DETERMINATION OF FLUOROTELOMER ALCOHOLS AND PERFLUOROALKYL CARBOXYLATES IN AIR ENVIRONMENT IN THAILAND

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Introduction

Perfluorinated compounds (PFCs) are used as processing additives, during fluoropolymer productions, and surfactants in consumer products for over 50 years[1].Perfluoroalkylcaboxylates (PFCAs) and sulfonates (PFASs), which are the most concerned groups of PFCs,are known to be persistent, bioaccumulative and toxic to human and animals[2]. PFCAs and PFASs arehighly water soluble but less volatile[3], and theyhave been detected in water environmentworldwide[4-5]. PFCAs are not found in significant quantities as a vapor but they can be associated with particulate matter in the air[6]. Precursor compounds such as fluorotelomer alcohols (FTOHs), which can be degraded to PFCAs[7-8] and are more volatile, were detected in the air not only in developed countries[9-13] but also in a global scale along Atlantic and Southern oceans[14]. Information on contamination of FTOHs and PFCAs in air environment has been developedbut mainly in developed countries, whereas very few studies have been conducted in developing countries including Thailand. PFCs contamination was observed in water and wastewater in Thailand[15-16] but the contamination in the air hasnever been studied before. This study is the first investigation ofFTOHs and PFCAs in outdoor and indoor air in Thailand, and the concentrations were compared with those in previous studies. In addition, composition profiles and particle-gas partitioning of the target compounds were examined in order to interpret their possible sources and behavior in the atmosphere.

Materials and methods

Sample Collection: Survey was conducted in the Central and Eastern parts of Thailand. Various outdoor and indoor areas, whichare suspected to be contaminated by FTOHs and PFCAs, were selected as sampling sites.Detailed characteristics of the sites; wastewater treatment plants (WWTPs) and residentialareas for outdoor air, and theplaces for indoor air, are demonstrated in **Table 1**. Samples were collected during 10 September - 29 October 2012 by using a high volume air sampler (Sibata, Japan) at the flow rate of approximately 500 L/min for24 h (~720 m^3). This study adapted three types of sampling media that comprised of glass fiber filters (GFFs, Advantec®, Japan), polyurethane foams (PUFs, Sibata, Japan) and activated carbon fiber felts (ACFs, Sibata, Japan). All the samplingmedia were pre-cleaned by soaking into ethyl acetate for 2 times and methanol for 3 times.One set of the sampling media(GFF and PUF–ACF–PUF) was used to collect the target compounds at each sampling site. Particle phase fractions of the target compounds were collected on GFF, while gas phase fractions were trapped in a column of PUF–ACF–PUF.Another set of the media was also prepared at four sampling sites (1, 2, 7 and 9) as a field blank to examine contamination during all of the procedures. The field blank set wasjust placed close to the sampling points without installation in the vacuum pump for sampling.

Sample Preparation: For particle phase FTOHs extraction, a half of GFF was soaked in 10 mL methanol and shaken for 1 hour. The extraction process was repeated for 4cycles (~40 mL in total). For gas phase FTOHs extraction, PUFs and ACF were separately soaked and shaken in methanol. The extraction was done for4cyclesand extracts were combined (~900 mL in total). Mass-labeled FTOH ($^{13}C_2$ 8:2 FTOH) was spiked into the sampling media before extractionto determine the recovery.Extracts of particle and gas phases FTOHs were separately evaporated to 3-5 mL by using a rotary evaporator. After that, the concentrated solutes were cleaned up by using 0.2 μm syringe filters and sodium sulfate (Na_2SO_4) cartridges to remove particles and water,respectively. The purified liquid extracts were concentrated to 1 mL under a gentle stream of nitrogen. 8:1 FA was added as an internal standard just prior to GC-MS analysis to correct sample volume variability. The other half of GFF was used to determine particle phase PFCAs. It was soaked in 10 mL methanol and shaken for 1 hour. Theextraction process was performed for 4cycles (~40 mL in total). Mass-labeled PFCAs ($^{13}C_2$-PFHxA, $^{13}C_4$-PFOA and$^{13}C_2$-PFDA) were spiked into the samples

to calculate their recoveries. The extracts were passed through ENVI-carb filter (Supelco, U.S.A.) to eliminate matrix. Then, the purified extracts were evaporated, and reconstituted into HPLC-MS/MS mobile phase (40% acetonitrile in ultrapure water) to a final volume 1 mL.

Chemicals and Instrumental analysis: **Table 2** shows analytical parameters of FTOHs and PFCAs. Ten target compounds; three FTOHs and seven PFCAs, and 8:1 FA (internal standard) were purchased from Wako Pure Chemicals (Osaka, Japan). Four mass-labeled ($^{13}C_2$ 8:2 FTOH, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA and $^{13}C_2$-PFDA) were purchased from the Wellington Laboratory Inc. (Ontario, Canada). Analytical or HPLC grade were used for all solvents and reagents. FTOHs were analyzed by an Agilent 6890 gas chromatography-Agilent 5973 mass spectrometer in electron ionization mode using selective ionmonitoring, while PFCAs were measured by an Agilent 1200SL high performance liquid chromatography coupled withan Agilent 6400 Triple Quadrupole mass spectrometer in electrospray ionization negative mode using multiple reactions monitoring.

Table 1 Locations and characteristics of the sampling sites

Sampling sites		Locations	Site characteristics		
Outdoor air-WWTPs			Capacity (m^3/d)	No. of industries	Industrial types
1.	Industrial WWTP1	Industrial estate1, at aeration tank	4,000	213	Chemical and related (55.4%), Petroleum and energy (19.2%), Plastic (7.0%)
2.	Industrial WWTP2	Industrial estate2, at aeration tank	16,000	244	Automotive (32.9%), Steel and metal (17.5%), Electronics and electrical (14.0%)
3.	Industrial WWTP3	Industrial estate3, near aeration tank	45,000	350	Steel and metal (15.0%), Paper and printing (13.0%), Chemical and related (12.0%)
4.	Domestic WWTP4	Suburban area, at aeration tank	157,000	Service area 44 km^2, 418,000 people	
Outdoor air-Residential areas			No. of households	Population density (capita/km^2)	Characteristics
5.	Residential area1	Industrial area	42,295	390	Northeast, 5 km from industrial estate1
6.	Residential area2	Urban area	55,575	6,441	~1 km from the main road
7.	Residential area3	Urban area	51,686	16,098	~10 m from traffic lanes of the main road
8.	Residential area4	Suburban area	14,568	640	at the university
Indoor air			Room size (m^2)	Activities/ characteristics	
9.	Condominium	Suburban area	30	Recently built, painted and decorated (new furniture and carpets)	
10.	Printing shop	Urban area	48	Document and poster printing	
11.	Office1	Suburban area	12	Instructor's room in the university, re-painted room	
12.	Office2	Urban area	225	Documenting and report preparing	
13.	Laboratory	Suburban area	74	Water analysis laboratory in the university	
14.	Furniture shop	Suburban area	150	Wood furniture, wind through opened door, window and porous wall	

Table2 Analytical parameters of FTOHs (by GC-MS) and PFCAs (by HPLC-MS/MS)

Compounds	Abbreviation	Ion1 (*m/z*)	Ion2 (*m/z*)	RT (min)	*MDL* (pg/m^3)	*MQL* (pg/m^3)	Blank (*n*=4) (pg/m^3)
2-Perfluorohexyl ethanol	6:2 FTOH	95	31, 69, 131	9.0	10.3	34.2	<10.3
2-Perfluorooctyl ethanol	8:2 FTOH	95	31, 69, 131	10.3	9.5	31.7	<9.5
2-Perfluorodecyl ethanol	10:2 FTOH	95	31, 69, 131	11.7	11.2	37.5	<11.2
Perfluorohexanoic acid	PFHxA	313	269	2.8	0.06	0.11	<0.06
Perfluoroheptanoic acid	PFHpA	363	319	4.7	0.06	0.17	<0.06
Perfluorooctanoic acid	PFOA	413	369	7.2	0.06	0.17	<0.06
Perfluorononanoic acid	PFNA	463	419	9.9	0.06	0.11	<0.06
Perfluorodecanoic acid	PFDA	513	469	12.7	0.06	0.22	<0.06
Perfluoroundecanoic acid	PFUnDA	563	519	15.4	0.39	1.22	<0.39
Perfluorododecanoic acid	PFDoDA	613	569	18.0	0.39	1.22	<0.39
1H,1H-Perfluoro-1-nonanol	8:1 FA	69	31, 95, 131	10.5	7.0	23.2	-
2-Perfluorooctyl-[1,1-$^2H_2$]-[1,2-$^{13}C_2$]-ethanol	$^{13}C_2$-8:2 FTOH	131	31, 69, 95	10.3	17.1	57.0	-
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	$^{13}C_2$-PFHxA	315	271	2.8	0.06	0.11	-
Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	$^{13}C_4$-PFOA	417	373	7.2	0.06	0.17	-
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	$^{13}C_2$-PFDA	515	471	12.7	0.06	0.17	-

Note: Ion1= quantification ion (GC-MS) and parent ion (HPLC-MS/MS), Ion2 = confirmation ion (GC-MS) and daughter ion (HPLC-MS/MS),RT = Retention time, *MDL* = Method detection limit, *MQL* = Method quantification limit

Calibration and Validation: The concentrations were calculated using five points standard curve analysis for FTOHs (10-1,000 pg/μL), and PFCAs (0.1-10 pg/μL), in which the determination coefficients (R^2) were more than 0.99.Instrument detection limits (*IDLs*) were defined as concentrations with signal to noise ratio (*S/N*) equal to 3:1. Instrumentquantification limits(*IQLs*) were used for quantifying analytes, which were defined by *S/N* 10:1. *MDLs* and *MQLs* were calculated from the *IDLs* and *IQLs*, respectively, which expressed as concentrations by dividing by an air sample volume of 720 m^3. FTOHs and PFCAs in field blanks were lower than *MDLs*, indicating no contamination during the process. PFDoDA was not detected in any samples,so that it was excluded in the next discussion. The recovery of $^{13}C_2$-8:2 FTOH was 61-119% and 73-132% for particle and gas phases, respectively.For PFCAs, the range of recovery rate of $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA and $^{13}C_2$-PFDA were 71-109%, 73-111% and 92-125%, respectively.

Results and discussion

FTOHs and PFCAs were detected from all indoor and outdoor air sampling sites in Thailand (**Fig.1**), which indicated their contamination in the study area. Total concentration of three FTOHs ranged from 1,690 to 13,030 pg/m^3, whiletotal concentration of sixPFCAs were 4-110 pg/m^3 which were two orders of magnitude lower than FTOHs**(Fig.2)**.The highest outdoor FTOHs and PFCAs concentrations were found at an aeration tank of the industrial WWTP1. Wastewater might contain FTOHs and PFCAs, and they could be release to the air by aeration process, which was reported by a previous study[9]. High FTOHs concentrations (7,260-13,030 pg/m^3) were also detected in condominium, printing shop, office1 and office2, which were higher than outdoor residential areas (1,830-3,020 pg/m^3). FTOHs are used as surfactants in several products such as carpet, textile, paper, paints, coatings and adhesives, and there is potential for residual FTOHs (unreacted and unbound)to be released from these products[17].High concentrations of FTOHs in such kind of indoor places were also reported by a previous study[18]. FTOHs were mainly distributed in gas phase fractions (89-100%). However, composition profiles of FTOHs and PFCAs were different in each sampling site. 10:2 FTOH (26-76%) was the dominant compound in most samples, followed by 8:2 FTOH (14-55%) and 6:2 FTOH (5-48%). For PFCAs, PFOA (9-72%) and PFHxA (3-50%) were dominant among the other compounds of PFCAs. This different distribution patterns might be caused by the variety of their emission sources in the measurement areas.

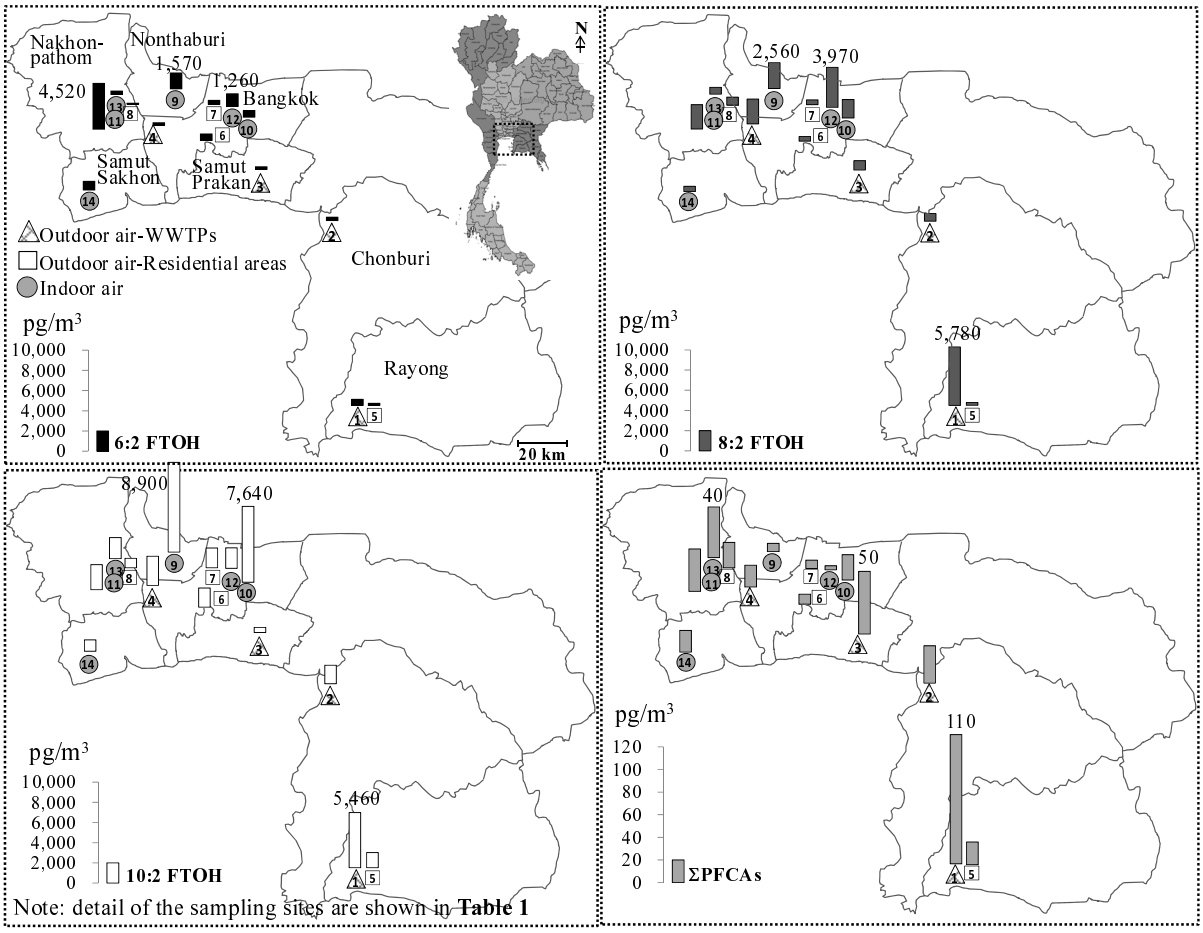

Figure 1 Distribution of FTOHs (gas and particle phases) and ΣPFCAs (particle phase) in the study areas

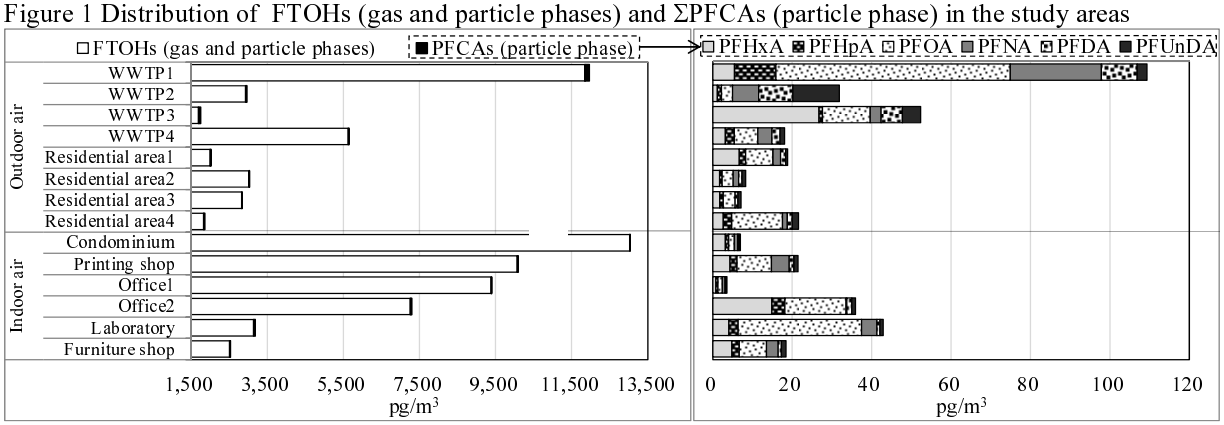

Figure 2 Concentrationsof FTOHs and PFCAs in outdoor and indoor air in Thailand

Compared to the studies in other countries(**Fig.3**), outdoor FTOHs concentrationsin Thailand were found at higherlevels in most sampling sites, while the indoor concentrations were found at similar high levels as the others.Outdoor and indoor PFCAs concentrationsin this study were about two orders of magnitude lower than FTOHs, which were also reported inmost of the mentioned studies.Therefore, high concentration levels of airborne FTOHs might have high possibility to contribute to PFCAs contamination worldwide. To confirm this hypothesis, it is needed to investigate deposition and degradation pathways of FTOHs in the air to PFCAs in water environment.

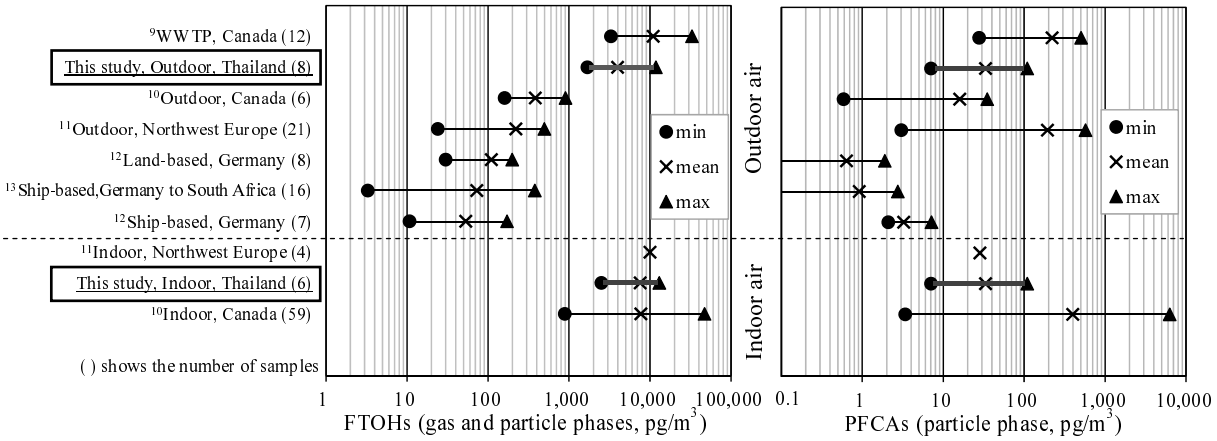

Figure 3 Comparison of FTOHs and PFCAs in outdoor and indoor air in Thailand with other countries

Acknowledgements

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