

Perfluorinated Compounds in the Asian Atmosphere

Jun Li,^{*,†,‡} Sabino Del Vento,[‡] Jasmin Schuster,[‡] Gan Zhang,[†] Paromita Chakraborty,^{†,§} Yuso Kobara,^{||} and Kevin C. Jones^{†,‡}

[†]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

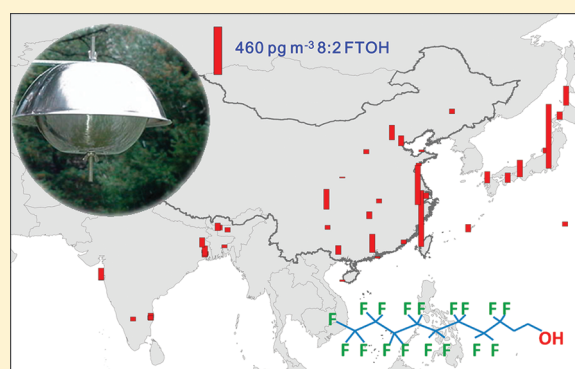
[‡]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, U.K.

[§]Department of Natural Science, Savannah State University, Savannah, Georgia 31404, United States

^{||}National Institute for Agro-Environmental Sciences, Tsukuba, Ibaraki 305-8604, Japan

S Supporting Information

ABSTRACT: There is interest in the production, use, and environmental occurrence of perfluorinated compounds (PFCs) across Asia and the Asian contributions to the burden of these compounds reaching the Arctic and other remote regions via long-range transport. A spatial survey of perfluorinated compounds was therefore undertaken across China, India, and Japan in 2009 using passive air samplers. Target analytes were fluorotelomer olefins (FTOs), acrylates (FTAs), alcohols (FTOHs), sulfonamides, and sulfonamidoethanols. Wide variations in concentrations and mixtures of compounds were apparent from the study. Generally the FTOHs were the most abundant, followed by 8:2 FTO in China and Japan and by the sulfonamides in India. There was a general decline in PFC concentration from urban, rural, to remote locations. Background stations reflected regional differences in air mass composition. A site in the west Pacific Ocean exhibited a Japanese profile in which 8:2 FTO and 8:2 FTOH were predominant. In contrast, a southern Indian profile with high 4:2 FTOH concentrations was observed at a background site in southern China.



INTRODUCTION

With a wide range of industrial uses, diffuse sources, environmental persistence, and the potential to form stable degradation products, the environmental occurrence of perfluorinated compounds (PFCs) has attracted significant interest in recent years.^{1,2} Atmospheric emissions and long-range atmospheric transport are important to the global dispersal of PFCs.^{3,4} Further understanding of the sources and fate in the atmosphere is needed to assess the relative importance of different classes of PFCs as precursors for two key breakdown products — namely perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) — which are the subject of international regulations.

Due to their properties and pattern of usage, most emissions of PFOS and PFOA will occur directly into water bodies. They are less efficient at direct entry to the atmosphere or partitioning into the gas phase, key requirements that make them available for long-range atmospheric transport (LRAT). Much of the recent attention has therefore focused on how they are transported from densely populated use areas to remote places. There are a range of pathways and hypotheses. One is the so-called ‘precursor’ hypothesis.² In addition to their presence in various perfluorinated products, PFOS and PFOA are also stable degradation products/metabolites of neutral PFCs. These precursor

compounds are more volatile,⁵ and therefore more likely to undergo LRAT, with sufficient atmospheric lifetimes to reach remote locations,⁶ where they can break down. Possible precursor compounds for other chain-length perfluorocarboxylates (PFCAs) and PFOS are fluorotelomer alcohols (FTOHs)² and fluorooctane sulfonamides/ethanols (FOSAs/FOSEs),^{7,8} respectively. It has also been suggested that fluorinated telomer olefins (FTO) will degrade to form PFCAs.⁹ Another mechanism predicts that the atmospheric transport of precursor PFCs is insignificant in comparison to direct oceanic transport;⁹ a comparison of measured oceanic concentrations coupled with oceanic transport models seems to support this theory.¹⁰ A third hypothesis is that PFOS and PFCAs may be emitted from primary sources in association with particulate matter and be directly transported long-distances in the atmosphere attached to particles,¹¹ supported by some studies which found PFOS and/or PFOA on environmental particles.^{12–14} Given the lack of consensus in the scientific community, transport pathways and

Received: May 22, 2011

Accepted: July 28, 2011

Revised: July 19, 2011

Published: July 29, 2011

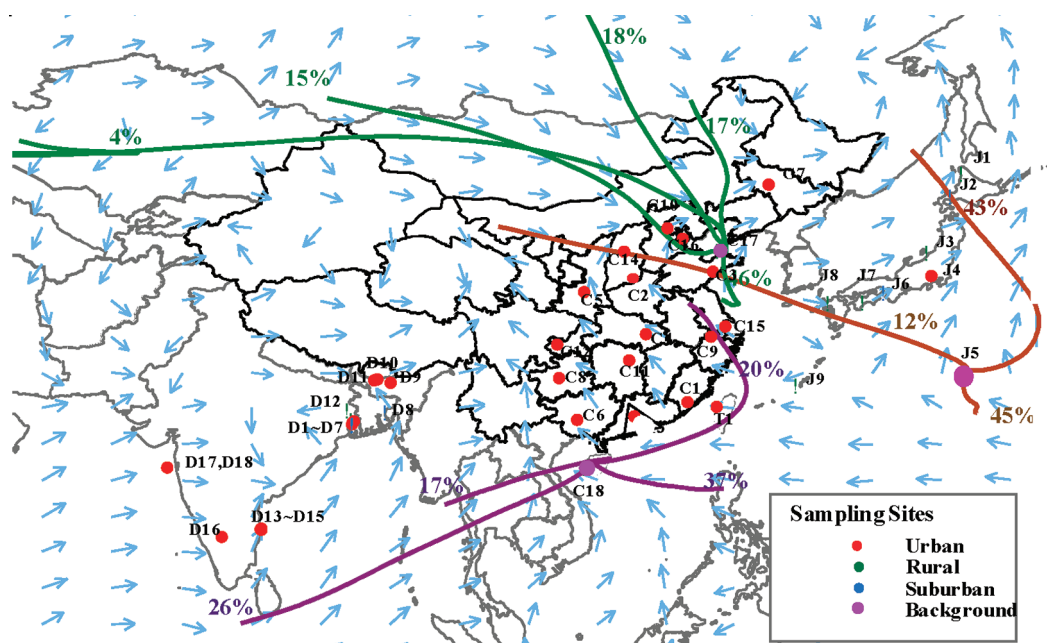


Figure 1. Map showing sampling sites, average wind direction between 20th March and 30th June 2009. Five-day back trajectories were calculated every 6 h during the sampling time, and several typical trajectories were classed at each of the background sites (J5, C17, and C18 see the text for details). The representative back-trajectories are shown in map, and the numbers (%) present the percentage of the typical trajectories that occurred in the whole sampling duration.

environmental fate of all fluorochemicals need further investigation. Therefore accurate measurements of the levels of these chemicals in important transport media such as water and air should be performed. There are still only a limited number of studies to determine atmospheric concentrations of PFCs.^{3,4,15–17} The aim of this current study was to screen a number of environmental air samples for a range of PFCs, including both neutral ‘precursor’ PFCs such as the previously investigated FTOHs and FOSAs/FOSEs and less well studied FTOs and fluorobutane sulfonamides/ethanols (FBSAs/FBSEs). So far most ambient measurements of PFCs have been made in North America and Europe.^{3,4,15–17} However, there is particular interest in Asia at the present time, because manufacture and use of PFCs continues there¹⁸ and LRAT can be important regionally and as a source to the Arctic and Pacific Ocean.^{3,4}

Ambient measurements can be made using active air samplers or passive sampling techniques. The latter has the advantage that large scale spatial surveys can be conducted relatively quickly, cheaply and easily. The purpose of this study was to investigate the general ambient levels and distributions of PFCs in key parts of Asia – China, India, and Japan – because of the size and economic significance of these countries. We deployed sorbent impregnated polyurethane foam (PUF) disk samplers (SIPs) adapted for PFC sampling from a design tested and regularly used for a range of persistent organic pollutants (POPs).^{16,19,20}

MATERIALS AND METHODS

Preparation of SIPs. PUF disks (Tisch Environmental) were pre-extracted in a Soxhlet with acetone (12 h) and petroleum ether (18 h). Amberlite XAD-4 was pre-cleaned with sonication in methanol, dichloromethane, and hexane (30 min each). The pre-cleaned Amberlite XAD-4 was ground to powder applying a Retsch planetary ball mill (particle diameter approximately 0.75 μm).²¹

Powdered Amberlite XAD-4 was pre-extracted with methanol (6 h), dichloromethane (DCM) (12 h), and hexane (6 h) consecutively. PUF disks were coated with XAD-4 by dipping the dried, pre-cleaned disks in a dispersion of the powdered Amberlite XAD-4 in hexane. SIPs were dried under vacuum and stored in metal tins at $-17\text{ }^{\circ}\text{C}$ until deployment. Further information for the SIP procedure can be found in Shoeib et al.¹⁹

Sampling Campaign. The SIP-PUF disk samplers used in this study have been described previously.^{19,20} Disks were pre-cleaned by extraction at Lancaster University, U.K., and then transferred to the sampling locations in sealed, solvent-cleaned metal tins. The samplers were assembled at the deployment sites to avoid contamination during transit. Samples were deployed for about 100 days from March to July 2009 in China, Taiwan, and Japan and from May to August 2009 in India. Rural sampling sites were chosen on the condition that they were distant from local sources or significant human activity. A total of 18 samplers were successfully deployed in 2 background sites and 16 urban sites in China, 1 suburban site in Taiwan, 9 locations in Japan (1 background, 5 rural, 2 suburban, 1 urban), and 18 in India (2 rural, 4 suburban, 12 urban) (see Figure 1). Three field blanks were collected at three sample sites (J2, D12, and C13), which were treated as regular samples, but only exposed to the environment for the duration of assembling and disassembling the field sampling devices. At the end of the deployment period, the SIP-PUF disks were retrieved, resealed in their original solvent-cleaned metal tins at the sampling locations, and returned by courier to Lancaster University. On receipt in Lancaster, they were stored frozen until extraction.

Sample Extraction and Analysis. The target analytes include fluorotelomer olefin (8:2 FTO), fluorotelomer acrylates (6:2, 8:2 FTA), fluorotelomer alcohols (4:2, 6:2, 8:2, 10:2, and 12:2 FTOH), sulfonamides (NMeFBSA, NMeFOSA, and NetFOSA), and sulfonamidoethanols (NMeFBSE, NMeFOSE, and NetFOSE),

Table 1. Summary of Measured PFC Concentrations (pg m^{-3})^c

analytes	MDL ^a	Japan (9) ^b			India (18)			China (18)			Taiwan (1)
		av \pm sta	range	median	av \pm sta	range	median	av \pm sta	range	median	
8:2 FTO	0.40	132 \pm 156	35.7–529	72.0	57.2 \pm 43.5	17.1–178	46.2	95.8 \pm 112	11.0–411	62.2	401
4:2 FTOH	1.51	29.5 \pm 22.5	2.29–71.9	24.1	76.0 \pm 78.1	2.21–235	60.3	20.8 \pm 25.8	ND ^c -78.2	7.92	6.22
6:2 FTOH	0.56	12.3 \pm 8.23	2.37–42.6	7.81	4.53 \pm 3.96	<MDL-15.3	3.31	36.2 \pm 73.0	ND-292	4.77	15.0
8:2 FTOH	0.45	204 \pm 234	59.4–808	121	60.9 \pm 32.1	19.4–135	48.3	108 \pm 121	14.4–498	56.2	709
10:2 FTOH	1.34	58.4 \pm 56	11.5–198	47.0	23.6 \pm 17.3	9.67–84.5	18.0	60.5 \pm 66.5	6.45–285	40.5	332
12:2 FTOH	0.09	30.2 \pm 31.6	7.48–112	21.0	12.9 \pm 8.02	5.92–41.2	10.7	27.6 \pm 25.2	3.32–98.7	18.2	134
Σ FTOHs		335 \pm 345	83.0–1210	206	178 \pm 84.4	54.0–311	194	253 \pm 216	51.4–936	183	1200
6:2 FTA	0.38	0.52 \pm 0.61	ND-2.00	0.19	0.19 \pm 0.37	ND-1.38	0.00	0.41 \pm 1.03	ND-3.45	ND	0.38
8:2 FTA	0.17	2.67 \pm 4.5	<MDL-14.6	1.17	1.22 \pm 1.11	<MDL-4.79	0.88	1.23 \pm 0.96	ND-3.13	0.78	3.78
Σ FTAs		3.19 \pm 4.64	0.28–15.3	1.36	1.41 \pm 1.22	0.32–4.98	0.88	1.64 \pm 1.56	0.20–5.80	0.90	4.16
NMeFBSA	0.11	1.16 \pm 0.26	0.81–1.57	1.12	3.92 \pm 3.27	1.47–13.9	2.50	1.21 \pm 0.55	ND-2.19	1.27	1.17
NMeFOSA	0.42	5.65 \pm 3.05	ND-10.2	5.91	6.51 \pm 2.89	ND-13.1	6.89	7.24 \pm 2.89	1.27–12.5	7.40	4.53
NEtFOSA	1.85	3.43 \pm 2.47	<MDL-7.23	2.65	72.3 \pm 201	ND-817	0.96	4.37 \pm 3.46	<MDL-14.2	2.99	3.25
Σ FOSAs		10.3 \pm 4.25	3.22–14.7	10.8	82.7 \pm 203	3.48–831	12.1	12.8 \pm 4.95	3.48–23.1	12.8	8.95
NMeFBSE	0.12	8.96 \pm 9.24	2.88–33.1	5.92	17.9 \pm 15.0	5.51–68.4	12.9	23.1 \pm 16.3	3.11–64.9	16.0	16.1
NMeFOSE	0.22	16.5 \pm 25.5	1.80–82.6	7.23	17.1 \pm 13.4	0.58–50.8	15.1	10.9 \pm 5.77	ND-18.5	10.8	16.4
NEtFOSE	0.48	8.16 \pm 18.1	0.67–56.2	2.27	5.15 \pm 2.93	1.43–11.4	4.24	6.02 \pm 5.89	ND-24.2	4.27	3.71
Σ FOSEs		33.6 \pm 52.4	8.20–172	17.9	40.1 \pm 23.9	11.4–88.1	34.2	40.0 \pm 18.9	7.44–94.0	36.8	36.2

^a MDL = method detection limit (pg m^{-3}). ^b Number of samples. ^c ND = not detected.

plus 11 Recovery Standards (RS) (5:1 FTOH, 7:1 FTOH, 9:1 FTOH, 11:1 FTOH, [M+4]6:2 FTOH, [M+5]8:2 FTOH, [M+4]10:2 FTOH, [M+3]NMeFOSA, [M+5]NEtFOSA, [M+7]NMeFOSE, and [M+9]NEtFOSE) and N,N-Me2FOSA, 13:1 FTOH and 13C-HCB as Internal Standards. 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, NMeFOSA, NEtFOSA, NMeFOSE, all of >98% purity, were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). 4:2 FTOH (>97% purity) and 5:1 FTOH (98% purity) were purchased from Matrix Scientific (Columbia, SC, USA). 8:2 FTO (>97% purity), 7:1 FTOH, 9:1 FTOH, 11:1 FTOH, and 13:1 FTOH were from Interchim (Montlucon Cedex, France). Native NEtFOSE, NMeFBSA, and NMeFBSE were donated by 3M. Native 12:2 FTOH and [M+5]8:2 FTOH were donated by DuPont. 13C-HCB (99% purity from Cambridge Isotope Laboratories, Inc. was used as Internal Standard. The following compounds of >98% purity were from Wellington Laboratories Inc. and were used as Recovery Standard: [M+4]6:2 FTOH, [M+4]10:2 FTOH, [M+3]-NMeFOSA, [M+5]NEtFOSA.¹⁵

Extraction of the SIPs was performed by sequential cold column extraction with ethyl acetate as the extraction solvent. Samples were spiked with recovery standard (25 μL of 200 $\text{pg } \mu\text{L}^{-1}$ RS solution in ethyl acetate) and extracted by 3 separate immersions for 30 min in ethyl acetate. The 3 extracts were then combined and reduced to a volume of 1 mL. The extracts were filtered 3 times through a 6 place Millipore Millex syringe filter unit (0.45 μm , 4 mm) adding 1 mL of ethyl acetate each time. The extracts were then reduced to a volume of 1 mL and cleaned-up by passing through 2 cm of Envi-Carb, reduced to a volume of 500 μL , spiked with performance internal standard (25 μL of 500 $\text{pg } \mu\text{L}^{-1}$ IS solution in ethyl acetate), and finally reduced to a volume of 50 μL for injection. Field blanks and lab blanks were extracted along with samples in the same way.

Analysis was performed using gas chromatography (Thermo Trace GC Ultra, Thermo Scientific) – mass spectrometry

(Thermo DSQ Quadrupole, Mass Spectrometer) (GC/MS) in selective ion monitoring (SIM) mode using positive chemical ionization (PCI). Aliquots of 2 μL were injected on a SUPEL-COWAX column (60 m, 0.25 mm inner diameter, 0.25 μm film, Supelco, Bellefonte, PA).

QA/QC. A total of 3 field blanks and 6 lab blanks were analyzed. In addition, recovery standards were added to each of the samples to monitor procedural performance. The average recoveries were 106 \pm 28%, 71 \pm 14%, 83 \pm 26%, 74 \pm 19%, 72 \pm 34%, 93 \pm 29%, 92 \pm 19%, 98 \pm 33%, and 98 \pm 30% for 5:1 FTOH, 7:1 FTOH, [M+5]8:2 FTOH, 9:1 FTOH, 11:1 FTOH, [M+3]-NMeFOSA, [M+5]NEtFOSA, [M+7]NMeFOSE, and [M+9]-NEtFOSE, respectively. Lab blanks and field blanks showed similar compound concentrations, typically below 1.0 pg/sample/day (assuming 100 day sampling duration), whereas for 4:2 FTOH, 10:2 FTOH, and NEtFOSA, the average concentrations were about 1.4, 1.2, and 2.8 pg/sample/day . All results were recovery and blank corrected. Method detection limits (MDLs) were calculated from the blanks (average of blanks +3 x standard deviation (σ)). The MDL ranged from 0.10–3.66 pg/sample/day for all compounds. Detailed information of the individual compound MDL were listed in Table S2, Table S3, and Table 1.

Data Presentation and Conversion. Data were initially expressed as the mass of PFC compound per SIP sample collected over the exposure period (Table S1). In order to facilitate comparison with available literature data, a calibration study by Shoeib et al.¹⁹ was used to estimate the ambient levels (as mass of PFC compound per m^3 air). For compounds which were estimated to approach equilibrium during the \sim 100 day exposure time (i.e., FTOs, FTOHs, and FTAs), eq 2 in the Shoeib et al.^{19,20,22} study was used. For those compounds which would not have equilibrated in 100 days (i.e., FOSAs and FOSEs), linear uptake was assumed at a sampling rate of 2.3 $\text{m}^3 \text{day}^{-1}$. The MDLs in Table 1 were also calculated based on the above method and 100 day exposure duration.

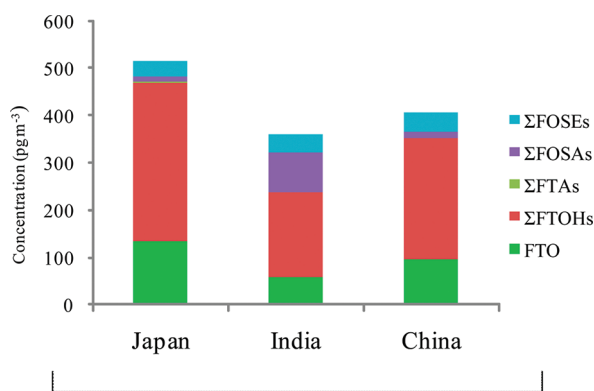


Figure 2. Average proportions of different compounds in Japan, India, and China.

RESULTS AND DISCUSSION

Summary of the PFC Concentrations. Table 1 presents a summary of the data arising from the study. Further details for each sampling site and the compounds detected in individual samples are available in the Supporting Information (Tables S1–S5). Although not all compounds were above the detection limit in each sample, some PFCs were detected in all the air samples, even at the background sites.

FT Olefins. In summary, the data indicate that the concentrations of 8:2 FTO, which was detected in all samples, were broadly in the range of tens to several hundreds of pg m^{-3} . Values ranged from 36 to 53, 17–180, and 11–410 pg m^{-3} in Japan, India, and China, respectively. These are generally higher than measured in a limited study in the UK ($<0.4\text{--}25 \text{ pg m}^{-3}$).¹⁵ Fluorotelomer olefins, which have high vapor pressures (typically up to several hundred Pa), are used to synthesize fluorotelomer acrylate monomer or ammonium perfluorononanoate (APFN). Several factories are located in Asia, including Japan, India, and China.⁹ The primary olefin used in the synthesis of APFN is 8:2 FTO.

FT Alcohols. The total concentrations of FTOHs (sum of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, and 12:2 FTOH) ranged from 83 to 1200, 54–310, and 51 to 940 pg m^{-3} in Japan, India, and China. Urban or suburban sites had highest concentrations (e.g., site J4 (1210 pg m^{-3}) in Japan, site C9 (940 pg m^{-3}) in China, and T1 (1200 pg m^{-3}) in Taiwan). The high concentrations of FTOHs in those cities may be related to the fluoropolymer manufacture activities and fluoropolymer use. These values were comparable to those results detected in Toronto, Canada,²³ Manchester city center, UK,¹⁵ Kyoto City and Osaka City in Japan,²⁴ and Hamburg, Germany (see Table S6).²⁵ Concentrations measured at the background sites (C17 and C18) were comparable to remote sites over the Atlantic Ocean²⁶ and in the Arctic.¹⁷

FT Acrylates. Measurements of FTAs have been attempted in a few studies.^{4,24,25,27,28} These compounds have relatively short atmospheric lifetimes (about several days).²⁹ Concentrations of FTAs were generally $<100 \text{ pg m}^{-3}$, except at Higashiyodogawa, in Osaka City, Japan where the highest value of 2950 pg m^{-3} was detected.²⁴ In this study, the concentrations of 6:2 FTA and 8:2 FTA ranged from ND–3.4 pg m^{-3} and ND–15 pg m^{-3} with frequencies of detection of 24% and 93%, respectively. Overall, these results are in the same range as previous studies (see Table S6).^{4,25,27,28}

Fluorinated Sulfonamides (FOSAs/FOSEs). As shown in Figure 3C and Table S5, FOSAs and FOSEs were frequently detected in Asia. The data are also summarized in Table 1. These compounds partition between the gas and particulate phases¹⁵ but appear to be found predominantly in the gas phase at higher ambient temperatures.²⁵ Average temperatures were 10–26 °C in Japan and China, while they were 21–35 °C in India in this study. Generally, individual compounds were $< \text{tens pg m}^{-3}$, in the same ranges as observed in North America and Europe.^{15,27,30} However, anomalously high values of NETFOSA were found in samples from Chennai, India ($\sim 820 \text{ pg m}^{-3}$). NETFOSA, commonly known as sulfluramide, is an insecticide used to control cockroaches, termites, and ants.³¹ It is sold in Asia, including China and India. These data suggested that large amounts of NETFOSA might be handled and used in the Chennai area.

PFC Composition. A comparison of the average concentrations for the different jurisdictions and the chemical distribution patterns is shown in Figure 2. Generally, the ΣFTOHs were the dominant class of compounds. In China and Japan this was followed by FTO, ΣFOSEs, ΣFOSAs, and ΣFTAs. In India, however, ΣFOSAs were the second dominant class, followed by FTO, ΣFOSEs, and ΣFTAs, although the latter was only caused by the anomalously high levels of NETFOSA in the four samples from Chennai.

Among the FTOHs, the 8:2 FTOH dominates in North American and European samples, followed by 6:2 FTOH and 10:2 FTOH.^{15,27} However, the trend was 8:2 FTOH, 10:2 FTOH, and 6:2 FTOH in Japan.²⁸ In this study, the composition of FTOHs in Japanese samples was consistent with previous data in Asian air masses,²⁸ and levels of 8:2 FTOH ($59 \pm 7\%$) were the highest, followed by 10:2 FTOH ($18 \pm 3\%$), 4:2 FTOH ($10 \pm 5\%$), 12:2 FTOH ($9 \pm 2\%$), and 6:2 FTOH ($4 \pm 2\%$). However, those compositions varied among the different sampling sites in China and India. In most cases in China and some parts of India, the compositions were similar to Japan, while at C8 and C14 in China, the proportions of 6:2 FTOH (63% and 75%, respectively) were dominant, followed by 8:2 FTOH, etc. At China site C18 and most sites in India, the 4:2 FTOH was the most abundant, followed by 8:2 FTOH and 10:2 FTOH. Fingerprint ratios of 6:2 FTOH to 8:2 FTOH and 10:2 FTOH to 8:2 FTOH for impregnating agents (0.02, 0.6, respectively) and lubricants (0.98, 0.74, respectively) in Germany were suggested by Fiedler et al.³² Moreover, 4:2 FTOH was detected only in small amounts in some impregnating agents and not detected in any of the lubricants in the previous study.³² The ratios of 6:2 FTOH to 8:2 FTOH and 10:2 FTOH to 8:2 FTOH determined for all the samples in this study were very different and ranged from zero to 5.4 and from 0.17 to 1.1, respectively. This, together with high 4:2 FTOH levels, suggests contributions from more sources or different FTOH compositions in these sources in the Asian market.

Among the FOSAs and FOSEs, the four samples collected in Chennai, India were significantly different from the other samples. In Chennai, NETFOSA occurred in the highest proportions (up to 83%), followed by NMeFBSE and NMeFOSE. In all other samples NMeFBSE, NMeFOSE, and NMeFOSA were the predominant compounds. The production of FOSE/FOSA chemistry stopped in 2002 and their use in 2003; these compounds have largely been replaced with their 4-C equivalents.²⁸ In Japan, more NMeFOSE ($30 \pm 13\%$) than NMeFBSE ($25 \pm 12\%$) was observed. Some samples in India and most samples in China contained elevated proportions of NMeFBSE.

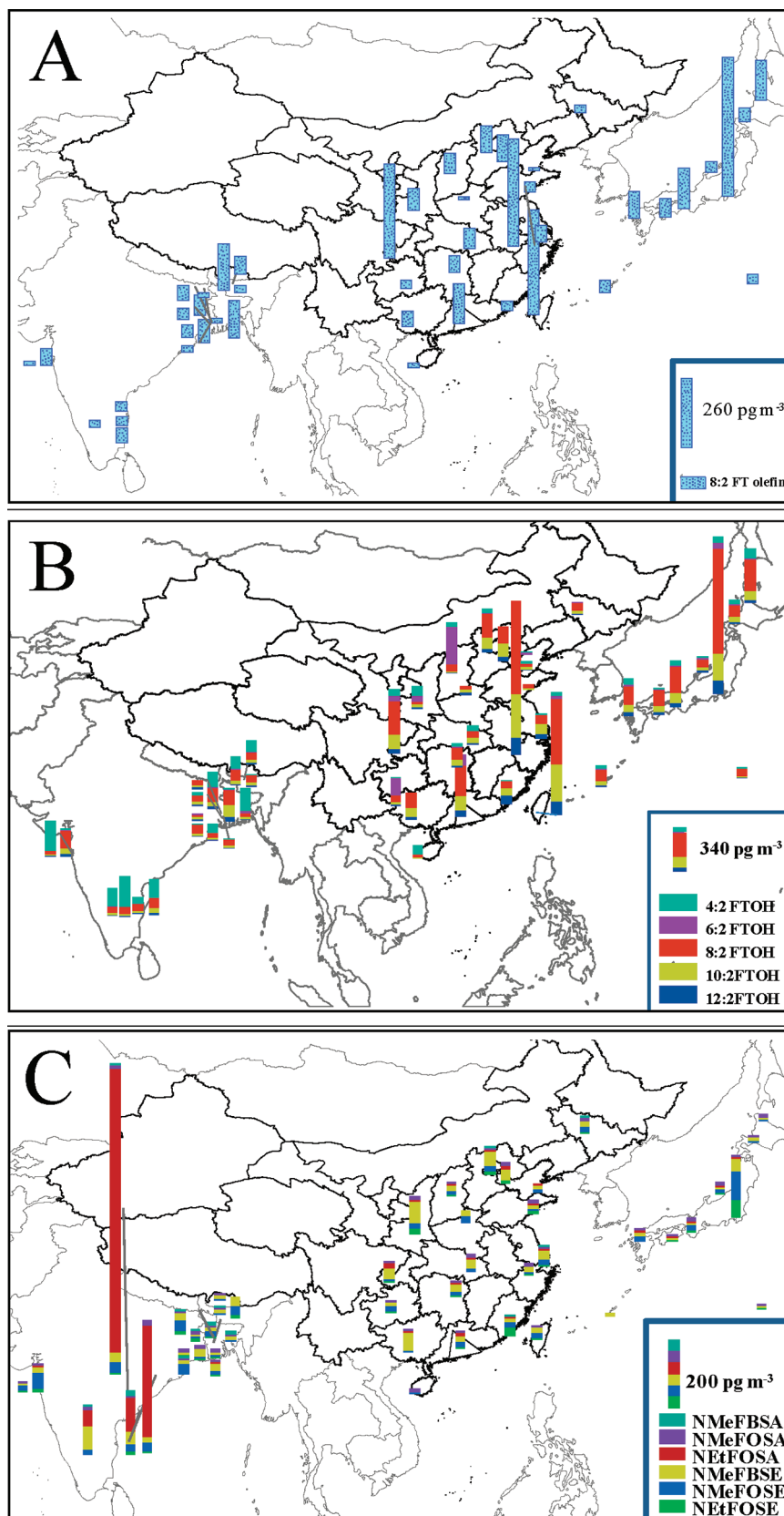


Figure 3. Spatial distribution of 8:2 FTO (A), FTOHs (B), and FOSAs and FOSEs (C).

Table 2. Correlation (r) of Individual Compounds among All the Samples in Asia^a

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTA	8:2 FTA	NMeFBSA	NMeFOSA	NEtFOSA	NMeFBSE	NMeFOSE	NEtFOSE
8:2 FTO			0.925	0.857	0.822		0.642					0.315	0.450
4:2 FTOH								0.492	0.201	0.235			
6:2 FTOH													
8:2 FTOH				0.908	0.903		0.710					0.433	0.504
10:2 FTOH					0.943		0.504					0.183	0.27
12:2 FTOH							0.616					0.319	0.475
6:2 FTA											−0.207	0.119	0.312
8:2 FTA											0.195	0.592	0.789
NMeFBSA										0.191	0.272		
NMeFOSA										0.267	0.283		
NEtFOSA												0.224	
NMeFBSE												0.185	0.284
NMeFOSE													0.743

^a Bold and italic are significant at $p < 0.01$ and $p < 0.05$, respectively.

The high concentration of the FBSE may be caused by the increasing use of perfluorobutane sulfonamide derivatives as substitutes for perfluorooctane sulfonamide derivatives, whereas the levels of NMeFOSE is likely due to their continued volatilization from consumer products manufactured prior to 2002 and 2003 in Japan.

Correlations between Compounds. Correlations between concentrations of contaminants may suggest common sources and similar fates. A correlation matrix was therefore prepared and showed that some compounds were significantly correlated (Table 2). Specifically, correlations were high ($r > 0.90$, $p < 0.01$) between 8:2 FTOH, 10:2 FTOH, and 12:2 FTOH, as observed at other sites in the world.^{24,25} However, 4:2 FTOH and 6:2 FTOH did not show significant correlation with other FTOHs. This implies that these FTOHs are sourced from the different products containing the different FTOH composition in Asia. The concentrations of 8:2 FTO significantly correlated with 8:2 FTA, and both of them also significantly correlated with 8:2 FTOH, 10:2 FTOH, and 12:2 FTOH. FTOs are formed as a byproduct during FTOHs synthesis, and FTOHs are used as precursors to produce FTAs for fluorotelomer-based polymers.⁹ NMeFOSE had a significant ($r = 0.74$, $p < 0.01$) correlation with NEtFOSE, and both were also significantly correlated with 8:2 FTO, 8:2 FTA, 8:2 FTOH, 10:2 FTOH, and 12:2 FTOH, suggesting that those compounds came from the same source regions. The two short-chain PFCs, 4:2 FTOH and NMeFBSA, were significantly ($r = 0.49$, $p < 0.01$) correlated with each other, suggesting these compounds are related to new products. For NEtFOSA and NMeFBSE, there were no significant correlations between each other and with any other major compound, suggesting different uses of different compounds in Asia.

Spatial Distributions. Spatial variations in air concentrations of PFCs across the sampling region are shown in Figure 3. The full data set is given in Table S3 and Table S5. As expected, the predominant declining gradient was urban, rural, and remote locations. On average, air concentrations of fluorotelomer compounds (FTO, FTOH, and FTA) were highest in Japan, followed by China and India, whereas comparable concentrations of perfluorosulfonamides (FOSA and FOSE) were found across the sampling regions (except for NEtFOSA which was found in abnormally high levels near Chennai, India) (D13–D16). However, various spatial trends of concentration and composition were displayed across the various jurisdictions.

In Japan, the highest concentration of PFCs was found at the urban site (J4, Tokyo). Apart from this, the concentrations of PFCs were quite uniform, with the ratio of the highest to lowest measured values (H/L ratio) less than 10. Strong correlations ($r > 0.95$, $p < 0.01$) of PFCs were observed for all the Japanese samples. This suggests similar sources and/or environmental processes of PFCs in Japan.

In India, the PFC concentrations at the rural sites (D1 and D12) did not show any difference to the urban/suburban sites, and the concentrations of all analytes varied strongly. The nonuniform spatial distributions of these PFCs indicate the importance of point sources for the dissemination of these contaminants in the Indian troposphere. Furthermore, clear differences in PFC composition were seen compared to those in Japan. Greater proportions of 4:2 FTOH to total FTOH, and NEtFOSA and NMeFBSE to total FOSA and FOSE were found in India than in Japan. Moreover, the patterns were also different between the samples collected in South India and North India, suggesting the different industrial activities.

In China, the concentrations of PFCs at the two background sites (C17 Tuoji and C18 Jianfeng Mountain) were significantly lower than at the urban sites. Among the urban sites, very high levels of 8:2 FTO, 8:2 FTOH, and 10:2 FTOH were measured in the three most developed and populated zones along the southeast coast, namely Beijing-Tianjing (C10 Beijing and C16 Tianjin), the Yangtze River Delta (C9 Hangzhou), and the Pearl River Delta (C13 Guangzhou), and in the west the new rapidly developed region of Chongqing (C12). This trend is not surprising, given that the source of these compounds appears to be directly related to human population density.⁹ Higher concentrations of 6:2 FTOH were measured at Guiyang (C8) and Taiyuan (C14), the cities with the largest coal and mine industries in China. Their use in lubricants in the mining machinery may be a factor here.³² The concentrations of FOSA and FOSE were consistent across China. A greater proportion of NMeFBSE was observed in the Chinese samples than in most Japanese samples (see Figure 3C).

Background Levels and Composition. Three background samples were collected in this study, J5 Ogasawara, Japan, located in the west Pacific Ocean; C17 Tuoji Island, China, located at the mouth of the Bohai Sea; C18 Jianfeng Mountain, located in the southwest of Hainan Island. The total PFC concentrations at the three background sites were comparable, with 140, 110, and

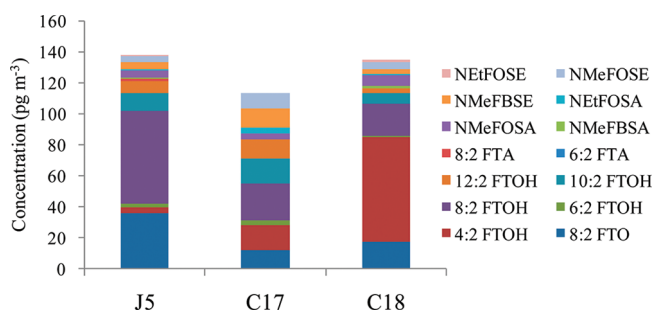


Figure 4. Concentration of individual PFC at the three background sites (J5 = Ogasawara, Japan; C17 = Tuoji Island, China; C18 = Jianfeng Mountain, China).

130 pg m^{-3} at J5, C17, and C18, respectively. These values are comparable to or a bit higher than those in the Atlantic Ocean and the Arctic region.^{4,17} However, clear differences in the PFC mixtures were seen between the three sites (see Figure 4), reflecting the regional differences discussed above. Figure 1 shows the average back-trajectories at 100 m AGL (above ground level) during the sampling period at the three sites. The back trajectories indicated that, at the J5 site, the air mass mainly (43% in Figure 1) came from Japan; this site reflects the typical composition of the Japanese samples, with 8:2 FTO and 8:2 FTOH the predominant compounds. At the C17 site, the air mass predominantly came from the east coast and north of China; the elevated contribution of 4:2 FTOH and NMeFBSE were displayed in this region. At the C18 site, the air mass came from South and Southeast Asia and South China. The dominant contribution of 4:2 FTOH may therefore reflect a regional Southeast and South Asia signal.

ASSOCIATED CONTENT

Supporting Information. Location of sampling sites, sampling duration, detailed information of the MDL, and the concentrations of the individual compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Phone: (86) 20 85291508. Fax: (86) 20 85290706. E-mail: junli@gig.ac.cn.

ACKNOWLEDGMENT

This work was supported by the Chinese Academy of Sciences (No. KZCX2-YW-GJ02), Natural Science Foundation of China (NSFC) (Nos. 40821003 and 41073080). The authors are grateful for the National Oceanic and Atmospheric Administration's Air Resources Laboratory to provide the HYSPLIT transport model and the READY website (<http://www.arl.noaa.gov/ready.html>).

REFERENCES

(1) Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-Ethyl Perfluorobutanesulfonamide. *Environ. Sci. Technol.* **2006**, *40* (3), 864–872.

(2) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* **2004**, *38* (12), 3316–3321.

(3) Stock, N. L.; Furdul, V. I.; Muir, D. C. G.; Mabury, S. A. Perfluoroalkyl contaminants in the Canadian Arctic: evidence of atmospheric transport and local contamination. *Environ. Sci. Technol.* **2007**, *41* (10), 3529–3536.

(4) Dreyer, A.; Weinberg, I.; Temme, C.; Ebinghaus, R. Polyfluorinated compounds in the atmosphere of the Atlantic and Southern Oceans: evidence for a global distribution. *Environ. Sci. Technol.* **2009**, *43* (17), 6507–6514.

(5) Lei, Y. D.; Wania, F.; Mathers, D.; Mabury, S. A. Determination of vapor pressures, octanol-air, and water-air partition coefficients for polyfluorinated sulfonamide, sulfonamidoethanols, and telomer alcohols. *J. Chem. Eng. Data* **2004**, *49* (4), 1013–1022.

(6) Wallington, T. J.; Hurley, M. D.; Xia, J.; Wuebbles, D. J.; Sillman, S.; Ito, A.; Penner, J. E.; Ellis, D. A.; Martin, J.; Mabury, S. A.; Nielsen, O. J.; Andersen, M. P. S. Formation of C7F15COOH (PFOA) and other perfluorocarboxylic acids during the atmospheric oxidation of 8:2 fluorotelomer alcohol. *Environ. Sci. Technol.* **2006**, *40* (3), 924–930.

(7) Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-Ethyl Perfluorobutanesulfonamide. *Environ. Sci. Technol.* **2005**, *40* (3), 864–872.

(8) D'Eon, J. C.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, C4F9SO2N(CH3)CH2CH2OH: Kinetics and mechanism of reaction with OH. *Environ. Sci. Technol.* **2006**, *40* (6), 1862–1868.

(9) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40* (1), 32–44.

(10) Armitage, J.; Cousins, I. T.; Buck, R. C.; Prevedouros, K.; Russell, M. H.; MacLeod, M.; Korzeniowski, S. H. Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. *Environ. Sci. Technol.* **2006**, *40* (22), 6969–6975.

(11) Simcik, M. F. Global transport and fate of perfluorochemicals. *J. Environ. Monit.* **2005**, *7* (8), 759–763.

(12) Boulanger, B.; Peck, A. M.; Schnoor, J. L.; Hornbuckle, K. C. Mass budget of perfluorooctane surfactant in Lake Ontario. *Environ. Sci. Technol.* **2005**, *39* (1), 74–79.

(13) Harada, K.; Nakanishi, S.; Saito, N.; Tsutsui, T.; Koizumi, A. Airborne perfluorooctanoate may be a substantial source contamination in Kyoto area, Japan. *Bull. Environ. Contam. Toxicol.* **2005**, *74* (1), 64–69.

(14) Harada, K.; Nakanishi, S.; Sasaki, K.; Furuyama, K.; Nakayama, S.; Saito, N.; Yamakawa, K.; Koizumi, A. Particle size distribution and respiratory deposition estimates of airborne perfluorooctanoate and perfluorooctanesulfonate in Kyoto area, Japan. *Bull. Environ. Contam. Toxicol.* **2006**, *76* (2), 306–310.

(15) Barber, J. L.; Berger, U.; Chaemfa, C.; Huber, S.; Jahnke, A.; Temme, C.; Jones, K. C. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *J. Environ. Monit.* **2007**, *9* (6), 530–541.

(16) Genualdi, S.; Lee, S. C.; Shoeib, M.; Gawor, A.; Ahrens, L.; Harner, T. Global pilot study of legacy and emerging persistent organic pollutants using sorbent-impregnated polyurethane foam disk passive air samplers. *Environ. Sci. Technol.* **2010**, *44* (14), 5534–5539.

(17) Shoeib, M.; Harner, T.; Vlahos, P. Perfluorinated chemicals in the Arctic atmosphere. *Environ. Sci. Technol.* **2006**, *40* (24), 7577–7583.

(18) Bao, J.; Jin, Y.; Liu, W.; Ran, X.; Zhang, Z. Perfluorinated compounds in sediments from the Daliao River system of northeast China. *Chemosphere* **2009**, *77* (5), 652–657.

(19) Shoeib, M.; Harner, T.; Lee, S. C.; Lane, D.; Zhu, J. P. Sorbent-impregnated polyurethane foam disk for passive air sampling of volatile fluorinated chemicals. *Anal. Chem.* **2008**, *80* (3), 675–682.

(20) Langer, V.; Dreyer, A.; Ebinghaus, R. Polyfluorinated compounds in residential and nonresidential indoor air. *Environ. Sci. Technol.* **2010**, *44* (21), 8075–8081.

(21) Lane, D. A. *Sorbent-coated diffusions denuders for direct measurement of gas/particle partitioning by semi-volatile organic compounds*; Gordon and Breach Science Publishers: Amsterdam, 1999.

(22) Dreyer, A.; Shoeib, M.; Fiedler, S.; Barber, J.; Harner, T.; Schramm, K. W.; Jones, K. C.; Ebinghaus, R. Field intercomparison on the determination of volatile and semivolatile polyfluorinated compounds in air. *Environ. Chem.* **2010**, *7* (4), 350–358.

(23) Martin, J. W.; Muir, D. C. G.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. Collection of airborne fluorinated organics and analysis by gas chromatography/chemical ionization mass spectrometry. *Anal. Chem.* **2002**, *74* (3), 584–590.

(24) Oono, S.; Matsubara, E.; Harada, K. H.; Takagi, S.; Hamada, S.; Asakawa, A.; Inoue, K.; Watanabe, I.; Koizumi, A. Survey of airborne polyfluorinated telomers in Keihan area, Japan. *Bull. Environ. Contam. Toxicol.* **2008**, *80* (2), 102–106.

(25) Dreyer, A.; Matthias, V.; Temme, C.; Ebinghaus, R. Annual time series of air concentrations of polyfluorinated compounds. *Environ. Sci. Technol.* **2009**, *43* (11), 4029–4036.

(26) Jahnke, A.; Berger, U.; Ebinghaus, R.; Temme, C. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53 degrees N–33 degrees S). *Environ. Sci. Technol.* **2007**, *41* (9), 3055–3061.

(27) Dreyer, A.; Ebinghaus, R. Polyfluorinated compounds in ambient air from ship- and land-based measurements in northern Germany. *Atmos. Environ.* **2009**, *43* (8), 1527–1535.

(28) Piekarz, A. M.; Primbs, T.; Field, J. A.; Barofsky, D. F.; Simonich, S. Semivolatile fluorinated organic compounds in Asian and Western U.S. air masses. *Environ. Sci. Technol.* **2007**, *41* (24), 8248–8255.

(29) Butt, C. M.; Young, C. J.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. Atmospheric chemistry of 4:2 fluorotelomer acrylate [C₄F₉CH₂CH₂OOC(O)CH=CH₂]: kinetics, mechanisms, and products of chlorine-atom- and OH-radical-initiated oxidation. *J. Phys. Chem. A* **2009**, *113* (13), 3155–3161.

(30) Stock, N. L.; Lau, F. K.; Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. Polyfluorinated telomer alcohols and sulfonamides in the North American troposphere. *Environ. Sci. Technol.* **2004**, *38* (4), 991–996.

(31) Su, N. Y.; Scheffrahn, R. H. Toxicity and lethal time of n-ethyl perfluorooctane sulfonamide against 2 subterranean termite species (isoptera, rhinotermitidae). *Fla. Entomol.* **1988**, *71* (1), 73–78.

(32) Fiedler, S.; Pfister, G.; Schramm, K.-W. Poly- and perfluorinated compounds in household consumer products. *Toxicol. Environ. Chem.* **2010**, *92* (10), 1801–1811.