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Time Trends and Transplacental Transfer of Perfluorinated Compounds in Melon-Headed Whales Stranded Along the Japanese Coast in 1982, 2001/2002, and 2006

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As a result of the phase-out of production of perfluorooctanesulfonyl-based compounds by a major producer, concentrations of perfluorooctanesulfonate (PFOS) in marine mammals from North American and European coastal waters have been declining since the early 2000s. Nevertheless, temporal trends in perfluorochemical (PFC) concentrations in marine mammals from Asian coastal waters have not been examined. In this study, PFCs were determined in livers of melon-headed whales (*Peponocephala electra*) collected along the coast of Japan, from three mass strandings that occurred during the past 25 years. Concentrations of nine PFCs were determined in livers of 48 melon-headed whales that were collected during strandings in 1982, 2001/2002, and 2006. In addition, concentrations in liver tissues obtained from two pregnant females and their fetuses were compared for determination of transplacental transfer rates of PFCs during gestation. PFOS and perfluorooctanesulfonamide (PFOSA) were the predominant PFCs found in livers of melon-headed whales collected in 1982 ($n = 22$). PFOS, PFOSA, perfluoroundecanoate (PFUnDA), perfluorododecanoate (PFDoDA), perfluorodecanoate (PFDA), and perfluorononanoate (PFNA) were found in whales collected in 2001/2002 ($n = 21$) and in 2006 ($n = 5$). Concentrations of PFOS and PFOSA were approximately 10-fold higher in 2001/2002 than in 1982. Whereas concentrations of PFOSA then declined by 2-fold from 2001/2002 to 2006, concentrations of PFOS and perfluorocarboxylates did not decline after 2001/2002. Conversely, concentrations of PFNA and PFDA increased significantly from 2001/2002 to 2006. The proportion of perfluoroalkylsulfonates in total PFC concentrations decreased from 75% in 1982 to 51% in 2006. Conversely, the contribution of perfluorocarboxylates to total PFC concentrations increased from 25% in 1982 to 49% in 2006. PFUnDA was the major perfluorocarboxylate found in whale livers collected after 2000. Analysis of paired samples of mother-fetus demonstrated that the transplacental transfer rates of PFCs were higher than those for PCBs and PBDEs.

Introduction

Perfluorochemicals (PFCs) have been manufactured for over half a century, for numerous consumer and industrial applications that entail their use as surfactants and surface protectors. In 2001, perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) were reported to be globally distributed in humans and wildlife (*1, 2*). As a result, the major producer, the 3M Company, announced the phase-out of the production of perfluorooctanesulfonylfluoride (POSF)-based compounds such as PFOS in 2000. However, a variety of related PFCs are still being produced by several manufacturers worldwide (*3*). Several current manufacturers of PFCs have voluntarily announced their intentions to reduce future emissions from manufacturing processes (*3*).

Temporal-trend studies are useful for evaluating the effectiveness of reduction in global production/emissions and for evaluating environmental clearance rates of persistent organic pollutants (*4*). Temporal-trend studies of PFCs, both near point sources and in remote locations in North America, have indicated a decline in PFOS concentrations, in biota and humans sampled after 2001. Concentrations of PFOS in sea otters from the California coast declined after 2001 (*5*). From 1993 to 2003/2004, concentrations of PFOS in Northern fulmar from the Canadian Arctic declined, while the concentrations in thick-billed murre increased (*6*). Ringed seals from the Canadian Arctic showed a decline in PFOS concentrations from 2000 to 2005 (*7*).

Despite the reports of recent declines in PFOS concentrations in the North American locations, only a few studies have reported temporal trends of PFCs in other global locations. PFOS concentrations in herring gull eggs from isolated colonies in northern Norway increased by 2-fold from 1983 to 1993, and then remained stable until 2003 (*8*). PFOS concentrations in guillemot eggs from the Baltic Sea increased by 25-fold from 1968 to 2003 (*9*). PFOS concentrations in seals from Lake Baikal, Russia, were higher in 2005 than they were in1992 (*10*). To our knowledge, there are no studies reporting comparable temporal trends of PFCs in Asia.

Melon-headed whales are found in tropical and warm-temperate waters throughout the world. Melon-headed whales have a life span of approximately 20−30 years and are thought to spend most of their time in the deep water, because their primary prey, mesopelagic squid and fish, are found in waters up to 1500 m deep (*11*). Since the 1980s, there have been at least three mass strandings of melon-headed whales along the Pacific coast of Japan; the causes of these strandings are unknown. Livers of melon-headed whales collected during the mass strandings in 1982, 2001/2002, and 2006 were analyzed in this study. The sampling periods covered before, during, and after the announcement of phase-out of production of POSF-based compounds by

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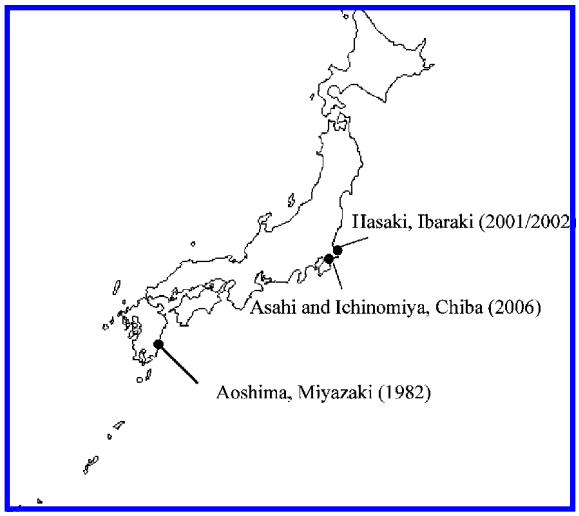

FIGURE 1. Map showing the sites of mass strandings of melon-headed whales along the coast of Japan.

the 3M Company in 2000. Tissues from two paired samples of mother and fetus were used to evaluate transplacental transfer of PFCs in whales. The objectives of this study were to gain an understanding of temporal trends in concentrations and profiles and transplacental transfer rates of PFCs in melon-headed whales mass stranded along the Japanese coast during the past 25 years.

Materials and Methods

Samples. Archived liver tissues of melon-headed whales (*Peponocephala electra*), stored at −20 °C in Environmental Specimen Bank (ES-Bank) at the Center for Marine Environmental Studies, Ehime University, Matsuyama, Japan, were used for the analysis. Selected samples from mass strandings occurred in January 1982 ($n = 22$; 11F, 11M), at Aoshima, Miyazaki Prefecture; in February 2001 ($n = 6$; 1F, 2M, 3 unknown) and February 2002 ($n = 15$; 8F, 5M, 2 unknown) at Hasaki, Ibaraki Prefecture; and in January−February 2006 ($n = 5$; 5M) at Asahi and Ichinomiya, Chiba Prefecture (Figure 1) were analyzed in this study.

Chemical Analysis. Concentrations of nine PFCs including perfluorohexanesulfonate (PFHxS), PFOS, perfluorodecanesulfonate (PFDS), perfluorooctanesulfonamide (PFOSA), PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), and perfluorododecanoate (PFDoDA) in livers of melon-headed whales were determined according to the procedure described previously (*12, 13*). A small quantity of the liver (0.7−0.9 g) was homogenized with 5 mL of Milli-Q water, and then 1 mL of the homogenate was transferred into a polypropylene tube (PP tube) with 500 pg each of internal standard mixture ($^{13}C_4$−PFOS, $^{13}C_4$−PFOA, $^{13}C_2$−PFDA, and $^{13}C_2$−PFNA), 2 mL of 0.25 M sodium carbonate buffer, 1 mL of 0.5 M tetrabutylammonium hydrogensulfate solution (adjusted to pH 10). The sample was mixed thoroughly. Extraction was carried out by addition of 5 mL of methyl-tert-butyl ether (MTBE) with vigorous shaking for 40 min. The sample was then centrifuged at 4000 rpm for 5 min to separate the organic layer from the aqueous layer. The aqueous layer was transferred into another PP tube, and the extraction was repeated with 3 mL of MTBE. After extraction, the two organic fractions were combined and evaporated to near-dryness under a stream of nitrogen. The sample was reconstituted with 1 mL of methanol, vortexed for 30 s, centrifuged at 4000 rpm for 2 min, and transferred into a 2 mL autosampler vial.

The target analytes were detected and quantified on an Agilent 1100 Series high performance liquid chromatography (HPLC), coupled with an Applied Biosystems API 2000 electrospray triple-quadrupole mass spectrometer (ESI-MS/MS). Ten microliters of the extract were injected into a Betasil C18 (100 × 2.1 mm) column with a (20 × 2.1 mm) guard column, both with a 5 μm particle size (Thermo Electron Corporation, Waltham, MA). The mobile phase consisted of a gradient elution of 2 mM ammonium acetate and methanol. The gradient started at 10% methanol and increased to 100% after 10 min; it was held at 100% for 2 min, and reverted to 10% methanol. The MS/MS was operated in a multiple reaction monitoring (MRM) mode; the mass transitions monitored were: 398.7 > 79.7 for PFHxS, 499 > 99 for PFOS, 503 > 99 for $^{13}C_4$−PFOS, 599 > 99 for PFDS, 497.7 > 77.7 for PFOSA, 413 > 369 for PFOA, 417 > 372 for $^{13}C_4$−PFOA, 463 > 419 for PFNA, 465 > 420 for $^{13}C_2$−PFNA, 513 > 469 for PFDA, 515 > 470 for $^{13}C_2$−PFDA, 563 > 519 for PFUnDA, and 613 > 569 for PFDoDA. The sum of the concentrations of the nine PFCs measured in this study is denoted as total PFCs (ΣPFC).

Quality Assurance/Quality Control. Known concentrations (10 ng each) of target compounds were spiked into an aliquot of the sample matrix (matrix spikes) and analyzed through the procedure, as a check for matrix effects through calculation of recoveries. Matrix spike recoveries for all target analytes ranged from 78 to 121% (mean ± SD: 89 ± 23%). Matrix spike recoveries for PFOSA were 51 ± 15%. The low recovery rate for PFOSA was likely due to the compound's neutral functional group, which is different from the anionic characteristic of the other target analytes. The matrix recoveries of PFOSA were consistent, however, and therefore the results were corrected for the mean recovery. Also, ^{13}C-labeled internal standards ($^{13}C_4$−PFOS, $^{13}C_4$−PFOA, $^{13}C_2$−PFDA, and $^{13}C_2$−PFNA) were spiked into all of the samples, for the calculation of recoveries. Mean internal standard recoveries in samples ranged from 82 to 86% (mean ± SD: 84 ± 8%). External calibration standards were prepared in methanol at concentrations ranging from 0.1 to 50 ng/mL. Calibration standards were injected every day before and after analyzing a batch of samples. A midpoint calibration standard was injected after every 10 samples, throughout the instrumental analysis, as a check for instrument response and drift. Procedural blanks were analyzed by passing water and reagents through the entire analytical procedure to monitor for contamination in reagents and glassware. The quantitation of PFCs was performed with a quadratic regression fit analysis weighted by 1/x of the external calibration curve. The limit of quantitation (LOQ) was considered to be the lowest acceptable standard within ± 30% of the theoretical value and has a peak area twice as large as that of the blanks. Dilution or concentration factors and the mass of samples taken for analysis were included in the calculation of LOQ. The LOQ for PFHxS, PFOS, and PFOSA, was less than 1 ng/g, wet wt, whereas the LOQs for PFDS, PFOA, PFNA, PFDA, PFUnDA, and PFDoDA were 5.5, 3.8, 5.3, 1.7, 4.6, and 4.2 ng/g, wet wt, respectively. Statistical analyses were performed using Statgraphics plus 5.1 (Manugistics, Inc., Rockville, MD) (Supporting Information). If a compound was consistently not detected above the detection limit within a year, then the compound was considered not detected. Otherwise, concentrations that were below the LOQ were assigned a value of half-the LOQ, for statistical analyses.

Results and Discussion

PFC Concentrations. Concentrations of PFCs in livers of melon-headed whales stranded along the Pacific coast of Japan in 1982, 2001/2002, and 2006 are shown in Table 1. PFOS and PFOSA were the predominant compounds found in melon-headed whales collected in 1982; other PFCs were rarely detected for that time point. The reasons for the lack of detection of PFCs other than perfluoroalkylsulfonates in

TABLE 1. PFC Concentrations (Mean and Range; ng/g, Wet Wt) in Livers of Melon-headed Whales Stranded Along the Japanese Coast in 1982, 2001/2002, and 2006[a]

collection year	sample location	age class (sex)	*n*	bodylength (cm)	PFOS	PFOSA	PFNA	PFDA	PFUnDA	PFDoDA	ΣPFCs[d]
1982	Miyazaki	mature (9F,3M)	12	243 (231–264)[b]	7.1 (5.2–8.9)	8.8 (6.0–12.3)	<1.1	ND[c]	<LOQ [1.8–5.1]	ND	20.3
		immature (1F,3M)	4	222 (214–236)	8.6 (6.8–10.3)	8.2 (6.9–10.2)	<1.1	ND [1.8–3.0]	<LOQ	ND	16.8
		fetus (3M)	3	91.0 (80–101)	8.6 (6.5–9.8)	4.1 (2.9–5.2)	<1.1	ND	<LOQ [3.1–4.5]	ND	12.7
		unknown (1F,2M)	3	253 (248–258)	6.2 (4.6–8.1)	6.4 (5.9–6.7)	<1.1	ND	<LOQ [1.3–2.3]	ND	12.6
2001/2002	Ibaraki	unknown (9F,7M,5UK)	21	227 (46–270)	51.1 (17.8–117)	65.8 (25.3–111)	7.8 (5.2–15.5)	9.3 (3.6–20.3)	32.5 (4.6–101)	14.7 (5.0–22.8)	184
2006	Chiba	mature (2M)	2	253 (249–256)	56.6 (52.6–60.6)	36.1 (35.9–36.3)	12.5 (12.5–12.6)	15.9 (15.6–16.2)	75.7 (74.9–76.6)	18.1 (17.5–18.8)	215
		unknown (3M)	3	246 (234–263)	51.6 (49.2–54.3)	24.5 (11.6–31.6)	14.1 (9.5–20.9)	16.3 (13.5–20.5)	<4.6 [1.4–1.8]	17.9 (15.2–20.6)	130

[a] Values in brackets [] are range of concentrations with >90% below LOQ, but above the detection limit. [b] Values in parenthesis () are range; For values below LOQ, a value of half-the LOQ was used for calculating a mean. [c] Not detected. [d] ΣPFC indicates the sum of nine PFCs. M = male, F = female, UK = unknown.

1982 are not known. It is possible that use patterns and volumes were such that the predominant compounds were derived from POSF/PFOS. In 2001/2002, PFOS, PFOSA, and PFUnDA were the predominant compounds, found at mean concentrations of 51.1, 65.8, and 32.5 ng/g, wet wt, respectively. PFNA, PFDA, and PFDoDA were also found in the livers of whales collected in 2001/2002, but at relatively lower concentrations (between 7.8 and 14.7 ng/g, wet wt). Mean concentrations of PFOS and PFUnDA were similar between 2001/2002 and 2006, whereas mean concentrations of PFNA and PFDA increased by approximately 2-fold during this 5-year period. PFOSA concentrations, in contrast, decreased by more than half-between 2001/2002 and 2006 (from 65.8 to 29.2 ng/g, wet wt).

PFOS concentrations in livers of melon-headed whales stranded in 2001/2002 off the coast of Japan were higher than the concentrations reported from livers of sperm whales stranded off the Florida coast, and along the Belgian coast (23 and 36 ng/g, wet wt, respectively *12, 14*). PFOSA concentrations were similar or greater than the concentrations of PFOS in whales collected prior to 2006. High concentrations of PFOSA were also reported in whales from the Mediterranean Sea (*15*). High concentrations of PFOSA in whales indicate lack of efficient biotransformation of PFOSA to PFOS, as has been reported in fish (*15*). In this study, high concentrations of PFUnDA were found in melon-headed whales collected after 2000. PFOS and PFUnDA were also the major contributors to total PFC concentrations in ringed seals from Greenland (*17*). PFHxS, PFDS, and PFOA were detected in our melon-headed whales less frequently than were the other six PFCs and at trace levels (<5 ng/g, wet wt). The low concentrations of PFOA in our samples are indicative of low bioaccumulation potential of this compound (*18*). Overall, the patterns of PFC contamination that we found in melon-headed whales suggest distinctive sources arising from the midlatitudes of the Eastern Asian countries.

Gender/Growth-Stage Related Differences in PFC Concentrations. Information on age was not available for all of the whales that we analyzed, although information on body length and growth stage was available for 19 of 21 individuals (12 mature (9F, 3M), four immature (1F, 3M), and 3 fetuses (3M)) collected in 1982 at Aoshima. Therefore, data from these individuals were used to determine the relationship between PFOS concentrations and body length (Figure 2). No significant difference in mean PFOS concentration was found, either between mature and immature whales, or between mature whales and fetuses ($p \geq 0.05$). Lack of age-related increase in PFOS concentrations in marine mammals has been reported earlier (*12, 19*). On the other hand, a significantly higher PFOS concentration was found in juvenile harbor porpoises than in adults of that species (*14*). For our melon-headed whales, concentrations of PFOS in livers of two of the fetuses were greater than that found in the livers of their mothers, suggesting considerable transplacental transfer of PFOS. Further details of rates of transplacental transfer of PFCs are discussed below.

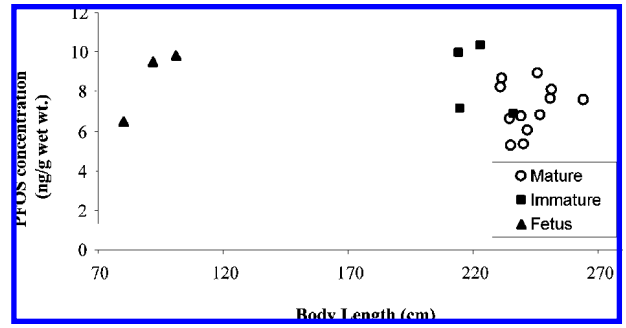

FIGURE 2. Relationship between body length, growth stage, and PFOS concentration (ng/g, wet wt.) in livers of melon-headed whales from Miyazaki, Japan, in 1982.

Relationship between gender and PFOS concentrations was examined in whales collected at Miyazaki in 1982 (n = 22; 11F, 11M). No significant difference was found in mean PFOS concentrations between males and females ($p \geq 0.05$). Lack of age- and gender-related differences in the concentrations of PFOS in whales suggest rapid turnover rates of this compound in marine mammals.

Transplacental Transfer. Concentrations of PFOS in the liver of fetus and the mother for the two pairs analyzed suggest gestational transfer to the fetus. An earlier study on harbor porpoises showed 2-fold higher PFOS concentration in fetuses than in the mothers (*14*). Transplacental transfer rates of PFCs were estimated based on the hepatic burdens in the two paired samples of mothers and fetuses. The body lengths of the fetuses were 80 and 92 cm, suggesting that these were in the advanced stages of development (*20*). Body weight (kg) of the whales in our study was estimated from the total body length, L (cm), according to the relationship developed for melon-headed whales by Miyazaki et al. (*21*):

$$\text{body weight} = 0.0000192L^{2.91}$$

TABLE 2. Transplacental Transfer Rates (%) of PFCs in Melon-Headed Whale Determined as a Ratio of Burden in Livers of Mothers to Burden in Livers of Fetuses Collected in 1982 in Japan

	liver wt (g)	conc. in liver (ng/g)	hepatic burden (ng)[a]	transfer rate (%)[b]
PFOS				
fetus A	167	6.48	1080	5.1
mother A	3810	5.33	20300	
fetus B	204	9.51	1940	7.2
mother B	3810	6.60	25100	
PFNA				
fetus A	167	1.42	236	9.5
mother A	3810	0.59	2260	
fetus B	204	1.38	280	7.2
mother B	3810	0.95	3630	
PFUnDA				
fetus A	167	3.45	575	6.4
mother A	3810	2.21	8400	
fetus B	204	3.09	630	7.3
mother B	3810	2.11	8040	

[a] Hepatic burden = Liver weight × individual PFC concentration in the liver. [b] Transfer rate (%) = (burden in fetus/burden in (mother + fetus)) × 100.

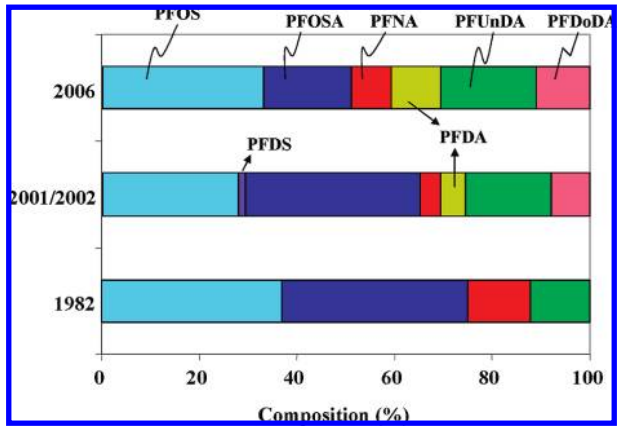

FIGURE 3. Composition profiles of various PFCs in melon-headed whales mass-stranded along the Japanese coast at three time points: 1982, 2001/2002, and 2006. If a compound was always below the detection limit within a time point, then the compound was considered not detected. If a compound was detected within a time point, but less than the LOQ, its concentration value was set to half-the LOQ.

The average liver weight in female melon-headed whales was 2.20−2.29% of the total body weight (*21*). Because PFOS accumulates predominantly in livers, PFC burden was calculated for liver tissues in both mothers and fetuses, for the calculation of transplacental transfer rates. The hepatic burdens (ng) of PFCs in the mother and the fetus were calculated based on the concentration in the liver (ng/g), multiplied by the whole liver weight (g). For our two pairs of samples, the transplacental transfer rates of PFOS, PFNA, and PFUnDA were 5.1 and 7.2%, 9.5 and 7.2%, and 6.4 and 7.3%, respectively (Table 2). The transplacental transfer rates of the three PFCs were approximately 2 times higher than the transfer rates reported for lipophilic contaminants such as PCBs and PBDEs in melon-headed whales (3.5 to 3.6% and 2.6 to 3.5%, respectively) (*20*). Higher transplacental transfer of PFCs than of PBDEs and PCBs from mother to fetus suggests that the pups of this species are subjected to elevated PFC exposures in utero and at early life stages.

PFC Profiles and Correlations. The percent composition of PFOS + PFOSA to ΣPFC concentrations decreased from 75% in 1982 to 51% in 2006 (Figure 3). From 1982 to 2006, the contribution of PFOSA to ΣPFC concentrations decreased by over half. In 1982, PFNA and PFUnDA were the only perfluorocarboxylates found in the whale livers at concentrations of <5 ng/g, wet wt. The contribution of perfluorocarboxylates to ΣPFC concentrations increased from 25% in 1982 to 49% in 2006. PFUnDA contributed 17.6 and 19.5% to ΣPFC concentrations in 2001/2002 and 2006, respectively. The PFC profiles in whale livers suggest that since the initial time point, 1982, concentrations of perfluoroalkylsulfonates increased until 2001/2002, when concentrations began to decrease. The concentrations of perfluorocarboxylates, particularly PFUnDA, have increased greatly since 1982. Concentrations of PFNA, PFDA, and PFDoDA in whale livers increased significantly after the initial 1982 time point; these results are similar to the trends reported for herring gull eggs from Norway, and in livers of polar bears and seals from the Canadian Arctic (*8, 22*).

The PFC profiles in our melon-headed whale livers were different from the profiles reported for the livers of seals from the Lake Baikal and the Dutch Wadden Sea (*10, 23*). A decrease in PFOSA concentrations was also found in Baikal seals from 1992 to 2005; however, in both seal populations, composition and concentrations of perfluorocarboxylates decreased with increasing chain length (*10, 23*). PFNA was the major perfluorocarboxylate in livers of Baikal seals and seals from the Dutch Wadden Sea followed by PFDA, PFUnDA, and PFDoDA.

The correlations among the six major PFCs found in our melon-headed whale livers (n = 21) in 2001/2002 are presented in Table S1 (Supporting Information). Concentrations of PFOS in these samples were significantly correlated with the concentrations of PFOSA, PFNA, PFDA, and PFDoDA ($p \leq 0.01$). This correlation suggests that the whales were exposed to PFOS and perfluorocarboxylates simultaneously, probably through the same pathways, and the compounds might have originated from similar sources. Despite the high concentrations of PFUnDA in whale livers, the concentrations of this compound were not correlated with the concentrations of other perfluorocarboxylates. The lack of correlation of the PFUnDA concentration with concentrations of other perfluorocarboxylates, and the large contribution of this compound to ΣPFC concentrations suggest a distinctive source in the mid latitudes of Eastern Asian countries. Degradation of 10:2 fluorotelomer alcohols (FTOHs) or related compounds could contribute to PFUnDA concentrations, as has been suggested for skipjack tuna sampled from a wider Asia-Pacific region (*23*). However, presence of PFUnDA as an impurity in other perfluorocarboxylate preparations cannot be ruled out. PFOA and PFNA have been used as fluoropolymerization aids, and the presence of PFUnDA as an impurity in PFNA mixture is plausible.

Temporal Trends. Temporal trends of ΣPFC concentrations in livers of melon-headed whales stranded along the Pacific coast of Japan in 1982, 2001/2002, and 2006 were examined (Figure 4). The concentration of ΣPFCs was approximately 10-fold higher in 2001/2002 than in 1982. No significant difference in ΣPFC concentrations was found between 2001/2002 and 2006. From 1982 to 2006, the concentrations of PFOS, PFOSA, PFNA, PFDA, PFUnDA, and PFDoDA in whale livers increased from 4- to 18-fold. PFOS, PFOSA, PFNA, and PFUnDA concentrations increased significantly from 1982 to 2001/2002 ($p < 0.05$). PFOS, PFNA, PFDA, and PFDoDA increased from 2001/2002 to 2006, although this increase was statistically significant only for PFNA and PFDA ($p < 0.05$). From 2001/2002 to 2006, PFOSA was the only compound whose concentration decreased significantly in whale livers ($p < 0.05$).

The decrease in PFOSA concentrations in melon-headed whales can likely be attributed to the phase-out of production

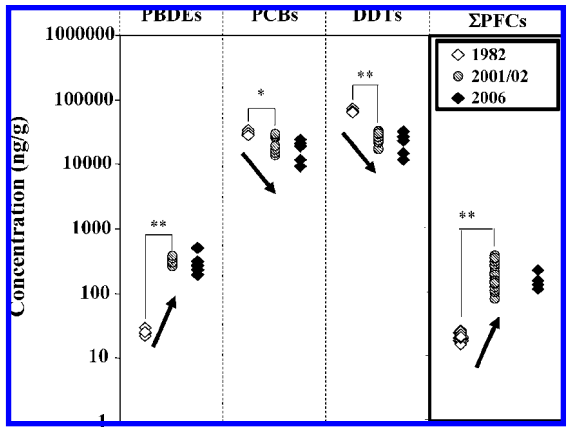

FIGURE 4. Trends in total PFC concentrations (ng/g, wet wt), compared with PBDEs, PCBs, and DDTs (ng/g, lipid wt) in melon-headed whales stranded along the Japanese coast in 1982, 2001/2002, and 2006. *$p < 0.05$; **$p < 0.01$. Data for PBDEs, PCBs and DDTs are from Kajiwara et al. (*20*). Arrows indicate upward or downward trends.

of POSF-based compounds. Between 2001/2002 and 2006, the concentrations and contributions of perfluorocarboxylates, such as PFNA, PFDA, PFUnDA, and PFDoDA increased in the whale livers. The release of perfluorocarboxylates in the environment could be derived from volatile precursors, such as FTOHs, which have been produced since the 1970s, or from direct uses of PFCAs in fluoropolymer manufacture (*3*).

Concentrations of PBDEs, PCBs, and DDTs have been reported in the set of melon-headed whales that we analyzed in the present study (*20*). Similar to the pattern for PFCs, concentrations of ΣPBDEs were found to have increased 10-fold between 1982 and 2001/2002 (*20*). ΣPFC concentrations were comparable between 2001/2002 and 2006 (184 and 163 ng/g, wet wt, respectively); the same was true for PBDEs (320 and 300 ng/g, lipid wt, respectively) (Figure 4). In contrast, concentrations of PCBs and DDTs in melon-headed whale decreased significantly from the 1982 values (*20*). The continuing exposure of certain PFCs, such as PFUnDA, in whales emphasizes the importance of further monitoring studies of PFCs in whales and other marine mammals from the Asia-Pacific region.

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Supporting Information Available

Information regarding standards and reagents used in the study, statistical analysis and a table showing correlation among perfluorochemicals in livers of melon-headed whales. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Giesy, J. P.; Kannan, K. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* **2001**, *35*, 1339–1342.

(2) Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Johnson, H. O. Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. *Environ. Sci. Technol.* **2001**, *35*, 766–770.

(3) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40*, 32–44.

(4) Loganathan, B. G.; Kannan, K. Global organochlorine contamination trends: an overview. *Ambio* **1994**, *23*, 187–191.

(5) Kannan, K.; Perrotta, E.; Thomas, N. J. Association between perfluorinated compounds and pathological conditions in southern sea otter. *Environ. Sci. Technol.* **2006**, *40*, 4943−4948.

(6) Butt, C. M.; Mabury, S. A.; Muir, D. C. G.; Braune, B. M. Prevalence of long-chained perfluorinated carboxylates in seabirds from the Canadian Arctic between 1975 and 2004. *Environ. Sci. Technol.* **2007**, *41*, 3521–3528.

(7) Butt, C. M.; Muir, D. C. G.; Stirling, I.; Kwan, M.; Mabury, S. A. Rapid response of Arctic ringed seals to changes in perfluroalkyl production. *Environ. Sci. Technol.* **2007**, *41*, 42–49.

(8) Verreault, J.; Berger, U.; Gabrielsen, G. W. Trends of perfluorinated alkyl substances in herring gulls from two coastal colonies in northern Norway: (1983−2003). *Environ. Sci. Technol.* **2007**, *41*, 6671–6677.

(9) Holmstrom, K.; Jarnberg, U.; Bignert, A. Temporal trends of PFOS and PFOA in guillemot eggs from the Baltic Sea, 1968−2003. *Environ. Sci. Technol.* **2005**, *39*, 80–84.

(10) Ishibashi, H.; Iwata, H.; Kim, E-Y.; Tao, L.; Kannan, K.; Amano, M.; Miyazaki, N.; Tanabe, S.; Batoev, V. B.; Petrov, E. A. Contamination and effects of perfluorochemicals in Baikal seal (*Pusa sibirica*). 1. Residue level, tissue distribution, and temporal trends. *Environ. Sci. Technol.* **2008**, *42*, 2295–2301.

(11) Jefferson, T. A.; Barros, N. B. *Peponocephala electra. Mammalian Species* **1997**, *533*, 1–6.

(12) Kannan, K.; Koistinen, J.; Beckman, K.; Evans, T.; Gorzelany, J.; Hansen, K. J.; Jones, P. D.; Giesy, J. P. Accumulation of perfluorooctane sulfonate in marine mammals. *Environ. Sci. Technol.* **2001**, *35*, 1593–1598.

(13) Tao, L.; Kannan, K.; Kajiwara, N.; Costa, M. M.; Fillman, G.; Takahashi, S.; Tanabe, S. Perfluorooctanesulfonate and relate fluorochemicals in albatrosses, elephant seals, penguins, and polar skuas from the Southern Ocean. *Environ. Sci. Technol.* **2006**, *40*, 7642–7648.

(14) Van de Vijver, K. I.; Hoff, P. T.; Das, K.; VanDongen, W.; Esmans, E. L.; Jauniaux, T.; Bonquegneau, J. M.; Blust, R.; de Coen, W. M. Perfluorinated chemicals infiltrate ocean water: link between exposure levels and stable isotope ratios in marine mammals. *Environ. Sci. Technol.* **2003**, *37*, 5545–5550.

(15) Sinclair, E.; Mayack, D. T.; Roblee, K.; Yamashita, N.; Kannan, K. Occurrence of perfluoroalkyl surfactants in water, fish, and birds from New York State. *Arch. Environ. Contam. Toxicol.* **2006**, *50*, 398–410.

(16) Bossi, R.; Riget, F.; Dietz, R. Temporal and spatial trends of perfluorinated compounds in ringed seal (*Phoca hispida*) from Greenland. *Environ. Sci. Technol.* **2005**, *39*, 7416–7422.

(17) Conder, J. M.; Hoke, R. A.; Wolf, W. D.; Russell, M. H.; Buck, R. C. Are PFCAs bioaccumulative? A critical review and

comparison with regulatory criteria and persistent lipophilic compounds. *Environ. Sci. Technol.* **2008**, *42*, 995–1003.
(18) Kannan, K.; Corsolini, S.; Falandysz, J.; Oehme, G.; Focardi, S.; Giesy, J. P. Perfluorooctanesulfonate and related fluorinated hydrocarbons in marine mammals, fishes, and birds from coasts of the Baltic and Mediterranean Seas. *Environ. Sci. Technol.* **2002**, *36*, 3210–3216.
(19) Kajiwara, N.; Kamikawa, S.; Amano, M.; Hayano, A.; Yamada, T. K., Miyazaki, N.; Tanabe, S. Polybrominated diphenyl ethers (PBDEs) and organochlorines in melon-headed whaled, *Peponocephala electra*, mass stranded along the Japanese coasts: Maternal transfer and temporal trend. *Environ. Pollut.* **2008**, doi: 10.1016/j.envpol.2007.12.034.
(20) Miyazaki, N.; Fujise, Y.; Iwata, K. Biological analysis of a mass stranding of melon-headed whales (*Peponocephala electra*) at Aoshima, Japan. *Bull. Natl. Sci. Mus., Ser A (Tokyo)* **1998**, *24*, 31–60.
(21) Smithwick, M.; Norstrom, R. J.; Mabury, S. A.; Solomon, K.; Evans, T. J.; Stirling, I.; Taylor, M. K.; Muir, D. C. G. Temporal trends of perfluoroalkyl contaminants in polar bears (*Ursus maritimus*) from two locations in the North American Arctic, 1972−2002. *Environ. Sci. Technol.* **2006**, *40*, 1139–1143.
(22) Van de Vijver, K. I.; Hoff, P. T.; Das, K.; Brasseur, S.; VanDongen, W.; Esmans, E. L.; Reijnders, P.; Blust, R.; de Coen, W. M. Tissue distribution of perfluorinated chemicals in harbor seals (*Phoca vitulina*) from the Dutch Wadden Sea. *Environ. Sci. Technol.* **2005**, *39*, 6978–6984.
(23) Hart, K.; Kannan, K.; Tao, L.; Takahashi, S.; Tanabe, S. Skipjack tuna as a bioindicator of contamination by perfluorinated compounds in the world's oceans. *Sci. Total Environ.* **2008**, *403*, 218–224.

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