570 ng/mL. Similarly, all fish eating bird tissues from Canada, Italy, Japan and Korea contained detectable concentrations of PFOS. The occurrence of PFOS in these birds suggests that the potential source of exposure is the fish they consume. PFOS concentrations of up to 300 ng/g were detected in the muscle of carp from Saginaw Bay, Michigan. Among aquatic mammals, mink from the midwestern United States contained the greatest concentrations of PFOS (970-4900 ng/g liver, wet wt). Mink are opportunistic predators and a proportion of their diet is fish. Average concentrations of PFOS in Saginaw Bay carp, which were fed to mink were 120 ng/g, wet wt, which suggests a biomagnification factor of 22 for PFOS in mink.

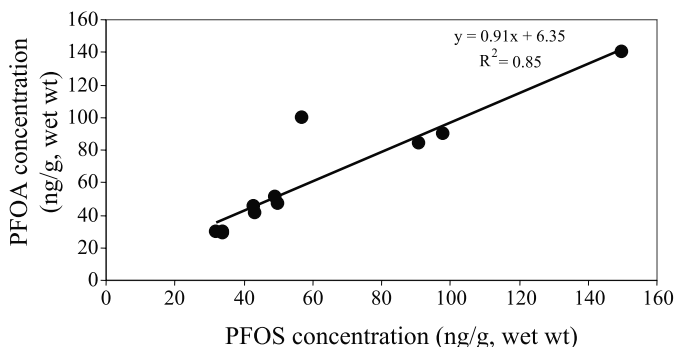
These results suggest that PFCs, particularly PFOS, are widely distributed on a global scale and can be persistent and bioaccumulative in the food chain. The mechanisms of transport and toxic effects of these compounds are the subjects of current investigations. The major route of transport of PFOS to remote marine locations is not known. The vapor pressures of PFOS parent compounds, such as *n*-ethylperfluorooctanesulfonamidoethanol (*n*-EtFOSEA; C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OH) and *n*-

## OTHER HALOGENATED POPs OF CONCERN

methylperfluorooctane sulfonamidoethanol (*n*-MeFOSEA) and ethylperfluorooctanesulfonamide (*n*-C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>NHCH<sub>2</sub>CH<sub>3</sub>) may exceed 0.5 Pa—1000-fold greater than that of PFOS. Moreover, the water solubility of *n*-EtFOSEA (<1 mg/L) is more than 100-fold lower than PFOS (300 mg/L). Possibly, volatile PFC precursors reach remote locations through the atmosphere or hydrosphere (water currents) and are subsequently metabolized to PFOS in animals. A recent study has reported the occurrence of *n*-EtFOSEA and *n*-MeFOSEA in atmospheric samples in North America <sup>7</sup>.

### Accumulation

Liver and blood tissues are the major accumulators of fluorochemicals in humans and animals. There was a positive correlation between PFOS concentrations in liver and blood of marine mammals. The relationship between accumulation of PFOS and other fluorochemicals did not follow a consistent trend. For instance, in the livers of cormorant from Sardinia, Italy, PFOS concentrations were significantly correlated with those of PFOA (Figure 1).



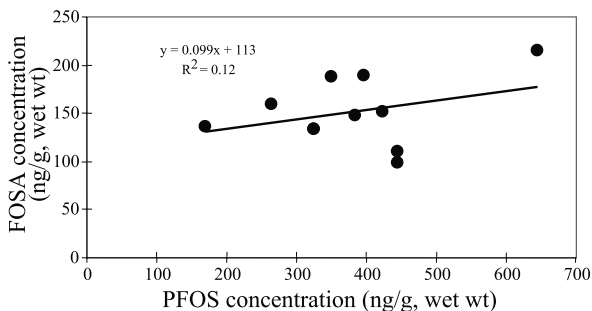
**Figure 1.** Relationship between PFOS and PFOA concentrations in cormorant livers from Cabras Lagoon, Sardinia, Italy

However, PFOS concentrations in livers of cormorants from Japan were not correlated with those of FOSA (Figure 2). Concentrations of PFOA were greater than those of PFOS in biota collected from certain locations. PFHS occurred in a few locations but at lesser concentrations. Perfluorodecanesulfonate (PFDS) was also found in some marine mammals and birds. Livers of California sealions contained PFDS at 8 ng/g, wet wt, whereas river otter livers contained 56 ng/g, wet wt. Concentrations of fluorochemicals did not increase with age (Figure 3) and there was no significant gender differences in concentrations in several species of wildlife. Eggs yolks from birds collected in the Great Lakes region retained several parts-per-million levels of PFOS. Time-trend analysis of PFOS concentrations in livers of white-tailed sea eagles collected since 1979 from Germany did not show a specific trend.

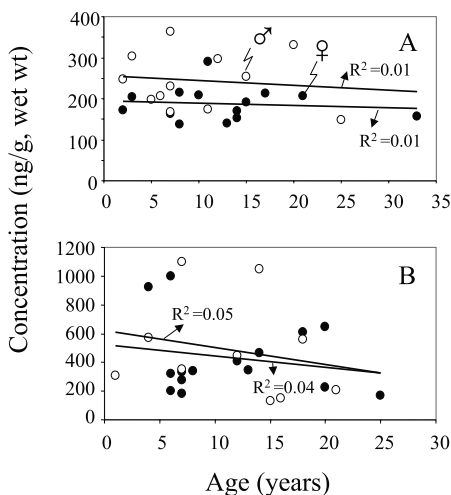
### References

1. Hansen, K.J., Clemen, L.A., Ellefson, M.E. and Johnson, H.O. (2001) *Environ. Sci. Technol.* 35, 766-770.
2. Giesy, J.P. and Kannan, K. (2001) *Environ. Sci. Technol.* 35, 1339-1342.

## OTHER HALOGENATED POPs OF CONCERN



**Figure 2.** Relationship between PFOS and FOSA concentrations in livers of cormorants from the Sagami River, Kanagawa Prefecture, Japan.



**Figure 3.** Relationship between PFOS concentrations and age in gray (A) and ringed (B) seal livers.

3. Taves, D.R. (1968) *Nature* 217, 1050-1051.
4. Olsen, G.W., Burris, J.M., Burlew, M.M. and Mandel, J.H. (2000) *Drug Chem. Toxicol.* 23, 603-620.
5. Kannan, K., Hansen, S.P., Franson, C.J., Bowerman, W.W., Hansen, K.J., Jones, P.D. and Giesy, J.P. (2001) *Environ. Sci. Technol.* 35, 3065-3070.
6. Kannan, K., Koistinen, J., Beckmen, K., Evans, T., Gorzelany, J., Hansen, K.J., Jones, P.D. and Giesy, J.P. (2001) *Environ. Sci. Technol.* 35, 1593-1598.
7. Martin, J.W., Muir, D.C.G., Moody, C.A., Ellis, D.A., Kwan, W.C., Solomon, K.R. and Mabury, S.A. (2002). *Anal. Chem.*, 74, 584-590.