

Accumulation of Perfluorooctane Sulfonate in Marine Mammals

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Perfluorooctane sulfonate (PFOS) is a perfluorinated molecule that has recently been identified in the sera of nonindustrially exposed humans. In this study, 247 tissue samples from 15 species of marine mammals collected from Florida, California, and Alaskan coastal waters; the northern Baltic Sea; the Arctic (Spitsbergen); and Sable Island in Canada were analyzed for PFOS. PFOS was detected in liver and blood of marine mammals from most locations including those from Arctic waters. The greatest concentrations of PFOS found in liver and blood were 1520 ng/g wet wt in a bottlenose dolphin from Sarasota Bay, FL, and 475 ng/mL in a ringed seal from the northern Baltic Sea (Bothnian Sea), respectively. No age-dependent increase in PFOS concentrations in marine mammals was observed in the samples analyzed. The occurrence of PFOS in marine mammals from the Arctic waters suggests widespread global distribution of PFOS including remote locations.

Introduction

Perfluorooctane sulfonate (PFOS) and associated salts are fully fluorinated organic molecules produced synthetically in an electrochemical fluorination process (1). Some of the fluorinated organic compounds, similar in structure to PFOS, are utilized in fire-fighting foams, herbicide and insecticide formulations, greases and lubricants, adhesives, paints, and polishes (1). Given the energy of the carbon–fluorine bond, it is expected that many fluorinated organic compounds will be resistant to hydrolysis, photolysis, biodegradation, or metabolism (2).

PFOS was recently identified in each of 65 nonindustrially exposed human sera samples previously characterized, indicating possible widespread distribution of this compound (3). Additionally, this analyte and organic fluorochemicals of similar structure have been identified in some water samples (4, 5). Our recent study has documented global distribution of PFOS in animals of various trophic levels in the food chain (6). In this study, PFOS was measured in the tissues of marine mammals from coastal and open ocean waters, including the Arctic Ocean. While our earlier paper has documented the presence of PFOS in marine mammals, this study provides detailed information on the accumulation of PFOS in marine mammals.

Materials and Methods

Samples. A total of 247 tissue samples from 15 species of marine mammals and a freshwater mammal (river otter; *Lutra canadensis*) were analyzed in this study. The species analyzed include pygmy sperm whale (*Kogia breviceps*), short-snouted spinner dolphin (*Stenella clymene*), striped dolphin (*Stenella coeruleoalba*), rough-toothed dolphin (*Steno bredanensis*), bottlenose dolphin (*Tursiops truncatus*), California sea lion (*Zalophus californianus*), northern elephant seal (*Mirounga augustirostris*), harbor seal (*Phoca vitulina*), northern fur seal (*Callorhinus ursinus*), southern sea otter (*Enhydra lutris nereis*), polar bear (*Ursus maritimus*), Steller sea lion (*Eumetopias jubatus*), ringed seal (*Phoca hispida*), gray seal (*Halichoerus grypus*), and Weddell seal (*Leptonychotes weddellii*). Samples included liver and blood as well as a few samples of brain and kidney from sea otters. The marine mammals analyzed in this study originated from coastal waters of Florida including the Gulf of Mexico, California, Alaska, northern Baltic Sea (Bothnian Bay), the Arctic (Spitsbergen), Sable Island in Canada, and Terra Nova Bay in the Antarctic.

Tissues of marine mammals were acquired from Federal or State agencies or university laboratories. All samples were collected under permission of relevant State or Federal agencies. Liver tissues of stranded cetaceans from the East Coast of the United States were acquired from Mote Marine Laboratory, Sarasota, FL, and had been originally collected under letters of authorization issued by the National Marine Fisheries Service. Pinniped tissues from the California Coast were acquired from the Marine Mammal Center (MMC), Sausalito, CA. The pinnipeds, which stranded on the coast of northern and central California in the 1990s, were diagnosed and treated at MMC. Dead animals were dissected, and samples were wrapped in aluminum foil, placed in airtight plastic bags, and frozen immediately at -20°C until analysis. Concentrations of organochlorine pesticides, polychlorinated biphenyls (PCBs), and butyltins residues in tissues of pinnipeds from California coastal waters have been previously reported (7). River otter tissues were obtained from licensed trappers in Oregon. Sea otter tissues were from the National Wildlife Health Center, Madison, WI. Blood and liver of northern fur seals from the Pribilof Islands in Alaska were acquired from archived tissues of the Institute of Arctic Biology, Fairbanks, AK, and the Northwest Fisheries Science Center, Seattle, WA. Polar bear livers were from native subsistence hunters and the U.S. Fish and Wildlife Service in Anchorage, AK, and were taken in northern and western Alaska. Blood samples of ringed and gray seals were collected from the Bothnian Bay in the Baltic Sea, from Spitsbergen in the Arctic Ocean (ringed seals), and from Sable Island in Canada (gray seals) (8, 9). The Weddell seal was collected from Terra Nova Bay in Antarctica. Information regarding

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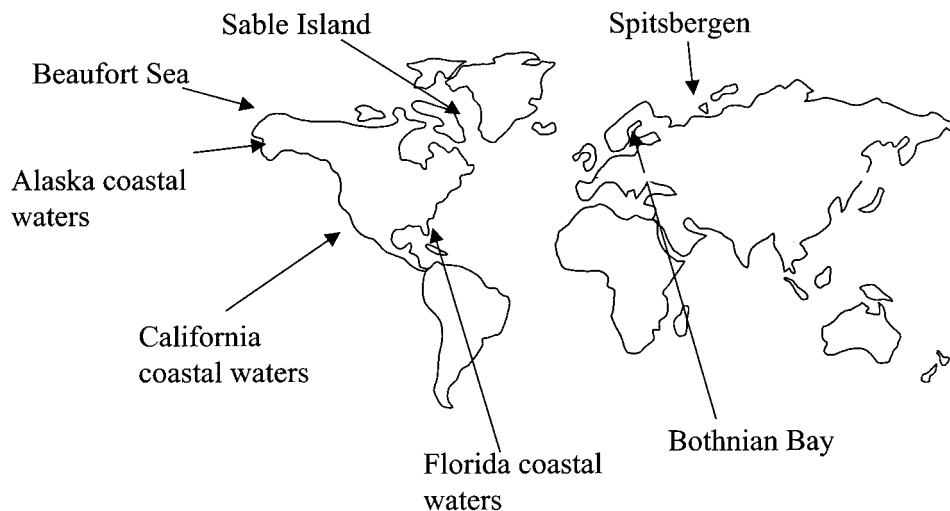


FIGURE 1. Map showing collection locations for marine mammal samples.

collection date, age, sex, and cause of death were recorded when available. The ringed and gray seals were aged by counting the annual layers of cementum from thin cross sections of a canine tooth (10). Tissues of most individual aquatic mammals were obtained from stranded dead animals. Sampling locations of various species are shown (Figure 1). Samples were obtained to represent various geographical locations including the Arctic and the Antarctic.

Analysis. Concentrations of PFOS in liver and blood plasma were measured using high-performance liquid chromatography (HPLC) with electrospray tandem mass spectrometry (5). The PFOS used as standards and as matrix spikes were purchased from Fluka (Milwaukee, WI). The internal standard, 1*H*,1*H*,2*H*,2*H*-perfluorooctane sulfonate (THPFOS), was purchased from ICN (Costa Mesa, CA). One milliliter of sera, 5 μ L of internal standard (100 ng), 1 mL of 0.5 M tetrabutylammonium hydrogen sulfate solution (adjusted to pH 10), and 2 mL of 0.25 M sodium carbonate buffer were added to a 15-mL polypropylene tube for extraction. After being thoroughly mixed, 5 mL of methyl *tert*-butyl ether (MTBE) was added to the solution, and the mixture was shaken for 20 min. The organic and aqueous layers were separated by centrifugation, and an exact volume of MTBE (4 mL) was removed from the solution. The aqueous mixture was rinsed with MTBE and separated twice; all rinses were combined in a second polypropylene tube. The solvent was allowed to evaporate under nitrogen before being reconstituted in 0.5–1 mL of methanol. The sample was vortex mixed for 30 s and passed through a 0.2- μ m nylon mesh filter into an autosampler vial. For the extraction of liver samples, a liver homogenate of 1 g of liver to 5 mL of Milli-Q water was prepared. One milliliter of the homogenate was added to a polypropylene tube, and the sample was extracted according to the procedure described above.

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 \times 2 mm (5 μ m) Keystone Betasil C₁₈ column with a 2 mM ammonium acetate/methanol mobile phase starting at 10% methanol. At a flow rate of 300 μ L/min, the gradient increased to 100% methanol at 11.5 min before reverting to original conditions at 13 min. Column temperature was maintained at 25 $^{\circ}$ C. Although PFOS eluted at about 7.5 min, the longer chromatographic run was necessary to completely elute all extractables from the column. 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 PFOS 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. In the electrospray tandem mass spectrometry (ESMSMS) system, the 499 \rightarrow 80 Da transition can provide a stronger signal than the 499 \rightarrow 99 Da transition of the PFOS analysis. However, in the analysis of tissue samples collected from some species of animals, an unidentified interferent was present in the 499 \rightarrow 80 Da transition. Although this interferent was rarely observed, to ensure complete selectivity, quantitation was based on the 499 \rightarrow 99 Da transition.

To verify the identity of the detected analyte, sample determined to contain PFOS at > 10 ng/mL (sera/plasma) to 70 ng/g (liver or other tissue), at least two transitions were monitored and showed quantitative agreement to within \pm 30%. Typically, 499 > 99 and 499 > 80 transitions were monitored. On the occasions that these two transitions differed by more than 30%, the sample was reanalyzed monitoring the 499 > 130 transition. This third transition showed quantitative agreement with the reported data from the 499 > 99 determination.

Because of the variety of matrixes analyzed (with respect to both species and tissues) and the evolving analytical methods, the limit of quantitation (LOQ) was variable. Data quality assurance and quality control protocols include matrix spike, surrogate spike, laboratory blank, and continuing calibration verification. Teflon or glass containers were avoided in this procedure; the former may cause analytical interferences, and the latter may bind the surfactants in an aqueous solution. Disposable polypropylene or plastic lab ware was used to minimize the possibility of sample contamination that can occur when glassware is reused. Any glassware used in the preparation of the reagents was thoroughly rinsed with methanol prior to use. Recoveries of PFOS spiked into rabbit plasma and liver and passed through the analytical procedure ranged from 85 to 101% (3). However, recoveries of PFOS spiked into liver or blood matrixes of marine mammal species analyzed in this study varied from 100 \pm 40%. The reported concentrations were not corrected for the matrix spike recoveries. Similarly, concentrations of PFOS were not corrected for the recoveries of the surrogate standard. For the estimation of the LOQ, the tissue (including plasma) samples were compared to an unextracted standard calibration curve. Concentrations in samples that were greater than the “lowest acceptable standard” were considered to

TABLE 1. Concentrations of PFOS in Livers (ng/g, wet wt) of Cetaceans Found Stranded along Florida Coastal Waters

species	sex	age	length (cm)	date	waterbody	PFOS	
pygmy sperm whale	M	na ^a	283	2/18/00	Atlantic Ocean	23.0	
	M	> 20	290	8/16/94	Anclote River	6.6	
						mean (n = 2)	14.8
short-snouted spinner dolphin	F	3	161	6/15/95	Gulf of Mexico	168	
	F	4	154	6/15/95	Gulf of Mexico	122	
	F	> 18	183	6/15/95	Gulf of Mexico	78.7	
						mean (n = 3)	123
						SD	36.3
striped dolphin	M	13–16	208	7/3/97	Gulf of Mexico	36.6	
	M	15	225	9/23/94	Venice Inlet	388	
						mean (n = 2)	212
rough-toothed dolphin	F	7	218	12/3/95	Tampa Bay	65.6	
	F	15	243	11/27/95	Anna Maria Sound	42.8	
						mean (n = 2)	54.2
bottlenose dolphin	F	25	245	7/16/97	Palma Sola Bay	734	
	F	22+	236	7/25/98	Palma Sola Bay	487	
	F		234	11/22/99	Sarasota Bay	716	
	F	20<	241	2/26/99	Anna Maria Sound	483	
	M	na	283	3/04/00	Gulf of Mexico	824	
	F	10	236	2/7/92	Gulf of Mexico	48.2	
	M	4	214	4/28/96	Sarasota Bay	1520	
	F	5	209	9/6/91	Gulf of Mexico	291	
	M	4	210	9/26/91	Anna Maria Sound	557	
	F	3.5	214	10/29/91	Gulf of Mexico	551	
	M	1.5	169	12/19/92	Gulf of Mexico	411	
	F	8	239	2/15/94	Peace River	402	
	F	16	258	4/12/92	Anna Maria Sound	97.1	
	M	11.5	199	8/16/94	Gulf of Mexico	60.9	
	F	44	250	8/9/96	Sarasota Bay	603	
	M	12	254	3/10/96	Gulf of Mexico	180	
	F	50+	251	1/5/94	Gulf of Mexico	75.3	
	M	18	274	12/24/95	Gulf of Mexico	141	
F	23+	239	8/27/95	Sarasota Bay	614		
M	8	229	3/24/95	Peace River	979		
						mean (n = 20)	489
						SD	356

^a NA, not available. Values below the detection limit were not included in calculating the mean.

be valid. A curve point was deemed acceptable if (i) it was back-calculated to be within 30% of the theoretical value when evaluated versus the 1/x weighted curve and (ii) the peak area of the standard was at least 2 times greater than the surrogate matrix blank (rabbit sera or rabbit liver). Concentration/dilution factors are included in the calculation of the LOQ. For instance, if the 5 ng/mL standard is the lowest acceptable standard, and the sample had been diluted by a factor of 7, the LOQ for that sample is reported as 35 ng/mL.

Results and Discussion

For the purpose of this discussion, the samples were grouped to represent five geographical regions: U.S. East Coast (Florida), U.S. West Coast (California, Oregon, and Washington), Alaska, temperate and polar regions (Baltic Sea, Spitsbergen, and Sable Island), and the Antarctic. Since perfluorinated compounds are used for applications to repel oils/lipids (oleophobic or amphiphatic) from surfaces, PFOS is not expected to concentrate in the blubber. Previous studies have shown that liver and blood are the tissues in which PFOS and related fluorochemicals concentrate (4, 11, 12). This feature is different from that observed for several neutral lipophilic compounds such as PCBs (13).

Florida Coastal Waters. PFOS was found in livers of all of the small cetaceans collected from the Florida Coast and the Gulf of Mexico (Table 1). Concentrations of PFOS in the livers of cetaceans ranged from 6.6 to 1520 ng/g, wet wt. The average concentration of PFOS in livers of bottlenose dolphins was 489 ± 356 ng/g, wet wt. Concentrations in cetaceans

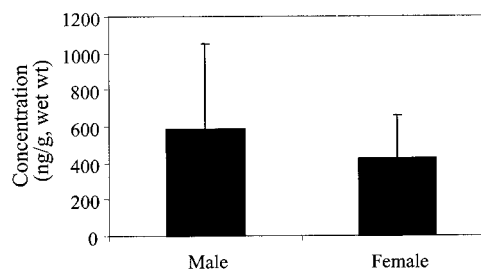


FIGURE 2. Concentrations (mean ± SD) of PFOS in livers of male and female bottlenose dolphins from Florida coastal waters.

were in the order of bottlenose dolphin > striped dolphin > spinner dolphin > rough-toothed dolphin > pygmy sperm whale. Greater concentrations of PFOS in bottlenose dolphin than in other cetaceans may be explained by this mammals' near-shore feeding habits. Pygmy sperm whales are oceanic, offshore feeders of small fish, squid, octopus, and other invertebrates. Therefore, exposure of pygmy sperm whales to fluorinated organic chemicals is expected to be minimal.

Concentrations of PFOS in livers of male bottlenose dolphins were greater than those in females, but the difference was not statistically significant ($p > 0.05$) (Figure 2). Hepatic concentrations of PFOS were not correlated with age in either the male or the female bottlenose dolphin (Figure 3). This is a different trend from that observed for persistent organochlorine compounds such as PCBs or DDTs, in which adult females generally contain lesser concentrations than those of males (7). These results suggest that the accumulation features of PFOS may be different from those observed for

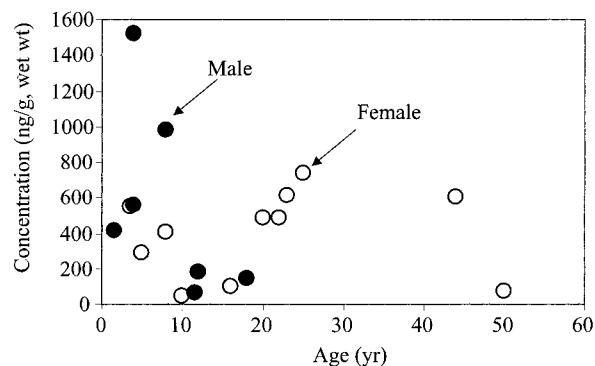


FIGURE 3. Relationship of PFOS concentrations with age in livers of bottlenose dolphin.

PCBs and other chlorinated pesticides, although more analyses are needed to confirm this hypothesis.

California Coastal Waters. Concentrations of PFOS in livers of pinnipeds (sea lions and seals) collected from the coastal waters of California were less than those found in cetaceans from coastal waters of Florida (Table 2). Among the four species of pinnipeds analyzed, the livers of northern fur seals contained the greatest PFOS concentration of 132 ng/g, wet wt. Mean concentrations of PFOS in livers of California sea lion and harbor seal were 27 ng/g, wet wt, approximately 20-fold less than those found for bottlenose dolphins from Florida. Relatively low concentrations of PFOS

in pinnipeds may suggest lesser exposure and/or a greater ability to metabolize and excrete fluorinated organic chemicals as compared to cetaceans. Pinnipeds undergo annual molting, and this feature has been shown to eliminate compounds that bind to the structural proteins of hair and other integuments. For example, butyltin compounds that bind to proteins are present in fur/hair and are eliminated during molting (7).

Livers collected from sea otters and elephant seals contained relatively low concentrations of PFOS (<15 ng/g, wet wt). Since sea otters do not possess blubber, to maintain the body temperature, they possess a greater basal metabolism than that of the pinnipeds. Greater metabolic capacity may explain the lower concentrations of PFOS in sea otters. Offshore feeding habits may be a reason for the lesser concentrations of PFOS in elephant seals.

River otters from inland and coastal waters of the Willamette River in Oregon and the Yaquina River in Washington contained 10–20-fold greater concentrations of PFOS than those found in pinnipeds from coastal waters of California. PFOS concentrations as great as 990 ng/g, wet wt, were found. The highest level was measured in the liver of a 4-year-old male river otter from the Willamette River in Oregon (Table 2). These results suggest greater exposures to aquatic mammals in inland waters than those in coastal or oceanic waters. The primary sources of fluorochemicals monitored in this study are postulated to be consumer products containing fluorinated surfactants, fire fighting foams, etc. Thus, greater concentrations would be expected

TABLE 2. Concentrations (ng/g, wet wt) of PFOS in Livers of Aquatic Mammals from the West Coast of the United States

species	location	date	sex	age class	cause of death	PFOS
California sea lion	Pismo Beach	11/20/97	F	adult	gunshot to head, early carcinoma	38.4
	San Simeon	10/24/97	F	adult	entangled in fishing net	49.4
	Oceano	7/26/96	F	adult	interstitial nephritis	4.6
	Cayucos	8/5/93	F	adult	renal disease	20.5
	San Francisco	10/22/95	M	adult	septicemia, interstitial nephritis	22.7
	Morro Bay	7/26/94	M	adult	hydronephrosis, paralysis	23.7
				mean (n = 6)	26.6	
elephant seal	Miramar Beach	4/14/97	F	1 yr	skin disease, septicemia	<5
	Lundborg Beach	5/13/97	M	weaner	pneumonia, otostrenglyus arteritis	<5
	Crecent City	3/13/92	M	yearling	skin disease, verminous pneumonia, pyothorax	8.7
	Pebble Beach	7/03/91	F	yearling	septicemia, skin disease	<5
	Pebble Beach	9/01/91	M	yearling	skin disease, hemorrhagic gastrointestinal tract	9.8
				mean (n = 5)	9.3	
harbor seal	coastal California	1991	F	pup		10.3
	Abbott's Lagoon	6/26/97	M	pup/calf	pneumonia	13.9
	Tiburon	10/02/97	F	adult	meningocephalitis, hepatitis	57.1
				mean (n = 3)	27.1	
northern fur seal	na	10/29/97	na ^a	na		133
	Willamette River	1996–97	M	adult	trapped	279
	Willamette River	1996–97	M	adult	trapped	994
	Fort Ward, WA	1996–97	M	adult	trapped	189
	Yaquina River	1996–97	M	adult	trapped	33.6
	Silverdale, WA	1996–97	M	adult	trapped	151
				mean (n = 5)	329	
sea otter liver	Monterey	2/16/94	M	adult	trauma	9.8
	San Luis Obispo	4/29/93	F	pup/calf	disease; acanthocephalan	9.6
	San Luis Obispo	8/1/94	F	subadult	disease; bacterial	5.7
	San Luis Obispo	2/4/93	M	adult	disease; coccidioidomycosis	<5
	San Luis Obispo	5/20/94	F	pup	disease; acanthocephalan	14.3
	Santa Barbara county	10/3/94	M	adult	trauma	<5
	San Luis Obispo	3/25/94	M	juvenile	disease; acanthocephalan	5.4
	San Luis Obispo	4/8/94	M	adult	miscellaneous	<5
				mean (n = 8)	8.9	
sea otter brain	Monterey	2/16/94	M	adult	trauma	<35
	San Luis Obispo	4/29/93	F	pup/calf	disease; acanthocephalan	<35
sea otter kidney	Monterey	2/16/94	M	adult	trauma	<35
	San Luis Obispo	4/29/93	F	pup/calf	disease; acanthocephalan	<35
	San Luis Obispo	8/1/94	F	subadult	disease; bacterial	<35

^a NA, not available.

TABLE 3. Concentrations of PFOS in Livers of Northern Fur Seals and Polar Bear from Alaska (ng/g, wet wt)

species	location	n	date	sex	age class	PFOS
northern fur seal	Pribilof Island	13	1995 or 1998	2 F; 11 M	3 pups (<4 m); 10 subadults (2–4 yr)	<10–122 [38] ^a
polar bear	Barrow; Nuiqsut; Point Lay; Gambell; Shishmaref; Little Diomedede; Savoonga	17	12/13/97–6/15/99	14 M; 3 F	13 adults (>5 yr); 4 subadults (3–4 yr)	175–678 (350)

^a Values in brackets [] indicate the percentage of detectable observations. Values in parentheses () indicate the mean.

TABLE 4. Concentrations (ng/mL) of PFOS in the Blood of Marine Mammals from Coastal Waters of Alaska

species	location	date	n	sex	age class	PFOS
northern fur seal pup	Pribilof Island	1995	19	10 F; 9 M	pup (<4 m)	<6–12 [5]
northern fur seal adult	Pribilof Island	1995	10	10 F	adult (>3 yr)	<6
northern fur seal subadult	Pribilof Island	1995	7	7 M	subadult (2–4 yr)	<6
northern fur seal	Pribilof Island	1995	8	6 M; 2 F	5 pups (<4 m); 3 subadults (2–4 yr)	<6
polar bear	Beaufort Sea	1999	14	7 M; 7 F	na ^a	26–52 (34)
Steller sea lion	southeast Alaska	1999	12	7 F; 5 M	3–4 months	<6

^a na, not available. Values in brackets [] indicate the percentage of detectable observations.

TABLE 5. Concentrations (ng/mL; Mean ± SD) of PFOS in Blood of Seals from the Northern Baltic Sea (Bothnian Bay), the Arctic (Spitsbergen), and Sable Island (Canada)

species	location	year	n	sex	age (yr)	PFOS
ringed seal	Baltic Sea	1996	10	1 M; 9 F	6–20	133 ± 47
	Baltic Sea	1997	9	3 M; 6 F	6–16	92 ± 81
	Baltic Sea	1998	10	5 M; 5 F	1.0–25	242 ± 142
	Spitsbergen	1996	10	4 M; 6 F	3.0–20	8.1 ± 2.5
gray seal	Spitsbergen	1998	8	3 M; 5 F	2.0–12	10.1 ± 2.7
	Baltic Sea	1996	9	5 M; 4 F	2.0–20	42 ± 21
	Baltic Sea	1997	10	4 M; 6 F	5.0–33	43.9 ± 19
	Baltic Sea	1998	7	3 M; 4 F	8.0–25	25.5 ± 9.6
	Sable Island	1998	12	7 M; 5 F	10.0–35	27.7 ± 11

in inland water bodies closer to direct discharges than at marine locations.

Alaska Waters. Livers of northern fur seals and polar bears and blood of northern fur seals, polar bears, and Steller sea lions from Pribilof Islands, Beaufort Sea, and southeastern coastal waters of Alaska were analyzed for the presence of PFOS (Tables 3 and 4). Livers of northern fur seal were from pups of less than 4 months or subadults of 2–4 yr. PFOS was detected in livers of 5 of 13 individuals (38%).

Livers from polar bears collected from Alaska contained PFOS at concentrations ranging from 175 to 678 ng/g, wet wt (mean: 350 ng/g) in livers. Concentrations of PFOS found in polar bear livers were similar to those found in river otters from Washington and Oregon states. Although the number of females analyzed in this study was less than males, there was no significant difference ($p > 0.05$) in concentrations of PFOS between males and females. Mean concentrations of PFOS in adult polar bears (>5 yr) were greater (383 ng/g, wet wt) than those in subadult (3–4 yr) animals (246 ng/g, wet wt), although the difference was not statistically significant ($p = 0.07$). The presence of PFOS in livers of polar bears and northern fur seals from locations such as the coastal waters of Alaska suggests the transport and distribution of PFOS to more remote marine locations.

PFOS was not found in the blood samples of northern fur seals collected from Pribilof Islands in 1995 at levels above the limits of quantitation (6 ng/mL) (Table 4). Similarly, blood of Steller sea lions collected from the southeast coast of Alaska did not contain quantifiable concentrations of PFOS. However, all of the blood samples collected from polar bears in the Beaufort Sea ($n = 14$) in 1999 contained PFOS concentrations ranging from 27 to 52 ng/mL (mean: 34 ng/mL). The ages of these polar bears were not available; there were

no significant differences in the concentrations of PFOS between males (32 ng/mL) and females (34 ng/mL). Although polar bear blood and liver samples were not collected from the same animals, the concentrations of PFOS in the blood samples analyzed were, on average, 10 times less than those found in the liver.

Temperate and Arctic Waters. All of the blood samples of ringed seals ($n = 46$) collected from Spitsbergen in the Arctic and from the northern Baltic Sea contained detectable concentrations of PFOS (Table 5). Concentrations of PFOS in the blood of ringed seals from the Bothnian Bay were 15-fold greater than those from the Arctic ($p < 0.01$) (Figure 4). Blood from a 4-year-old male ringed seal collected in 1998 from the Baltic Sea was determined to contain the greatest PFOS concentration of 475 ng/mL. The mean concentration of PFOS in the blood of male ringed seals was 2-fold greater (204 ng/mL) than those of females (123 ng/mL). Similarly, there was no age-dependent increase in the concentrations of PFOS in the blood of ringed seals. Concentrations of PFOS in ringed seal collected from the Bothnian Bay in 1998 were significantly greater than those collected in 1996 and 1997 ($p < 0.05$). Concentrations of PFOS in the blood of ringed seals collected from Spitsbergen in 1998 were greater than those collected in 1996.

Similar to ringed seals, gray seal blood collected from animals in the northern Baltic Sea and Sable Island in Canada was determined to contain PFOS (Table 5). There was no significant difference between the concentration of PFOS in the blood of gray seals collected from the Bothnian Bay and those from Sable Island collected in 1998 ($p > 0.05$) (Figure 5). Concentrations of PFOS in gray seal blood were significantly less than those found in ringed seals from the Baltic Sea ($p < 0.01$). Concentrations of PFOS in the blood of male

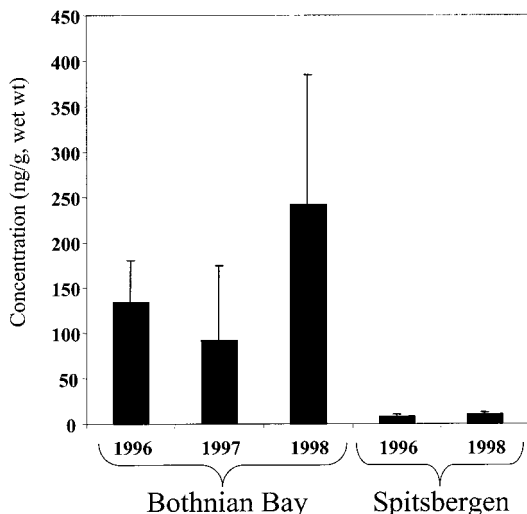


FIGURE 4. Concentrations (mean \pm SD) of PFOS in blood of ringed seals from the northern Baltic Sea (Bothnian Bay) and Spitsbergen (Arctic).

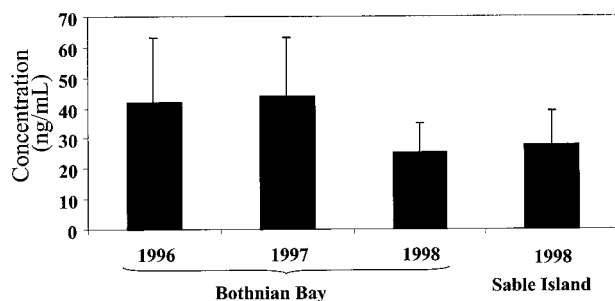


FIGURE 5. Concentrations (mean \pm SD) of PFOS in blood of gray seals from the northern Baltic Sea (Bothnian Bay) and Sable Island (Canada).

gray seals from the Baltic (mean: 51 ng/mL) were significantly greater than those found in the blood of females (mean: 28 ng/mL) ($p < 0.01$). This observation of gender-related concentration was different than that hypothesized for ringed seals from the Baltic Sea. However, as with ringed seals there was no age-specific increase in the concentrations of PFOS in the blood of gray seals. A comparison of the PFOS concentrations with previously reported concentrations of PCBs and DDT in ringed and gray seals revealed similar geographical and species differences (8, 9).

Antarctica. Only one sample of Weddell seal liver was available for the analysis of fluorinated organic chemicals. PFOS was not measured above the limit of quantitation of 35 ng/g.

In summary, these results suggest occurrence of PFOS in marine mammals from a wide range of geographical regions. Accumulation features of PFOS were different from those observed for other, well-studied compounds such as PCBs and DDT. PFOS concentrations did not appear to increase with age of marine mammals. Toxic effects of PFOS are unknown. Structurally similar perfluorinated compounds have been shown to affect cell-cell communication, membrane transport and process of energy generation, and peroxisome proliferation (14, 15). Further studies are needed to evaluate the potential of PFOS to exert toxic effects in wildlife.

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Literature Cited

- (1) Rogers, R. S. *Chem. Eng. News* **1999**, 77 (April 12), 30.
- (2) Banks, R. E.; Smart, B. E.; Tatlow, J. C. *Organofluorine Chemistry Principles and Commercial Applications*; Plenum Press: New York, 1994.
- (3) Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Johnson, H. O. *Environ. Sci. Technol.* **2001**, 35, 766–770.
- (4) U.S. Environmental Protection Agency, Office of Pollution and Prevention and Toxic Substances, Docket AR-226.
- (5) Moody, C. A.; Field, J. A. *Environ. Sci. Technol.* **2000**, 34, 3864–3870.
- (6) Giesy, J. P.; Kannan, K. *Environ. Sci. Technol.* **2001**, in press.
- (7) Kajiwara, N.; Kannan, K.; Muraoka, M.; Watanabe, M.; Takahashi, S.; Olsen, H.; Blankenship, A. L.; Jones, P. D.; Tanabe, S.; Giesy, J. P. *Arch. Environ. Contam. Toxicol.* **2001**, in press.
- (8) Mattson, M.; Raunio, H.; Pelkonen, O.; Helle, E. *Aquat. Toxicol.* **1998**, 43, 41–50.
- (9) Nyman, M.; Raunio, H.; Pelkonen, O. *Environ. Toxicol. Pharmacol.* **2000**, 8, 217–225.
- (10) Laws, R. M. *Nature* **1952**, 169, 972.
- (11) Ylinen, M.; Auriola, S. *Pharmacol. Toxicol.* **1990**, 66, 45–48.
- (12) Olsen, G. W.; Burris, J. M.; Mandel, J. H.; Zobel, L. R. *J. Occup. Environ. Health* **1999**, 41, 799–806.
- (13) Tanabe, S.; Iwata, H.; Tatsukawa, R. *Sci. Total Environ.* **1994**, 154, 163–177.
- (14) Upham, B. L.; Deocampo, N. D.; Wurl, B.; Trosko, J. E. *Int. J. Cancer* **1998**, 78, 491–495.
- (15) Sohlenius, A.-K.; Eriksson, A. M.; Högström, C.; Kimland, M.; DePierre, J. W. *Pharmacol. Toxicol.* **1993**, 72, 90–93.

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