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A Survey of Perfluorooctane Sulfonate and Related Perfluorinated Organic Compounds in Water, Fish, Birds, and Humans from Japan

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Occurrence of perfluorooctane sulfonate (PFOS) in the tissues of humans and wildlife is well documented. In this study, concentrations and distribution of PFOS, perfluorohexane sulfonate (PFHS), and perfluorobutane sulfonate (PFBS) were determined in samples of surface water, fish and bird blood and livers, and human blood collected in Japan. Notable concentrations of PFOS were found in surface water and fish from Tokyo Bay. PFOS was found in all of the 78 samples of fish blood and liver analyzed. Based on the concentrations of PFOS in water and in fish livers, bioconcentration factors were calculated to range from 274 to 41 600. Concentrations of PFOS in the blood of Japanese human volunteers ranged from 2.4 to 14 ng/mL. PFHS was detected in 33% of the fishes analyzed, at concentrations severalfold less than those of PFOS.

Introduction

Perfluorooctane sulfonate (PFOS) and its salts are fully fluorinated organic compounds that can be produced synthetically or through the degradation of other perfluorochemical products. Recent studies have shown that PFOS is a persistent and bioaccumulative global contaminant (*1*−*6*). Sulfonyl-based perfluoroalkylated compounds have been produced and used for over 40 years (*1*) for soil/stain resistance and surfactant applications and are used in various textiles, upholstery, carpeting, and specialty papers, including food-contact materials and fire-fighting foams. Perfluorohexane sulfonate (PFHS) and perfluorobutane sulfonate (PFBS) are impurities in certain fluorochemical formulations, including aqueous film-forming foams (AFFF). Occurrence of perfluorocarboxylates in groundwater and AFFF products has been shown (*7, 8*). The 3M Company, a major manufacturer of sulfonyl-based perfluorochemicals, announced the phase-out of production of POSF-based chemicals from December 2000, because of concerns about the persistence of PFOS in the environment and the potential for long-term environmental effects (*9*). The discovery of fluorinated organic compounds in human serum and in the environment has led to the initiation of studies to characterize the distribution, dynamics, and fate of such chemicals in the environment. PFOS and related perfluorinated chemicals are also thought to be produced by other manufacturers in other countries. Since July 2000, the Organization of Economic Cooperation and Development (OECD) led an international collaboration on the scientific assessment of PFOS. Therefore, data on the occurrence and distribution of perfluorochemicals in the environment are needed for accurate risk assessment in all countries.

Studies on the occurrence of perfluorinated compounds in wildlife have focused on samples collected from North America and Europe (*3*−*6*). Studies describing the occurrence of perfluorinated compounds in coastal surface waters and fishes have not been previously reported. Japan is one of the most highly industrialized nations in the world, and the use of perfluorinated compounds is expected to have occurred there in various applications. In 2000, the first national project on PFOS in Japan was started at the National Institute for Advanced Industrial Science and Technology, with the support of New Energy and Industrial Technology Development Organization (NEDO). A preliminary survey was conducted in 2001 to estimate PFOS in Japanese humans; this survey showed measurable concentrations (a few tens of parts-per-billion) in blood (*10*−*12*). In the present study, we report results of a survey of PFOS, PFHS, and PFBS in samples of water, fish, birds, and humans, collected in Japan. Additionally, this study provides evidence for the field-based bioconcentration factors of PFOS in fish.

Materials and Methods

Sample Collection. Twenty-two surface seawater samples were collected from Ishikari Bay and Lake Shikotsu in Hokkaido, Tokyo Bay, Osaka Bay, Hiroshima Bay, Ariake Bay, and Kin Bay in Okinawa (Figure 1). Three freshwater samples were collected from Lake Biwa, the largest lake in Japan, located in central Shiga Prefecture. Samples were collected using a clean stainless steel grab sampler and stored in new 1 L polypropylene containers with narrow mouths and screw tops. The containers were rinsed with methanol, deionized water, and water from the particular sampling location prior to use. Teflon bottles and Teflon-lined caps were avoided throughout the analysis, as interference might have been introduced into the sample extracts. The amount of suspended matter was kept to a minimum. To reduce residual chlorine, we added 200 μL of 250 mg/mL solution of sodium thiosulfate to each bottle. In most cases, samples were extracted within 24 h after collection; otherwise, samples were kept at 4 °C until analysis. All of the water samples were collected during March to September, 2002.

Forty-eight blood samples and 30 liver samples were collected from 23 species of fish during March-August, 2002, from Tokyo Bay, Osaka Bay, Hiroshima Bay, Ariake Bay, Kin Bay (Okinawa), and Lake Biwa (Figure 1). Fish were caught by hook and line or obtained from local fisherman. All species were coastal fishes except those from Lake Biwa. Fish were captured alive for the collection of blood and liver samples. Blood samples were drawn from the caudal artery of fish that were still alive, and liver samples were obtained after dissection. Samples from biota and seawater were placed on dry ice and kept in the dark from the time of collection until

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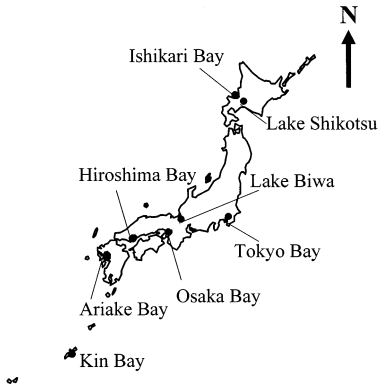

FIGURE 1. Map of Japan, highlighting the sampling locations.

transport to the laboratory and then stored at −30 °C for biota samples and 4 °C for seawater samples, until analysis.

Blood and liver samples were also collected from carrion crow (*Corvus corone corone*), mallard (*Anas platyrhynchos*), and pintail duck *(Anas acuta) (n* = 17) around Tokyo Bay in December 2000. In addition, blood and serum samples were collected from two species of pets, rabbits, and domestic duck ($n = 7$). Serum was prepared by centrifugation of the blood at 2500 G for 15 min. Human blood and serum were collected from Japanese volunteers ($n = 10$, ages 23−44) in June, 2002. Three of the blood samples were analyzed both as whole blood and as serum after centrifugation, to allow comparison of the concentrations in whole blood and in serum.

Extraction. The analytical procedure for the extraction of water samples was similar to that described elsewhere (*13*), with some modifications. The modifications include the use of 10-g solid-phase extraction (SPE) tC18 cartridges instead of 1-g cartridges, and extraction of 500 mL of water instead of 40 mL of water. C18 SPE cartridges (10 g, 35 mL, Waters Corporation, Milford, MA) were preconditioned by passage of 100 mL of methanol followed by 50 mL of milli-Q water, prior to passage of samples. A sample aliquot of water (500 mL) was passed through the preconditioned cartridges at a rate of 1 drop/s, and the cartridges were not allowed to go dry at any time throughout the extraction process. The cartridges were then washed with 20 mL of 40% methanol in water, which was then discarded. The target analytes were eluted with 30 mL of methanol and collected in a polypropylene tube. The solvent was evaporated under nitrogen to 0.4 mL and transferred into a vial for analysis.

The analytical procedure for the extraction of blood and liver samples was similar to that described elsewhere (*2*, *3*). One milliliter of 0.5 M tetrabutylammonium hydrogensulfate solution and 2 mL of sodium carbonate buffer (0.25 M, pH 10) were added to 1 mL of blood or serum sample in a polypropylene tube and thoroughly mixed for extraction. Five milliliters of methyl *tert*-butyl ether (MTBE) was added to the above mixture and shaken for 20 min. After centrifugation, the MTBE layer was transferred into another polypropylene tube. The solvent was evaporated under nitrogen and replaced with 0.5 mL of methanol. This extract was passed through a nylon mesh filter (0.2 μm) into an HPLC vial. For the extraction of liver samples, 1 g of liver was homogenized with 5 mL of milli-Q water. One milliliter of this homogenate was transferred into a polypropylene tube and extracted similarly to the procedure described for blood.

Analysis. Concentrations of PFOS in liver and blood plasma were measured using high performance liquid chromatography (HPLC) interfaced with an electrospray mass spectrometer (MS), followed by confirmation with electrospray tandem mass spectrometry (MS/MS). The PFOS used as standards and as matrix spikes were purchased from Fluka (Milwaukee, WI). HPLC-MS/MS measurement was performed using an Agilent HP1100 liquid chromatograph interfaced with LCQ TermoQuest (Finnigan, San Jose, CA) and Micromass (Beverly, MA) Quattro II mass spectrometer operated in the electrospray negative mode. Twenty microliters of the extract was injected onto a CAPCELL PAK C18 column (2.0 mm i.d. × 50 mm length, 3 μm; Shiseido Fine Chemicals, Tokyo, Japan) with 2 mM ammonium acetate/methanol as mobile phase starting at 30% methanol. At a flow rate of 300 μL/min, the gradient was increased to 100% methanol at 10 min before reversion to original conditions at 18 min. The capillary was held between 1.6 and 3.2 kV. Desolvation gas flow was kept at 750 L/h, and desolvation temperature was kept at 420 °C. Cone voltage was kept at 90, 60, and 50 V for PFOS, PFHS, and PFBS, respectively. Collision energies were 33, 29, and 23 eV for PFOS, PFHS, and PFBS, respectively. The MS/MS parameters were optimized to transmit the $[M - K]^-$ ion for PFOS using atmospheric pressure ionization, operated in the electrospray negative ion mode. Ions were monitored using selected reaction monitoring for ions 499 and 99 for quantitative determination of PFOS, m/z 399 and 99 for PFHS, and m/z 299 and 99 for PFBS.

Data quality assurance and quality control protocols included matrix spikes, laboratory blanks, and continuing calibration verification. Matrix spikes were analyzed for each sample type and species. Blanks were analyzed with each set of water and tissue samples as a check for possible laboratory contamination and interferences. Blanks did not contain any interference. Recoveries of PFOS, PFHS, and PFBS spiked into distilled water samples and passed through the analytical procedures were 101, 154, and 113% ($n = 3$ each), respectively. Recoveries of PFOS, PFHS, and PFBS spiked into blood and liver matrices were 85, 87, and 61% ($n = 4$ each), respectively. Reported PFOS concentrations were not corrected for recovery. The limit of detection (LOD) was variable, depending on the matrix used. The LODs for PFOS, PFHS, and PFBS in water samples varied from 4 to 9, 4 to 11, and 39 to 60 ng/L, respectively. The LODs of PFOS in liver tissues varied from 1 to 4 ng/g, wet wt. The LODs for PFHS and PFBS varied from 2 to 200 ng/g, wet wt, depending on the sample.

TABLE 1. Concentrations of Perfluoroalkane Sulfonates [ng/L] in Surface Water Samples from Japan[a]

location	*n*	PFOS	PFHS	PFBS
Ishikari Bay (Hokkaido)	1	<2.5	<3.1	<27
Lake Shikotsu (Hokkaido)	1	<2.5	<3.1	<27
Tokyo Bay	4	8−59 (26)[b]	<7.1	<48
Osaka Bay	3	<4−21 (8.7)	<8.8	<60
Lake Biwa	3	<4−7.4 (3.8)	<8.8	<60
Hiroshima Bay	4	<4	<8.8	<60
Ariake Bay	5	<9−11 (4.8)	<11	<38
Kin Bay (Okinawa)	4	<2.5	<3.1	<27

[a] Values below the detection limit were assigned a value of 2 (half the MDL) for calculation of the mean. [b] Values in parentheses indicate the means.

Results and Discussion

PFOS was found in nine of the 25 surface water samples at levels above the LOD. PFOS was detected in all of the surface seawater samples collected from Tokyo Bay, at concentrations ranging from 8 to 59 ng/L (mean; 26 ng/L) (Table 1). PFHS and PFBS were not detected in any of the water samples analyzed. The measured concentrations of PFOS in Tokyo Bay water samples were similar to those reported (17−54 ng/L) for waters collected upstream of a fluorochemical manufacturing facility in the Tennessee River in the United States but lower than concentrations downstream (75−144

ng/L) of that fluorochemical manufacturing facility (*13*). The highest PFOS concentration, 144 ng/L, measured in the Tennessee River was 2.4-fold greater than the highest concentration found in Tokyo Bay. Similarly, PFOS concentrations in our seawater samples were 3−4 orders of magnitude lower than those reported (<0.1−2210 μg/L) for water samples collected after a spill of fire-fighting foam in Etobicoke Creek near Toronto, Canada (*14*). PFOS was not found in Hiroshima Bay (Seto Inland Sea), Kin Bay (Okinawa), Ishikari Bay (Hokkaido), or Lake Shikotsu (Hokkaido). Higher concentrations of PFOS in Tokyo Bay relative to other locations in Japan indicate that the chemical sources are concentrated in industrialized and urbanized areas. Tokyo Bay receives discharges of waters from several rivers, including the Tama River, which flows through suburban and metropolitan areas of Tokyo. Discharge of industrial and municipal wastewaters is suspected as a source of fluorochemicals found in surface and coastal waters analyzed in this study. A nationwide survey of PFOS in freshwaters conducted recently in Japan showed that the Tama River has the highest concentration, 157 ng/L, whereas surface waters from coastal locations contained PFOS concentrations at 25 ng/L (*15*). The highest concentration of PFOS found in Tokyo Bay water in our study was approximately 20-fold lower than the drinking water health advisory level of 1 μg/L (*13*).

PFOS was found in all blood and liver samples analyzed from fish (n = 78; Table 2). Fish 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 in 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 ranged from 2 to 488 ng/mL. The highest concentrations, 834 ng/mL in blood and 7900 ng/g in liver, were respectively found in bluegill (*Lepomis macrochirus*) from Lake Biwa and ornate jobfish (*Pristipomoides argyrogrammicus)* from Kin Bay (Okinawa). Both of these species are carnivorous, near-bottom feeders. An electric power plant and an army base (U.S. Marine Corps) are located at Kin Bay. Use of PFOS in fire-fighting operations on army bases may provide a possible source of PFOS in Kin Bay. Perfluoroalkane sulfonate salts and perfluorocarboxylates are present in AFFF fire-fighting foam formulations (*7*). AFFFs are found at military bases, fire departments, and airports, where large volumes of flammable liquids, and the potential for a major fire, exist. Further investigation is necessary to identify and confirm the presence of PFOS-related sources in Kin Bay. The coastal water samples (n = 4) collected in Kin Bay did not contain measurable PFOS concentrations.

The ratios of concentrations of PFOS between liver and blood samples from fish varied widely from 0.02 to 179 (mean; 19). Concentrations of PFOS in livers of ornate jobfish collected from Kin Bay were 170-fold higher than blood concentrations. Alternatively, fishes collected from Tokyo Bay and Osaka Bay contained higher PFOS concentrations in blood than in liver. This may be indicative of inequilibrium in PFOS concentrations between liver and blood, indicating an ongoing exposure of fish to PFOS. Liver to blood concentration ratios increased with increasing hepatic concentrations of PFOS (Figure 2). Water-borne exposure of rainbow trout to PFOS has been shown to result in a higher accumulation in blood than in liver (*16*). Additionally, the distribution of perfluorinated acids among various tissues has been linked to the presence of fatty acid binding proteins (*17*).

PFHS was detected in approximately 33% of the fish blood samples. Fishes from Tokyo Bay and Osaka Bay contained measurable concentrations of PFHS. The maximum concentrations 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 fish from Tokyo Bay were relatively higher than levels that have been found (<17−380 ng/g, wet wt, in livers) in some fish samples from the Great Lakes region of the United States (*1*). Similarly, the concentrations of PFOS in livers of fishes from Tokyo Bay were greater than those that have been reported for bluefin tuna and swordfish from the Mediterranean Sea (*6*).

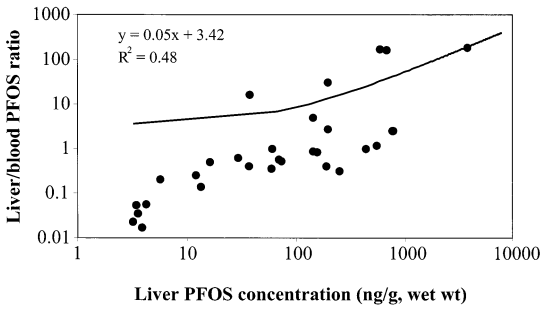

FIGURE 2. Relationship between hepatic PFOS concentrations and liver:blood concentration ratios in fish.

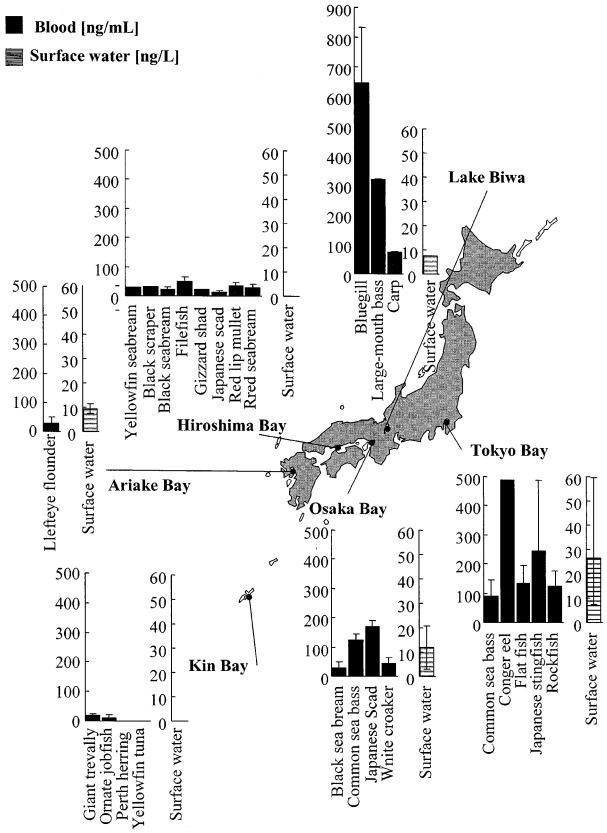

FIGURE 3. Spatial distribution of PFOS in fish and surface water samples collected in Japan.

The spatial distribution in the concentrations of PFOS in Japanese fish and water samples is shown in Figure 3. To calculate the bioconcentration factor (BCF: ratio of concentration in fish to concentration in water) for PFOS in fish liver tissue, we utilized the data for the water samples that had been collected simultaneously with the fish to be sampled from various locations. Although concentrations in whole fish are appropriate for the calculation of BCF, whole fish were not analyzed in this study. Nevertheless, the fact that PFOS is preferably concentrated in liver together with the availability of laboratory-derived liver BCFs (*16*), enabled an

TABLE 2. Concentrations of Perfluoroalkane Sulfonates in Liver (ng/g, wet wt) and Blood (ng/mL) of Fishes Collected in Japan

location	species	tissue	*n*	PFOS	PFHS	PFBS
Tokyo Bay	Common seabass (*Lateolabrax japonicus*)	liver	3	37−144 (85)[a]	4−10 (7)	<138
		blood	3	30−146 (91)	4 (4)	<16
	Conger eel (*Conger myriaster*)	liver	1	558	18	<151
		blood	1	489	121	<61
	Flatfish (*Pleuronectiformes pleuronectidae*)	liver	2	158−198 (178)	7−19 (13)	<142
		blood	2	74−194 (134)	28−38 (33)	<21
	Japanese stingfish (*Sebastiscus marmoratus*)	liver	2	38−192 (115)	<11 (8.8)	<67
		blood	2	2−488 (245)	<2−4 (2.5)	<13
	Rockfish (*Sebastes inermis*)	liver	3	62−70 (64)	9[b]	<85
		blood	3	63−176 (123)	2−5 (4.1)	<11
Osaka Bay	Black seabream (*Acanthopagrus schlegeli*)	liver	1	6	<6.1	<43
		blood	1	29	<3	<11
	Common seabass (*Lateolabrax japonicus*)	liver	2	3−4 (4)	<5.7	<40
		blood	2	104−142 (123)	3.6−3.8 (3.7)	<8
	Japanese scad (*Trachurus japonicus*)	liver	2	4−14 (9)	<7.6	<53
		blood	2	108−238 (170)	<2.7	<15
	White croaker (*Argyrosomus argentatus*)	liver	2	12−16 (14)	<5.7	<40
		blood	2	33−50 (42)	<2.8	<10
Lake Biwa	Blue gill (*Lepomis macrochirus*)	liver	2	254−310 (282)	<5.2	<36
		blood	2	455−834 (645)	<4.3	<15
	Largemouth bass (*Micropterus salmoides*)	liver	2	159−309 (234)	<5.8	<40
		blood	2	322−317 (320)	<4.3	<15
	Carp (*Cyprinus carpio*)	liver	2	3−4 (4)	<6.2	<43
		blood	2	68−77 (73)	<4.3	<15
Hiroshima Bay	Black scraper (*Thamnaconus modestus*)	blood	2	31−35 (33)	<5.5	<14
	Blake seabream (*Acanthopagrus schlegeli*)	blood	2	30−31 (31)	<5.5	<14
	Filefish (*Stephanolepis cirrhifer*)	blood	2	33−66 (35)	<5.5	<14
	Gizzard shad (*Konosirus punctatus*)	blood	1	23	<5.5	<14
	Japanese scad (*Trachurus japonicus*)	blood	2	7−19 (13)	1 (1)	<9
	Redlip mullet (*Liza haematocheila*)	blood	2	23−47 (35)	1[c]	<14
	Red seabream (*Pagrus major*)	blood	2	17−41 (29)	<5.5	<14
	Yellowfin sea bream (*Acanthopagrus schlegeli*)	blood	1	27	<5.5	<14
Ariake Bay	Lefteye flounder (*Paralichthys olivaceus*)	liver	2	30−199 (115)	NA[d]	NA
		blood	2	7−50 (29)	<0.7−11 (5.7)	<7.5
Okinawa (Kin Bay)	Giant trevally (*Caranx ignobilis*)	blood	3	15−24 (19)	<1.93	<23
	Ornate jobfish (*Tropidinius amoenus*)	liver	4	593−7900 (3250)	NA	NA
		blood	3	4−21 (9.7)	NA	NA
	Perth herring (*Nematalosa come*)	blood	1	1	<4.4	<53
	Yellowfin tuna (*Thunnus albacares*)	blood	1	1	<2.2	<27

[a] Values in parentheses indicate the means. [b] One sample above the detection limit; others had detection limits of 14 and 26 ng/g. [c] One sample above the detection limit, another sample with an LOD of 5.5 ng/mL. [d] NA = not analyzed.

approximate comparison. Concentrations of PFOS measured in the livers of fishes collected from Tokyo Bay, Osaka Bay, and Lake Biwa, and the corresponding mean concentrations of PFOS in water, were used for the calculation (Figure 3). Based on these data, BCF for PFOS in livers of fishes ranged from 274 to 41 600 (mean; 8540). The corresponding log BCF values in fishes were 2.4−4.6 (mean; 3.9). BCFs of PFOS in the livers of common shiner (*Notropus cornutus*) collected

TABLE 3. Concentrations of Perfluoroalkane Sulfonates in Liver (ng/g, wet wt) and Blood or Serum of [ng/mL] Birds, Pet Animals, and Human Volunteers Collected from the Tokyo Bay Area

species	tissue	*n*	PFOS	PFHS	PFBS
carrion crow (*Corvus corone*)	liver	6	68−1200 (464)[a]	<5.7	<45
	blood	5	11−150 (56)	<1	NA[d]
mallard (*Anas platyrhynchos*)	liver	1	493	<5.5	<44
	blood	1	130	9	NA
pintail duck (*Anas acuta*)	liver	2	239−497 (368)	2.6[b]	<45
	blood	2	84−167 (126)	6−20 (13)	NA
sea gull (*Larus crassirostris*)[c]	liver	1	230	<7.5	NA
black-eared kite (*Milvus lineatus*)	liver	1	180	<7.5	NA
common cormorant (*Phalacrocorax carbo*)	liver	10	390 (170−650)	<7.5−10[b]	NA
domestic duck (pet bird) (*Anas platyrhynchos var. domestica*)	blood	2	0.3−1 (0.65)	NA	NA
	serum	2	6−9 (7.5)	NA	NA
rabbit (pet animal) (*Oryctolagus cuniculus*)	serum	3	<0.1−0.4 (0.17)	NA	NA
human	blood	3 ♂	5−14 (11)	<2.7	<19
	serum	3 ♂	19−41 (27)	<2.7	<19
	blood	5 ♂	2.4−8.6 (5.9)	<1−3.8 (2.0)	NA
	blood	2 ♀	9.1−11	<1−1	NA

[a] Values in parentheses indicate the means. [b] One sample above the LOD, another sample with a LOD of 5.5 ng/g, wet wt. [c] From ref *22*. [d] NA = not analyzed.

from Etobicoke Creek in Toronto, Canada, ranged between 6300 and 125 000 (14). The highest BCF in our study, 41600, was found in bluegill collected from Lake Biwa. The average water concentration of PFOS in Lake Biwa was 7.4 ng/L, whereas the concentrations in the livers of bluegill from that lake ranged from 254 to 310 ng/g, on a wet weight basis. The mean BCF for PFOS in fishes from Tokyo Bay was 5500 (1400−21 100), which is similar to the laboratory-derived value of 5400 that has been reported for the liver of rainbow trout exposed to PFOS (*16*). The calculated field-based BCFs for PFOS were greater than those reported for chlorophenols and PAHs but less than those obtained for more highly chlorinated PCBs and DDT (*18*, *19*). BCFs for PFOS were comparable to, or greater than, values that have been reported for anionic linear alkylbenzene sulfonates (6−990; laboratory based) in fathead minnows (*20*). Nevertheless, it should be noted that the mechanisms of bioconcentration and the compartments of accumulation of neutral organic pollutants such as PCBs and DDT are different from those of ionic compounds such as PFOS.

PFOS was also found in the blood of Japanese human volunteers, at concentrations ranging from 2.4 to 14 ng/mL (Table 3). The mean PFOS concentration in blood samples from adult females was 10 ng/mL ($n = 2$), whereas the level in males ($n = 8$) was 8 ng/mL. There was no significant correlation between PFOS concentration in blood and age of the donor (Figure 4). Concentrations of PFOS were measured in the serum of three individuals and were 1.4−4-fold (mean; 2.5) greater than concentrations in the corresponding whole blood samples. The measured range of PFOS concentrations was similar to the range of 2−20 ng/mL that has been reported previously (*21*). Concentrations of PFOS ranging from 6.7 to 82 ng/mL have been reported in the sera of United States citizens (*2*). Assuming that concentrations of PFOS in serum were 2.5-fold greater than concentrations in whole blood, the mean PFOS concentration in sera of Japanese volunteers can be estimated to be 21 ng/mL. This is slightly lower than the average concentration of 28 ng/mL, that was reported for United States citizens (*2*). PFHS was also found in the humans in our study at concentrations ranging from 1 to 3.8 ng/mL. These results provide baseline data on the extent of PFOS exposure of Japanese citizens; however, the number of human samples in our study was small, and the results may not reflect exposures in general Japanese population. Further studies with larger numbers of samples are necessary to understand the sources and pathways of exposures and the levels of risk.

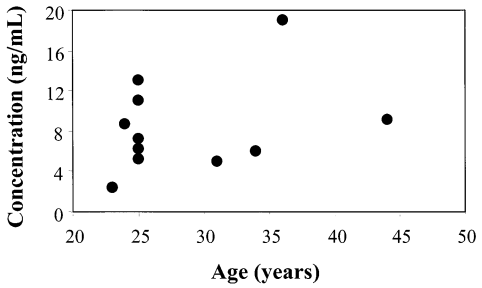

FIGURE 4. Relationship between age of human volunteer subjects and PFOS concentrations in their blood in Japan.

Birds (carrion crow, mallard, and pintail duck) and pets (rabbit and domestic duck) contained detectable concentrations of PFOS in liver and blood. In the birds, concentrations in livers were greater than those determined in corresponding blood samples. Occurrence of PFOS in pet animals suggests exposure from food sources. Mallard ducks may be exposed to PFOS via fish meal, which may be incorporated in their diet. Perfluorinated compounds, as perfluoroalkylated organophosphates, have been reported to be impregnated/used in folding cartons used for pet food supplies (*9*). Carrion crows, which are omnivorous birds, that consume a diet ranging from worms, insects, fruits, and seeds to kitchen scraps, had PFOS concentrations ranging from 11 to 150 ng/mL (mean; 56) in their blood and from 68 to 1200 ng/g (mean; 464) in liver samples. These concentrations of PFOS in livers of carrion crows were similar to the liver concentrations reported for several fish-eating water bird species collected from around Tokyo Bay (*22*). Overall, these results provide the first evidence of the presence of PFOS in surface seawater and in coastal fishes from various locations in Japan. Furthermore, field-based BCFs of PFOS in livers of fishes

have been reported. Additional studies are needed to characterize the exposure routes and fate of perfluorochemicals in the environment.

Acknowledgments

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