Presence and Partitioning Behavior of Polyfluorinated Iodine Alkanes in Environmental Matrices around a Fluorochemical Manufacturing Plant: Another Possible Source for Perfluorinated Carboxylic Acids?

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The indistinct origins of some ubiquitous perfluorinated alkyl acids have attracted great attention in recent decades. In this present work, even-chained polyfluorinated iodides (PFIs), a group of volatile perfluorinated compounds (PFCs), including four perfluorinated iodine alkanes (FIAs) and three polyfluorinated telomer iodides (FTIs) were confirmed to be present in the environment. A wide concentration range was found for FIAs at 1.41 to 3.08×10^4 pg/L, and for FTIs at 1.39 to 1.32×10^3 pg/L in the ambient air collected around a fluorochemical manufacturing plant in Shandong province, northern China. Whereas for surface soils, most of these PFIs were below detection limits and only small amounts of analytes with higher carbon chain (such as perfluorododecyl iodide and 1H,1H,2H,2H-perfluorodecyl iodide, 16.6−499 pg/g) could be sporadically detected. The presence of the PFIs in different environmental matrices in the investigated area and calculated vapor pressures (0.095−20.4 Torr) verify that they can be considered as volatile organic chemicals and easily be released into the atmosphere. Together with reported degradation ability and long-range transport potential, the identification of these PFIs indicates that unintentional release during the telomer reaction process might also be another route for the formation and distribution of certain polyfluorinated alcohols, aldehydes, and carboxylic acid derivatives under oxidative conditions in the environment.

Introduction

Polyfluorinated compounds (PFCs) are industrial additive chemicals that have been found worldwide in environmental matrices (*1, 2*), humans (*3, 4*), and other biological species including those living in pristine areas (*5, 6*). Global distribution of these PFCs showed that, among all of these polyfluorinated substances, the most frequently detected compounds are perfluoroalkyl sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs). However, as these perfluorinated anions are nonvolatile in the ambient environment, their long-range transport pathways are still a subject of debate. Hypotheses were postulated that oceanic transport, aerosol enrichment followed by water−air transfer (*7–9*), or emission and degradation of volatile precursors as indirect sources (*10–12*) are the main responsible pathways. Recent studies assessing the transport pathways of PFCs revealed that mass flux from direct sources (e.g., emission during manufacture) are responsible for the main contributions to the global-scale environmental fate of PFCAs (*7, 13, 14*). However, formation of perfluorooctanoate and other related substances from potential precursors such as fluorotelomer alcohols (FTOHs) via biodegradation and atmospheric oxidation have also been confirmed by model deduction (*15*), laboratory experiments (*10, 16, 17*), and field evidences (*11, 12*). Meanwhile, other overlooked indirect source precursors such as nonpolymeric polyfluoroalkyl phosphate surfactants and fluoroacetates have also been found, which could be transformed into related fluorocarboxylic acids through biodegradation and photo-oxidation routes (*18–20*).

Polyfluorinated iodides (PFIs) are intermediates and products of telomerization process in the synthesis of FTOHs, ammonium perfluorooctanoate (APFO), and related compounds through iodide oxidation and iodide carboxylation (*7, 21*). Following a recent discontinued utilization of the electrochemical fluorination (ECF) process in the production of certain perfluorochemicals, the production volumes of some PFI homologues dramatically rose to ten thousand to ten million pounds per year (*22*) and have thus been added into the high production volume (HPV) list (*23*). Computer models predicted that some homologues of these groups of chemicals have physical−chemical properties and atmospheric oxidation half-lives that might result in long-range transport potential (*24*). Smog chamber experiment also showed that 1H,1H,2H,2H-perfluorohexyl iodide (PFHxHI) could react with OH radicals and Cl atoms to form several perfluorocarboxylic acids (*25*). However, detailed investigation has yet to be conducted on the presence and environmental fate of these PFIs, as they should only recently be emitted at large quantities into the environment.

In this study, a thermal desorption/gas chromatography/high-resolution mass spectrometry (TD-GC-HRMS) method for ambient air and a solid-phase microextraction/gas chromatography/low-resolution mass spectrometry (SPME-GC-LRMS) method for surface soil samples were established and applied to determine the presence and distributions of these PFIs around a manufacturing area.

Materials and Methods

Materials. All materials and standards were obtained from suppliers as shown below (Figure 1). Perfluorohexyl iodide (acronym: PFHxI), perfluorooctyl iodide (PFOI), perfluorodecyl iodide (PFDeI), perfluorododecyl iodide (PFDoI), 1H,1H,2H,2H-perfluorohexyl iodide (PFHxHI), 1H,1H,2H,2H-perfluorooctyl iodide (PFOHI), 1H,1H,2H,2H-perfluorodecyl iodide (PFDeHI), 1H,1H,2H,2H-perfluorododecyl iodide (PFDoHI), 1,8-diiodoperfluorooctane (PFODiI), and 1H,1H,2H,2H,3H,3H-perfluorononyl iodide (internal standard, IS) were purchased from Sigma-Aldrich (St. Louis, MO). 1,4-Diiodoperfluorobutane (PFBuDiI) and 1,6-diiodoperfluorohexane (PFHxDiI) were from Alfa Aesar (WardHill, MA). HPLC grade methanol and acetone were supplied by Fisher Scientific (Hampton, NH) and Dima Technology Inc. (Richmond Hill, ON), respectively. Ultrapure water (18.3 MΩ) was generated from a Milli-Q system (Millipore, Billerica, MA), and 100-μm polydimethylsiloxane (PDMS), 65-μm polydim-
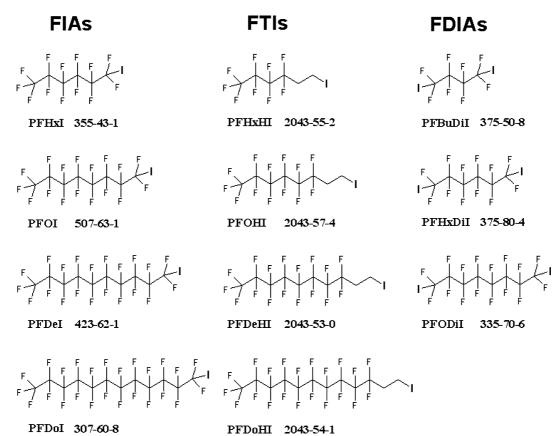
FIGURE 1. Analyte structure, acronym, and CAS Registry Number.

FIAs

PFHxI   355-43-1

PFOI   507-63-1

PFDeI   423-62-1

PFDoI   307-60-8

FTIs

PFHxHI   2043-55-2

PFOHI   2043-57-4

PFDeHI   2043-53-0

PFDoHI   2043-54-1

FDIAs

PFBuDiI   375-50-8

PFHxDiI   375-80-4

PFODiI   335-70-6

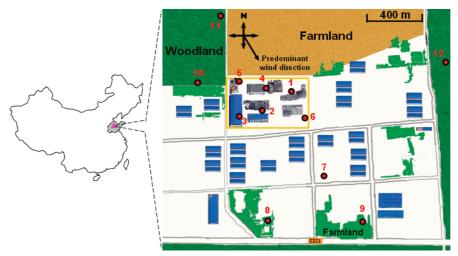**FIGURE 2. Ambient air and soil sampling sites in the investigated area. Facilities in the fluorochemical manufacturing sites are: Site 1 and Site 2, reaction tower; Site 3, warehouse; Site 4, precursor synthesis workshop and wastewater treatment facility; Site 5, wastewater pumping station; and Site 6, cooling facility. Buildings outside the fluoro-manufactory are workshops of various unrelated factories.**

ethylsiloxane/divinylbenzene (PDMS-DVB), and 75-μm carboxen/PDMS solid-phase microextraction (SPME) fibers were from Supelco (Bellefonte, PA). Tenax TA (150 mg, 35/60 mesh)/Carbograph 1TD (200 mg, 40/60 mesh) multisorbent cartridges were purchased from Markes International (Llantrisant, UK).

Sample Collection. Ambient air and surface soil samples were collected around a fluorotelomer manufacturing plant at an industrial zone located in Shandong Province, northern China (Figure 2) in September, 2009. The predominant wind direction was mainly from the northwest with wind strength grade between 1 and 2 (1−11 km/h) for the 1-day sampling period. As our preliminary experiment suggested that air

concentrations of the PFIs might decrease rapidly with distance, sampling sites were chosen densely around the plant to investigate potential emission points and pollution pathways. Most sampling sites (Sites 1−9) were located near possible emission sources and at downwind direction. Three control sites (Sites 10−12) were located at the other three perpendicular wind directions. Ambient air samples were collected following a previously described procedure with some minor modifications (26). In short, each Tenax TA/ Carbograph 1TD multisorbent cartridge was connected to a portable membrane pump through a piece of silicone tube. Air samples were collected in triplicate at each site. The samplers were placed at a height of 1.5 m above ground

level, 5 m apart from each other and distant from roads. A volume of 3.75 L of ambient air was passed through the desorption tubes within 25 min at a constant gas flow rate of 150 mL/min. Ambient temperature (22.4−27.9 °C), humidity (30−61%), and atmospheric pressure (101.2−101.5 kPa) were recorded in order to correct for actual air sampling volume. Additional backup tubes were connected after the sampling cartridges to check possible breakthrough during the sampling procedures. Three field blank tubes were also taken to the field, uncapped and exposed to the air for one sampling cycle and used to subtract possible diffusive contamination. After the sampling cycles, the cartridges were well packed and stored inside a metal container with activated charcoal. Corresponding surface soil samples were collected at depths of about 2 cm at the sampling sites, packed in aluminum foil, and sealed in polypropylene bags. All samples were kept in an ice-box and immediately transported back to the laboratory.

Analysis of Air Samples. Detailed optimization of instrumental parameters and analysis procedures were published elsewhere (26) and only summarized here. Before analysis, 200 pg of internal standard in 1 μL of methanol was spiked into the cartridges through a solution loading rig. The solvent was vaporized with the application of helium makeup gas at a flow rate of 30 mL/min for 5 min, allowing the IS and analytes to be adsorbed onto the sorbents. The sampling tubes, backup tubes, and field blanks were loaded directly onto the UNITY series 2 (Markes International, Llantrisant, UK) thermal desorption instrument. After interferents had been removed by the split purge steps, analytes of interest were first released from the cartridges at 280 °C for 8 min, refocused on a cold trap, and then rapidly injected into a TRACE GC Ultra gas chromatograph. A high-resolution double-focusing magnetic sector (DFS) mass spectrometer (Thermo Fisher Scientific, Waltham, MA) was used as detector for its low method detection limits (MDL, 0.04−1.22 pg/L). A DB-624 GC column (6% cyanopropyl-phenyl, 94% dimethyl polysiloxane, 0.25 mm i.d., 30 m long, 1.4 μm film thickness, J&W Scientific, Folsom, CA) was chosen for the separation. Initial GC oven temperature program was at 35 °C for 6 min, then 5 °C/min to 135 °C, and 2 °C/min to 145 °C. Electron impact (EI) positive mode was chosen at electron energy of 45 eV. Source temperature was set at 250 °C and MS resolution was tuned to 5000 (5% valley) with perfluorotributyl amine as the instrument reference compound. If the PFI concentrations exceeded the upper limit of the method linear range (5−1000 pg), the analysis was performed with a higher amount of IS loaded into another triplicate sample cartridge. Split mode was then used in the sample desorption procedure allowing the analyte concentrations to be within the extended method linear range.

Analysis of Soil Samples. Headspace SPME coupled with an Agilent 6890 GC/5973 MS system was used for the determination of the PFI concentrations in soil samples. Detailed optimization procedures for pretreatment parameters are given in the Supporting Information (SI). Briefly, approximately 1 g of soil sample was introduced into a 150-mL glass vial and 50 mL of ultrapure water was added into the vial and the soil was subsequently homogenized into water slurry. Supernatant fluid was kept at 25 °C and 2 ng of 1H,1H,2H,2H,3H,3H-perfluorononyl iodide in 50 μL methanol was added as the internal standard. Afterward, the glass vial was sealed with a septum cap, placed aside for 5 min, and the slurry was intensively mixed by a custom-made magnetic glass stirrer. The PDMS-DVB fiber was inserted into the vial and exposed at the headspace through a custom-made handle. After exposure for 30 min, the SPME fiber was withdrawn into the needle, immediately inserted into the GC injector, and left for 7 min at 200 °C to ensure complete analyte desorption. The GC separation column and oven

temperature program used for soil sample analysis were the same as for the air sample analysis mentioned above. EI positive mode was also chosen while electron energy of 70 eV was used as the instrument default setting. As abundance of high m/z characteristic ions decrease at high collision energy, smaller fragments ($m/z < 300$) were also selected as confirmation ions in the selective ion monitoring (SIM) mode and are shown in Table S1 (SI).

Quality Assurance and Quality Control. Before ambient air sample collection, each cartridge was baked twice at 325 °C for 30 min and then quickly sealed with prerinsed brass screw caps to eliminate possible contamination. Before sample analysis, three blank tubes were checked and analytes of interest were all below their limits of detection (LOD, 0.16−4.6 pg) in the TD-GC-HRMS system. The recoveries for all of the PFIs were around 100% when spiked cartridges (200 pg for each PFI and IS) were analyzed in triplicate, and residue concentrations were very low (<1%) when the spiked cartridges were reanalyzed for another desorption cycle. For each batch of seven samples, a laboratory blank and a laboratory check standard (200 pg of each analytes plus IS) were analyzed to eliminate possible systematic residues and check the status of the GC/MS instrument. If more than 15% deviation was observed, a new calibration curve was performed. Once samples with high concentrations were analyzed (especially analyte concentration >100 LOD), additional desorption procedures with laboratory blanks were employed to ensure that residues were properly eliminated. Three field blanks were also used to check possible field contamination. PFDoHI was found to be present in two field blanks and an average concentration of 1.3 pg/L was subtracted from the PFDoHI concentrations in sampling tubes as the background contamination level. The backup tubes collected at the sampling sites were also analyzed and the analyte concentrations in backup tubes were under the LODs or very low (<1.5%) compared with those in the corresponding sampling tubes, indicating no obvious breakthrough occurred during the sampling procedure.

Before the analysis of soil samples, all glassware was thoroughly rinsed with acetone and water, each in triplicate. One method blank (50 mL of pure water) was also included for each batch of seven samples to check possible cross-contamination.

Result and Discussion

PFI Concentrations in Ambient Air. Spatial concentrations of the detected analytes are summarized and presented in Table 1. Four perfluorinated iodine alkanes (FIAs) and three polyfluorinated telomer iodides (FTIs) were positively identified. PFDoI and PFDoHI were detectable in all air samples, whereas the presence of PFHxI, PFOI, PFDeI, PFOHI, and PFDeHI was restricted to the manufacturing plant and related downwind areas. PFHxHI and diiodofluoroalkanes (FDIAs) such as PFBuDiI, PFHxDiI, and PFODiI were also included in the analytical method but none of these analytes could be found in any of the air samples. Briefly, PFI levels varied widely from a few picograms per liter to several nanograms per liter, with highest individual concentrations of 3.08×10^4 pg/L for PFOI and 2.07×10^4 pg/L for PFHxI.

As noted in Table 1, the concentrations of PFOI were higher than the other even carbon-numbered homologues at most of the sampling sites, and the concentrations were then successively followed by PFHxI, PFDeI, and PFDoI (Figure 3). The results indicate that PFOI and PFHxI were the major FIA homologues in the ambient air and might also be the main products during the FIA synthesis procedures. This is further supported by reported literature that new APFO production is based on >99% pure PFOI in the U.S. (7). However, the positive identification of PFHxI, PFDeI, and PFDoI also proved that other homologues of FIAs were

TABLE 1. PFI Concentrations Found in Ambient Air and Soil Samples

site	PFHxI	PFOI	PFDeI	PFDoI	PFOHI	PFDeHI	PFDoHI
ambient air samples [average ± standard deviation, pg/L]							
site 1	2.07×10^4	3.08×10^4	9.11×10^3	5.43×10^2	1.57	3.01	4.28
site 2	$(9.53 \pm 0.32) \times 10^2$	$(6.23 \pm 2.55) \times 10^3$	$(1.26 \pm 0.30) \times 10^2$	$(2.89 \pm 1.54) \times 10^2$	$(2.29 \pm 0.38) \times 10^2$	$(4.63 \pm 0.20) \times 10^3$	88.4 ± 15.6
site 3	7.50×10^2	1.58×10^3	2.53×10^2	69.3	3.68×10^2	1.32×10^3	1.30×10^2
site 4	$(2.73 \pm 0.44) \times 10^2$	50.7 ± 12.2		1.68 ± 0.44	1.60 ± 0.28	2.76 ± 0.76	3.37 ± 0.58
site 5	52.1 ± 18.0	82.3 ± 14.1	2.41 ± 1.37	3.84 ± 1.41	18.6 ± 4.4	53.1 ± 8.9	11.3 ± 1.9
site 6	33.4 ± 6.2	28.1 ± 8.4	8.34 ± 2.24	2.80 ± 0.64	2.69 ± 0.42	13.1 ± 3.3	4.95 ± 0.93
site 7	56.9 ± 7.9	69.0 ± 8.4	6.15 ± 1.25	2.66 ± 0.34	1.55 ± 0.05	1.87 ± 0.08	3.11 ± 0.46
site 8	4.78 ± 0.29	11.7 ± 1.0		1.95 ± 0.03	1.46 ± 0.03	1.46 ± 0.50	2.82 ± 0.05
site 9	7.48 ± 2.18	11.3 ± 0.2		1.82 ± 0.21	1.42 ± 0.04	1.39 ± 0.49	2.82 ± 0.44
site 10				1.41 ± 0.35			2.66 ± 0.05
site 11				1.45 ± 0.18			2.56 ± 0.06
site 12				1.57 ± 0.10			2.39 ± 0.29
soil samples [pg/g][a]							
site 1		194	67.7	101	16.6	145	303
site 2							
site 3						499	
site 4						227	

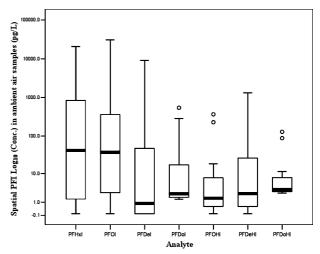[a] PFIs were all < LOD in soil samples at sites 5–12.

FIGURE 3. Spatial PFI concentrations (logarithmic scale) in ambient air samples. The broad lines represent the 5th, 50th, and 95th percentiles; the boxes represent the 25th–75th percentiles; data outside of 5th–95th percentiles are given in dots. Nondetects were set as null.

present as well during the manufacturing processes in the investigated area, and these chemicals could as well be leaked into the environment. A similar trend was also observed for FTIs in that PFDeHI was the most abundant contaminant at most sampling sites with highest concentration of 1.32×10^3 pg/L, and sequentially followed by PFOHI and PFDoHI (Figure 3). Distinguished from that of FIAs, the median concentration of FTIs was highest for the C-10 homologue (PFDoHI). This could be explained by the fluorotelomer-based manufacturing process (Figure S1, SI), where FTIs are synthesized from FIAs through ethylene insertion and thus a relationship exists between FIAs and their corresponding FTI homologues (7, 21). PFHxHI is usually used as intermediate in the production of 4-carbon-fluorinated compounds, such as 4:2 olefins, 4:2 acrylate monomer, and ammonium perfluoropentane during the telomer-based manufacture process, but the absence of this compound in the collected samples indicated that short-chain FIAs (C ≤ 4) might not be produced in this manufacturing plant. This is consistent with previous reported estimation that PFOHI, PFDeHI, and PFDoHI might be the most environmentally relevant FTIs based on the production of FTOHs and related products (27). Although FDIAs have chemical structures and physical–chemical properties similar to those of the FIAs and FTIs, they were not detected in any of the collected samples. This might hint that these fluorinated telechelics, which were also reported to be used as synthesis precursors in telomerization process to form fluoroelastomers (Figure S1, SI) (28), were not used as intermediates or present as byproducts in the investigated manufacturing plant. The compositions of FIA production mixtures from the investigated fluorochemical plant consisted of 32−38% PFHxI, 30−35% PFOI, 20−26% PFDeI, and 6−8% PFDoI. For FTIs, the proportions were: PFOHI (32−38%), PFDeHI (30−35%), PFDoHI (20−26%), and other homologues (C ≥ 14, 6−8%). However, as shown in Figure 4, the composition profiles of FIA and FTIs in the ambient air are somewhat different from those in the production mixtures. The proportions of higher molecular weight homologues (such as PFDeI (1.7−15%) and PFDoI (0.9−8.8%)) for FIAs in most air samples were lower than those in the production mixture. A similar pattern was also observed for the FTI homologues. Relative amounts of 7.1−14% for PFDoHI in the samples near the emission source were also much lower than what is reported in the production mixture, whereas the proportion increased to 24−50% in the downwind areas. Pearson correlation test revealed that there
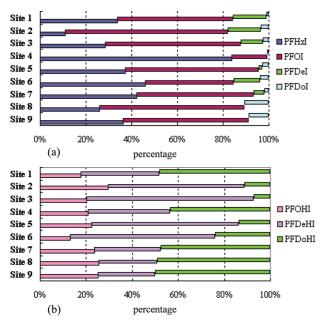
FIGURE 4. Composition profiles of FIAs (a) and FTIs (b) in the ambient air samples in the manufacturing plant and related downstream area.

were good relationships (two-tailed, $p < 0.01$) among the individual FIA homologues in all collected air samples, indicating that they might have been emitted into the environment in a similar pattern. A similar observation was also found for the FTIs. It is hypothesized that FIAs with short carbon chain, such as PFHxI and PFOI, have higher vapor pressures than the long chain homologues, thus leading to higher relative amounts of these short chain chemicals to be emitted into the ambient environment during the manufacturing process. Also seen in Table 1, at most sampling sites, concentration of ΣFIAs was higher than ΣFTIs. It is possible that the usage of FIAs is higher in this manufacturing plant, or FIAs have higher potential to be volatilized and thus emitted into the environment. This is supported by previous publications which suggested that vapor pressures for perfluorinated chemicals are equal to or greater than those of the analogues with fluorine atoms replaced by hydrogen atoms (29, 30).

To evaluate the spatial distributions and long-distance transport abilities of these PFIs, sampling sites were chosen at places in the range of 1 km near the manufactory. As shown in Table 1, there is a large variation in concentrations for the FIAs (e.g., 141 to 6.12×10^4 pg/L for ΣFIAs) and the content decreased by a factor of ~400 even within the manufacturing area (Sites 1−6). Highest contents of FIAs were observed at the sampling point near a chemical reaction tower (Site 1). Two-way ANOVA analysis ($p < 0.05$) showed that the concentrations of FIAs at that site were significantly higher than those of the other sites, indicating that a large amount of FIAs might have been emitted into the ambient environment during chemical production. A similar trend was obtained for the FTIs, as sampling sites with high FTI concentrations were converged at the western part of the plant. The rapid decreasing pattern was even more obvious when the PFI contents at the downwind areas were taken into account. The concentrations declined to low pg/L levels for most of the analytes at about 1 km away from the source (Sites 8, 9). PFDeI was below the MDL (0.860 pg/L) while reduction factors of approximately 2700 and 940 were observed for PFOI and PFDeHI, respectively. It is speculated that photodegradation and transformation might not be sufficient to explain the sudden drop of airborne PFI concentrations in such a short distance, as computer models

and smog chamber experiments predicted the atmospheric oxidation half-lives to be several days for FTIs (24, 25). A more probable explanation is a rapid distribution of PFIs in the atmosphere and/or to other matrices once emitted into the environment. Similar rapid distribution phenomena were also found for atmospheric tracers such as volatile cyclic perfluoroalkanes, which were purposely released from a point source near ground level and allowed to be quickly diffused in the atmosphere to study the local-scale atmospheric transport and dispersion processes (31, 32).

PFI Concentrations in Soil Samples. The detection frequency of PFIs in soil samples was far lower than that in ambient air. The analytes were almost all below detection limits and only found at the most contaminated air sampling sites in the plant. PFOI (194 pg/g), PFDeI (67.7 pg/g), and PFDoI (16.6, 101 pg/g) were sporadically detected at the site near the chemical reaction tower, while PFDeHI (227, 499 pg/g) and PFDoHI (303 pg/g) were detectable only at two sites in the western part of the plant. Different concentration profiles were found in soil samples compared with the air samples. None of the lower molecular weight homologues, such as PFHxI and PFOHI, were detected in any of the soil samples, whereas heavier homologues accounted for a large part of the mass composition. The result might partly be explained by their physical−chemical properties, which are related to the partitioning between matrices. Stoichiometric model (33) showed that the calculated vapor pressures ranged from 0.122 (PFDoI) to 20.4 Torr (PFHxI) for the FIAs and 0.095 (PFDoHI) to 2.9 Torr (PFOHI) for the FTIs, which were almost the same as or even higher than the calculated values for FTOHs (0.008 Torr (10:2 FTOH) to 9.94 Torr (4:2 FTOH)) and measured results (1.08 Torr (10:2 FTOH) to 7.44 Torr (4:2 FTOH)) (29). It is widely accepted that chemicals with vapor pressures above 0.1 Torr are usually classified as volatile organic compounds (VOCs) (34) and consequently most of the PFIs can also be considered as neutral volatile fluorinated substances, which would mostly be evaporated from soil or directly emitted into the atmosphere under ambient conditions. However, heavier homologues of the FIAs and FTIs have relatively higher predicted octanol−air partition coefficient (Log K_{oa}, e.g., 4.70 for PFDoHI and 3.23 for PFHxHI) and coefficient of fraction sorbed to atmospheric particulates (Log phi, e.g., −4.80 for PFDoHI and −6.90 for PFHxHI) (33). They might therefore be more prone to be associated to particles and soil, leading to relatively higher background concentrations in these matrices.

PFI Degradation Potentials to Form Other Fluorinated Compounds in the Environment. A literature report suggests that a considerable amount of perfluorinated chemicals could be emitted during the synthesis processes, such as a 5−10% perfluorooctanoate loss in total ECF manufacturing and an approximate 10% of ammonium perfluorononanoate emission (7). As thousands of tonnes of PFIs have been produced worldwide in recent years and also used as commercial feedstock in various telomer-based manufacturing processes, it is possible that a considerable proportion of PFIs might have been released into the environment from these point sources. However, although there are similarities in physical−chemical properties between these PFIs and some PFC precursors such as FTOHs and N-alkyl perfluorooctane sulfonamides, to our knowledge, only a few studies have reported the transformation pathways of PFIs through degradation processes such as hydrolysis and photolysis in the environment. Rayne and co-workers were the first to consider both the SN_1 and SN_2 abiotic hydrolysis reaction mechanisms of FTIs and showed that both the temperature and pH were key factors to the hydrolysis dynamics (35). In considering marine and landfill conditions (typically 0−40 °C, pH 4−9), FTI half-lives were estimated to be between 10 and 1000 days and the hydrolysis product formation might

be important in aquatic systems, while it was considered to be negligible in the atmosphere. Further detailed investigation on the atmospheric fate of PFIs was conducted by reacting PFHxHI with OH radicals and Cl atoms (25). It was suggested that rate constants of the two reactions were at the same magnitude while photolysis would dominate the PFHxHI atmospheric half-life. $C_4F_9CH_2CHO$ was affirmed as the primary product, which could be transformed to related PFCAs by subsequent radical reactions. The reported FTI photolysis was initiated by an α-hydrogen abstraction, which is similar to the atmospheric chemistry of FTOHs and alkyl iodides (16, 36). By comparing the PFHxHI oxidation pathways with that previously published for 4:2 FTOH, it is judged that almost the same products were formed during the oxidation pathways (16, 25). Although the transformation rate of PFHxHI reacting with chlorine atoms was approximately an order of magnitude lower than for 4:2 FTOH, the observed yield of the primary and other products did not differ significantly. Hence, the similarities between PFHxHI and 4:2 FTOH indicated that PFHxHI has the potential to be another PFCA precursor. Although PFHxHI was not detected in our investigated area, the mentioned photolysis process is considered to be unaffected by reactant chain length (25), and the long chain FTIs detected in our work might also be subjected to similar atmospheric fate. On the other hand, studies concerning the environment fate of FIAs are very rare. Currently, stoichiometric models such as VOPWIN V1.92 (33) could not estimate the rate constant for the reactions between FIAs and atmospheric hydroxyl radicals. This might be mainly because there is no abstractable hydrogen in the FIA molecular structures for OH radicals to react with, which is different from that for FTOHs and FTIs. Calvert and co-workers discussed that photolysis is the major atmospheric loss mechanism for methyl-, ethyl-, and *n*-propyl iodides by donating alkyl radicals and iodine atoms, and their half-lives are approximately a few days (37). The FIAs could photochemically form perfluorinated alkyl radicals and may have different atmospheric fates in various conditions. It might be possible that the perfluorinated alkyl radicals and peroxy radicals formed by reacting with oxygen can undergo backbone "unzipping" process by cleavage to form smaller molecules such as COF_2 and CF_3OH, or they might further react with $CH_3O_2\cdot$ to form perfluoroalcohols and related PFCAs (Scheme S1, SI). However, the importance of each transformation mechanism still remains to be confirmed by further studies to assess the environmental behaviors and fate of the PFIs from potential point sources.

In this study, a rudimentary investigation was conducted, for the first time, to assess the environmental fate and behaviors of polyfluorinated iodine alkanes in the vicinity of a fluorochemical manufacturing plant. FIAs and FTIs detected in ambient air and surface soils suggested unintentional release of PFIs during the telomer-based manufacturing process. As a majority of the PFIs partition to the gas phase, it is considered that long-range transport is possible for these chemicals. As PFIs have been reported to have the potential to be converted into related PFCAs, more research is warranted to elucidate their environmental fate, long-range transport abilities, and the atmospheric transformation mechanisms. Because PFOI was also detected in fluorotelomer raw materials at high parts-per-million level (38), research for other possible emission sources and consumer usages, as well as estimating total PFI mass flux in different environment compartments and influences on the dissemination of other well-known PFCs to pristine areas should also be carried out.

Supporting Information Available
Detailed information about telomer reaction scheme of polyfluorinated iodine alkanes, possible reaction scheme of perfluorinated alkyl radicals, and SPME-GC-LRMS parameter optimization. This material is available free of charge via the Internet at http://pubs.acs.org.

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