Bull. Environ. Contam. Toxicol. (2003) 71:408–413
© 2003 Springer-Verlag New York Inc.
DOI: 10.1007/s00128-003-0179-x

Bulletin of Environmental Contamination and Toxicology

Impact of Airborne Perfluorooctane Sulfonate on the Human Body Burden and the Ecological System

K. Sasaki,[1] K. Harada,[2] N. Saito,[1] T. Tsutsui,[3] S. Nakanishi,[3] H. Tsuzuki,[3] A. Koizumi[2]

[1] Research Institute for Environmental Sciences and Public Health of Iwate Prefecture, Morioka Iwate, Japan
[2] Department of Health and Environmental Sciences, Kyoto University School of Public Health, Kyoto 606-8501, Japan
[3] Kyoto Prefectural Institute of Hygienic and Environmenal Sciences, Kyoto, Japan

Received: 2 January 2003/Accepted: 17 April 2003

PFOS (perfluorooctane sulfonate) is an environmental contaminant with special public health concerns because it demonstrates stability, long-term persistence and bio-accumulativeness in the ecological environment. Since the 1950s, PFOS has been produced for many uses including lubricants, paints, cosmetics, and firefighting foam.

PFOS is reported to be globally distributed in living organisms (Giesy and Kannan 2001, Kannan et al. 2001a, Kannan et al. 2001b, Kannan et al. 2002) and humans (Hansen et al. 2001). However, mainly because of difficulties in measuring trace amounts of PFOS, little data has been reported on the levels of PFOS contamination in the natural environment, such as in surface waters and in air-borne particulate matter.

We have recently developed a robust, yet simple and sensitive method that enables the determination of trace concentrations of PFOS at the pg/mL level in surface waters (*Saito et al. submitted for publication*). Using this method, we conducted a nationwide survey of surface water contamination in Japan, and found that contamination levels are generally much less than those reported in the USA, although there were comparable levels of contamination in some urban areas (*Saito et al. submitted for publication*). In another study (*Harada et al. submitted for publication*) we also showed that the levels of drinking (tap) water contamination in Japan were estimated to be in the range of 0.1-51 pg/mL.

To evaluate the exposure levels and effects on ecological systems, the determination of air-borne PFOS is critically important. To date, there has been no analytical method available to determine the level of PFOS in air-borne particulate matter. In the present study, we began by establishing an analytical method. Using this, we measured air-borne PFOS contamination in Japan. We then evaluated human exposure through respiration on the basis of the observed data.

MATERIALS AND METHODS

Heptadecafluorooctane sulfonic acid potassium salt (FW 538.22), used as a standard for PFOS and as matrix spikes, was purchased from Fluka (Milwaukee, WI). The purity of the PFOS used as the standard was 98%, and the reported

---

Correspondence to: A. Koizumi

concentrations were not corrected for purity. In our preliminary study, water samples, including deionized water, were found to be contaminated with PFOS. Therefore, even the deionized water was only used after passing it through a Presep-C Agri cartridge (Solid phase: Styrenedivinylbenzene polymethacrylate on a polyethylene housing) (Wako Pure Chemicals, Osaka Japan) to remove the contaminating PFOS. Methanol and acetonitrile were HPLC grades, and the ammonium acetate was a special grade.

Air dust samples were collected every month from 2001 Apr. to 2002 Mar. at sampling stations in the town of Oyamazaki and in Fukuchiyama City (Kyoto Pref. Japan). At each sampling station, approximately 1,400 m^3 of air was collected over a period of 24 hours by a vacuum sampler MODEL-120V (Kimoto Electric Co., LTD, Osaka Japan) from air collecting orifices, which were located 1.5 m above ground level. Air dust particles were collected on a quartz membrane filter (PALLFLEX 2500QAT-UP, 8 x 10 in., Pallflex Products Corporation, USA). The sampling stations were located on a national road, R171, in the town of Oyamazaki and on a local road in Fukuchiyama City. The filter samples were stored at room temperature, along with a blank, until analyzed.

An automated extraction system (Dionex AES 200, Accelerated Solvent Extractor) was used for the extraction of the PFOS adsorbed on the quartz membrane filter under the conditions shown in Table 1. The halves of the filter samples were cut into small pieces and loaded into 11 mL stainless steel extraction cells. The PFOS was eluted into vials with 30 ml of 10% methanol solution. The eluted solution was adjusted to pH>6 to increase the recovery of PFOS from the cartridges (*Saito et al. submitted for publication*). The solutions were then passed through Presep-C Agri columns (250 mg cartridge) (Wako Pure Chemicals, Osaka Japan), which were equipped with a membrane filter cartridge (Advantec DISMIC-13HP, pore size 0.45 μm)(Advantec, Tokyo Japan) to remove the suspended materials or insoluble particles. Presep-C cartridges were eluted with 1.5 mL of methanol and the eluted solutions were concentrated at room temperature under nitrogen gas flow to 1 mL for analysis by LC/MS.

Table 1. Optimized conditions for PFOS extraction using an accelerated solvent extractor.

Instrument	:	DIONEX ASE-200 (DIONEX CO. Sunnyvale CA)		
Cell size	:	11	mL	.
Oven temperature	:	100	℃	
Pressure	:	1,500	psi	(=10.5MPa)
Static time	:	10	min	
Flush volume	:	120	%	of extraction cell volume
Solvent	:	methanol 10 % solution		
Nitrogen purge	:	150	psi	(=1MPa) for 120sec.
Extraction cycle	:	twice		

The details of the LC/MS and quantification have been previously described (*Saito et al. submitted for publication*). Briefly, standard compounds were infused by flow injection at a flow rate of 0.2 mL/min to adjust the ion sprayer and tune the mass spectrometer. Methanol extracts (10 μL injection volume) were chromatographed using HPLC with a flow rate of 0.2 mL/min. The total runtime was 20 min, without any equilibration time between samples. Mass spectra were taken on a liquid chromatography mass spectrometer equipped with an orthogonal spray interface; employing electron spray ionization in a negative mode. The fragmentor and Vcap voltages were 200V and 4000V, respectively. The nebulizer pressure was 50 psig and the drying N_2 gas flow rate was 10.0 mL/min, 350^0C. A selected negative-ion monitoring mode was employed for quantification of the PFOS. A Zorbax XBD C-18 (Agilent Narrow-Bore 2.1x150mm, 5-mm) column was used and eluted with a mixture containing acetonitrile and 10 mM ammonium acetate at 45:55 to obtain a retention time of about 10 min. The monitoring of the parent ion $(M\text{-}K)^-$ for PFOS m/z 499 ($C_8F_{17}SO_3^-$) revealed a major peak, considered to be PFOS, at a retention time of 11.15 min. The calibration curves constructed for the PFOS ranged from 0.1 to 100 pg/μL, and were linear with correlations of $r>0.999$. The instrumental detection limits were approximately equal to 0.4 pg.

Spike and recovery experiments were performed to determine the precision and accuracy of the method. One set of spike and recovery experiments was performed using quartz membrane filters that contained known amounts of PFOS. Six filter samples were spiked to a final concentration of 2.5 ng/mL PFOS.

RESULTS AND DISCUSSION

Standard addition experiments revealed that the mean recoveries for air dust samples collected on the quartz membrane filters were 97.2±2.29(Table 2). The CV for the blank filter samples was 30.4% after 6 repeated determinations (Table 2). Although the S:N ratio permitted a lower detection limit of 0.04 pg/μL, we considered the actual limit of quantification for the air dust samples to be 0.1 pg/μL; expressed in consideration of the limit of quantification based on the lowest calibration curve.

The PFOS concentrations of all the samples, including the blank filters, were larger than the limit of quantification. The PFOS concentrations in the blank filters ranged from 0.11 pg/μL to 0.27 pg/μL. Most of the PFOS concentrations of the air dust samples were significantly higher than the blanks. To quantify the PFOS concentration in air, we subtracted the background levels from the sample values. The annual geometric means (GM) (geometric standard deviation: GSD) of the PFOS concentrations in the air (pg/m^3) were 5.3 (1.2) for the town of Oyamazaki and 0.6 (1.3) for Fukuchiyama City, respectively. It was significantly higher in the town of Oyamazaki than in Fukuchiyama City ($p<0.01$). The annual GMs (GSDs) of the concentrations in dust (ng/g) and the dust concentrations in the air (μg/m^3) were significantly higher for the town of Oyamazaki than for

Fukuchiyama City ($p<0.01$)(Table 3). Differences in PFOS the concentrations in the dust samples (ng/g) and the dust concentrations ($\mu g/m^3$) can account for the differences in the concentrations in air (pg/m^3) from the two sampling sites.

Table 2. Recovery and spiked test of PFOS using silica fiber filters.

	Blank concentration a) (ng/mL)	Spiked concentration b) Found (ng/mL)	Recovery (%) c)
	0.11	2.68	101
	0.19	2.55	95
	0.16	2.60	97
	0.24	2.54	95
	0.11	2.64	99
	0.17	2.55	95
Mean	0.163	2.593	97.213
S.D.(n-1)	0.050	0.057	2.286
CV(%)	30.4	2.2	2.4

a) Silica fiber filters(ADVANTEC QR-100) used for sampling air-borne dust.
b) 2.5 ng of PFOS was added to the silica fiber filter paper (101.5x127mm).
c) Recovery (%) was defined as;

Recovery (%) = (Found - mean of the blank concentration)*100/2.5

Table 3. PFOS concentrations in Fukuchiyama City and the town of Oyamazaki.

Sampling Month	Fukuchiyama City			Oyamazaki Town		
	PFOS (pg/m^3)	Dust ($\mu g/m^3$)	PFOS in dust (ng/g)	PFOS (pg/m^3)	Dust ($\mu g/m^3$)	PFOS in dust (ng/g)
Apr.	0.46	27	16.88	2.96	78	37.99
May	0.38	53	7.19	4.08	53	77.00
Jun.	0.92	18	50.86	3.74	33	113.32
Jul.	2.12	35	60.64	6.55	41	159.72
Aug.	0.61	28	21.89	21.80	51	427.41
Sep.	0.10	14	7.00	2.34	25	93.77
Oct.	0.94	39	24.08	10.66	77	138.44
Nov.	0.75	29	25.80	4.67	51	91.50
Dec.	0.36	43	8.35	2.32	56	41.35
Jan.	0.60	37	16.26	10.93	108	101.20
Feb.	0.82	31	26.44	6.68	41	163.02
Mar.	0.00	39	0.00	3.51	88	39.89
GM	0.6^{A**}	30.9^{B**}	19.2^{C**}	5.3^{A}	54.0^{B}	97.4^{C}
GSD	1.30	1.10	1.20	1.20	1.10	1.20

** T-test $p<0.01$ between the two counterparts with the same letter of the alphabet.

There was a tendency for the PFOS concentrations to be higher during summer (July to August) than in the winter (December to February) at both sites. The values obtained in the town of Oyamazaki can be assumed to be representative of those in typical urban air in Japan, while those in Fukuchiyama City may represent those in rural air. Although the samples from both areas showed similar seasonal variations, the former values were significantly larger than the latter ones, suggesting that urban air is more heavily contaminated with PFOS. Although we do not have direct evidence in terms of the source of the PFOS, it is believed that the traffic density had a significant impact on the contamination levels of PFOS.

The determination of PFOS concentrations in the air allowed us to estimate human exposure to PFOS. Assuming that adult humans inspire 15 m^3 of air per day, and that the PFOS inspired on dust particles was absorbed completely into the body, the estimated daily intake became 10 pg/day and 100 pg/day in Fukuchiyama City and in the town of Oyamazaki, respectively. A one-compartment pharmacokinetic model predicts that the corresponding air contamination levels can be assumed to result in 1.2 pg/mL and 12 pg/mL excess of plasma PFOS levels, respectively (*Harada et al. submitted for publication*). It should be pointed out that the mean of the serum PFOS levels in humans was reported to be 28.4 ng/mL (Hansen et al. 2001). If this is the case, the PFOS exposure from air is quite low compared with exposure via a gastrointestinal route.

It is of interest that in Japan, the PFOS concentrations in air-borne particulate matter were much higher than those in water (pg/mL orders) (*Saito et al. submitted for publication*). Although the direct human exposure to PFOS from air is almost negligible, air-borne PFOS is a discernible source of contamination for the ecological system and should be addressed. If so, a target may be the wildlife. Obviously, if the bioconcentrations in microorganisms and the wildlife were taken into account, human exposure through the food chain would be greater.

This is the first report on PFOS in air. The present paper shows definitive evidence that air-borne PFOS is not a negligible source of PFOS in the ecosystem. Although the pulmonary route of exposure to PFOS seems to be negligible for humans, air-borne PFOS very likely contaminate the Earth. Together, this information offers a toxicological basis for human and ecological risk assessments. Further studies are necessary to investigate the fate of PFOS in the Earth's ecological system.

Acknowledgment. This project is supported by a grant from Nihonseimei Zaidan (2002).

REFERENCES

Giesy JP, Kannan K (2001) Global distribution of perfluorooctane sulfonate in wildlife. Environ Sci Technol 35: 1339-1342

Hansen KJ, Clemen LA, Ellefson ME, Johnson HO (2001) Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. Environ Sci Technol 35: 766-70

Kannan K, Franson JC, Bowerman WW, Hansen KJ, Jones PD, Giesy JP (2001a) Perfluorooctane sulfonate in fish-eating water birds including bald eagles and albatrosses. Environ Sci Technol 35: 3065-3070

Kannan K, Hansen J, Wade TL, Giesy JP (2002) Perfluorooctane sulfonate in Oyster, *Crassostrea virginica*, from the Gulf of Mexico and the Chesapeake Bay, USA. Arch Environ Contam Toxicol 42: 313-318

Kannan K, Koistinen J, Beckmen K, Evans T, Gorzelany JF, Hansen KJ, Jones PD, Helle E, Nyman M, Giesy JP (2001b) Accumulation of perfluorooctane sulfonate in marine mammals. Environ Sci Technol 35: 1593-1598