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Particle Size Distribution and Respiratory Deposition Estimates of Airborne Perfluorooctanoate and Perfluorooctanesulfonate in Kyoto Area, Japan

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Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are environmental contaminants used in a variety of applications, such as lubricants, paints, chemical process aids and fire-fighting foams. They pose special public health concerns because of their stability, long-term persistence and bioaccumulation in the environment.

We have determined PFOS and PFOA in surface water all over Japan and have found intensive contamination of surface water by PFOA in the Keihanshin (Kobe-Osaka-Kyoto) area (Harada et al. 2004; Saito et al. 2004). In addition, serum levels of PFOA in Kyoto residents were significantly higher than those in residents from other areas of Japan (Harada et al, 2004). These data collectively suggest area-specific sources of PFOA in the Keihanshin area.

To determine the sources of PFOA in the Keihanshin area, we investigated the levels of PFOS and PFOA in drinking water, and found that it is one of the major sources of human exposure in the Keihanshin area (Harada et al. 2003; Saito et al. 2004). The air-borne PFOA and PFOS levels were found to be considerably higher at sampling sites on a busy traffic route (Oyamazaki, Kyoto) than on an urban road (Harada et al. 2005b; Sasaki et al. 2003). In Kyoto, the estimated daily intake of PFOA from this route was comparable to that from tap water. However, in the previous study, the absence of fractionation data for airborne dusts made it impossible to evaluate daily intakes from this route.

The aim of the present study was to characterize particle size distributions and to evaluate respiratory deposition of air-borne PFOA. For this reason, we measured air-borne PFOA and PFOS contamination in Kyoto, Japan using Andersen air samplers.

MATERIALS AND METHODS

Heptadecafluorooctane sulfonic acid potassium salt (FW.538.22), used as a standard for PFOS, and pentadecafluorooctanoic acid ammonium salt (FW. 431.10), used as a standard for PFOA, were purchased from Fluka (Milwaukee, WI). The purity of the PFOS and PFOA used as standards was higher

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than 98%. We did not correct the reported concentrations according to purity. [1,2-$^{13}C_2$] Perfluorooctanoate was donated by the Environmental Protection Agency of the U.S.A. as an internal standard (originally synthesized by Perkin Elmer, Boston, MA). Methanol and acetonitrile were of HPLC grade. The purity of the ammonium acetate was higher than 99%.

Air dust samples were collected in the town of Oyamazaki and in Fukuchiyama City (Kyoto Pref., Japan). The sampling stations are located on a national road (Route 171) and at a junior high school 0.5 km north of Route 171 in the town of Oyamazaki, and on a local road in Fukuchiyama City. Route 171 is one of the busiest trunk routes in Japan.

Approximately 1,080 m^3 of air was collected over a period of 30 days, with an eight-stage Andersen cascade impactor sampler (AN-200, Tokyo Dylec Co., Tokyo, Japan), which was located 3 m above ground level. The stage specific effective cut-off diameter (ECD) values provided by the manufacturer were used in this study. The upper limit for the ECD was taken to be 100 μm for the first stage and 0.46 μm for the final filter stage. Air dust particles were collected on a quartz membrane filter (PALLFLEX 2500QAT-UP, Pallflex Products Corporation, USA). Samples were collected from April to May 2005 for Fukuchiyama and Route 171 and from May to June for the school in Oyamazaki. The filter samples were stored at room temperature, along with a blank, until analyzed.

The internal standard was added to each sample prior to extraction. An automated extraction system (Dionex AES 200, Accelerated Solvent Extractor) was used to extract PFOA and PFOS, as previously reported (Sasaki et al. 2003). Extract solutions were concentrated to 1 mL for analysis by LC/MS. Details of the LC/MS and the quantification have been described previously (Saito et al. 2004; Saito et al. 2003). The methanol extracts (10 μl injection volume of the 1 mL extract) were chromatographed by HPLC with a flow rate of 0.2 mL/min as previously reported (Sasaki et al. 2003).

Mass spectra were obtained using an LC/MS system equipped with an orthogonal spray interface, employing electrospray ionization in the negative mode. The selected ion monitoring (SIM) mode was employed for quantification of analytes. In the selected negative-ion mode monitoring of ions, the fragment ions for PFOA (m/z 413, $C_7F_{15}CO_2^-$) and PFOS (m/z 499, $C_8F_{17}SO_3^-$) were monitored for quantification. To avoid interference and ensure complete selectivity, the m/z 369 fragment of PFOA ($C_7F_{15}^-$) and the m/z 99 fragment of PFOS (FSO_3^-) were monitored. The limits of detection (LOD) and quantification (LOQ) were calculated by measuring the blank silica fiber filters.

RESULTS AND DISCUSSION

The LOQs for both PFOA and PFOS were determined to be 0.1 pg/m^3 in the samples. The PFOA and PFOS concentrations of all the samples were larger than the quantification limit (Table 1).

The sum of the PFOA concentrations and the sum of the PFOS concentrations from the individual fractions from Route 171 were comparable to the concentrations previously reported using high volume samplers [geometric means (geometric standard deviation) (pg/m^3): 262.8 (1.4) for PFOA, 5.2 (1.2) for PFOS] (Harada et al. 2005b). The concentrations of PFOA were higher than those of PFOS at all sampling sites, particularly in Oyamazaki. There was not much

Table 1. Particle size distributions of PFOA and PFOS in Oyamazaki and Fukuchiyama.

	Fraction	Dust amount	PFOA concentration		PFOS concentration	
Sampling site	µm	mg	pg/m^3-air	ng/g-dust	Pg/m^3-air	ng/g-dust
Fukuchiyama	100-11.4	7.0	2.3	355	0.3	42.6
	11.4-7.4	4.7	2.2	513	0.3	64.1
	7.4-4.9	6.8	2.2	351	0.3	43.8
	4.9-3.3	7.5	2.0	294	0.3	40.1
	3.3-2.2	5.4	1.9	371	0.3	55.7
	2.2-1.1	6.1	1.0	179	0.2	32.5
	1.1-0.7	6.6	1.1	181	0.2	30.2
	0.7-0.46	3.6	1.1	336	0.2	56.1
	0.46>	4.4	1.3	319	0.3	68.3
Total	100>	52.2	15.2	314	2.2	46.0
Respirable	1.1-11.4	30.5	9.4	331	1.3	45.8
School in Oyamazaki	100-11.4	12.9	27.2	2100	0.1	9.4
	11.4-7.4	13.2	34.7	2624	0.2	13.2
	7.4-4.9	7.2	34.5	4790	0.3	48.4
	4.9-3.3	13.7	41.5	3036	0.9	63.8
	3.3-2.2	15.7	23.7	1507	0.7	44.3
	2.2-1.1	12.4	15.5	1253	0.5	42.2
	1.1-0.7	7.4	11.2	1513	0.2	23.6
	0.7-0.46	0.9	11.2	12962	<0.1	<120
	0.46>	4.7	5.4	1162	<0.1	<20
Total	100>	88.0	204.8	2326	2.9	33.1
Respirable	1.1-11.4	62.2	149.9	2410	2.6	42.0
Route 171	100-11.4	10.5	43.1	4427	0.7	76.2
	11.4-7.4	7.0	50.3	7791	0.6	86.1
	7.4-4.9	8.4	54.7	7010	0.9	118.6
	4.9-3.3	8.9	53.0	6421	1.3	157.1
	3.3-2.2	7.4	45.9	6699	1.3	189.1
	2.2-1.1	5.6	24.9	4778	0.9	177.6
	1.1-0.7	7.6	19.8	2818	0.4	52.7
	0.7-0.46	6.8	17.1	2710	0.2	29.3
	0.46>	8.0	10.9	1478	0.5	62.6
Total	100>	70.2	319.7	4916	6.8	103.9
Respirable	1.1-11.4	44.9	228.8	5499	5.0	120.2

difference in the PFOA and PFOS concentrations or distributions between the school and Route 171 in Oyamazaki, although the traffic densities were significantly higher at Route 171 than at the school.

The particle size distributions of PFOA and PFOS show similar trends among the sampling sites (Table 1). The proportion of PFOA and PFOS in the respirable fraction (1.1 – 11.4 μm) ranged from 58.3 to 89.8%. The fraction smaller than 1.1 μm had a small peak for PFOA and PFOS concentrations in airborne dust.

The present study suggests two possible sources of PFOA and PFOS. First, de novo formation may occur on the airborne particles of many of their derivatives such as heptadecafluoro-1-decanol and perfluorooctane sulfonamides, as was shown in airborne particulates at 10-80 pg/m^3 and 48-95 pg/m^3 in Ontario (Stock et al. 2004). Second, they may be derived from automobile exhaust. Further study on the degradation of perfluorochemical derivatives on particulate matter will provide more insight for identifying the source of contamination in Kyoto.

We reported previously that the daily intake of airborne PFOA was estimated to be 3.9 ng/day around Route 171, on the assumption that all dusts were respirable and that adult humans inhale 15 m^3 of air per day (Harada et al. 2005b). Based on the present findings that include particle size distributions, the estimated human exposure to PFOA through inhalation around Route 171 in Oyamazaki is 3.4 ng/day. The daily intake by inhalation accounts for about 20% of the daily urinary excretion of PFOA (20.8 ng/day) in this area (Harada et al. 2005a).

This study demonstrated that the daily intakes of PFOA and PFOS through inhalation are comparable to those through drinking water ingestion, and are a significant source of human exposure in the Keihanshin area. Further studies are necessary to clarify the environmental source of airborne PFOA in the Keihanshin area.

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