

## Temporal Trends (1992–2007) of Perfluorinated Chemicals in Northern Sea Otters (*Enhydra lutris kenyoni*) from South-Central Alaska

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**Abstract** Perfluorinated chemicals (PFCs) have been detected in abiotic and biotic matrices worldwide, including the Arctic Ocean. Considering these chemicals' persistent and bioaccumulative potentials, it was expected that levels of PFCs, like those of many legacy organic pollutants, would respond slowly to the restrictions in production and usage. Temporal trend studies in remote areas, such as the Arctic, can help determine the chronology of contamination and the response of the environment to regulations on PFCs. Prior to this study, temporal trends of PFCs in Alaskan coastal waters had not been examined. In the present study, concentrations of six PFCs were determined in livers of northern sea otters (*Enhydra lutris kenyoni*) collected from three areas in south-central Alaska (Prince William Sound,  $n = 36$ ; Resurrection Bay,  $n = 7$ ; Kachemak Bay,  $n = 34$ ) from 1992 to 2007. Additionally, previously published profiles and concentrations of PFCs in southern sea otters from California and Asian sea otters from Kamchatka (Russia) were compared to our new data, to determine the geographical differences in PFC profiles among these three regions in the Pacific Ocean. Perfluorooctanesulfonate (PFOS), perfluorooctanesulfonamide (PFOSA), and perfluorononanoate (PFNA) were the predominant PFCs found in the livers of northern sea otters from 1992 to 2007. Other PFCs, such as perfluorooctanoate (PFOA), perfluoroundecanoate (PFUnDA), and

perfluorodecanoate (PFDA), were detected less frequently, and at low concentrations. Overall, from 2001 to 2007, a decrease in concentrations of PFOS was found in northern sea otters, suggesting an immediate response to the phase-out in 2000 of perfluorooctanesulfonyl-based compounds by a major producer in the United States. In contrast, concentrations of PFNA in northern sea otters increased by 10-fold from 2004 to 2007. These results indicate that the contribution by PFNA to  $\Sigma$ PFC concentrations is increasing in northern sea otters. The profiles (i.e., composition of individual PFC to  $\Sigma$ PFC concentration) of PFCs in northern sea otters from Alaska were similar to those reported for southern sea otters from California, but were considerably different from the profiles reported for Asian sea otters from Russia, suggesting differences in point sources of exposure.

Perfluorinated chemicals (PFCs) have received worldwide attention, because of their persistent and toxic properties (Giesy and Kannan 2001, 2002). Several of the PFCs are ubiquitous in the environment, due to their widespread usage and dispersive nature. PFCs have been produced for more than 50 years in a range of applications, to render products resistant to oil and grease, stains, heat, and water. Following the discovery of PFCs in humans and wildlife worldwide (Giesy and Kannan 2001; Hansen et al. 2001), a voluntary phase-out of production of perfluorooctanesulfonate (PFOS) was undertaken in 2000 by, 3M Company, a leading manufacturer in the USA. Furthermore, global perfluorocarboxylate (PFCA) emissions have been reported to have decreased by 60% between 1999 and 2004, following implementation of emission control strategies in

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manufacturing processes, by other PFC manufacturers (Prevedouros et al. 2006).

Within the past 5 years, studies have reported the pathways of transport of PFCs to the remote regions of the world such as the Arctic (Ellis et al. 2004; Prevedouros et al. 2006). Temporal-trend studies of PFCs can aid in the determination of the chronology of contamination and the potential sources and modes of transport to remote marine locations. Time-trend studies are valuable tools used by regulatory agencies to assess changes in environmental burdens of pollutants with time and to evaluate implications for the future (Loganathan and Kannan 1994). Temporal trends of PFCs in polar bears, ringed seals, and seabirds have been studied in the Canadian Arctic (Smithwick et al. 2006; Butt et al. 2007a, b). Livers of polar bears collected from the Canadian Arctic showed remarkable increases in concentrations of PFOS, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), and perfluoroundecanoate (PFUnDA) from 1972 to 2002 (Smithwick et al. 2006). Ringed seals from the Canadian Arctic showed a significant decrease in PFOS concentrations from 2000 to 2005 (Butt et al. 2007a). From 1993 to 2004, two species of Arctic seabirds, thick-billed murres and northern fulmars from the Canadian Arctic, showed variable trends for PFOS; PFCAs increased significantly in thick-billed murres, but remained steady for northern fulmars, after 1993 (Butt et al. 2007b). The differences in temporal trends of PFCs in Arctic seabirds from Canada were suggested to be due to migratory patterns of these birds. Concentrations of PFOS and several PFCAs increased considerably in livers of polar bears collected from eastern Greenland during 1984–2006 (Dietz et al. 2008). Between 1982/1986 and 2003, ringed seals from two locations in Greenland showed significant increases in PFOS, PFDA, and PFUnDA concentrations (Bossi et al. 2005). Overall, the trends and patterns of PFC contamination varied among species, locations, and compounds. Prior to this study, temporal trends of PFCs in Alaskan coastal waters had not been examined. Availability of archived tissues of northern sea otters collected during 1992–2007 from Alaska provided an opportunity to examine temporal trends of PFCs in this keystone species.

Sea otters are considered to be sentinel species, in the understanding of the health of the nearshore-marine ecosystem (Jessup et al. 2004). Sea otters are nonmigratory, and their diet primarily consists of sedentary benthic invertebrates (Riedman and Estes 1990); thus, their behavioral characteristics and limited home ranges cause them to exhibit contamination patterns dominated by local influences (Kannan et al. 1998). In addition, sea otters neither fast (unlike polar bears) nor molt (unlike birds and seals); therefore, contaminant burdens in sea otters are not modulated by such physiological processes. In the present

study, archived liver tissues from northern sea otters (*Enhydra lutris kenyoni*) collected from south-central Alaska during 1992–2007 were utilized to assess temporal trends of PFCs. This choice of time frame permits an assessment at points both before and after the voluntary phase-out in 2000 of the production of PFOS by a leading manufacturer, the 3M Company in the United States. In addition, the profiles of PFCs found in northern sea otters from Alaska were compared to previously published PFC profiles for southern sea otters from California and Asian sea otters from Kamchatka, Russia (Kannan et al. 2008). The objectives of the present study were twofold: (1) to determine the concentrations and profiles of PFCs, and the temporal trends from 1992 to 2007, in northern sea otters from south-central Alaska and (2) to examine the spatial variations in PFC profiles among northern, southern, and Asian sea otters. The differences in PFC profiles among the three populations should indicate regional variations in sources of PFC exposures.

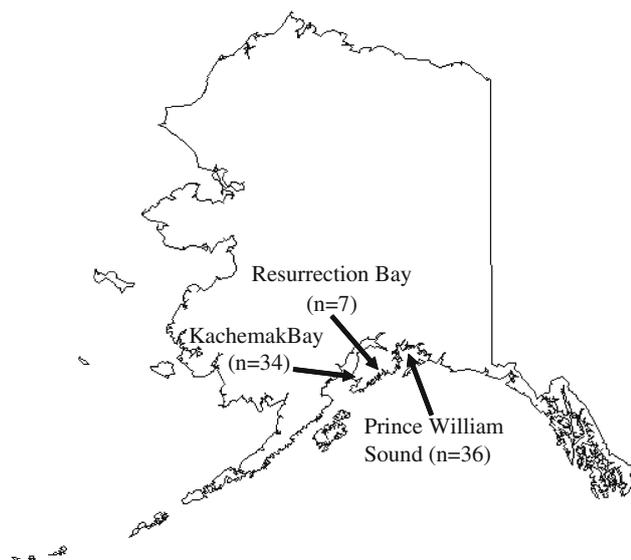
## Materials and Methods

### Standards and Reagents

Potassium salts of PFOS and PFOA were purchased from Tokyo Chemical Industries (Portland, OR). PFNA and PFDA were from Fluorochem Ltd. (Glossop, Derbyshire, UK). PFUnDA was from Aldrich (St. Louis, MO). Perfluorooctanesulfonamide (PFOSA),  $^{13}\text{C}_2$ -PFNA, and  $^{13}\text{C}_2$ -PFDA were provided by the 3M Company (St. Paul, MN).  $^{13}\text{C}_4$ -PFOS and  $^{13}\text{C}_4$ -PFOA were purchased from Wellington Laboratories (Guelph, ON, Canada). Purities of all standards were  $\geq 95\%$ . All solvents were HPLC grade, and reagents were ACS grade (J.T. Baker, Phillipsburg, NJ).

### Samples

Archived liver tissues of northern sea otters from Alaska, stored at  $-20^\circ\text{C}$ , were obtained from the U.S. Fish and Wildlife Service (USFWS), Anchorage, Alaska. A subsample of liver tissues from 77 male northern sea otters collected from south-central Alaska population stock from 1992 to 2007 was selected for this study. Livers were obtained from sea otters that were either beach-cast or killed in the native hunt at several locations in Prince William Sound ( $n = 36$ ), Resurrection Bay ( $n = 7$ ), and Kachemak Bay ( $n = 34$ ) (Fig. 1). Liver samples were stored in clean polyethylene bags at  $-20^\circ\text{C}$  after collection. Individuals were chosen for the analysis based on gender (males only) and geographical location, to eliminate possible confounding variables. The coastal distance between the two farthest locations in the coastal waters of



**Fig. 1** Map showing the locations of sampling sites for northern sea otters (*Enhydra lutris kenyoni*) from south-central Alaska, 1992–2007

south-central Alaska (Kachemak Bay and Knight Island in Prince William Sound) is approximately 430 km. The sea otters analyzed were predominantly adults and subadults (88%). Liver tissues from nine pups were included in the analysis, but were not used in the temporal-trend evaluation. Postmortem examinations were performed on a few sea otters analyzed in this study ( $n = 18$ ), from 2003 to 2007 at USFWS, for determination of the cause of death. Animals were grouped into two categories, those that died from infectious diseases (diseased) and animals that died from trauma and other causes (nondiseased).

PFC profiles previously reported (Kannan et al. 2008) for five Asian sea otters found stranded along the southern Kamchatka Peninsula in 1997 ( $n = 5$ ; 1 male, 4 females) and 13 southern sea otters beach-cast along the central California coast during 1998–2001 ( $n = 13$ ; 2 males, 11 females) were compared with the profiles reported here for PFCs in northern sea otters from Alaska. For the interstudy comparison of PFC profiles, only northern sea otters collected during 1998–2001 (to eliminate time as a confounding factor) were utilized.

#### Chemical Analysis

Concentrations of PFCs in livers of northern sea otters were determined according to a procedure described previously (Kannan et al. 2001; Tao et al. 2006). A small quantity of the liver (0.7–0.9 g) was homogenized with 5 ml of Milli-Q water. One milliliter of the homogenate was transferred into a polypropylene tube (PP tube), and 50  $\mu\text{L}$  of 5 ng/mL internal standard mixture ( $^{13}\text{C}_4$ -PFOS,  $^{13}\text{C}_4$ -PFOA,  $^{13}\text{C}_2$ -PFDA, and  $^{13}\text{C}_2$ -PFNA), 2 ml of 0.25 M

sodium carbonate buffer, and 1 ml of 0.5 M tetrabutylammonium hydrogensulfate solution (adjusted to pH 10) were added and mixed thoroughly. Extraction was carried out by the addition of 5 ml of methyl-tert-butyl ether, with vigorous shaking for 40 min. The sample was centrifuged at 4,000 rpm for 5 min, and the organic layer was separated from the aqueous layer and transferred into a new PP tube. The organic layer was evaporated to near-dryness under a gentle stream of nitrogen. The sample was then reconstituted with 1 mL of methanol, vortexed for 30 s, centrifuged at 4,000 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 chromatograph, coupled with an Applied Biosystems API 2000 electrospray triple-quadrupole mass spectrometer (ESI-MS/MS). Ten microliters of the extract was injected onto a Betasil C18 (100  $\times$  2.1-mm) column with a (20  $\times$  2.1-mm) guard column, both with a 5- $\mu\text{m}$  particle size (Thermo Electron Corp., 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 then reverted to 10% methanol. The MS/MS was operated in a multiple reaction monitoring mode, and the mass transitions monitored were 499 > 99 for PFOS, 503 > 99 for  $^{13}\text{C}_4$ -PFOS, 497.7 > 77.7 for PFOSA, 413 > 369 for PFOA, 417 > 372 for  $^{13}\text{C}_4$ -PFOA, 463 > 419 for PFNA, 465 > 420 for  $^{13}\text{C}_2$ -PFNA, 513 > 469 for PFDA, 515 > 470 for  $^{13}\text{C}_2$ -PFDA, and 563 > 519 for PFUnDA. The sum of the concentrations of the six PFCs measured in this study is denoted as the total PFCs ( $\Sigma\text{PFC}$ ).

#### Quality Assurance/Quality Control

A known concentration (10 ng each) of the target compounds was spiked into an aliquot of the sample matrix (matrix spikes) and passed through the analytical procedure, as a check for matrix effects through the calculation of recoveries. Matrix spike recoveries of most of the target compounds were within an acceptable range of 75% to 125%. Matrix spike recoveries for PFOSA fluctuated from 25% to 135% (mean: 79%) among the three batches of samples analyzed. Matrix spike recoveries for PFUnDA in three batches were between 61% and 154% (mean: 135%).  $^{13}\text{C}$ -Labeled internal standards ( $^{13}\text{C}_4$ -PFOS,  $^{13}\text{C}_4$ -PFOA,  $^{13}\text{C}_2$ -PFDA, and  $^{13}\text{C}_2$ -PFNA) were spiked into all of the samples for the calculation of recoveries. The concentrations of PFOS, PFOA, PFNA, and PFDA were corrected by their  $^{13}\text{C}$ -labeled internal standard recoveries in each sample. External calibration standards were prepared in methanol at concentrations ranging from 0.1 to 50 ng/ml

for quantification. Calibration standards were injected every day before and after a batch of samples was analyzed. A midpoint calibration standard was injected after every 10 samples, throughout the instrumental analysis, to check for instrument response and drift. Procedural blanks were analyzed by passage of water and reagents through the entire analytical procedure, to monitor for contamination in reagents and glassware. The quantitation of PFCs was performed using a quadratic regression fit analysis weighted by  $1/x$  of the matrix extracted calibration curve. The limit of quantitation (LOQ) was the lowest acceptable standard within  $\pm 30\%$  of the theoretical value with 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. LOQs, varying for each batch, and on a wet weight basis, were 0.8–0.9 ng/g for PFOS, 0.8–1.7 ng/g for PFOSA, 2.0–6.0 ng/g for PFOA, 0.9–2.0 ng/g for PFNA, 1.0–4.0 ng/g for PFDA, and 0.8–1.8 ng/g for PFUnDA.

#### Statistical Analysis

Statistical analyses were performed using Statgraphics plus 5.1 (Manugistics, Inc., Rockville, MD). Concentrations that were below the LOQ were assigned a value of half the LOQ, in the statistical analyses. ANOVA was used to compare the means within and between groups. The Kruskal-Wallis test was used to determine which medians were statistically different, for temporal trend evaluation. Correlations between compounds were tested using Spearman's rho test.

## Results and Discussion

### PFC Concentrations in Northern Sea Otters

PFOS, PFOSA, and PFNA were the predominant PFCs found in livers of northern sea otters from 1992 to 2007 (Table 1). PFOS concentrations were similar at the start and end of the 15-year span, i.e., in 1992 and 2007 (2.3 and 2.8 ng/g wet weight [wt], respectively), while the highest mean concentration was found in 2001 (21.2 ng/g wet wt). Concentrations of PFOSA were similar to the concentrations of PFOS, and the highest mean concentration was found in 1999 (15.2 ng/g wet wt). Concentrations of PFNA fluctuated markedly, from 0.9 to 8 ng/g wet wt, during the 1992–2004 span; nevertheless, in the latter portion of it, 2004–2007, PFNA concentrations increased by almost 10-fold ( $<2$  to 9.4 ng/g wet wt). Concentrations of PFNA were higher than concentrations of PFOS in sea otters collected after 2003 (Table 1). The other three PFCs measured,

**Table 1** Concentrations of the predominant perfluorochemicals (PFCs; mean  $\pm$  SD ng/g, wet wt) and  $\Sigma$ PFC in livers of male northern sea otters from south-central Alaska, collected during 1992 to 2007

Collection year	<i>n</i>	PFOS	PFOSA	PFNA	$\Sigma$ PFCs
1992	1	2.3	2.3	1.3	9.9
1993	1	1.6	11.1	<0.9	17.3
1994	6	10.4 $\pm$ 11.4	5.2 $\pm$ 4.7	8.0 $\pm$ 12.4	28.5
1996	3	2.7 $\pm$ 1.3	6.8 $\pm$ 2.6	3.4 $\pm$ 4.1	16.9
1997	7	6.0 $\pm$ 4.8	9.8 $\pm$ 3.2	2.8 $\pm$ 2.2	23.4
1998	11	4.2 $\pm$ 5.7	6.6 $\pm$ 5.2	2.1 $\pm$ 2.2	17.7
1999	7	5.1 $\pm$ 2.4	15.2 $\pm$ 8.6	1.9 $\pm$ 2.5	27.1
2000	7	10.8 $\pm$ 5.6	12.7 $\pm$ 5.3	2.3 $\pm$ 1.5	32.6
2001	2	21.2 $\pm$ 22.7	3.3 $\pm$ 1.3	6.0 $\pm$ 5.2	34.6
2002	6	7.0 $\pm$ 7.5	4.2 $\pm$ 4.3	5.6 $\pm$ 4.7	21.1
2003	8	4.2 $\pm$ 3.5	2.3 $\pm$ 2.3	5.9 $\pm$ 4.2	18.7
2004	2	<0.9	<1.7	<2.0	7.1
2005	3	1.3 $\pm$ 0.6	<1.7	3.9 $\pm$ 4.9	9.9
2006	11	1.9 $\pm$ 1.1	<1.7	4.3 $\pm$ 3.0	10.9
2007	2	2.8 $\pm$ 2.1	<1.7	9.4 $\pm$ 10.4	18.5

Note:  $\Sigma$ PFCs is the sum of PFOS, PFOSA, PFOA, PFNA, PFDA, and PFUnDA. Values below the LOQ were assigned half the value of the LOQ for the calculation.

PFOA, PFDA, and PFUnDA, were detected in sea otters at concentrations less than their corresponding LOQs.

Concentrations of PFOS in livers of northern sea otters from south-central Alaska were considerably lower, between 3- and 11-fold, than the concentrations previously reported for southern sea otters from the California coast (Kannan et al. 2006), signifying spatial differences in the magnitude of contamination. Nevertheless, concentrations of PFOS and PFOSA in livers of northern sea otters collected in 1997 were fivefold higher than concentrations in Asian sea otters collected in the same year. Furthermore, the mean PFOS concentrations in livers of northern sea otters were 7- to 13-fold lower than in the livers of seals from western Greenland (Bossi et al. 2005) and Lake Baikal (Ishibashi et al. 2008) in 2003 and 2005. These results suggest relatively low levels of PFC contamination along the south-central coast of Alaska.

Among the four PFCAs (PFOA, PFNA, PFDA, and PFUnDA) analyzed in northern sea otters from Alaska, concentrations of PFNA were the highest. The high concentrations of PFNA found in the northern sea otters are different from the profiles found in the livers of tuna and whales collected from East Asia; for the latter, PFUnDA was the predominant PFCa (Hart et al. 2008a, b).

We compared hepatic concentrations of PFOS and PFNA between two groupings (diseased and nondiseased) among 18 of the northern sea otters for which pathological information was available. No significant difference was

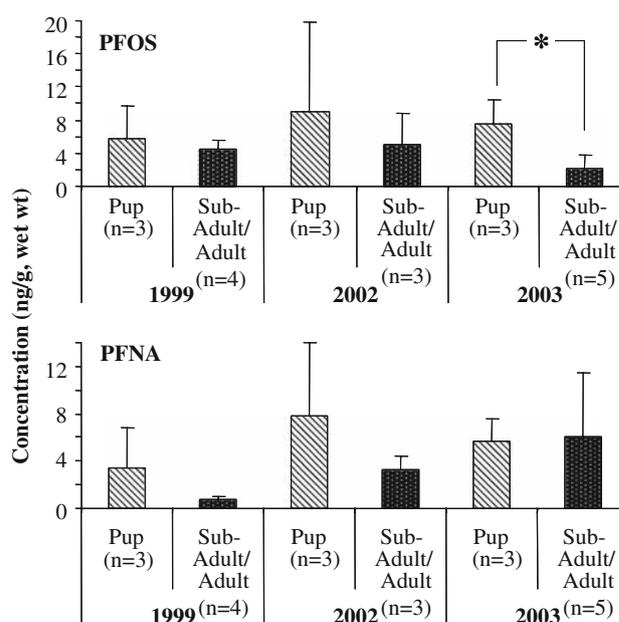
found in the concentrations of PFOS and PFNA between the diseased and the nondiseased groups (data not shown). The lack of association is contrary to what was previously found for southern sea otters; for these, the diseased group was characterized by significantly higher PFOS and PFOA concentrations (Kannan et al. 2006). Further studies with a large number of samples are needed for examining the association between PFC concentrations and disease in northern sea otters. In addition, the presence of other contaminants such as PAHs, PCBs, and pesticides in northern sea otters should be examined. Concentrations of PAHs reported in only three northern sea otters collected in the mid-1990s from Alaska were elevated relative to concentrations in sea otters from California, Washington, and Kamchatka (Kannan et al. 2008).

#### Age-Related Accumulation Patterns

The northern sea otters analyzed in this study were categorized as adults (3+ years), subadults (1–3 years), or pups (0–1 years), based on premolar teeth counts. Concentrations of PFOS and PFNA were compared between pups and adult/subadults collected in 1999, 2002, and 2003 (Fig. 2). The mean concentrations of PFOS and PFNA in pups were higher than in adults/subadults. PFOS concentrations were significantly higher ( $P < 0.05$ ) in pups than in adults/subadults for the samples collected in 2003. Similarly, an earlier study reported significantly higher concentrations of PFCs in livers of juvenile seals (<0.3–2 years) than in adult/subadult seals (>2 years) from Lake Baikal (Ishibashi et al. 2008). For melon-headed whales, transplacental transfer of PFCs has been suggested as a major route of in utero exposure (Hart et al. 2008b). Similarly, concentrations of PFOS were higher in pups than in adult harbor seals collected from the northwest Atlantic (Shaw et al. 2008). These comparable sets of results suggest that elevated exposures to PFCs occur in the early life stages of marine mammals. It is probable that the rate of elimination of PFCs is slower in pups than in adults, which results in higher concentrations in the former than the latter.

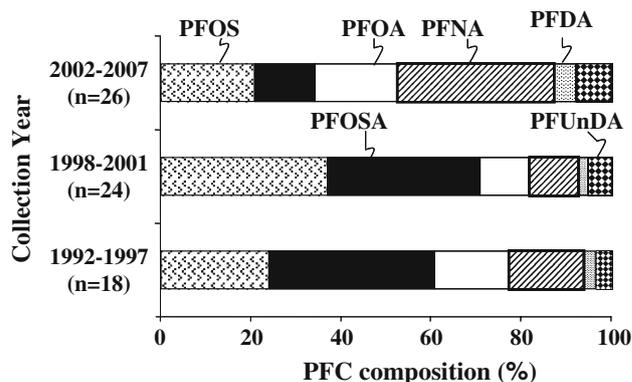
#### Spatial and Temporal PFC Profiles and Correlations

For temporal comparisons, in order to increase the sample size for each time period, the northern sea otter samples analyzed here were grouped into three sampling periods: 1992–1997, 1998–2001, and 2002–2007 (Fig. 3). PFC profiles were dominated by perfluoroalkylsulfonates (PFOS and PFOSA) during 1992–1997 and during 1998–2001 (61% and 71%, respectively, of the  $\Sigma$ PFC concentrations). In the 2002–2007 period, the contributions of PFOS and PFOSA to  $\Sigma$ PFC concentrations were lower by



**Fig. 2** Relationship between age class and concentrations (ng/g wet wt) of PFOS (top) and PFNA (bottom) in the livers of pup (0–1 year) and subadult/adult (>1 year) northern sea otters from south-central Alaska, in 1999, 2002, and 2003. \*Statistically significant difference ( $P < 0.05$ )

approximately 34% compared to the contributions in the previous two sampling periods. Conversely, in the 2002–2007 period, the proportion of PFCAs (PFNA, PFOA, PFUnDA, and PFDA) in  $\Sigma$ PFC concentrations was twofold (66%) higher than in the previous two time periods. In the 2002–2007 period, PFNA was the predominant carboxylate, contributing 35% of the  $\Sigma$ PFC concentration. The changing PFC concentrations and profiles in northern sea otters across the three time periods spanning more than 15 years are indicative of a shift in sources from sulfonyl-



**Fig. 3** Composition profiles of six PFCs in livers of northern sea otters from south-central Alaska collected during 1992–1997, 1998–2001, and 2002–2007, i.e., before, during, and after the phase-out of PFOS production. Values below the limit of quantitation (LOQ) were assigned a value of half the LOQ for calculation.  $\Sigma$ PFCs is the sum of PFOS, PFOSA, PFOA, PFNA, PFDA, and PFUnDA

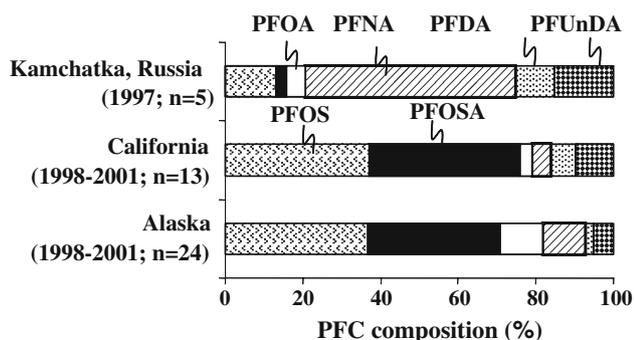
to carboxyl-based compounds after 2001. The PFC profiles in northern sea otters suggest a response to the phase-out of perfluorooctanesulfonyl-based compounds (i.e., PFOS) in 2000 by 3M Company in the United States. The correlations among the three predominant PFCs in northern sea otters ( $n = 77$ ) from Alaska, spanning the 1992–2007 range, are presented in Table 2. Concentrations of PFOS in sea otters were significantly correlated with concentrations of PFOSA and PFNA ( $P < 0.01$ ), indicating common pathways of exposure to PFOS, PFOSA, and PFNA.

The PFC profiles in livers of northern sea otters from Alaska were similar to those found for southern sea otters from California, for the period 1997/1998–2001 (Kannan et al. 2008) (Fig. 4). PFOS and PFOSA were the major PFCs in both northern and southern sea otters, accounting for >60% of the  $\Sigma$ PFC concentration. Similarities in PFC profiles between northern and southern sea otters suggest a commonality in the sources of exposures. However, the profiles of PFCs in Asian sea otters from Russia (Kannan et al. 2008) were considerably different from the profiles in both the northern and the southern sea otters (Fig. 4). PFNA and PFUnDA were major PFCs in Asian sea otters (Fig. 4) and the profiles of PFCs in these sea otters were

**Table 2** Spearman's correlation values among the three major perfluorochemicals found in livers of northern sea otters from Alaska ( $n = 77$ ; 1992–2007)

	PFOSA	PFNA
PFOS	0.346**	0.589**
PFOSA		−0.238*

Note: Correlation significant at the \* 0.05 or the \*\* 0.01 level (two-tailed)

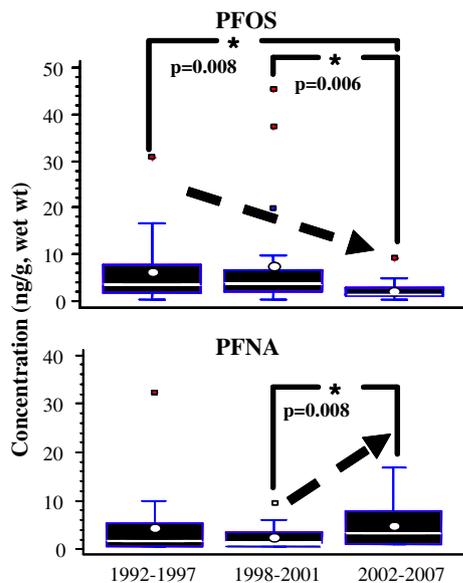


**Fig. 4** Composition profiles of six PFCs in livers of sea otters from south-central Alaska (1998–2001 samples only), compared with the previously published profiles reported for southern sea otters from 1998 to 2001 and for Asian sea otters from Russia collected in 1997. Values below the limit of quantitation (LOQ) were assigned a value of half the LOQ for calculation.  $\Sigma$ PFCs is the sum of PFOS, PFOSA, PFOA, PFNA, PFDA, and PFUnDA. Profiles of PFCs in southern (for the specific time period) and Asian sea otters are from Kannan et al. (2008)

similar to the profiles reported for seals from Lake Baikal, Russia (Ishibashi et al. 2008). The distance between Kamchatka (Russia) and south-central Alaska (USA) is comparable to the distance between south-central Alaska (USA) and California (USA) (~3500 km). Therefore, the spatial differences in the concentrations and profiles of PFCs in sea otters from the three locations may be indicative of local sources of contamination.

#### Temporal Trends

Temporal trends of PFCs in northern sea otters collected during 1992 to 2007 from south-central Alaska were examined. Although the number of samples analyzed per time point was small for certain years, restricting the dataset to adult/subadult males and grouping of samples into three sampling periods, 1992–1997 ( $n = 18$ ), 1998–2001 ( $n = 24$ ), and 2002–2007 ( $n = 26$ ), helped to reduce the variability in this analysis and increased the sample size, providing a more robust dataset for statistical analysis. Pups were not included in the temporal trend analysis due to higher concentrations of PFOS and PFNA than in subadults/adults. The groupings represented before, during, and after phase-out of PFOS production in 2000 by the 3M Company in the United States. The concentrations of  $\Sigma$ PFCs increased by 3.5-fold between the 1992–1997 period and the 1998–2001 period, in livers of northern sea otters, whereas the concentrations decreased by 1.9-fold between the 1998–2001 period and the 2002–2007 period. Concentrations of PFOS decreased significantly between the 1992–1997 and the 2002–2007 periods ( $P = 0.008$ ), and between the 1998–2001 and the 2002–2007 periods ( $P = 0.006$ ) (Fig. 5). In contrast, concentrations of PFNA increased significantly between 1998–2001 and 2002–2007 ( $P = 0.008$ ). Time trends of PFOSA were similar to the trends found for PFOS; PFOSA decreased by more than eightfold from the 1998–2001 period to the 2002–2007 period. A recent temporal trend study showed that PFOS and PFOSA declined in the livers of melon-headed whales from Japanese coastal waters, whereas concentrations of PFUnDA increased during 1982–2006 (Hart et al. 2008b). The mean concentrations of PFNA and PFDA in livers of seals collected from Lake Baikal (Russia) in 2005 were twofold higher than in seals collected in 1992 (Ishibashi et al. 2008). Increased prevalence of long-chain PFCAs in livers of seabirds from the Canadian Arctic and coastal birds from Korea has been reported (Butt et al. 2007b; Yoo et al. 2008). Overall, our results suggest that the concentrations of PFOS and PFOSA are declining in the Alaska coast, in response to the reductions in production/emission, while the concentrations of PFCAs such as PFNA and PFUnDA are increasing. These results suggest continuing emissions of long-chain PFCAs and their precursor



**Fig. 5** Box-plots for PFOS and PFNA concentrations (ng/g wet wt) in the liver of adult/subadult northern sea otters from south-central Alaska over three time periods: 1992–1997 ( $n = 18$ ), 1998–2001 ( $n = 24$ ), and 2002–2007 ( $n = 26$ ). Values below the limit of quantitation (LOQ) were assigned a value of half the LOQ for calculation. \*Statistically significant difference. Arrows indicate upward or downward trends

compounds into the environment. Unless adequate emission control strategies are implemented, the levels of PFCAs may supercede those of perfluoroalkylsulfonates in biota in the future.

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