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Perfluorooctanesulfonate and Related Fluorinated Hydrocarbons in Marine Mammals, Fishes, and Birds from Coasts of the Baltic and the Mediterranean Seas

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Perfluorooctanesulfonate (PFOS; $C_8F_{17}SO_3^-$), perfluorooctanesulfonamide (FOSA; $C_8F_{17}SO_2NH_2$), perfluorohexanesulfonate (PFHxS; $C_6F_{13}SO_3^-$), and perfluorooctanoate (PFOA; $C_7F_{15}CO_2^-$) were detected in 175 samples of liver and blood of bluefin tuna (*Thunnus thynnus*), swordfish (*Xiphias gladius*), common cormorants (*Phalacrocorax carbo*), bottlenose dolphins (*Tursiops truncatus*), striped dolphins (*Stenella coeruleoalba*), common dolphins (*Delphinus delphi*), fin whales (*Balenoptera physalus*), and long-finned pilot whales (*Globicephala melas*) from the Italian coast of the Mediterranean Sea and in livers of ringed seals (*Phoca hispida*), gray seals (*Halichoerus grypus*), white-tailed sea eagles (*Haliaeetus albicilla*), and Atlantic salmon (*Salmo salar*) from coastal areas of the Baltic Sea. PFOS was detected in all of the wildlife species analyzed. Concentrations of PFOS in blood decreased in order of bottlenose dolphins > bluefin tuna > swordfish. Mean PFOS concentrations (61 ng/g, wet wt) in cormorant livers collected from Sardinia Island in the Mediterranean Sea were less than the concentrations of PFOA (95 ng/g, wet wt). PFOS concentrations in cormorant livers were significantly correlated with those of PFOA. FOSA was found in 14 of 19 livers or blood samples of marine mammals from the Mediterranean Sea. The highest concentration of 878 ng FOSA/g, wet wt, was found in the liver of a common dolphin. Livers of ringed and gray seals from the Bothnian Bay in the Baltic Sea contained PFOS concentrations ranging from 130 to 1100 ng/g, wet wt. No relationships between PFOS concentrations and ages of ringed or gray seals were observed. Concentrations of PFOS in livers of seals were 2.7−5.5-fold greater than those in corresponding blood. A significant positive correlation existed between the PFOS concentrations in liver and blood, which indicates that blood can be used for nonlethal monitoring of PFOS. Trend analysis of PFOS concentrations in livers of white-tailed sea eagles collected from eastern Germany and Poland since 1979 indicated an increase in concentrations during the 1990s. Livers of Atlantic salmons did not contain quantifiable concentrations of any of the fluorochemicals monitored. PFOS is a widespread contaminant in wildlife from the Baltic and the Mediterranean Seas, while FOSA and PFOA were detected only in certain locations indicating their sporadic spatial distribution.

Introduction

Perfluorinated sulfonates have been commercially produced by an electrochemical fluorination process for over 40 years (*1*). A major fluorochemical produced by this process is perfluorooctane sulfonylfluoride (POSF; $C_8F_{17}SO_2F$). Using this fluorinated compound as a building block, further reactions produce several other fluorinated compounds, including perfluorooctanesulfonate (PFOS) (*1, 2*). These compounds repel water and oil, reduce surface tension, catalyze oligomerization and polymerization, and maintain their properties under extreme conditions. Depending upon the specific functional derivatization or the degree of polymerization, POSF-based compounds may degrade or metabolize to PFOS (*2, 3*). PFOS is stable, chemically inert, and nonreactive and has the potential to bioaccumulate (*4*−*6*). PFOS has been identified in serum samples from both occupationally and nonoccupationally exposed human populations and in various species of wildlife (*2, 6*−*11*), and PFOS, FOSA, PFHxS, and PFOA have been detected in human blood (*7*). However, studies describing the occurrence of FOSA, PFHxS, and PFOA in wildlife are scarce (*6, 11, 12*).

The mechanisms and pathways leading to the presence of perfluorinated compounds in wildlife and humans are not well characterized, but it is likely that there are multiple sources of the compound. To understand the spatial distribution of perfluorinated compounds, exposure concentrations were measured in a range of species with different natural histories from various parts of the world. In this study, concentrations of PFOS, FOSA, PFHxS, and PFOA were measured in marine mammals including bottlenose dolphins (*Tursiops truncatus*), striped dolphins (*Stenella coeruleoalba*), common dolphins (*Delphinus delphi*), fin whales (*Balenoptera physalus*), long-finned pilot whales (*Globicephala melas*) and fishes such as northern bluefin tuna (*Thunnus thynnus*), swordfish (*Xiphias gladius*), and in common cormorants (*Phalacrocorax carbo*) collected from Italian coast of the Mediterranean Sea. Furthermore, livers of ringed seals (*Phoca hispida*), gray seals (*Halichoerus grypus*), and Atlantic Salmon (*Salmo salar*) were collected from the Bothnian Bay in the northern part of the Baltic Sea. Similarly, concentrations of target compounds were measured in livers of white-tailed sea eagles (*Haliaeetus albicilla*) collected from inland and coastal regions of eastern Germany and Poland since 1979 until 1999. This provided to an opportunity to evaluate temporal trends in concentrations of fluorochemicals during 20 years. The objectives of this study were to determine the current concentrations of target fluorochemicals in biota from the Mediterranean and the Baltic Seas and to determine their accumulation features.

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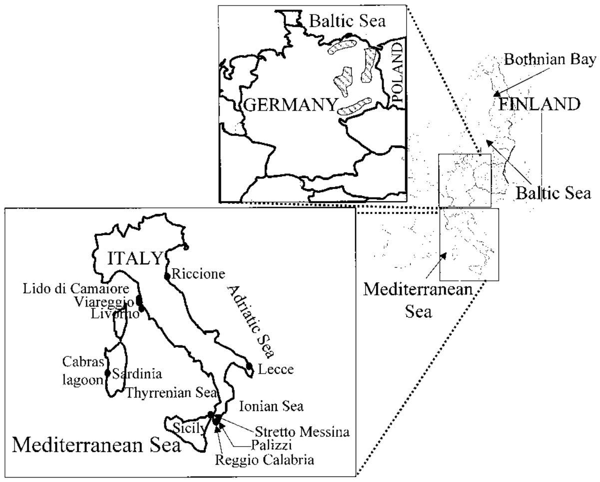

FIGURE 1. Map showing sampling locations (shaded, patterned areas in Germany are eagle sampling sites).

Materials and Methods

Samples. One hundred and seventy five samples of liver and blood of cetaceans (dolphins and whales), fishes, and birds were analyzed in this study. Blood samples of bottlenose dolphins were collected by bleeding (10 mL) captive animals born in delphinariums. In the delphinarium, these dolphins were fed mackerel and herring caught in the Mediterranean Sea and capelin from the North Sea. Livers of common, bottlenose and striped dolphins were collected during mass mortality events along the Italian coast in 1991 (Figure 1). All the dolphins were found stranded, dead along the Adriatic and Thyrrenian Seas. The livers of striped and bottlenose dolphins were freeze-dried prior to analysis. Tissues of long-finned pilot whale and fin whales were taken from animals stranded in the Thyrrhenian Sea. Liver and blood samples of sexually mature (fork length > 110 cm) bluefin tuna were collected in Palizzi, southern coast of Italy. Liver and blood were taken from mature swordfish, which were caught by harpooning in the Ionian − Thyrrenian Seas. Livers of cormorant (*Phalacrocorax carbo*) were collected from the birds that were originally sacrificed in 1997 by the Department of Sanitation-Division of Rearing and Zootechnical Resources due to sanitary regulations. Age class and sex of cormorants were recorded when available. Livers of ringed (*Phoca hispida*) and gray seals (*Halichoerus grypus*) and Atlantic Salmon (*Salmo salar*) collected from the Bothnian Bay in the Baltic Sea were obtained from Finnish Game and Fisheries Research Institute. Salmon were taken from the Rivers Simojoki and Kymijoki in Finland during spawning. All were female salmon, which migrate to the Bothnian Sea, the southern Gulf of Bothnia or the Gulf of Finland. The salmon fast up to 4 months before spawning. Livers of white-tailed sea eagles (*Haliaeetus albicilla*) collected since 1979 until 1999 from eastern Germany and Polish coastal areas of the Baltic Sea were analyzed. Liver samples were wrapped in aluminum foil cleaned with solvents or whirlpac bags and stored frozen at −20 °C until analysis. Sampling locations of fishes, marine mammals, and birds are shown in Figure 1.

Analysis. Concentrations of PFOS, FOSA, PFOA, and PFHxS in liver and blood were measured using high performance liquid chromatography (HPLC) with electrospray tandem mass spectrometry (*7*). Details of preparation of tissues, reagents, and standards have been described earlier (*7*). Analyte separation was performed using a Hewlett-Packard HP1100 liquid chromatograph modified with low dead-volume internal tubing. Ten microliters of extract was injected onto a 50×2 mm (5 μm) Keystone Betasil C_{18} column with a 2 mM ammonium acetate/methanol mobile phase starting at 10% methanol at a flow rate of 300 μL/minute, to 100% methanol at 11.5 min before reverting to original conditions at 13 min. For quantitative determination, the HPLC system was interfaced to a Micromass (Beverly, MA) Quattro II atmospheric pressure ionization tandem mass spectrometer operated in the electrospray negative mode. Instrumental parameters were optimized to transmit the $[M-K]^-$ ion for all analytes before fragmentation to 1 or more product ions. When possible, multiple daughter ions were monitored, but quantitation was based on a single product ion. In all cases, the capillary was held between 1.6 and 3.2 kV.

Recoveries of PFOS and other fluorochemicals spiked at the 250 ng level onto sample matrices and carried through the analytical procedure varied (Table 1; Supporting Information). The standards (5 μL of 50 ppm stock) were spiked into liver or blood prior to homogenization. While the recoveries of PFOS spiked to tuna, swordfish, and dolphin livers were 66−140%, the recoveries of PFOS spiked to tuna blood were low (37−47%). The reason for low recoveries of PFOS spiked to tuna blood is not known. Concentrations of PFOS were not corrected for the recoveries of surrogate standard. Similarly, recoveries of FOSA, PFHxS, and PFOA varied depending on the sample matrix. For instance, recoveries of FOSA and PFOA in seal livers were 70 ± 50% and PFHxS was 50%. Recoveries of FOSA, PFHxS, and PFOA in salmon livers were less than 40%, and therefore the data for salmon liver should be considered qualitative. Recoveries of PFOS and PFOA in sea eagle livers were 90 ± 30%, whereas those of FOSA and PFHxS were 54 and 71%, respectively. Based on the duplicate analysis of matrix spike samples, accuracy of the analytical results under the best conditions were ±30% of the reported values. For the estimation of the LOQ, the tissue samples were compared to an unextracted standard calibration curve. For instance, if 5 ng/mL standard is the lowest acceptable standard, and sample had been diluted by a factor of 7, the LOQ is reported as 35 ng/mL. LOQs for fluorochemicals varied from 1 to 72 ng/g, wet wt, depending on the matrix.

Results and Discussion

Mediterranean Sea. Of the four fluorochemicals monitored, PFOS was the most predominant fluorochemical in the tissues analyzed (Tables 2 and 3). PFOS was found in blood of captive bottlenose dolphins at concentrations ranging from 42 to 210 ng/mL (Table 2). The greatest PFOS concentration found in the liver of a common dolphin was 940 ng/g, wet wt (Table 3). Muscle tissue from the same individual contained a PFOS concentration that was 12-fold less than that in liver. Four of five livers of bottlenose dolphins collected from the Adriatic and Thyrrenian Seas contained quantifiable concentrations of PFOS. The mean (±SD) concentration of PFOS in livers of bottlenose dolphins was 54 ± 35 ng/g, wet wt (Table 3). The mean (±SD) concentration of PFOS in livers of striped dolphins was 26 ± 9 ng/g, wet wt. Concentrations of PFOS in livers of bottlenose and striped dolphins were less than those found in cetaceans from the coastal waters of Florida (*8*). Nevertheless, the concentration of PFOS measured in common dolphin liver was similar to those reported for dolphins from the Florida coast. Concentrations of PFOS in muscle and liver of long-finned pilot whales were 52 and 270 ng/g, wet wt, respectively.

Of the other fluorochemicals measured, FOSA was a prominent compound found in livers of dolphins and whales. Concentrations of FOSA in blood of bottlenose dolphins were 1−5-fold greater than those of PFOS (Table 2). Livers of most of the cetaceans (except striped dolphin) contained quantifiable concentrations of FOSA (Table 3). The greatest concentration of 878 ng FOSA/g, wet wt, was found in the liver of a common dolphin. Concentrations of FOSA in bottlenose

TABLE 2. Concentrations of Perfluorinated Organic Compounds in Blood (ng/mL) of Bottlenose Dolphin and Fishes from Italian Coasts[a]

species	sampling area	date of collection	PFOS	FOSA	PFOA	PFHxS	remarks
bottlenose dolphin ($n = 4$)	Riccione (Adriatic Sea)	1997	143 (42−210)	223 (190−270)	3.1 (<2.5−3.8)	4.5 (<1−6.1)	3 males, 1 female; 2−19 years
bluefin tuna ($n = 6$)	Palizzi	Oct-Nov 1999	40 (27−52)	15 (13−19)	<2.5	<1	4 males, 2 ND; 113−158 cm fork length; 25−61 kg
swordfish ($n = 7$)	Stretto Messina (Ionian-Thyrrenian Sea)	July 1999	7.2 (4−14)	15 (1.1−28)	<2.5	<1	3 males, 3 females, 1 ND; 107−190 cm; 15−83 kg

[a] ND = not determined. Values below the quantitation limit were assigned zero when calculating mean.

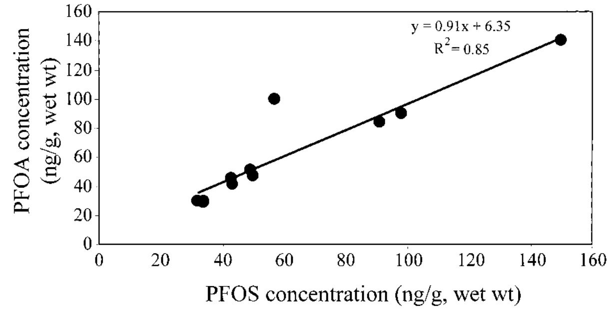

FIGURE 2. Relationship between PFOS and PFOA concentrations in cormorant livers from Cabras Lagoon, Sardinia, Italy.

dolphins, common dolphins, and long-finned pilot whales were similar to those of PFOS (Table 3). The greatest concentration of FOSA found in the liver of a common dolphin was greater than those found in mink from Illinois (*11*). Occurrence of FOSA in marine mammals from the Mediterranean region indicates the presence of specific sources. PFOA and PFHxS were found in blood of a few individuals of bottlenose dolphins at concentrations ranging from <2.5 to 6.1 ng/mL. PFOA was not found in livers of cetaceans at the quantitation limit of 38−72 ng/g, wet wt. PFHxS was detected in a striped dolphin and swordfish liver at concentrations of 6.8 and 10 ng/g, wet wt, respectively. While PFOS is a metabolic product of several sulfonated perfluorochemicals such as *n*-methyl perfluorooctanesulfonamidoethanol [$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$] (*13*), FOSA, PFOA, and PFHxS are intermediates in the production of several perfluorinated compounds. FOSA and PFOA are also products used in various applications. FOSA is also a metabolic product of *n*-ethyl perfluorooctanesulfonamide, which is used as an insecticide (Sulfluramid) to control cockroaches, termites, and ants (*14*). PFOA is an impurity in various formulations of perfluorochemicals including aqueous film fire-fighting foams (*5*).

Concentrations of PFOS in cormorant livers collected from Cabras Lagoon in Sardinia ranged from 32 to 150 ng/g, wet wt (mean: 61 ng/g) (Table 3). Mean PFOS concentrations in juvenile birds were not significantly different from those in adults ($p < 0.05$). This is similar for bald eagles collected from the midwestern U.S. (*9*). In general, PFOS concentrations in cormorants were similar to or less than those found in cormorants and other fish-eating water birds collected from the North American Great Lakes (*9*).

PFOA was consistently found in all the livers of cormorants at concentrations ranging from 29 to 450 ng/g, wet wt. Mean concentration of PFOA (95 ng/g, wet wt) in cormorant livers was, on average, 1.7-fold greater than the PFOS concentrations (61 ng/g, wet wt). A juvenile, female cormorant contained the greatest PFOA concentration of 450 ng/g, wet wt, which appeared to qualify as an outlier as this concentration was 4.5 times greater than the standard deviation of the mean. When this outlier value is eliminated, there was a significant correlation between PFOS and PFOA concentrations in cormorant livers (Figure 2). These results indicate that the sources of PFOS and PFOA may be similar for cormorants from Cabras Lagoon in Sardinia. FOSA was found in one of the 12 cormorant livers at a concentration of 89 ng/g, wet wt.

Concentrations of PFOS in blood of bluefin tuna and swordfish ranged from 27 to 52 (mean: 40) and 4 to 21 ng/mL (mean: 10), respectively (Table 2). Similarly, livers of 12 of 13 tuna and swordfish contained quantifiable concentrations of PFOS. The average concentration of PFOS in livers of bluefin tuna (21−87 ng/g; mean: 47) was greater than that determined in swordfish (<1−13 ng/g; mean: 7) (Table 3). The ratios of concentrations of PFOS in liver to blood of

TABLE 3. Concentrations of Perfluorinated Organic Compounds in Livers (ng/g, Wet Wt) of Cormorants, Marine Mammals, and Fishes from the Italian Coast of the Mediterranean Sea

species/tissue	location; date	PFOS	FOSA	PFOA	PFHxS	sample details[b]
cormorant liver	Cabras Lagoon (Sardinian Sea); 1997	43	<38	41	<7	M, adult, 2.4 kg
		57	<38	100	<7	F, adult, 2.2 kg
		49	<38	51	<7	F, adult, 2.3 kg
		98	<38	90	<7	F, adult, 2.33 kg
		34	<38	30	<7	F, adult, 2.7 kg
		150	<38	140	<7	F, adult, 2.2 kg
		91	89	84	<7	F, juvenile, 2 kg
		47	<38	450	<7	F, juvenile, 1.4 kg
		50	<38	47	<7	F, juvenile, 1.96 kg
		43	<38	45	<7	M, juvenile, 2 kg
		32	<38	30	<7	M, juvenile, 2.4 kg
		34	<38	29	<7	M, juvenile, 2.4 kg
bottlenose dolphin liver[a]	Marina di Grosseto (North Thyrrenian Sea); 1991	45	55	<36	<7	
	Livorno (North Thyrrenian Sea); 1991	75	90	<72	<7	240 cm
	Croatia (North Adriatic Sea); 1992	42.5	32.5	<72	<7	M, 288 cm
	Lecce (South Adriatic Sea); 1991	108	32.5	<72	<7	M, 235 cm
	Lido di Camaiore (North Thyrrenian Sea); 1991	<1.4	30	<72	<7	279 cm
	Mar Tirreno; NA	110	139	<38	<19	NA
striped dolphin liver[a]	Lecce (South Adriatic Sea); Aug 1991	40	<38	<72	<7	M, 201 cm
	Viareggio (North Thyrrenian Sea); 1991	22.3	<38	<72	<7	F, 200 cm
	Lecce (South Adriatic Sea); Aug 1991	23.5	<38	<72	<7	F
	Lecce (South Adriatic Sea); Aug 1991	16.3	<38	<72	6.8	F, 201 cm
common dolphin muscle	Giglio Island, North Thyrrenian Sea; Feb 1998	77	142	<38	<19	F, 203 cm
common dolphin liver	Giglio Island, North Thyrrenian Sea; Feb 1998	940	878	<38	<19	F, 203 cm
fin whale muscle	Livorno, coast of Tuscany; Feb 1998	<19	<19	<38	<19	M, 13.8 m, 13.7 tons
long-finned pilot whale muscle	Elba Island, North Thyrrenian Sea; Sep 1996	52	48	<38	<19	160 cm, pup, suckling
long-finned pilot whale liver	Elba Island, North Thyrrenian Sea; Sep 1996	270	50	<38	<19	160 cm, pup, suckling
swordfish liver	Stretto Messina (Ionian-Thyrrenian Sea); Jul 1999	3	<38	<36	10	150 cm, 44 kg
		5	<38	<36	<7	156 cm, 45 kg
		8	<38	<36	<7	140 cm, 53 kg
		<1	<38	<36	<7	161 cm, 61 kg
		13	<38	<36	<7	F, 70 kg
tuna liver	Reggio Calabria (Ionian Sea); Oct-Nov 1999	35	<38	<36	<7	M, 250 cm,
		43	<38	<72	<7	156 cm
	Palizzi; Oct-Nov 1999	87	<38	<36	<7	M, 147 cm, 54 kg
		57	<38	<72	<7	M, 157 cm, 61 kg
		49	<38	<36	<7	M, 158 cm, 51 kg
		21	<38	<36	<7	139 cm
		56	<38	<36	<7	M, 149 cm, 46 kg
		25	<38	<72	<7	152 cm, 56 kg

[a] Values were converted from dry weight basis to wet wt assuming a moisture content of 75%. [b] M = male; F = female. Length of fish and dolphin represents fork length.

TABLE 4. Concentrations of Fluorochemicals in Gray and Ringed Seals and Atlantic Salmon Livers (ng/g, Wet Wt)

species	sex	*n*	age (yrs)	PFOS	FOSA	PFOA	PFHxS
gray seal	male	12	10 (2−25)	243 (148−360)	42[a] (<19−47)	<19	<7.5
	female	15	12.6 (2−33)	190 (140−290)	<38	<19	<7.5
ringed seal	male	10	11.5 (1−21)	490 (130−1100)	<38	34[a] (<19−39)	<38
	female	15	11.5 (4−25)	430 (170−1000)	<38	<19	<38
Atlantic salmon	female	22	Adult	<8	<19	<19	<7.5

[a] Mean of two detectable observations.

bluefin tuna and swordfish were 0.85 and 1.4, respectively. These ratios are 7−12-fold less than those calculated for polar bears from Alaska (*8*). Although the PFOS concentrations in bottlenose dolphins blood were 4−14-fold greater than those in bluefin tuna and swordfish, blood-to-liver ratios of PFOS were less in dolphins than in fishes. This suggests that the distribution of PFOS between liver and blood in fishes is different than in mammals. FOSA was found in all the 13 blood samples of fishes. Concentrations of FOSA (mean: 15 ng/mL) in the blood of bluefin tuna were 2−4-fold less than those of PFOS (40 ng/mL), which was different from that observed in bottlenose dolphins. Mean concentrations of FOSA in swordfish blood was 1.5-fold greater than that of PFOS. Despite the occurrence of FOSA in blood of swordfish and tuna, it was not found in the livers at the quantitation limit of 38 ng/g, wet wt. PFHxS was detected in one of the five livers of swordfish at a concentration of 10 ng/g, wet wt. PFOA was not found at the quantitation limit in any of fish tissue samples.

Baltic Sea. Concentrations of PFOS in livers of gray seals ranged from 140 to 360 ng/g, wet wt (Table 4). Concentrations of PFOS in ringed seals were significantly greater ($p < 0.01$) than those in gray seals. Concentrations of PFOS of up to 1100 ng/g, wet wt, were found in ringed seals from the Bothnian Bay. The greatest concentration was found in a 7-year old male ringed seal, while the second greatest

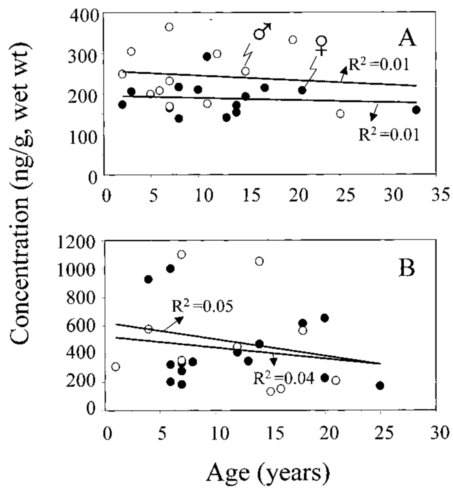

FIGURE 3. Relationship between PFOS concentrations and age in gray (A) and ringed (B) seal livers.

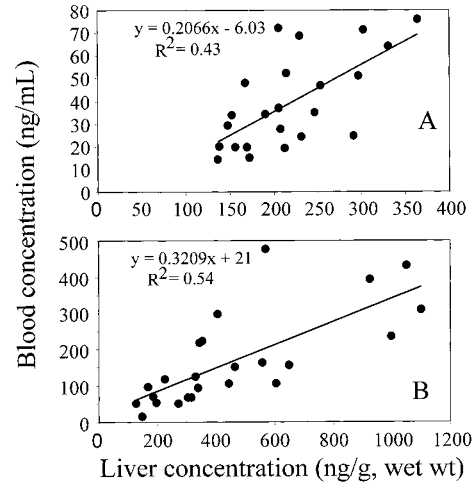

FIGURE 4. Relationship between PFOS concentrations in liver and blood of gray (A) and ringed (B) seals.

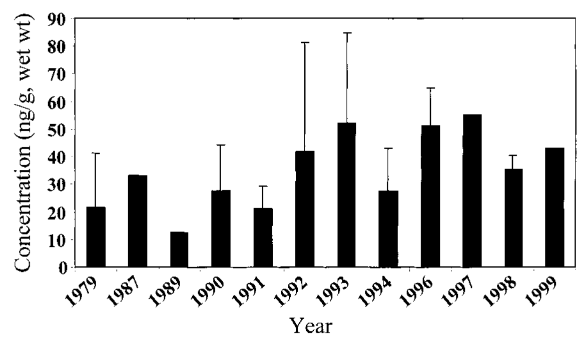

FIGURE 5. Concentrations (mean ± SD) of PFOS in livers of white-tailed sea eagles collected from 1979 to 1999. Sample collected in 1995 was removed from this graph.

concentration was found in a 6-year old female ringed seal. There was no significant difference in the concentration of PFOS between sexes of ringed seals (p > 0.05). However, PFOS concentrations in male gray seals were significantly greater than those in females (p < 0.05). Earlier studies have reported the lack of significant differences in PFOS concentrations between gender (*8*). The observed differences in the accumulation of PFOS between genders of ringed and gray seals could be due to specific reproductive parameters. Female ringed seals are reproductively mature at about 6 years of age, whereas female gray seals start to reproduce from ages 3 to 5. Earlier parturition may be a reason for lesser PFOS concentrations in female gray seals than in ringed seals. However, several other biological parameters associated with samples such as age may limit the interpretation. Concentrations of PFOS did not increase with age in either ringed or gray seals (Figure 3). This is similar to results observed for mink and marine mammals from the U.S.A. (*8, 11*). In an earlier study, we reported PFOS concentrations in blood of ringed and gray seals (*8*). The ratios of PFOS concentrations in ringed and gray seal liver and blood were 2.7 and 5.5, respectively. These values were greater than those found in bluefin tuna and swordfish analyzed in this study, suggesting preferential enrichment of PFOS in livers of mammals than in fishes. There was a significant correlation between PFOS concentrations in livers and blood of both ringed and gray seals (p < 0.05) (Figure 4). This indicates that blood can be used as a matrix for nonlethal monitoring of PFOS exposures in marine mammals.

FOSA and PFOA were found only in 2 of the 52 samples of seals analyzed. PFHxS was not detected in any of the samples. This was different from that observed in marine mammals from the Mediterranean Sea, where FOSA was relatively prominent in marine mammals. PFHxS was not found in any of the seal livers analyzed.

Livers of 22 Atlantic salmon collected from the northern Baltic Sea were analyzed for target fluorochemicals (Table 4), and none of the salmon livers contained the fluorochemicals at the quantification limit of between 8 and 19 ng/g, wet wt. All Atlantic salmon were adult females and were collected during spawning. The salmon fast for 4 months prior to spawning and the lack of quantifiable concentrations of fluorochemicals in salmon could be attributed to their long fasting periods.

White-tailed sea eagles collected from eastern Germany and Poland contained quantifiable concentrations of PFOS (Table 5), ranging from <3.9 to 127 ng/g, wet wt. These concentrations were severalfold less than those found in bald eagles from the United States (*9*). Concentrations of PFOS varied widely within the sampling years. However, comparison of concentrations in livers of sea eagles from the 1970s and 1980s (25 ng/g, wet wt) with those from the 1990s (40 ng/g, wet wt) indicated an increase in the 1990s compared to those in the 1970s or 1980s (Figure 5). For instance, mean concentration of PFOS in eagles collected in 1979, 1990, 1992, 1993, 1996, and 1999 were 22, 28, 42, 52, 52, and 45 ng/g, wet wt, respectively. There was a statistically significant increase in the concentration of PFOS in sea eagle livers with time (p < 0.05). Sulfonyl-based fluorinated hydrocarbons have been manufactured since the 1950s (*13*). PFOS concentrations in sea eagle livers may be influenced by several factors related to the matrix and accumulation features of fluorinated organics. Livers of birds analyzed in this study were from different ages and sexes. However, no significant correlation existed between PFOS concentrations and age or sex of birds (*9*). Unlike neutral organic pollutants such as PCBs, PFOS covalently binds to proteins in liver and blood plasma (*15, 16*). Therefore, accumulation of PFOS in higher trophic predators is controlled by a dynamic equilibrium between uptake and elimination or is related protein turnover. On the other hand, neutral lipophilic contaminants such as PCBs tend to accumulate in fatty tissues over a period of time, which results in an age-related increase of concentrations. Therefore, abiotic matrices such as dated sediment or lower trophic organisms may be better indicators for temporal trend analysis of PFOS. FOSA, PFHxS, and PFOA were not detected in livers of white-tailed sea eagles at the quantitation limits of 38, 7, and 40 ng/g, wet wt, respectively. This is different from that observed in the Mediterranean Sea, in which PFOA

TABLE 5. Concentrations of PFOS in Livers of White-Tailed Sea Eagles (ng/g, Wet Wt) from Eastern Germany and Poland[a]

sample	sex	date	wt (g)	location[b]	PFOS	remarks
79/6	F	1979	5700	National Park Muritz	3.9	adult
79/8	F	12/6/1979	4200	Stegelitz	11.3	subadult
79/5	F	17/4/79	6640	Waldlewitz	49.5	immature
87/18	M	4/11/1987	4374	Dassow	40.5	juvenile
M 87/21	F	29/3/87	4325	Dabelow	25.8	adult
89/1	F	24/2/89	6060	Kustrinchen	21	adult
89/6	NA	25/5/89	1445	Rodenskrug	<3.9	juvenile- 8 d old
MV 90/9	F	4/12/1990	3445	Schlicht	35.1	juvenile
90/4	F	12/4/1990	5640	Kotzow	43.2	adult
90/7	M	15/8/90	2970	Melzower Forst	3.9	adult, emaciated
190/3	M	28/3/90	4425	Babke	<3.9	adult
MV91/4	F	1/3/1991	5800	National Park Muritz	8	immature
MV 91/8	M	6/4/1991	4105	Bergfeld	25.6	adult, emaciated
MV 91/10	F	6/5/1991	5517	Julchendorf	20.8	adult
MV 91/12	F	25/6/91	4830	Bossow	30.1	juvenile-70d old
S92/1	F	2/1/1992	4230	Kamenz	38	immature 2yrs
MV 92/21	M	4/11/1992	4315	Axelshof	12.4	immature
MV 92/2	M	5/1/1992	NA	Lahnvitz	23.8	juvenile
MV92/3	F	6/2/1992	3805	Lewitz, Bahlenhusch	127	decomposed, emaciated, juvenile
MV 92/9	M	28/04/92	4280	Near Torgelow	11.9	adult, 6 yrs
BB 92/20	F	28/10/92	5255	Milmersdorf	36.8	adult
BB 93/19	F	1/10/1993	4750	Wilmersdorf	39.8	juvenile
SA 93/17	F	4/9/1993	5420	Stackelitz	23.3	immature
S93/7	F	8/4/1993	5710	Konigswartha	108	subadult
MV 93/2	F	15/2/93	4505	National Park Muritz	37.5	adult, moderate decomposition
MV 94/11	F	10/4/1994	3620	Dobbin/Glave	28.1	adult, emaciated
BB 94/18	M	12/5/1994	3595	Kuhzer lake n. Ruhhof	32.8	adult, emaciated, decomposed
BB 94/2	F	15/1/94	4300	Thomsdorf	10.5	adult
BB 94/4	M	17/2/94	5116	Angermunde-Tantow	16.6	adult
MV 94/19	M	17/5/94	4225	near Karow	58.5	adult
94/6	F	25/2/94	3460	lake at Sproitz	11.5	emaciated, juvenile
BB 94/9	M	26/3/94	4500	Chorin	33.8	immature, moderate decomposition
MV 95/5	F	21/2/95	6500	Kolpinsee/Usedom	120	5 yrs
S96/7	F		3400	Niederspree	65	immature, emaciated
S 97/22	M	28/8/97	3800	Ebersbach-Rodern	99.6	adult
S 98/18	F	28/7/98	4920	klein Krauscha	42.1	immature, moderate decomposition
No3, 28/02/00	M	1996		Western Poland	31.8	immature, emaciated
No4, 2001	F	1996		Western Poland	63.4	adult, liver disease
No5, 3/06/00	M	1996		Poland	44.4	immature, emaciated
No7, 2000	M	1997		Poland	10.7	adult, emaciated
No1, 11/02/00	F	1998		Poland	29.7	adult
No2, 20/01/00	F	1998		Wolsztyn, Poland	33.5	adult, healthy
No6, 2000	F	Oct 2000		Krucza, Poland	62	young
No8, UNK	NA	1999		Poland	24.4	adult

[a] FOSA, PFHxS, and PFOA were not found in any of the sea eagle livers at the quantitation limits of 38, 7, and 40 ng/g, wet wt, respectively.
[b] All the locations are in eastern Germany except those indicated as Poland, which are collected from the Baltic coast of Poland.

was relatively prominent in cormorants. This indicates region-specific distribution of these fluorochemicals in biota.

The results of this study suggest widespread occurrence of PFOS in fishes, birds, and marine mammals from the Mediterranean and the Baltic Seas. Concentrations of FOSA in blood of bottlenose dolphins and swordfish from the Mediterranean Sea were greater than those of PFOS. Despite the occurrence of FOSA in blood tissues of fishes, it was not detected in livers. Similarly concentrations of PFOA were greater than those of PFOS in cormorant livers from the Mediterranean Sea. FOSA, PFOA, and PFHxS were found less frequently in seals from the Baltic Sea. Concentrations of PFOS in livers of white-tailed sea eagles collected from eastern Germany and Poland from 1979 to 1999 did not exhibit clear temporal trends. In general, FOSA and PFOA are distributed sporadically in certain species and locations. PFHxS was not found in blood and liver of most of the samples analyzed.

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Supporting Information Available

Recoveries (%) of PFOS spiked at the 250 ng level onto liver and blood matrices (Table 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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