Perfluorooctanesulfonate and Related Fluorochemicals in the Amur Tiger (*Panthera tigris altaica*) from China

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Perfluorinated compounds (PFCs) are used in a variety of industrial applications. We tested the hypothesis that, in Amur tigers (*Panthera tigris altaica*), captivity in industrialized areas increases PFC levels, potentially presenting a health risk to these animals. Serum samples were collected from 100 tigers from industrialized or nonindustrialized regions in China with nonpoint sources of PFCs. Mean concentrations of PFCs in these samples ranged from 1.57 ± 0.83 ng/mL in nonindustrial Hailin to 4.31 ± 2.90 ng/mL in industrial Beijing. PFC concentrations were significantly higher in tigers from the industrial city of Harbin than those from Hailin ($p < 0.05$). Perfluorooctanesulfonate (PFOS) was the most abundant PFC in all tigers and increased with age, regardless of industrial/nonindustrial background ($p < 0.01$). However, PFOS concentrations were 2−4 orders of magnitude less than the current no-observed-effect level. In addition, overall PFC levels in Amur tigers were low compared with various species living in other countries, consistent with the relatively short history of PFC use in China. These results are consistent with the hypothesis that captivity in industrialized areas increases PFC levels in Amur tigers. They also suggest that PFC accumulation will persist, and even increase, with continued use of PFCs in China.

Introduction

Perfluorinated compounds (PFCs) are a diverse group of chemicals that are used in a variety of specialized consumer and industrial products, such as paper products, food packaging, fire-retarding foams, cosmetics, upholstery, surfactants, and surface protectors in carpets, textiles, and leather (reviewed in refs *1, 2)*. PFCs contain a carbon−fluorine covalent bond that confers resistance to hydrolysis, photolysis, biodegradation, and metabolism (*3*). Indeed, PFCs are present throughout all global environments (*4*), including remote locations such as the Arctic (*5*). PFCs alter cholesterol and steroid levels, mitochondrial bioenergetics, and lipid metabolism (*6, 7*). PFC exposure is also associated with endocrine, reproductive, and developmental problems (*8, 9*).

PFC accumulation has been reported to occur in several wildlife species, including marine animals and sea birds (*4, 10*−*13*). Only a few studies have investigated PFC accumulation in terrestrial mammals (*14*−*16*). In many cases, the source and mode of transmission of PFCs to wildlife are unknown. However, a likely source is atmospheric fluorotelomer alcohol (FTOH), which is emitted through industrial activities and produces perfluorinated carboxylic acids (PFCAs) upon degradation (*17*). For this reason, animals residing in environments with high levels of industrial activity might be expected to accumulate high levels of PFCs, making them vulnerable to the adverse effects of these contaminants. The Amur tiger (*Panthera tigris altaica*) may be one such example. The Amur tiger is a Category I protected species under the Wild Animal Protection Law in China. It is found in only northeast China, far eastern Russia, and North Korea. Illegal poaching and habitat destruction have brought this species to the brink of extinction, with a total wild population of approximately 450 and wild population of only about 20 in China (*18*). Fortunately, captive tiger breeding in China has expanded the captive population to over 4000 animals in recent years (*19*). However, captivity in industrialized areas may increase the exposure of these animals to PFCs, possibly adversely affecting their health.

The objective of the current study was to assess PFC exposure in Chinese Amur tigers relative to other species worldwide. It was also performed to test the hypothesis that captivity in industrial areas increases serum PFC levels in Amur tigers. Blood PFC levels were analyzed in tigers from five separate centers situated in industrialized and nonindustrialized regions of China. Since little information exists on gender- and age-specific PFC accumulation within a single species, the relationship of each variable with PFC accumulation was also analyzed (*20*−*22*).

Materials and Methods

Sample Collection. From April to December 2006, blood samples were collected from 100 animals located in industrial areas or nonindustrial areas. According to the international criterion of industrial level assessment, the area will be of early industrial level if its GDP per capita exceeds 1000 U.S. dollars. The average GDP per capita of Beijing, Harbin, Guilin, Hailin, and Antu were about 3156, 2339, 2022, 736, and 726 dollars one year during 2000−2006, respectively (*23, 24*). Harbin ($n = 31$), Beijing ($n = 3$), and Guilin (Guangxi Province) ($n = 22$) were selected as industrial areas. The nonindustrial areas were Hailin (Helongjiang Province) ($n = 17$) and Antu (Jilin Province) ($n = 27$) (Figure S1, Supporting Information). All Amur tigers had been present in their respective centers for at least 0.5−1 year prior to sample collection. The blood collection protocol was approved by the Institute of Zoology, Chinese Academy of Sciences Institutional Animal Care Committee and State Forestry Administration of China. In all cases, the anesthesia protocol was identical to that used for routine handling of felids in the zoos. Briefly, the animals

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TABLE 1. Mean Plasma PFC Concentrations in Terrestrial and Marine Mammals

species	N	location	PFC concentration (ng/mL or ng/g wet wt)[a] PFOS	PFHxS	PFDA	PFNA	PFOA	ref
Amur tiger	100	China	1.41	0.11	0.07	0.32	0.11	
polar bear (*Ursus maritimus*)	NR	Svalbard	1290 (914)	2940 (26727)	43 (614)	102 (318)	21 (190)	*28*
bottlenose dolphin (*Tursiops truncates*)	2	Bermuda	49 (34)	5.9 (53)	9.6 (137)	17 (53)	0.8 (7)	*33*
	42	Indian River Lagoon, FL	642 (455)	73 (663)	18 (257)	13 (40)	12 (109)	*33*
	5	New Jersey	751 (532)	164 (1490)	45 (642)	326 (1018)	72 (90)	*33*
	13	Sarasota Bay, FL	780 (553)	40 (363)	22 (314)	25 (78)	6.3 (57)	*33*
	47	Charleston, SC	1315 (932)	46 (418)	159 (2271)	63 (196)	44 (400)	*33*
giant panda (*Ailuropoda melanoleuca*)	9	Beijing, China	11.10 (7)	–	–	–	0.80 (7)	*16*
red panda (*Ailurus fulgens*)	12	Chongqing, China	15.65 (11)	–	–	–	2.29 (20)	*16*

[a] Values in parenthesis represent the mammal-to-tiger ratio of PFC concentrations.

were sedated with darts containing xylazine (1.0 mg/kg) and ketamine (10.0 mg/kg). If more prolonged relaxation was required, 0.5 mg/kg diazepam was administered. After anesthetization by a veterinarian, animals underwent blood collection (3−5 mL) from the left forearm. Samples were transferred to polypropylene cryovials and kept at −20 °C until analysis. The age, gender, and sampling locations were recorded (Table S1, Supporting Information).

Extraction and Cleanup Methods. Chemical extraction from blood/serum was performed similarly to a previously described procedure, with an additional cleanup step (*20*). The chemicals used are provided in the Supporting Information, along with the details of the extraction procedure.

High-Performance Liquid Chromatography−Tandem Mass Spectrometery (HPLC−MS/MS). Final extracts were analyzed using an Agilent HP1100 liquid chromatography system interfaced with a Micromass (Beverly, MA) Quattro Ultima Pt mass spectrometer, which was operated in electrospray negative ionization mode as previously reported (*25*). In brief, a 10 μL aliquot of the sample extract was injected onto a guard column (XDB-C8, 2.1 mm i.d. × 12.5 mm, 5 μm; Agilent Technologies, Palo Alto, CA) connected to a Betasil C18 column (2.1 mm i.d. × 50 mm length; Thermo Hypersil-Keystone, Bellefonte, PA). The mobile phase consisted of 2 mM ammonium acetate−methanol, with 10% methanol serving as the starting mobile phase. MS/MS parameters were optimized to transmit the $[M - K]^-$ or $[M - H]^-$ ion (Table S2, Supporting Information). Detailed instrumental parameters are described elsewhere (*25*).

Data Quality Assurance and Quality Control. Data quality control and assurance included instrumental blanks, procedural (method) blank, matrix spikes, and duplicated analysis. All HPLC components were free of polytetrafluorethylene (PTFE) to minimize perfluorocarboxylic acid (PFCA) contamination and achieve lower detection limits. Recoveries of native chemicals were tested in a series of preliminary experiments. Mean analyte recoveries ranged from 86 to 145% ($n = 4$ per analyte) (Table S2, Supporting Information). PFC concentrations were not corrected for recoveries. Procedural blanks were tested with every eight samples to check for possible laboratory contamination and interference, and all were below the limit of quantification (LOQ). For all analytes, concentrations measured in methanol washes from blank sample collection tubes were less than 7 pg/mL. LOQs were defined as the value corresponding to the peak with a signal-to-noise ratio of 10. The LOQ was 50 pg/mL for perfluorooctanesulfonate (PFOS), perfluorohexanesulfonate (PFHxS), perfluorobutanesulfonate (PFBS), perfluorodecanoic acid (PFDA), perfluorononanoic acid (PFNA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), and unsaturated fluorotelomer carboxylate (8:2 FTUCA). The LOQ for perfluorohexanoic acid (PFHxA) and saturated fluorotelomer carboxylate (8:2 FTCA) was 250 pg/mL.

PFC concentrations were extrapolated from calibration curves that were generated using a concentration series of 0, 2, 10, 50, 200, 1000, 5000, 20 000 pg/mL. The deviation of every point from the standard was less than 20%. The linearity and repeatability of these calibration curves were confirmed prior to each set of determinations. In addition, the reliability of this method was verified through participation in the First International Laboratory Calibration Study coordinated by ASG-RIVO and Örebro University (*26*).

Statistical Analysis. PFC concentrations for all samples were logarithmically (ln) transformed to ensure a normal distribution of the data. The normality of the data was analyzed using a Kolmogorov−Smirnov test. A *t*-test was used to compare PFC concentrations between genders. Pearson correlation analysis was performed to examine the relationship between PFCs. The differences in PFC levels among tiger populations were analyzed using one-way analysis of variance (ANOVA), following by Duncan's multiple range test. Linear regression was performed to evaluate relationships between age and PFC concentrations. Samples with concentrations below the LOQ were assigned zero. All statistical analyses were conducted with SPSS software (Version 13.0 for Windows, SPSS Inc., Chicago, IL).

Results and Discussion

PFC Levels in the Amur Tiger. In all tigers examined, PFBS, PFHpA, PFHxA, 8:2 FTCA, and 8:2 FTUCA were below the LOQs. The mean concentrations of remaining PFCs (i.e., PFOS, PFNA, PFHxS, PFOA, and PFDA) were above the LOQs in all locations. The mean concentrations, in order of decreasing abundance, were 1.41 ± 0.15 ng/mL for PFOS, 0.32 ± 0.03 ng/mL for PFNA, 0.11 ± 0.02 ng/mL for PFHxS, 0.11 ± 0.01 ng/mL for PFOA, and 0.07 ± 0.01 ng/mL serum for PFDA ($n = 100$) (Table 1).

For PFOS, concentrations ranged from 0.10 to 9.82 ng/mL (Table S3, Supporting Information), with the highest and lowest PFOS concentrations being found in male tigers (age 16 years) and juvenile female tigers (age 1 year) from Guilin, respectively. The highest mean PFOS concentration (3.95

ng/mL) was found in tigers from Beijing and was 1−4 fold higher than concentrations found in tigers from other locations.

PFNA, the second most prevalent PFC in Amur tigers, had mean concentrations ranging from 0.13 to 0.89 ng/mL and detection frequencies from 59% to 100%. These results are consistent with the observations of Martin et al. (*7*) and Smithwich et al. (*10*), who found that PFNA was the dominant PFCA in the liver of polar bears and ringed seals.

For PFHxS, mean concentrations ranged from 0.03 to 0.29 ng/mL and the detection frequency from 25% to 81%. PFHxS concentrations were approximately 5−34-fold less than PFOS concentrations. PFHxS is only sporadically detected in the environment because PFHxS is the sulfonate form of perfluorohexanesulfonyl fluoride (PHSF), a component of fire-fighting foams, an intermediate in the production of PFCs, and an impurity in PFOS-based formulations (*27*).

PFOA, the third or fourth most abundant PFC, had mean concentrations ranging from 0.04 to 0.18 ng/mL in Amur tigers. In a previous study, PFOA was the second highest PFC in wildlife serum samples (*28*). Nevertheless, the finding that PFOA comprises about 8% of total PFCs (i.e., the sum of PFOS, PFHxS, PFDA, PFNA, and PFOA) in Hailin Amur tigers is consistent with its contribution in polar bears, which is about 3% of total PFCs (*7*). The low PFOA composition of total PFCs might be indicative of the relatively low bioaccumulation and concentration potential of PFOA (*28*). Odd-number chain-length PFCs generally accumulate more than even-number chain-length PFCs. The PFC profiles observed here support the hypothesis that FTOH degradation may be one source of PFCs. For example, the atmospheric degradation of 8:2 FTOH yields similar PFOA and PFNA quantities (*17*). However, longer-chain PFCs are more bioaccumulative (i.e., PFNA > PFOA), resulting in higher biota concentrations of PFNA than PFOA (*29*).

Finally, the least abundant PFC was PFDA, which had concentrations that ranged from <LOQ to 0.33 ng/mL. The highest mean PFDA concentrations (0.15 ± 0.08 ng/mL for female tigers and 0.10 ± 0.07 ng/mL for male) were found in tigers from Antu at a detection frequency of 81%. Taken together, these results reveal that detectable levels of PFCs are present in captive tigers. All locations sampled in this study were at least 400 miles from PFC plants (i.e., Shanghai, Shangdong, Jiangsu, Sichuan, Zhejiang, Jinan, and Liaoning), implying that PFCs were derived from nonpoint sources (*30*). The degradation of FTOH in the atmosphere might be one such source (*17*).

Comparison of PFCs Concentrations in Amur Tigers and Wild Animals. A comparison of PFC concentrations in Amur tigers with values reported for other wildlife revealed that overall PFC concentrations in Amur tigers were lower than those reported in other terrestrial and marine mammals. The mean PFOS and PFOA concentrations in Amur tigers were both 7-fold less than concentrations in the captive giant panda and 11- and 20-fold less than those in the red panda in China, respectively (*16*). Similarly, PFOS and PFOA concentrations were 34- and 7-fold less in Amur tigers than those in bottlenose dolphins in Bermuda, respectively (Table 1). Concentrations of PFHxS, PFDA, and PFNA in Amur tigers were at least 40-fold less than those found in bottlenose dolphins around the world (Table 1). Mean PFOS concentrations in Amur tigers were similar to those in the northern fur seal from the coastal waters of Alaska and also similar to the loggerhead turtle from the southeastern coast of the United States (*31, 32*). In contrast, mean PFOS concentrations were slightly greater in Amur tigers than in ringed seals from the Canadian Arctic (*33*). The overall lower PFC concentrations in Amur tigers may be attributable to the lack of direct PFC point source at all sampling locations. It is also consistent with the fact that PFCs have been used for a relatively short

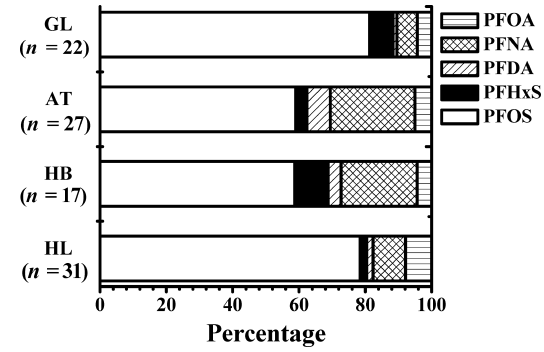

FIGURE 1. Composition of serum PFCs in Amur tigers from Harbin (HB), Hailin (HL), Guilin (GL), and Antu (AT).

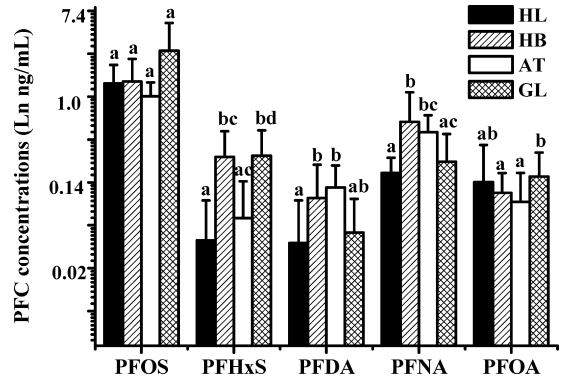

FIGURE 2. Serum PFC concentrations in Amur tigers from Harbin (HB), Hailin (HL), Guilin (GL), and Antu (AT). Data are expressed as mean ± standard derivation. Columns with different letters are significantly different ($p < 0.05$, ANOVA with Duncan's multiple range test).

period in China compared with other developed countries such as America and Japan.

Geographic Trends. An analysis of PFC concentrations by geographic location revealed that, although most PFC compositions differed among each location, PFOS and PFNA were the major components in all locations (Figure 1). Figure 2 shows the serum PFCs concentrations in Amur tigers from Harbin, Guilin, Hailin, and Antu. (PFC concentration data for Beijing Amur tigers were omitted from this and subsequent analyses due to the small sample size). PFOS levels did not significantly differ among tigers in the four locations. PFHxS, PFDA, and PFNA concentrations were significantly higher in Amur tigers from Harbin (most industrialized area included in this study) than those from Hailin ($p < 0.05$ for all) (Figure 2). The sources of PFCs in these four areas have not been documented, and only sparse information concerning PFC production in China is available. Nevertheless, the finding that PFCs are present at higher concentrations in tigers from industrialized region (Harbin) than in those from remote region (Hailin) is consistent with the idea that the degree of PFCs exposure is related to the level of industrial activities in a particular area. These results were similar to our previous study that PFC blood concentrations of an individual from Shenyang (industrial area) were generally higher than those from Jintan (remote area) (*20*).

Gender- and Age-Related PFC Accumulation. The influence of gender on the accumulation of PFCs is unknown, although experimental trials suggest that females have higher PFOS clearance rates and accumulate lower concentrations of these compounds than males (*32*). We investigated possible gender- and age-related PFC accumulation in a pooled sample group consisting of 47 males with ages ranging from 1 to 16 years and 50 females with age ranges of 1 to 15 years. However, both PFDA ($p = 0.058$) and PFNA ($p = 0.076$) were

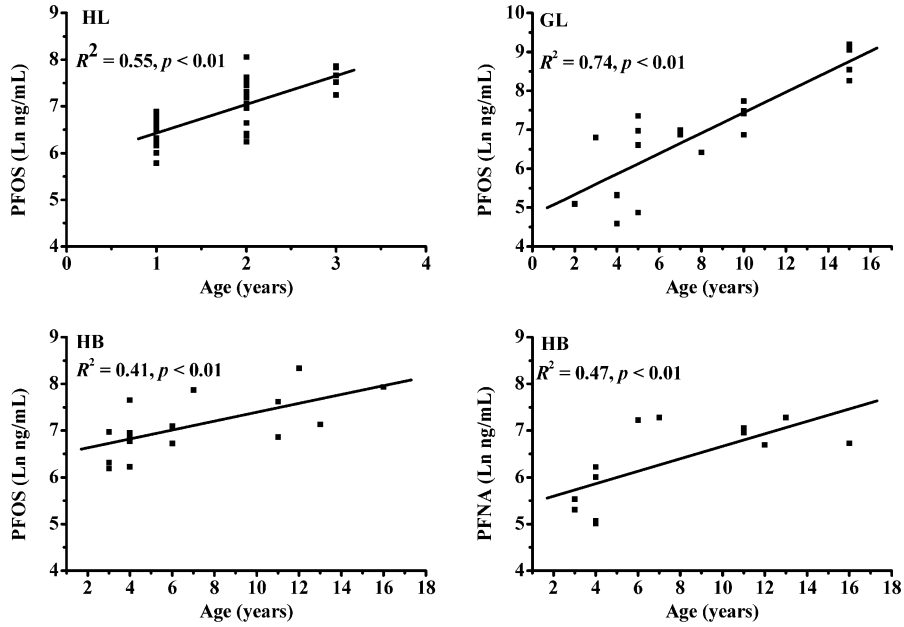

FIGURE 3. Linear regression analysis of age and PFC concentrations in Amur tigers from Harbin (HB), Hailin (HL), and Guilin (GL). Coefficients of variation (*R*) and *p* values are shown.

slightly higher in females ($n = 50$) than males ($n = 47$). PFOS, PFHxS, and PFOA did not differ between genders ($p > 0.05$). Analysis of gender differences by location revealed that significant differences existed only in PFDA and PFNA levels. PFDA concentrations were greater in juvenile (<3 years) females than juvenile males ($p < 0.05$) in Hailin, although the percentage of samples above the LOQ for PFDA was less than 50% and the sample size was small (female, $n = 5$; male, $n = 6$). In the Harbin and Antu, females had higher PFNA concentrations than males ($p < 0.05$). The finding that a trend existed toward increased PFOS levels in females is consistent with findings in harbor porpoises (*34*). Contrastingly, the mean PFOS concentrations in adult male minks in Massachusetts were greater than those in adult females, but this finding was not statistically significant (*13*). In addition, gender-related differences in PFCs concentrations were not found in panda (*16*), humans (*20*), bottlenose dolphins (*T. truncates*) (*32*), polar bears, or ringed seals (*11*).

PFOS levels increased with age at three of the sampling locations ($p < 0.01$), with the exception being Antu (Figure 3). PFHxS and PFOA increased with age only at Guilin ($p < 0.01$). A significant negative relationship between age and PFDA concentrations was present in juvenile Amur tigers (<3 years) in Hailin ($R^2 = 0.31$, $p < 0.05$) and Antu ($R^2 = 0.25$, $p < 0.01$). PFNA concentrations significantly increased with age at Harbin and Guilin ($p < 0.01$). Since PFNA concentrations significantly differed according to both age and gender in tigers from Harbin, we investigated age-related changes in PFNA and PFDA levels within each gender. No significant relationship was present between age and C_{9-10} PFCA (PFDA and PFNA) concentrations within the same gender, suggesting that only gender affects PFDA and PFNA concentrations. When the sex-specific data was pooled, only PFOS (female, $n = 50$, $p < 0.05$; male, $n = 47$, $p < 0.01$) and PFHxS (female, $n = 22$, $p < 0.05$; male, $n = 21$, $p < 0.01$) significantly increased with age. Several studies have demonstrated age-related effects in PFC levels. For example, PFC concentrations increase with age in mallards (*Anas platyrhynchos*) for PFOS (*32*), in juvenile male bears for PFOS, PFNA, and C_{10}–C_{14} PFCAs (*10*), in Arctic ringed seals for perfluorododecanoic acid (PFDoA) and PFOS (*35*), and in ridley turtles for PFOS (*36*). Conversely, PFCs decrease with age in bottlenose dolphins (*32*) and juvenile harbor porpoises (*34*). No correlations were observed between PFCs and age in gray and ringed seals from the Baltic or Mediterranean Sea for PFOS (*37*) or in panda (*16*) and humans (*20*) in China for PFOA and PFOS. Our results clearly demonstrate that PFOS concentrations are related to age and that PFDA and PFNA concentrations are related to gender in Amur tigers. However, since PFC bioaccumulation is a complex process, multiple other factors may contribute to the gender- and age-related PFC bioaccumulation observed here.

Relationships between PFCs. This analysis included data sets only for PFCs that were detected at frequencies greater than 50%. We found significant positive correlations between multiple PFCs in Harbin (Figure S2, Supporting Information), Guilin (Figure S3, Supporting Information), and Antu (Figure S4, Supporting Information). Positive correlations between PFOS and PFHxS concentrations were observed in both Harbin ($R^2 = 0.61$, $p < 0.01$, $n = 14$) and Guilin ($R^2 = 0.78$, $p < 0.01$, $n = 12$). This finding suggests that sources of PFOS and PFHxS exposure may be similar in Harbin and Guilin. Positive correlations between PFOS and PFNA ($R^2 = 0.79$, $p < 0.01$, $n = 12$) as well as between PFOS and PFOA ($R^2 = 0.52$, $p < 0.01$, $n = 13$) were observed in the Guilin samples. In addition, positive correlations were observed between PFDA and PFNA in Harbin ($R^2 = 0.58$, $p < 0.05$, $n = 9$) and Antu ($R^2 = 0.40$, $p < 0.01$, $n = 22$) as well as between PFNA and PFOA in Guilin ($R^2 = 0.54$, $p < 0.01$, $n = 12$).

Analysis of data combined from the four locations (Antu, Guilin, Hailin, and Harbin) revealed that PFOS concentrations were positively correlated with PFHxS ($p < 0.01$), PFOA ($p < 0.05$), and PFNA concentrations ($p < 0.01$). PFDA concentrations were positively correlated with PFNA ($p < 0.01$) and PFOA concentrations ($p < 0.05$), while PFHxS concentrations were positively correlated with PFNA concentrations ($p < 0.01$). The positive linear association between these PFCs suggests that they arise from a common source in all regions.

Risk Assessment. Since PFOS was the dominant PFC in captive tigers, we performed a basic risk assessment of this compound. PFOS may disrupt homeostasis of DNA metabolism by inducing DNA strand breaks and/or affecting DNA repair (*38*). PFOS also has deleterious effects on membrane integrity, resulting in necrosis of liver cells (*38*). The risk of PFOS exposure to Amur tigers was assessed using a previously described method (*20*) in which PFOS risk is estimated by comparing the probability of exceedance to

several points of departure or toxicity reference values (TRVs). Protective values, the benchmark internal concentrations (BMICs), were chosen as "points of departure" for risk characterization. Three TRVs were selected for points of departure. The first was 33 μg/mL, which was derived from the lower 95% confidence limit of the BMIC based on rat pup weight during lactation. The second was 44 μg/mL, the no-observed adverse effect level of rat liver toxicity. The final TRV was 62 μg/mL, the lower 95% confidence limit of the BMIC (10% response) for liver tumor formation in rats. PFOS concentrations in all Amur tigers were lower than the TRVs. Thus, all PFOS concentrations were 2−4 orders of magnitude less than the current no-observed-effect level (NOEL). Nevertheless, this risk assessment needs further refinement due to inherent limitations of the information regarding the physiological, toxicological, ecological effects of PFCs in terrestrial mammals, and the potential combined effects of various PFCs.

In conclusion, our results are consistent with the hypothesis that captivity in industrialized areas increases serum PFC levels in Amur tigers. The overall low PFC levels in these animals compared to terrestrial wildlife in other countries is consistent with the relatively short duration of PFC use in China and suggests that continued use of these compounds will lead to greater PFC accumulation in Amur tigers. Additional studies using larger sample sizes and measurable PFC sources will be necessary to fully understand the mode of transmission and biological consequences of these industrial chemicals.

Acknowledgments

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Supporting Information Available

The chemicals used and the full methods details are provided. Additional information regarding sampling and geographic locations is provided in Table S1 and Figure S1. Mass determination of analytes and matrix spike recoveries are presented in Table S2. The mean, standard deviation, and range of serum PFC concentrations (ng/mL) in tigers from different locations in China are provided in Table S3. Correlations between PFCs are shown in Figure S2 for Harbin, Figure S3 for Guilin, and Figure S4 for Antu. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Hekster, F. M.; Laane, R. W. P. M.; de Voogt, P. Environmental and toxicity effects of perfluoroalkylated substances. *Rev. Environ. Contam. Toxicol.* **2003**, *179*, 99–121.

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

(3) Key, B. D.; Howell, R. D.; Criddle, C. S. Fluorinated organics in the biosphere. *Environ. Sci. Technol.* **1997**, *31*, 2445–2454.

(4) Giesy, J. P.; Kannan, K. Perfluorochemical surfactants in the environment. *Environ. Sci. Technol.* **2002**, *36*, 146A–152A.

(5) Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C.; Mabury, S. A. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environ. Sci. Technol.* **2004**, *38*, 373–380.

(6) Kennedy, G. L., Jr.; Butenhoff, J. L.; Olsen, G. W.; O'Connor, J. C.; Seacat, A. M.; Perkins, R. G.; Biegel, L. B.; Murphy, S. R.; Farrar, D. G. The toxicology of perfluorooctanoate. *Crit. Rev. Toxicol.* **2004**, *34*, 351–384.

(7) Guruge, K. S.; Yeung, L. W. Y.; Yamanaka, N.; Miyazaki, S.; Lam, P. K. S.; Giesy, J. P.; Jones, P. D.; Yamashita, N. Gene expression profiles in rat liver treated with perfluorooctanoic acid (PFOA). *Toxicol. Sci.* **2006**, *89*, 93–107.

(8) Sonne, C.; Dietz, R.; Leifsson, P. S.; Born, E. W.; Letcher, R. J.; Kirkegaard, M.; Muir, D. C.; Riget, F. F.; Hyldstrup, L. Do organohalogen contaminants contribute to histopathology in liver from East Greenland polar bears (*Ursus maritimus*). *Environ Health Perspect.* **2005**, *113*, 1569–1574.

(9) Martin, J. W.; Whittle, D. M.; Muir, D. C.; Mabury, S. A. Perfluoroalkyl contaminants in a food web from Lake Ontario. *Environ. Sci. Technol.* **2004**, *38*, 5379–5385.

(10) Smithwick, M.; Muir, D. C.; Mabury, S. A.; Solomon, K. R.; Martin, J. W.; Sonne, C.; Born, E. W.; Letcher, R. J.; Dietz, R. Perfluoroalkyl contaminants in liver tissue from East Greenland polar bears (*Ursus maritimus*). *Environ. Toxicol. Chem.* **2005**, *24*, 981–986.

(11) 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 the Mediterranean Seas. *Environ. Sci. Technol.* **2002**, *36*, 3120–3126.

(12) Kannan, K.; Hansen, K. J.; Wade, T. L.; Giesy, J. P. Perfluorooctanesulfonate in oysters, *Crassostrea virginica*, from the Gulf of Mexico and the Chesapeake Bay, USA. *Arch. Environ. Contam. Toxicol.* **2002**, *42*, 313–318.

(13) Kannan, K.; Newsted, J.; Halbrook, R. S.; Giesy, J. P. Perfluorooctanesulfonate and related fluorinated hydrocarbons in mink and river otters from the United States. *Environ. Sci. Technol.* **2002**, *36*, 2566–2571.

(14) Hoff, P. T.; Scheirs, J.; Van de Vijver, K.; Van Dongen, W.; Esmans, E. L.; Blust, R.; De Coen, W. Biochemical effect evaluation of perfluorooctane sulfonic acid-contaminated wood mice (*Apodemus sylvaticus*). *Environ Health Perspect.* **2004**, *112*, 681–686.

(15) Guruge, K. S.; Taniyasu, S.; Miyazaki, S.; Yamanaka, N.; Yamashita, N. Age dependent accumulation of perfluorinated chemicals in beef cattle. *Organohalogen Compd.* **2004**, *66*, 4029–4035.

(16) Dai, J.; Li, M.; Jin, Y.; Saito, N.; Xu, M.; Wei, F. Perfluorooctanesulfonate and periluorooctanoate in red panda and giant panda from China. *Environ. Sci. Technol.* **2006**, *40*, 5647–5652.

(17) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. Degradation of fluorotelomer alcohol; A likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* **2004**, *38*, 3316–3321.

(18) Andrew, C. K.; Andrew, J. D. Biogeographical change in the tiger *Panthera tigris*. *Anim. Conserv.* **2000**, *3*, 113–124.

(19) Government of China. Fact Sheet. Information document issued by the delegation of the People's Republic of China to the 54th meeting of the CITES standing committee, Geneva, Switzerland, 2−6 October, 2006.

(20) Yeung, L. W.; So, M. K.; Jiang, G.; Taniyasu, S.; Yamashita, N.; Song, M.; Wu, Y.; Li, J.; Giesy, J. P.; Guruge, K. S.; Lam, P. K. Perfluorooctanesulfonate and related fluorochemicals in human blood samples from China. *Environ. Sci. Technol.* **2006**, *40*, 715–720.

(21) Jin, Y.; Saito, N.; Harada, K. H.; Inoue, K.; Koizumi, A. Historical trends in human serum levels of perfluorooctanoate and perfluorooctane sulfonate in Shenyang, China. *Tohoku J. Exp. Med.* **2007**, *212*, 63–70.

(22) Liu, B.; Jin, Y.; Yu, Q.; Wang, K.; Dong, G.; Li, H.; Saitou, N.; Sasaki, K. Investigation of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) pollution in the surface water of the Songhua River (in Chinese, English abstract). *Acta Sci. Circumstantiae* **2007**, *27*, 480–486.

(23) http://www.eeffee.com/index.php/viewnews-132397.html.

(24) http://www.antu.gov.cn/government/class_index_zx.htm.

(25) Taniyasu, S.; Kannan, K.; So, M. K.; Gulkowska, A.; Sinclair, E.; Okazawa, T.; Yamashita, N. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. *J. Chromatogr. A* **2005**, *1093*, 89–97.

(26) Lindstrom, G.; Karrman, A.; Zammitt, A.; Van Bavel, B.; Van der Veen, I.; Kwadijk, C.; de Boer, J.; van Leeuwen, S. The 1st worldwide interlaboratory study on perfluorinated compounds in environmental and human samples. *Proceedings of the 2005 International FLUOROS Symposium. An International Symposium on Fluorinated Alkyl Organics in the Environment; Toronto, Canada*; August 18−20, 2005; Mabury, S., Ed.; University of Toronto, Toronto, Canada; p ANA040.

(27) Lang, C. C. *Biodegradation screen study for telomere type alcohol*; U.S. EPA Public Docket AR226−1149; 3M Environmental Laboratory: St. Paul, MN, 2002.

(28) Kannan, K.; Yun, S. H.; Evans, T. J. Chlorinated, brominated, and perfluorinated contaminants in livers of polar bears from Alaska. *Environ. Sci. Technol.* **2005**, *39*, 9057–9063.

(29) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* **2003**, *22*, 189–195.
(30) Yan, J. J. Application and market situation of fluoropolymers at home and abroad (in Chinese). *Fine Specialty Chem.* **2006**, *14*, 17–20.
(31) Smithwick, M. M.; Mabury, S. A.; Solomon, K. R.; Sonne, C.; Martin, J. W.; Born, E. W.; Dietz, R. E; Derocher, A. E.; Letcher, R. J.; Evans, T. J.; Gabrielsen, G. W.; Nagy, J.; Stirling, I.; Taylor, M. K.; Muir, D. C. G. Circumpolar study of perfluoroalkyl contaminants in polar bears (*Ursus maritimus*). *Environ. Toxicol. Chem.* **2005**, *24*, 5517–5523.
(32) Houde, M.; Wells, R. S.; Fair, P. A.; Bossart, G. D.; Hohn, A. A.; Rowles, T. K.; Sweeney, J. C.; Solomon, K. R.; Muir, D. C. Polyfluoroalkyl compounds in free-ranging bottlenose dolphins (*Tursiops truncatus*) from the Gulf of Mexico and the Atlantic Ocean. *Environ. Sci. Technol.* **2005**, *39*, 6591–6598.
(33) Giesy, J. P.; Kannan, K. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* **2001**, *35*, 1339–1342.
(34) Van de Vijver, K. I.; Hoff, P.; Das, K.; Van Dongen, W.; Wsmans, E.; Jauniaux, T.; Bouquegneau, J. M.; Blust, R.; De Coen, W. Perfluorinated chemicals infiltrate ocean waters: Link between exposure levels and stable isotope ratios in marine mammals. *Environ. Sci. Technol.* **2003**, *37*, 5545–5550.
(35) Butt, C. M.; Muir, D. C.; Stirling, I.; Kwan, M.; Mabury, S. A. Rapid response of Arctic ringed seals to changes in perfluoroalkyl production. *Environ. Sci. Technol.* **2007**, *41*, 42–49.
(36) Keller, J. M.; Kannan, K.; Taniyasu, S.; Yamashita, N.; Day, R. D.; Arendt, M. D.; Segars, A. L.; Kucklick, J. R. Perfluorinated compounds in the plasma of loggerhead and Kemp's ridley sea turtles from the southeastern coast of the United States. *Environ. Sci. Technol.* **2005**, *39*, 9101–9108.
(37) Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Gorzelany, J. F.; Hansen, K. J.; Jones, P. D.; Helle, E.; Nyman, M.; Giesy, J. P. Accumulation of perfluorooctane sulfonate in marine mammals. *Environ. Sci. Technol.* **2001**, *35*, 1593–1598.
(38) Hoff, P. T.; Van Dongen, W.; Esmans, E. L.; Blust, R.; De Coen, W. M. Evaluation of the toxicological effects of perfluorooctane sulfonic acids in the common carp (*Cyprinus carpio*). *Aquat. Toxicol.* **2003**, *62*, 349–359.

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