

Survey of Airborne Polyfluorinated Telomers in Keihan Area, Japan

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Abstract Perfluorooctanoate (PFOA) are environmental contaminants posing special public health concerns because of their long-term persistence and bioaccumulation in the environment. Fluorotelomer alcohols are volatile and may undergo long-range transport. Air samples were collected at five sites in the Keihan area, Japan: Sakyo, Morinomiya and three sites in Higashiyodogawa. Except for Higashiyodogawa, the highest concentrations of fluorotelomer alcohols (FTOHs) were for 8:2 FTOH (median 447 pg m^{-3}) followed by 10:2 FTOH (56 pg m^{-3}) and 6:2 FTOH (22 pg m^{-3}). In contrast, 8:2 FTOAcryl (median 865 pg m^{-3}) and 8:2 FTOH ($1,864 \text{ pg m}^{-3}$) were both major components in Higashiyodogawa. Compared to data published for North America and Europe, 8:2 FTOH levels are significantly higher in Keihan, suggesting a possible point source.

Keywords Air · Fluorotelomer · GC/MS · Japan

Sayoko Ohno and Eriko Matsubara contributed equally to this study.

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Perfluorochemicals such as perfluorooctanoate (PFOA) are environmental contaminants posing special public health concerns because of their long-term persistence and bioaccumulation in the environment. They have been used widely in surfactants, lubricants, firefighting foam and other applications (Kissa 2001).

PFOA and perfluorinated carboxylic acids (PFCAs) with various chain lengths have been detected in a variety of environmental compartments. The sources of PFCAs in the environment remain unclear, however degradation of fluorotelomers, particularly fluorotelomer alcohols (FTOHs), might be indirect sources of PFCAs (Ellis et al. 2004). Fluorotelomer alcohols are volatile and may undergo long-range transport. FTOHs are currently produced and used as intermediates for the synthesis of coatings, polymers, inks, adhesives, waxes and so on.

PFOA and related compounds have also been detected in the environment in Japan (Nakayama et al. 2005). We have determined PFOA in surface water all over Japan and have found intensive contamination of surface water by PFOA in the Keihan (Osaka–Kyoto) area (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, 2007). These data collectively suggest area-specific sources of PFOA in the Keihan area. The air-borne PFOA 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. 2005, 2006). In Kyoto, the estimated daily intake of PFOA from this route was comparable to that from tap water.

The aim of the present study was to evaluate the concentrations of airborne FTOHs in the Keihan area. This information may provide an insight into the origin of PFOA in the environment.

Materials and Methods

The test materials, 1H,1H,2H,2H-perfluorooctanol (6:2 FTOH; purity >98%), 1H,1H,2H,2H-perfluorodecanol (8:2 FTOH; >97%) and 1H,1H,2H,2H-perfluoro-1-dodecanol (10:2 FTOH; >96%) were purchased from Alfa Aesar (Ward Hill, MA). 1H,1H,2H,2H-perfluorodecyl acrylate (8:2 FTOAcryl; >96%), was purchased from Lancaster Synthesis (Lancashire, UK). 1H,1H,2H,2H-heptadecafluorodecyl methacrylate (8:2 FTOMethacryl; >98%) was from Fluorochem (Derbyshire, UK). 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro-1-nonanol (8:1 FA; >98%) was purchased from Wako Pure Chemicals (Osaka, Japan). 1D,1D,2D,2H, ^{13}C -perfluorodecanol was donated by the Environmental Protection Agency of the USA (originally synthesized by DuPont, Wilmington, DE).

Air samples were collected on quartz fiber filters (QF 8" \times 10"; QR-100, Sibata, Tokyo, Japan) for particulate phase and glass columns (90 mm i.d.) with a polyurethane foam (PUF 50 mm) followed by activated carbon fiber felts (ACF 10 mm; KF-1700F, Toyobo, Osaka, Japan) for the gaseous phase, using high-volume air samplers (HV-700F, Sibata, Tokyo, Japan) at approximate flow rates of 700 L min^{-1} for 24 h, as previously reported (Takazawa 2006). ACF and PUF slices were prepared by soaking in ethyl acetate, followed by drying under vacuum. QF filters were rinsed several times with methanol and ethyl acetate, and dried in a clean room. All sampling media were wrapped in polyethylene bags for transport to the sampling site.

Air samples were collected at five sites in the Keihan area, Japan: Sakyo (SA: Kyoto city, population 1,472,764), Morinomiya (MO: Osaka city, 2,636,680) and three sites in Higashiyodogawa (HI1, HI2 and HI3: Osaka city) (Fig. 1). Ten samples were collected at Sakyo (October 2–December 19). Four samples were collected at Morinomiya (September 29–December 19). Ten samples were collected at Higashiyodogawa (October 16–November 12). Field

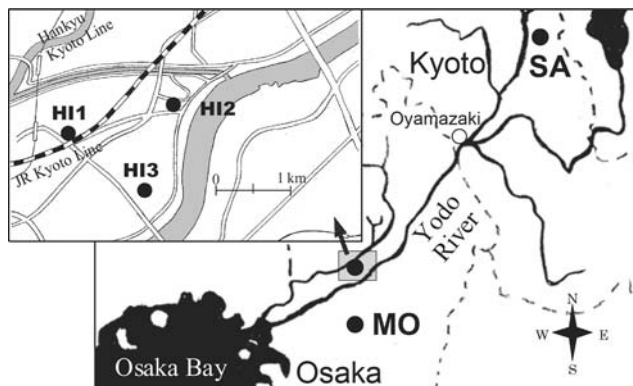


Fig. 1 Geographic locations of the air sampling sites in Keihan area, Japan

blanks (ACF, PUF and QF) were sent to the sampling sites with each set of samples, placed in the same sites for 24 h, and returned with the environmental samples.

For extraction of samples, the three sampling media were analyzed separately. Each media was soaked for 10 min in 50 mL of ethyl acetate, and this was repeated three more times (200 mL total). The aliquots were combined and dried with sodium sulfate. Isotope-labeled 8:2 FTOH was added to all extracts to determine recoveries. The extracts were rotoevaporated and reconstituted into hexane. The solutes were then rotoevaporated again and the concentrates were cleaned on a silica gel column (Presep[®]-C Silica Gel, Wako Pure Chemicals). The FTOHs were eluted with 5 mL of 25% ethyl acetate in hexane and the eluates were then evaporated to 1 mL under a gentle stream of high-purity nitrogen. 8:1 FA was added as an internal standard just prior to the GC/MS analysis to correct for volume differences.

Each extracted solution was analyzed by gas chromatography–mass spectrometry (Agilent 6890GC/5973MSD) in electron impact ionization mode (GC-EIMS) using single ion monitoring. Analytes were separated on an HP-5MS column (30 m \times 0.25 mm i.d. \times 0.25 μm film thickness) with a helium carrier gas. Pulsed splitless injections (2 μL) were performed at an initial pressure of 30 psi for 1.5 min, with the injector set at 200°C, and the split was opened after 1.5 min. The initial oven temperature was 50°C for 4 min, ramped at 20°C min^{-1} to 140°C, and then at 40°C min^{-1} to 240°C, followed by a 1-min hold. The ion source and quadrupole were 230 and 150°C, respectively. Quantification was performed using standard curve analysis and the internal standard 8:1 FA.

Results and Discussion

Instrumental detection limits (IDL) were defined as the mass of analyte producing a peak with a signal-to-noise ratio of 3, and ranged from 1 pg (8:2 FTOAcryl and 8:2 FTOMethacryl) to 10 pg (6:2 FTOH). Method quantification limits (MQL) were defined as the mean blank concentration producing a quantifiable response +10 standard deviations with 10 repetitions, and ranged from 3 pg m^{-3} (8:2 FTOAcryl and 8:2 FTOMethacryl) to 24 pg m^{-3} (8:2 FTOH) for 1,008 m^3 of sample (Table 1). Breakthrough experiments were conducted by spiking 1,000 ng of analytes onto PUF slices (Table 1).

Reported concentrations were not corrected for blanks and recoveries. For statistical analyses, data below the MDL and MQL were converted to half these values.

The field blank response was not significantly different from the clean sampling media. Though there was occasionally a blank concentration of 8:2 FTOH and 10:2

Table 1 Limit of detection and recovery of fluorotelomers

Analyte	Q ion (m/z)	IDL (pg)	MQL (pg m ⁻³)	Recovery of breakthrough experiment (%)					Cleanup recovery (%)	
				PUF	Rsd	ACF	Rsd	Total	Mean	Rsd
6:2 FTOH	344	10	14	6	3	87	19	93	69	8
8:2 FTOH	405	10	24	5	4	88	29	93	91	6
10:2 FTOH	505	5	16	3	2	79	16	82	98	7
8:2 FTOAcryl	518	1	3	8	3	88	11	96	92	15
8:2 FTO Methacryl	532	1	3	8	3	89	14	97	89	23

Q ion: Quantifier ion, Rsd:
Relative standard deviation

FTOH associated with ACF and PUF, the response was always low enough (<10 pg m⁻³).

FTOHs air concentrations determined are presented in Table 2. All analytes could be determined in the gaseous

phase of air samples. 8:2 FTOH and 10:2 FTOH were above the MDL in all samples, while 6:2 FTOH, 8:2 FTOAcryl and 8:2 FTO Methacryl were detectable in 75, 79 and 50%, respectively, of samples.

Table 2 Airborne fluorotelomer concentrations (pg m⁻³) in Keihan area, Japan

Date	Temp (°C)	6:2FTOH	8:2FTOH	10:2FTOH	8:2FTOAcryl	8:2 FTOMethacryl	ΣFTOH
(SA)							
23-August	28.4	<MDL	884	134	<MDL	<MDL	1,024
2-October	20.1	28	277	37	<3	<MDL	345
7-October	18.6	15	580	67	<3	<MDL	664
11-October	19.0	22	217	34	<3	<MDL	280
24-October	18.5	26	229	<16	<3	<MDL	276
1-November	15.8	<14	151	<16	<3	<3	169
23-November	11.9	<MDL	48	<MDL	<3	4	68
28-November	14.7	<MDL	314	29	<3	4	362
5-December	5.6	<MDL	1,743	106	101	6	1,959
19-December	5.3	21	1054	197	21	<MDL	1,294
GM (GSD)	10(2.4)	352(2.9)	39(3.0)	4(4.9)	2(2.1)	424(2.8)	
(MO)							
29-September	23.0	44	866	89	<MDL	<MDL	1,001
28-November	15.9	27	199	45	45	10	325
5-December	7.7	41	999	143	22	3	1208
19-December	7.2	30	729	75	74	<MDL	909
GM (GSD)	35(1.3)	595(2.1)	81(1.6)	16(6.9)	2(3.1)	773(1.8)	
(HI1)							
16-October	20.9	<MDL	2,745	48	1062	<MDL	3,860
17-October	20.9	170	4,585	250	2953	<MDL	7,959
18-October	21.7	83	1,910	166	974	<MDL	3,135
(HI2)							
6-November	19.6	<MDL	1,818	347	820	6	2,995
7-November	15.1	16	549	116	188	5	873
8-November	13.0	83	3,071	368	2,453	29	6,003
(HI3)							
9-November	17.0	124	3,778	518	909	9	5,338
10-November	19.4	28	1,030	284	341	7	1,690
11-November	15.6	22	512	156	<MDL	<MDL	699
12-November	10.8	19	310	35	235	5	604
GM (GSD)	29(3.8)	1,465(2.5)	173(2.4)	485(5.4)	3(3.4)	2,377(2.5)	

Temp: Average temperature of ambient air; GM: Geometric mean; GSD: Geometric standard deviation

Table 3 Nonparametric correlation (Kendall's τ) among airborne fluorotelomers

		Total τ	p value	HI τ	p value	SA & MO τ	p value
8:2 FTOH	6:2 FTOH	0.25	0.093	0.48	0.058	0.13	0.542
10:2 FTOH	6:2 FTOH	0.34	0.021	0.43	0.087	0.23	0.267
10:2 FTOH	8:2 FTOH	0.67	<0.001 ^a	0.47	0.060	0.77	<0.001 ^a
8:2 Acryl	6:2 FTOH	0.20	0.182	0.34	0.176	−0.01	0.955
8:2 Acryl	8:2 FTOH	0.54	<0.001 ^a	0.78	0.002 ^a	0.17	0.400
8:2 Acryl	10:2 FTOH	0.43	0.004 ^a	0.24	0.325	0.19	0.368
8:2Methacryl	6:2 FTOH	−0.03	0.830	0.12	0.640	−0.29	0.194
8:2Methacryl	8:2 FTOH	0.07	0.651	0.07	0.781	−0.12	0.583
8:2Methacryl	10:2 FTOH	0.18	0.264	0.45	0.078	−0.13	0.541
8:2Methacryl	8:2 Acryl	0.40	0.011	0.12	0.643	0.52	0.021

^a $p < 0.005$ corresponding to
 $p < 0.05$ after Bonferroni
correction

Except for Higashiyodogawa, the highest concentrations of FTOHs were for 8:2 FTOH (median 447 pg m^{−3}; range 48–1,743 pg m^{−3}) followed by 10:2 FTOH (56 pg m^{−3}; <16–196 pg m^{−3}) and 6:2 FTOH (22 pg m^{−3}; <MDL–44 pg m^{−3}). 8:2 FTOH represents 83% (range 61–89%) of the total FTOHs. In contrast, 8:2 FTOAcryl (median 865 pg m^{−3}; range 9–2,952 pg m^{−3}) and 8:2 FTOH (median 1,864 pg m^{−3}; range 310–4,585 pg m^{−3}) were both major components in Higashiyodogawa. Three airborne FTOHs (8:2 FTOH, 10:2 FTOH and 8:2 FTOAcryl) and Σ FTOH concentrations were significantly higher in the samples from Higashiyodogawa than those from Sakyo (Steel-Dwass test: $p < 0.05$), indicating possible point and diffuse sources. 8:2 FTOAcryl concentrations in Higashiyodogawa were also significantly higher than those in Morinomiya (Steel-Dwass test: $p < 0.05$). Between Morinomiya and Sakyo, 6:2 FTOH concentrations in Sakyo samples were significantly lower (Steel-Dwass test: $p < 0.05$). The average temperature of the ambient air did not influence the levels of fluorotelomers (Kendall's τ : $p > 0.05$).

The proportions of the three fluorotelomer alcohols (6:2 FTOH, 8:2 FTOH and 10:2 FTOH) were 3.7 ± 2.9 , 85 ± 6.0 and $11 \pm 5.1\%$ (mean \pm standard deviation), respectively. These proportions did not differ between the three sampling sites (Kruskal-Wallis's test: $p > 0.05$ for each FTOH). Correlations between analytes are shown in Table 3. There were significant correlations between 8:2 FTOH, 10:2 FTOH and 8:2 FTOAcryl (Kendall's τ : $p < 0.05$ after Bonferroni correction for each combination). These correlations suggest that these compounds might have a common source in the environment.

Fluorotelomer alcohols (FTOH) concentrations determined in this study and reported by North American and European researchers are presented in Table 4 (Berger et al. 2005; Jahnke et al. 2007; Shoeib et al. 2007; Stock et al. 2004). Compared to data published for North America and Europe, 8:2 FTOH levels are significantly

Table 4 Comparison of FTOH concentrations (pg m^{−3}) with literature data

Location	6:2 FTOH	8:2 FTOH	10:2 FTOH	Reference
Higashiyodogawa	55	2031	229	This study
Morinomiya	35	698	88	This study
Sakyo	14	550	64	This study
Arctic Cruise	3	7	4	Shoeib et al. (2007)
Toronto, Canada	9	20	11	Shoeib et al. (2007)
North America, urban ^a	53	80	<MDL	Stock et al. (2004)
North America, rural ^a	14	7	<MDL	Stock et al. (2004)
Hazelrigg, England	81	103	75	Berger et al. (2005)
Manchester, England	188	240	67	Berger et al. (2005)
Hamburg, Germany	66	119	35	Jahnke et al. (2007)
Waldhof, Germany	64	75	23	Jahnke et al. (2007)

^a North American urban cities includes Reno, Griffin, Cleves and Toronto; rural cities, Winnipeg, Long Point

Each concentration was an arithmetic mean

higher in Keihan. However, 6:2 FTOH levels in Europe are slightly higher than in Keihan and North America. These different patterns of FTOHs might result from the formulations for industrial applications, although the environmental fate of the FTOHs is unclear.

To the best of our knowledge, the study presented here provides the first environmental survey of 8:2 FTOAcryl and 8:2 FTOAcryl. The fluorotelomer alcohol acrylate and methacrylate are unpolymerized intermediates used in the manufacture of telomer-based polymers. These esters could be rapidly degraded under aerobic conditions into FTOH and acids (Berger et al. 2005). Since 8:2 FTOAcryl was only present as a small portion of FTOHs in the areas other than Higashiyodogawa, it was suggested that there might be a point source of the acrylate ester and that degradation of the ester into 8:2 FTOH might progress rapidly.

The GM (GSD) of the airborne PFOA concentrations (pg m^{-3}) was 262.8 (1.4) for Oyamazaki, Kyoto (Fig. 1) in 2001–2002 (Harada et al. 2005), which is comparable to the 8:2 FTOH concentrations in Sakyo. FTOHs have an atmospheric lifetime of approximately 10–20 days (Ellis et al. 2004). Therefore, airborne PFOA in Oyamazaki seems to originate, in part, from fluorotelomer alcohols.

This paper gives evidence suggesting that the level of airborne FTOHs is considerably higher in the Keihan area than in other areas, suggesting a possible point source. Further studies are necessary to investigate the contribution of airborne FTOHs to PFCA contamination in the Keihan area, including that of humans.

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