

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/11277557>

Perfluorooctanesulfonate and Related Fluorinated Hydrocarbons in Mink and River Otters from the United States

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · JULY 2002

Impact Factor: 5.33 · DOI: 10.1021/es0205028 · Source: PubMed

CITATIONS

171

READS

19

4 AUTHORS:



Kurunthachalam Kannan

Wadsworth Center, NYS Department of Health

637 PUBLICATIONS 28,629 CITATIONS

SEE PROFILE



John L Newsted

Michigan State University

112 PUBLICATIONS 3,392 CITATIONS

SEE PROFILE



Richard S Halbrook

Southern Illinois University Carbondale

61 PUBLICATIONS 752 CITATIONS

SEE PROFILE



John P Giesy

University of Saskatchewan

1,067 PUBLICATIONS 35,523 CITATIONS

SEE PROFILE

Perfluorooctanesulfonate and Related Fluorinated Hydrocarbons in Mink and River Otters from the United States

KURUNTHACHALAM KANNAN,^{*,†}
JOHN NEWSTED,[‡]
RICHARD S. HALBROOK,[§] AND
JOHN P. GIESY[†]

National Food Safety and Toxicology Center, Department of Zoology, Institute of Environmental Toxicology, Michigan State University, East Lansing, Michigan 48824, Entrix Inc., Okemos, Michigan 48864, and Cooperative Wildlife Research Laboratory and Department of Zoology, Southern Illinois University, Carbondale, Illinois 62901

Mink and otters are good integrators of their aquatic environments and useful sentinel species for determining exposure to environmental contaminants. In this study, 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 measured in livers of mink and river otters collected from various locations in the United States. PFOS was found in all mink livers analyzed. Frequencies of occurrence of FOSA, PFHxS, and PFOA were less. The greatest concentration of PFOS measured in liver of mink was 5140 ng/g, wet weight. Maximum concentrations of FOSA, PFHxS, and PFOA in mink livers were 590, 39, and 27 ng/g, wet weight, respectively. There were no significant positive relationships between concentrations of PFOS and PFHxS or PFOA in mink livers. Concentrations of PFOS were positively correlated with those of FOSA in mink livers from Illinois. There was no significant correlation between concentrations of PFOS and lipid content in mink livers. There were no age- or sex-related differences in the concentrations of fluorochemicals in mink livers. Greater concentrations are associated with those individuals collected near urbanized and/or industrialized areas. PFOS was detected in livers of all river otters collected from Washington and Oregon at concentrations ranging from 25 to 994 ng/g, wet wt.

Introduction

Due to their unique properties, fluorinated surfactants are used in a wide variety of commercial products for over 50 years (1). Sulfonated fluorochemicals repel both water and oil and can reduce surface tension much lower than other hydrocarbon surfactants. Furthermore, sulfonated fluorochemicals can function in environmental conditions where

other compounds would rapidly degrade. Sulfonated fluorochemicals have been used for surface treatment of fabrics, upholstery, carpets, leather, paper, and packaging (2). The production of sulfonyl-based fluorochemicals has been estimated to be 6.5 million pounds in the year 2000 (2).

The extensive use of perfluorinated compounds over a relatively long period of time (50 years) and their stability has resulted in exposure of humans and wildlife (3–7). The strength of the carbon–fluorine bond contributes to the stability of fluorochemicals (1, 8). Recent studies have reported the occurrence of sulfonated fluorochemicals such as perfluorooctanesulfonamide (FOSA), perfluorohexanesulfonate (PFHxS), and perfluorooctanoate (PFOA) in human sera (3). Perfluorooctanesulfonate (PFOS) is an end product of the biological metabolism of various sulfonated fluorochemicals (9). PFOS has been detected in liver and blood plasma of wildlife on a global scale (4–7). While screening wildlife tissues for PFOS across a range of species and habitats, American mink (*Mustela vison*) collected from the Great Lakes region contained some of the greatest concentrations observed (4). Mink are top carnivores in aquatic ecosystems and are used as sentinel species for assessing the effects of environmental contaminants in aquatic environments (10–12). Mink are mostly piscivores, have a fairly small home range, live close to, and prefer to catch prey in rivers, streams, and ponds. Similarly, river otters (*Lutra canadensis*), which belong to the same family as mink, are piscivores and top predators of riverine food chains. This makes otters and mink good integrators of their aquatic environments and useful sentinel species for determining exposure to environmental contaminants. Mink have been identified as an indicator species of water quality and ecosystem integrity for the Great Lakes basin (13). To evaluate accumulation characteristics of perfluorinated compounds, livers of mink collected from Illinois, Massachusetts, South Carolina, and Louisiana were analyzed in this study. In addition, livers of mink that were fed with carp from Saginaw Bay, MI, were analyzed to estimate biomagnification of perfluorochemicals in mink. Livers of river otters collected from Washington and Oregon were also analyzed for the presence of PFOS, FOSA, PFHxS, and PFOA.

Materials and Methods

Mink Samples. One hundred and twelve mink livers comprised of 65 from Illinois, 31 from Massachusetts, 9 from South Carolina, and 7 from Louisiana were obtained. Mink were collected by licensed trappers during November–February, 1995–1996, from various watersheds in Illinois. Skinned carcasses were obtained from licensed commercial trappers in Massachusetts during November–December, 1996. Mink were captured in Acadia Parish, LA, in December 1999. Mink were collected from tidal brackish marshes of the Ashepoo, Combahee, and Edisto River basin of South Carolina in May 2000. Sampling locations or watershed information of mink samples are shown in Figure 1.

Liver samples were dissected from the carcasses, wrapped in clean aluminum foil or whirlpac bags, and stored frozen at -20°C until analysis. Livers of mink from Massachusetts were freeze-dried prior to analysis. The use of mink carcasses taken by trappers utilizes a resource that would normally have been discarded and reduces the need for collecting additional animals. Age and sex of individuals were recorded when available. Body and liver weights were available for mink from Illinois, while body weight was available for mink from South Carolina and Louisiana.

In addition to wild mink, livers of mink that were fed to diets that contained 10, 20, and 40% carp taken from Saginaw

* Corresponding author phone: (517)432-6321; fax: (517)432-2310; e-mail: kuruntha@msu.edu. Corresponding author address: 213 National Food Safety and Toxicology Center, Michigan State University, East Lansing, MI 48824.

[†] Michigan State University.

[‡] Entrix Inc.

[§] Southern Illinois University.

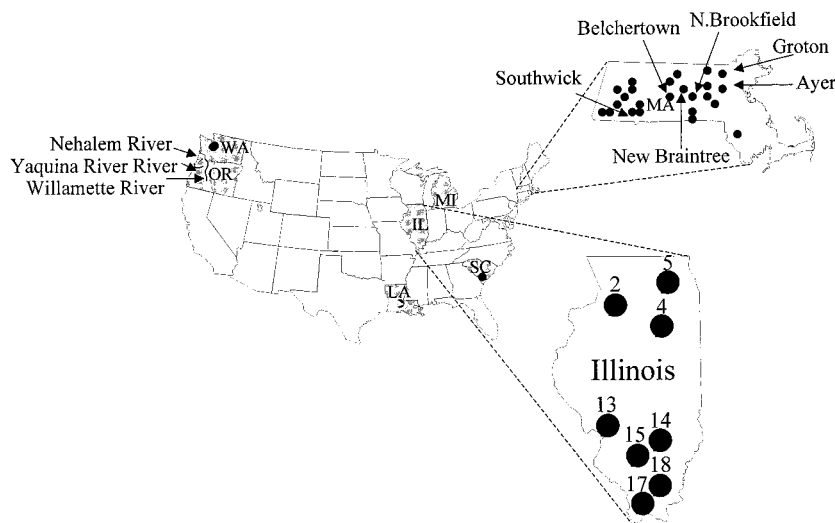


FIGURE 1. Map of the United States showing sampling locations of mink from Illinois (IL), Massachusetts (MA), South Carolina (SC), and Alabama (AL). River otters were collected from Washington (WA) and Oregon (OR). Circles represent sampling locations or watershed; numbers above the circles represent watershed numbers.

Bay, MI, were analyzed to estimate biomagnification of perfluorochemicals from diet to livers of mink. The feeding study was conducted in 1988, and the details of the study have been discussed elsewhere (14, 15). The study was conducted to examine the accumulation of persistent organochlorine compounds such as PCBs, PCDDs, and PCDFs and their effects on mink. Archived tissues of mink and diet available from the feeding study provided an opportunity to calculate biomagnification factors of fluorochemicals in mink. Mink feeding was conducted for 182 d and all mink analyzed were adult females. Samples of the blended raw carp and experimental diets collected during the study were analyzed for perfluorochemicals.

River Otter Samples. Carcasses of river otters were collected from trappers in 1997–1998 in Washington and Oregon. All the river otters analyzed were adult males. Age and body weights of the individuals were recorded.

Analysis. Concentrations of perfluorochemicals in mink livers were determined by use of high performance liquid chromatography (HPLC) coupled with electrospray tandem mass spectrometry (ESMSMS) (3). Briefly, a liver homogenate of 1 g of liver to 5 mL of Milli-Q water was prepared and 1 mL of the homogenate was pipetted into a polypropylene tube. To the homogenate were added 1 mL of 0.5 M tetrabutylammonium hydrogen sulfate solution (adjusted to pH 10) and 2 mL of 0.25 M sodium carbonate buffer. After thorough mixing, 5 mL of methyl *tert*-butyl ether (MTBE) was added, 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 vortexed for 30 s and passed through a 0.2 μ m nylon filter into an autosampler vial.

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. 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. When possible, multiple daughter ions were monitored, but quantitation was based on a single product ion. For all analyses, the capillary was held between 1.6 and 3.2 kV. For the ESMSMS analysis of PFOS 499 Da \rightarrow 99 Da transition was monitored. For PFOA, FOSA, and PFHxS, 413 Da \rightarrow 169 Da, 498 Da \rightarrow 78, and 399 Da \rightarrow 80 Da transitions, respectively, were monitored. The presence of perfluorochemicals was verified by quantitative agreement ($\pm 30\%$) between two or more product ions.

The limit of quantitation (LOQ) was variable depending on the instrumental conditions and samples. For the estimation of the LOQ, samples were compared to an unextracted standard calibration curve. Concentrations in samples that were greater than the “lowest acceptable standard” were considered to be valid. A curve point was acceptable if (1) it was back calculated to be within 30% of the theoretical value when evaluated versus the 1/x weighted curve, and (2) the peak area of the standard was at least 2 times greater than the matrix blank. Concentration/dilution factors are included in the calculation of the LOQ. The LOQ for PFOS was 7 ng/g, wet weight, whereas for FOSA, PFHxS, and PFOA, it varied from 4.5 to 75 ng/g, wet weight. Data quality assurance and quality control protocols included matrix spikes, laboratory blanks, and continuing calibration verification. For rabbit, rat, and bovine tissue, recoveries of PFOS through the analytical procedure ranged from 85 to 101% (3). The reported concentrations of PFOS were not corrected for the recoveries of the surrogate standard.

Results and Discussion

Recoveries. Recoveries of fluorochemicals spiked to mink livers varied (Table 1). In particular, recoveries of PFOS spiked into mink livers varied from 131 to 160%. Recoveries of FOSA and PFHxS were generally less, ranging from 40 to 70%. Matrix spike recoveries of PFOA ranged from 53 to 140%. Reasons for the variability in recoveries are not known. It is more likely due to matrix-related characteristics rather than due to instrumental or sample preparation introduced variability in the overall recoveries. Recoveries of fluorochemicals spiked to river otters ranged from 65 to 79%. The data were not corrected for the recoveries of matrix spikes. Accuracy of the analytical data for PFOS was in the range of $\pm 30\%$, whereas that for FOSA, PFHxS, and PFOA was in the range of $\pm 50\%$.

TABLE 1. Mean Matrix Spike Recoveries (%) of Fluorochemicals Spiked to Mink Livers^a

| sample ID | PFOS | FOSA | PFHxS | PFOA |
|-------------------|------|------|-------|------|
| mink liver S19 | 160 | 71 | 48 | 140 |
| mink liver P09 | 160 | 70 | 50 | 107 |
| mink liver MA1 | 131 | 54 | 63 | 107 |
| mink liver MA2 | 136 | 40 | 67 | 53 |
| river otter liver | 75 | 65 | 79 | 71 |

^a PFOS = perfluorooctanesulfonate, FOSA = perfluorooctanesulfonamide, PFHxS = perfluorohexanesulfonate, PFOA = perfluorooctanoate.

TABLE 2. Concentrations (ng/g, Wet Wt) of PFOS in Mink Livers from the United States

| sex | age group | n | body wt ^a (g) | liver wt ^a (g) | PFOS ^e |
|-----------------------------------|--------------|----|--------------------------|---------------------------|-------------------|
| Illinois | | | | | |
| female | adult | 11 | 612 | 23 | 1610 (93–5140) |
| | juvenile | 10 | 591 | 25 | 1450 (243–3650) |
| male | adult | 21 | 1267 | 39 | 680 (47–1990) |
| | juvenile | 21 | 1169 | 40 | 1210 (64–4870) |
| unidentified | | 2 | | | 2290 (1900–2700) |
| Massachusetts^b | | | | | |
| female | adult | 14 | NA ^d | NA ^d | 220 (50–620) |
| | juvenile | 2 | NA ^d | NA ^d | 110 (70–140) |
| | unidentified | 1 | NA ^d | NA ^d | 410 |
| male | adult | 12 | NA ^d | NA ^d | 450 (20–1100) |
| | juvenile | 1 | NA ^d | NA ^d | 67 |
| | unidentified | 1 | NA ^d | NA ^d | 74 |
| South Carolina^c | | | | | |
| female | juvenile | 2 | 790 | NA ^d | 1070 (650–1500) |
| male | juvenile | 7 | 1143 | NA ^d | 2370 (1240–3110) |
| Louisiana^c | | | | | |
| male | juvenile | 7 | 1148 | NA ^d | 140 (40–320) |

^a Mean value. ^b Data for Massachusetts are converted from dry weight basis to wet weight basis assuming a liver moisture content of 75%. ^c Fat content of livers varied from 3.6 to 6.4%. ^d NA = data not available. ^e Values in parentheses indicate range.

PFOS Concentrations in Mink. Concentrations of PFOS were above the LOQ of 7 ng/g, wet wt, in all the mink livers analyzed. The greatest concentration of 5140 ng PFOS/g, wet wt, was found in an adult female mink collected from northwest McHenry County, IL (watershed number 5; Fox River and its environs; Figure 1). PFOS concentrations in livers of adult and juvenile mink from Illinois were not statistically significant ($p > 0.05$; two-tailed t -test) (Table 2). In contrast, concentrations of PFOS in adults were 2-fold greater than those measured in juvenile female mink from Massachusetts. The observed variations in PFOS concentrations between adults and juveniles could be explained by differences in feeding rates. A similar observation has been made for accumulation of butyltin compounds in dolphins, in which age-related increase in concentrations was less prominent (16). However, due to relatively great variability in the data, no conclusions regarding the mechanism for the observed differences can be made at this time. Mean PFOS concentrations were greater in females (1540 ng/g, wet wt) than those in males from Illinois (940 ng/g, wet wt), but the difference was not statistically significant ($p = 0.09$; two-tailed t -test). The greater mean concentration of PFOS in adult females from Illinois was due to the presence of elevated concentrations of PFOS in a few individuals collected from watershed 5 (Figure 2). There was no significant relationship between PFOS concentrations and body weight or liver weight for mink from Illinois ($p > 0.05$).

Mean PFOS concentrations in adult male mink livers from Massachusetts (450 ng/g, wet wt) was greater than those in

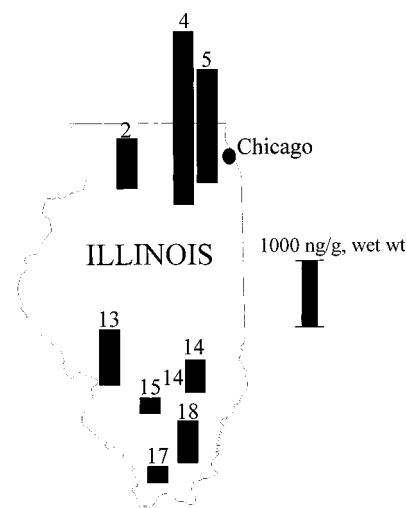


FIGURE 2. Spatial distribution in concentrations of PFOS in mink livers from Illinois. Bars indicate concentration (ng/g, wet wt) in livers. Numbers indicate watersheds.

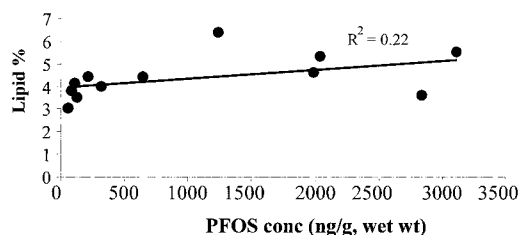


FIGURE 3. Relationship between concentrations of PFOS and lipid content in mink livers from South Carolina and Louisiana.

adult females (220 ng/g, wet wt), but this was not statistically significant ($p = 0.07$, two-tailed t -test). This result differs from that observed for persistent organochlorine compounds such as PCBs or DDTs, in which adult females generally contain significantly lesser concentrations than do males (17). This is attributed to excretion of organochlorines by females through parturition and lactation. Nevertheless, accumulation feature of PFOS is similar to those observed for butyltin compounds (16), in which no difference between genders was observed. These results indicate that the factors controlling accumulation of PFOS are different from those of organochlorines. PFOS, like butyltin compounds, binds to specific proteins in liver and blood plasma and are expected to undergo entero-hepatic circulation due to their ionic properties (18). In contrast, neutral, lipophilic contaminants such as organochlorines tend to accumulate in fatty tissues over a period of time, which results in an age-related increase of concentrations. To examine the relationship of PFOS concentrations to lipid content in livers, lipid content in livers was measured gravimetrically from methylene chloride and hexane (3:1, 400 mL) extracts of mink collected from South Carolina and Louisiana. Lipid content in liver tissues of mink varied from 3.6 to 6.4%. Concentrations of PFOS in mink livers were not significantly related to lipid content (Figure 3), which further supports the conclusion that PFOS accumulation was not determined by lipophilicity.

A spatial evaluation of PFOS concentrations in mink showed that mink from Illinois and South Carolina had significantly greater concentrations than those from Massachusetts and Louisiana ($p < 0.05$). Furthermore, a considerable spatial difference in concentrations of PFOS was observed among different sampling locations within a state. For instance, concentrations of PFOS varied among various watersheds in Illinois. The greatest concentrations (mean: 2590 ng/g, wet wt) of PFOS were found in mink collected

TABLE 3. Concentrations (ng/g, Wet Wt) of PFOA, FOSA, and PFHxS in Mink Livers from the United States

| location | statistics | FOSA | PFHxS | PFOA |
|--------------------------------|---------------------------------|------------------|---------|-----------------|
| Illinois (<i>n</i> = 65) | % detects | 33.8 | 17 | 8 |
| | range ^a | <37–590 | <7–85 | 24 ^a |
| | mean (LOQ as zero) | 47 | 3.1 | 1.5 |
| | mean (LOQ at detection limit) | 65 | 7.4 | 27 |
| | mean of detectable observations | 138 | 18 | 20 |
| Massachusetts (<i>n</i> = 31) | % detects | 12.9 | 16 | 58 |
| | range | 170 ^b | <4.5–12 | <4.5–27 |
| | mean (LOQ as zero) | 12 | 1.7 | 4.6 |
| | mean (LOQ at detection limit) | 65 | 5.5 | 6.5 |
| | mean of detectable observations | 92 | 10 | 8 |
| South Carolina (<i>n</i> = 9) | % detects | 0 | 89 | 0 |
| | range | <75 | <7.5–39 | <19 |
| | mean (LOQ as zero) | 0 | 22 | 0 |
| | mean (LOQ at detection limit) | 75 | 23 | 19 |
| | mean of detectable observations | 0 | 25 | 0 |
| Louisiana (<i>n</i> = 7) | % detects | 0 | 0 | 0 |
| | range | <75 | <7.5 | <19 |
| | mean (LOQ as zero) | 0 | 0 | 0 |
| | mean (LOQ at detection limit) | 75 | 7.5 | 19 |
| | mean of detectable observations | 0 | 0 | 0 |

^a LOQs varied from 8 ng/g to 40 ng/g; only maximum concentration reported. ^b LOQs varied from 18 to 75 ng/g.

from watershed 4 in Kendall and Kane counties which are located within 40–50 km from Chicago, IL. Concentrations of PFOS in mink from watershed 4 were significantly greater than those from other watersheds except those from watershed 5 in McHenry county (mean: 1690 ng/g, wet wt). Watersheds 4 and 5 are close to urbanized and industrialized areas in the vicinity of Chicago, Illinois (Figure 2). The lowest concentrations of PFOS were found in mink collected from watersheds 15 and 17 in southern Illinois (240 ng/g, wet wt).

FOSA, PFHxS, and PFOA Concentrations in Mink. While PFOS was found in all of the mink livers analyzed, FOSA, PFHxS, and PFOA were detected in certain individuals at relatively lesser concentrations compared to those of PFOS (Table 3). Among FOSA, PFHxS, and PFOA, FOSA was the most frequently detected fluorochemical in mink livers from Illinois. PFOA occurred frequently in mink from Massachusetts, while PFHxS was frequently found in mink from South Carolina. Mink livers from Louisiana did not contain detectable concentrations any of these fluorochemicals. While PFOS is a metabolic product of several sulfonated perfluorochemicals such as *n*-methyl perfluorooctanesulfonamidoethanol [C₈F₁₇SO₂N(CH₃)CH₂CH₂OH], FOSA, PFOA, and PFHxS are intermediates in the production of several perfluorinated compounds. FOSA and PFOA are also products used in various commercial applications. For instance, FOSA is a metabolic product of *n*-ethyl perfluorooctanesulfonamide, which is used as an insecticide (Sulfluramid) to control cockroaches, termites, and ants (19). PFOA is an impurity in various formulations of perfluorochemicals including aqueous film fire-fighting foams (20). The greatest concentrations of FOSA, PFHxS, and PFOA in mink livers were 590, 85, and 27 ng/g, wet wt, respectively (Table 3). Spatial differences in the distribution pattern of PFOA, PFHxS, and FOSA indicated the existence of sources of the four analytes that are independent of each other. Nevertheless, FOSA, which was next in abundance to PFOS in mink from Illinois, was found in those individuals that contained elevated concentrations of PFOS. Concentrations of FOSA averaged 12% of the concentrations of PFOS in mink livers from Illinois. A significant positive relationship between concentrations of PFOS and FOSA was observed in mink livers that contained detectable concentrations of FOSA (Figure 4). These results indicate that the sources of exposure of mink to PFOS and FOSA are similar or coexistence of these compounds in sources.

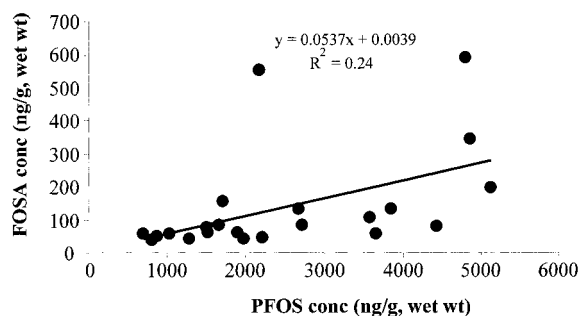


FIGURE 4. Relationship between concentrations of PFOS and FOSA in mink livers from Illinois (only those individuals with detectable concentrations of both PFOS and FOSA were compared).

PFHxS was not detected in most samples from Illinois, Massachusetts, or Louisiana. However, eight of nine samples from South Carolina contained detectable concentrations of PFHxS. Mean concentration of PFHxS in mink from South Carolina (25 ng/g, wet wt) was 1.2% of the concentrations of PFOS (2100 ng/g, wet wt). There was no significant correlation between concentrations of PFOS and PFHxS in mink livers from South Carolina (Figure 5a). Mink from Massachusetts had relatively greater frequencies of detection of PFOA. The mean concentration of PFOA (8 ng/g, wet wt) was 2.7% of the concentrations of PFOS (298 ng/g, wet wt) in mink livers from Massachusetts. There was no significant positive relationship between PFOS and PFOA or PFOA and PFHxS in mink livers from Massachusetts (Figure 5b). These results suggest that the sources of PFOA and PFHxS to mink are independent of PFOS. This is the first report to document the concentrations of FOSA, PFHxS, and PFOA in wildlife tissues although we have reported the occurrence of these compounds in wildlife tissues earlier (4).

Laboratory Mink Feeding Study. Carp collected from Saginaw River, MI, were substituted for marine fishes at levels of 10, 20, and 40% in the diets (feed) of adult ranch mink (Table 4). The mean concentration of PFOS in carp tissue was 270 ng/g, wet wt (range: 240–300 ng/g, wet wt). The mean concentration of PFOS in mink diet was 87 ng/g, wet wt (60–110 ng/g, wet wt). Thus, substitution of carp to mink diet at 10, 20, and 40% would result in final dietary concentrations of PFOS of 105, 124, 160 ng/g, wet wt, respectively. Concentrations of PFOS in livers of mink fed 10, 20, and 40% carp were 1120, 2830, and 3250 ng/g, wet wt,

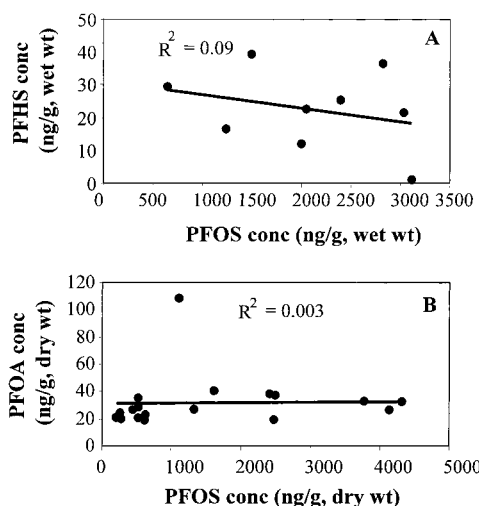


FIGURE 5. Relationship between concentrations of PFOS and PFHxS (South Carolina, top) PFOS and PFOA (Massachusetts, bottom) in mink livers.

TABLE 4. Mean Concentrations (ng/g, Wet Wt; Ranges in Parentheses) and Biomagnification Factors (BMF) of PFOS and FOSA in Livers of Mink Fed to Carp from Saginaw Bay, MI

| % of carp in diet | n | PFOS | FOSA | BMF ^a (av) |
|---------------------|-----|------------------|-------------|-----------------------|
| diet | 8 | 87 (60–110) | <19 | |
| carp | 2 | 270 (240–300) | <19 | |
| 10% carp fed mink | 5 | 1120 (590–1880) | 52 (33–83) | 11 |
| 20% carp fed mink | 6 | 2830 (1960–3680) | 51 (27–70) | 23 |
| 40% carp fed mink | 10 | 3250 (2130–4850) | 28 (<19–37) | 20 |
| 10% carp + 90% diet | 105 | | | |
| 20% carp + 80% diet | 124 | | | |
| 40% carp + 60% diet | 160 | | | |

^a BMF is for PFOS only.

respectively, suggesting a dose-related increase in concentrations of PFOS with an increase in the proportion of carp in the diet. Based on the dietary concentrations of PFOS, biomagnification factors in mink livers were estimated to range from 11 to 23 with a mean value of 18. This value is similar to or greater than those reported for PCBs or PCDDs/DFs in mink livers (15). The mink feeding study was originally designed to examine the effects of persistent organochlorine compounds in mink, and, therefore, effects associated with the study cannot be directly interpreted with fluorochemical concentrations measured in this study. Mink are relatively sensitive to the effects of dioxin-like compounds (15), and reproductive effects were observed even in the lowest treatment group (10% carp in the diet) (see ref 15 for details). Relative risks of fluorochemical concentrations in mink are discussed elsewhere (21). FOSA was detected in mink livers although this was not found in the diet at a quantitation limit of 19 ng/g, wet wt. Concentrations of FOSA in mink

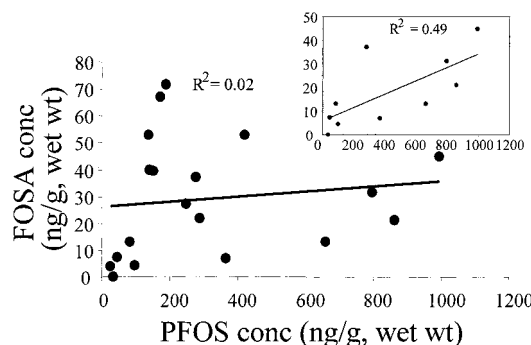


FIGURE 6. Relationship between concentrations of PFOS and FOSA in livers of river otters from Washington and Oregon (inset, plot of mink from Oregon alone).

livers were not related to the proportion of carp in the diet. The reason for this is not known, but it is possible that FOSA was present in the diet at low concentrations that accumulation into mink liver proceeded according to zero-order kinetics and was not dependent on concentration in the diet. It is also possible that FOSA was further metabolized in mink, although there exists no evidence to support this hypothesis. PFOA and PFHxS were neither found in the diet nor in mink livers at the LOQ of 35 ng/g, wet wt.

Fluorochemicals in River Otters. PFOS was detected in livers of all river otters collected from Washington and Oregon at concentrations ranging from 25 to 994 ng/g, wet wt (mean: 303 ng/g, wet wt) (Table 5). The greatest concentration of 994 ng/g, wet wt, was found in an adult male otter from the Willamette River in Albany, OR. Relatively lower concentrations were found in otters collected from the Yaquina, Soleduck, and Nehalem Rivers, which are coastal rivers that discharge into the Pacific Ocean. Greater concentrations were observed in relatively more urbanized areas such as Bremerton, Eglon, Fort Ward, and Silverdale in Puget Sound, WA. This further suggests that urbanized areas are the primary sources of fluorochemicals in the environment. FOSA was found in 95% of the river otters analyzed at concentrations ranging from <4 to 72 ng/g, wet wt (Table 5). The mean concentration of FOSA was 10% of the concentrations of PFOS in river otter livers. There was no significant relationship between concentrations of PFOS and FOSA in livers of river otters (Figure 6). However, when concentrations were grouped by state, there was a significant correlation between concentrations of PFOS and FOSA in livers of river otter from Oregon (Figure 6, inset). This may indicate location-specific differences in the sources of fluorochemicals. There was no significant relationship between body weight or age and concentrations of fluorochemicals in river otters ($p > 0.05$). This is similar to those found for marine mammals (6). In addition, this may indicate that the accumulation of fluorochemicals is not controlled by lipophilicity as has been observed for neutral organochlorine compounds (17).

TABLE 5. Concentrations of Perfluorochemicals (ng/g, Wet Wt; Ranges Are Given in Parentheses) in River Otters from Washington and Oregon

| state | location | n | age (yr) | body wt (kg) | PFOS | FOSA | PFHxS | PFOA |
|------------|------------------|---|-----------|--------------|---------------|-------------|-------|----------|
| Washington | Bremerton | 1 | 6 | 10.2 | 288 | 22 | <4 | <7.5 |
| | Eglon | 2 | 5 | 9.75 | 297 (173–422) | 60 | <4 | <7.5 |
| | Fort Ward | 3 | 5.7 (2–8) | 9.07 | 156 (139–189) | 55 (40–72) | <4–76 | <7.5–19 |
| | Silverdale | 2 | 2.5 (2–3) | 8.05 | 199 (151–248) | 33 (27–39) | <4–52 | <7.5–11 |
| | Soleduck River | 2 | 3.5 (3–4) | 8.85 | 43 (25–62) | <4–4 | <4 | <7.5 |
| Oregon | Willamette River | 7 | 3.6 (1–5) | 8.42 | 579 (97–994) | 23 (4.4–44) | <4–68 | <7.5–19 |
| | Yaquina River | 2 | 3 (2–4) | 7.83 | 39 (34–45) | <4–7.4 | <4 | <7.5–9.9 |
| | Nehalem River | 1 | 2 | 8.16 | 82.8 | 13 | <4 | <7.5 |

These results suggest that perfluorochemicals, in particular, PFOS is a widespread contaminant in mink and river otters from the United States. Unlike the more studied organochlorines, the accumulation of perfluorochemicals is not determined by their lipophilicity, which is evidenced by the lack of age or sex-related differences in concentrations. Toxic effects of PFOS are unknown, but related fluorochemicals have been shown to affect cell-cell communication, membrane transport, and process of energy generation and peroxisome proliferation (18). In particular, FOSA is one of the most potent uncouplers of oxidative phosphorylation (22). Toxic effects of PFOS to mink and river otters are unknown and are subjects of further investigation.

Acknowledgments

This study was supported by 3M (St. Paul, MN) with technical assistance of Drs. Kris Hansen, Lisa Clemen, and Harold Johnson. We thank several individuals who assisted in sample collection and analysis. We thank Dr. William W. Bowerman, Clemson University, for providing samples from South Carolina and Louisiana.

Literature Cited

- (1) Kissa, E. *Fluorinated Surfactants and Repellents*, 2nd ed.; Revised and updated; Marcel Dekker: New York, 2001.
- (2) U.S. Environmental Protection Agency. Perfluorooctyl Sulfonates: Proposed Significant New Use Rule. *Fed. Regist.* **2000**, *65*, 62319–62333.
- (3) Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Johnson, H. O. *Environ. Sci. Technol.* **2001**, *35*, 766–770.
- (4) Giesy, J. P.; Kannan, K. *Environ. Sci. Technol.* **2001**, *35*, 1339–1342.
- (5) Kannan, K.; Franson, J. C.; Bowerman, W. W.; Hansen, K. J.; Jones, P. D.; Giesy, J. P. *Environ. Sci. Technol.* **2001**, *35*, 3065–3070.
- (6) Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Gorzelany, J.; Hansen, K. J.; Jones, P. D.; Giesy, J. P. *Environ. Sci. Technol.* **2001**, *35*, 1593–1598.
- (7) Kannan, K.; Hansen, K. J.; Wade, T. L.; Giesy, J. P. *Arch. Environ. Contam. Toxicol.* **2002**, *42*, 313–318.
- (8) Key, B. D.; Howell, R. D.; Criddle, C. S. *Environ. Sci. Technol.* **1997**, *31*, 2445.
- (9) Olsen, G. W.; Burris, J. M.; Mandel, J. H.; Zobel, L. R. *J. Occup. Environ. Med.* **1999**, *41*, 799–806.
- (10) Aulerich, R. J.; Bleavins, M. R. In *Blue Book of Fur Farming*; Lamb, B. Ed.; Comm Marketing Inc.: Eden Prairie, MN, 1981; p 30.
- (11) Poole, K. G.; Elkin, B. T.; Bethke, R. W. *Arch. Environ. Contam. Toxicol.* **1998**, *34*, 406–413.
- (12) O'Brien, D. J.; Kaneene, J. B.; Poppenga, R. H. *Environ Health Perspect.* **1993**, *99*, 351–368.
- (13) U.S. Environmental Protection Agency. *Wildlife Criteria Portions of the Proposed Water Quality Guidance for the Great Lakes System*; Office of Science and Technology and Office of Water: Washington, DC, 1993.
- (14) Heaton, S. N.; Bursian, S. J.; Tillitt, D. E.; Render, J. A.; Jones, P. D.; Verbrugge, D. A.; Kubiak, T. J.; Aulerich, R. J. *Arch. Environ. Contam. Toxicol.* **1995**, *28*, 334–343.
- (15) Tillitt, D. E.; Gale, R. W.; Meadows, J. C.; Zajicek, J. L.; Peterman, P. H.; Heaton, S. N.; Jones, P. D.; Bursian, S. J.; Kubiak, T. J.; Giesy, J. P.; Aulerich, R. J. *Environ. Sci. Technol.* **1996**, *30*, 283–291.
- (16) Kannan, K.; Senthilkumar, K.; Loganathan, B. G.; Takahashi, S.; Odell, D. K.; Tanabe, S. *Environ. Sci. Technol.* **1997**, *31*, 296–301.
- (17) Kajiwara, N.; Kannan, K.; Muraoka, M.; Watanabe, M.; Takahashi, S.; Gulland, F.; Olsen, H.; Blankenship, A. L.; Jones, P. D.; Tanabe, S.; Giesy, J. P. *Arch. Environ. Contam. Toxicol.* **2001**, *41*, 90–99.
- (18) Giesy, J. P.; Kannan, K. *Environ. Sci. Technol.* **2002**, *36*, 147A–152A.
- (19) Vitayavirasuk, B.; Bowen, J. M. *Pestic. Sci.* **1999**, *55*, 719–725.
- (20) Moody, C. A.; Field, J. A. *Environ. Sci. Technol.* **2000**, *34*, 3864–3870.
- (21) Newsted, J. L.; Kannan, K.; Giesy, J. P. *Environ. Sci. Technol.* Submitted for publication.
- (22) Schnellmann, R.; Manning, R. *Biochim. Biophys. Acta* **1990**, *1016*, 344–348.

Received for review January 6, 2002. Revised manuscript received April 5, 2002. Accepted April 10, 2002.

ES0205028