Partitioning behavior and occurrence of airborne polyfluorinated alkyl substances in Singapore

Wu, Yaoxing

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**PARTITIONING BEHAVIOR AND OCCURRENCE OF
AIRBORNE POLYFLUORINATED ALKYL
SUBSTANCES IN SINGAPORE**

WU YAOXING

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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WU YAOXING

School of Civil and Environmental Engineering

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Abstract

Polyfluorinated alkyl substances (PFASs) are a large group of organic chemicals, many of which are persistent in the environment, bioaccumulative and pose potential adverse effects to human health. The presence of neutral, volatile PFASs in air are of particular concern, as air quality is an important determinant in terms of public health. However, little experimental information is available on the physicochemical properties of volatile PFASs. The short-term concentration variations of airborne PFASs also remain unknown due to the lack of a highly sensitive analytical method which can also achieve satisfying temporal resolution. Therefore, the aim of current work is to improve our understanding of the partitioning behavior, occurrence and source strength of neutral, volatile PFASs in Singapore.

Firstly, air–water partition coefficient (K_H) of 4 fluorotelomer alcohols (FTOHs), a subgroup of volatile PFASs, was measured using inert gas-stripping method (IGS). K_H values of FTOHs showed strong propensity to partition into air. However, the expected linear dependence of K_H on molecular weight was not observed. The unique molecular geometry of FTOHs, with hydrogen bonding and molecular contortion, was probably responsible for the unusual phenomenon. The results were compared to predictions made by SPARC and EPI suite. The erroneous predications given by modeling software packages appeared to confirm the unusual behavior of the compounds.

Secondly, the study attempted to develop a novel method based upon thermal desorption and GC–MS for determination of indoor airborne volatile PFASs, including four FTOHs, two fluorooctane sulfonamides (FOSAs), and two fluorooctane sulfonamidoethanols (FOSEs) through low-volume active air sampling. The optimization of sorbent combination was also conducted. The method recovery exhibited significant improvement compared with other existing methods such as passive air sampling method. The approach also achieved relatively high temporal resolution and low noise level. It has been successfully

applied to routine quantitation of targeted PFASs in indoor office environment of Singapore, which provided further insights toward the indoor source strength of PFASs and performance of building air handlings.

Thirdly, the developed thermal desorption method was further applied for determination of target PFASs in urban atmosphere through low-volume active air sampling (0.108 m³). It displayed greatly improved method recovery but higher detection limits in comparison with the conventional protocol, which employs high-volume sample collection (450 m³) and solvent-based sample extraction. Comparison of their performances in the real samples of urban atmosphere showed a higher portability and temporal resolution of thermal desorption method, which would be very useful in source apportionment analysis and assessment of concentration variations in highly-urbanized regions. In addition, the concentration levels of PFASs detected in the ambient air of Singapore were more in line with the European pattern and might indicate an increasing tendency toward using FTOHs in these regions.

List of Publications

Wu, Y. and V. W. C. Chang (2012). "Development of analysis of volatile polyfluorinated alkyl substances in indoor air using thermal desorption-gas chromatography–mass spectrometry." Journal of Chromatography A **1238**(0): 114-120.

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List of Symbols

ΔH	enthalpy of phase change
ΔS	entropy of phase change
C_0	concentration from preceding time
C_A	gas phase concentration
C_{Air}	concentration in the incoming air
C_t	concentration at time t
C_w	aqueous phase concentration
G	emission rate
I	air exchange rate
k	first order loss rate constant through other mechanisms
K_{AW}	Henry's law constant in dimensionless form
K_H	Henry's law constant
K_{OA}	octanol-air partition coefficient
P_g	vapor pressure
R	ideal gas constant
T	thermodynamic temperature
V	volume

List of Abbreviations

AFFF	aqueous fire-fighting foam
CI	chemical ionization
ECF	electrochemical fluorination
EI	electron ionization
EIC	extracted ion chromatogram
EPI	estimation programs interface suite
ETOA	ethyl acetate
FBSAs	N-alkyl fluorobutane sulfonamides
FBSEs	N-alkyl fluorobutane sulfonamidoethanols
FOSAs	N-alkyl fluorooctane sulfonamides
FOSEs	N-alkyl fluorooctane sulfonamidoethanols
FTOHs	fluorotelomer alcohols
GC–MS	gas chromatography – mass spectrometry
GFFs	glass-fibre filters
GJIC	gap junctional intercellular communication
HS	headspace
HVS	high-volume sampling
IDL	instrumental detection limit
IGS	inert-gas stripping
IQL	instrumental quantitation limit
IS	internal standard (spiked before sample analysis)
LOD	limit of detection
LOQ	limit of quantitation
LVS	low-volume sampling
MDL	method detection limit
MLQ	method quantitation limit
MTBE	methyl <i>tert</i> -butyl ether
m/z	ion mass to charge ratio
NCI	negative chemical ionization
PCI	positive chemical ionization

LIST OF ABBREVIATIONS

PFASs	polyfluorinated alkyl substances
PFCs	perfluorinated compounds
PFCAs	perfluoroalkyl carboxylates
PFOA	perfluorooctanoic acid
PFSAs	perfluoroalkyl sulfonates
PUF	polyurethane foam
S/N	signal-to-noise ratio
SIM	selected ion monitoring
SIP	sorbent impregnated polyurethane foam
SPARC	sparc performs automated reasoning in chemistry
SPE	solid-phase extraction
TD	thermal desorption
TIC	total ion chromatogram
TM	telomerization
U.S. EPA	United States Environmental Protection Agency

Chapter 1

Introduction

1.1 Problem statement

In recent years, long-chain ionic polyfluorinated alkyl substances (PFASs) including perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSA), have become an increasing public health concern, since they are persistent in environment and bioaccumulative in wildlife and humans (Conder et al. 2008, Sáez et al. 2008). The long-range atmospheric transport and subsequent oxidation of neutral, volatile precursor PFASs, including fluorotelomer alcohols (FTOHs), fluorooctane sulfonamides/-ethanols (FOSAs/FOSEs), is considered as the major contributor to the ubiquitous environmental occurrence of ionic PFASs (Ellis et al. 2004, Wallington et al. 2006). Therefore, it is important for us to understand the physicochemical properties of volatile PFASs and develop a highly sensitive analytical method for the determination of these analytes in gaseous phase.

Despite numerous reports on environmental concentrations and toxicological concerns of PFASs (Renner 2006, Shoeib et al. 2006, Jahnke et al. 2007b), little experimental information is available on the physicochemical properties of volatile PFASs such as FTOHs. Henry's law constant (K_H), which describes the equilibrium partitioning between gaseous and aqueous phases, is essential to predict the environmental behavior, transport and fate of volatile/semivolatile organic chemicals. For the limited number of existing studies on determination of K_H of neutral PFASs (Lei et al. 2004, Goss et al. 2006), equilibrium headspace gas chromatography (HS) approach using small size glass vials (10 or 20 mL) was employed. However, these measurements were reported to suffer severe bias resulting from the surface adsorption of long-chain FTOHs (Goss, Bronner et al. 2006).

For the sampling and analysis of neutral, volatile PFASs in indoor environment, most of past studies have used passive sampler for sample collection and solvent-based sample extraction, followed by chromatographic analysis. The long sampling period (> 7 days) leaves poor temporal resolution (Jahnke et al. 2007d, Shoeib et al. 2008). Moreover, evaporative losses of the most volatile PFASs in solvent extraction process compromise the reliability and accuracy of the reported concentration data (Barber et al. 2007, Jahnke et al. 2007a).

Furthermore, the majority of studies employed high-volume active air sampler in combination with solvent extraction for measurement of PFAS occurrence in outdoor air. In addition to evaporative losses encountered in solvent extraction, the analyte breakthrough during air sampling has always been another issue. The sampling sometimes takes more than 3 days, making the observation of daily concentration variation difficult. A highly sensitive analytical method which can achieve both satisfying resolution and high accuracy for determination of neutral, volatile PFASs in gaseous phase has not yet been developed.

1.2 Objective

The objectives of this study were to

- 1) Determine Henry's law constants of some neutral, volatile PFASs using inert gas-stripping (IGS) method.
- 2) Develop, optimize and validate a new trace-analytical method for the compound-specific determination of neutral, volatile PFASs in indoor and outdoor air samples.
- 3) Apply the protocol to routine quantitation of targeted analytes in indoor and outdoor environment.

1.3 Scope and outline

This thesis contains seven chapters and one appendix. **Chapter 1-2** and **Chapter 7** present the introduction, literature review and conclusions, respectively. The major results and discussions are presented in **Chapters 3-6**. Chapter 3 has been published in the Journal of Chemical and Engineering Data. Chapter 4 has been published in the Journal of Chromatography A. Chapter 5 and 6 have been submitted for potential publication. Brief descriptions of Chapter 3-6 and the appendix are as follows:

Chapter 3 determined Henry's law constants (K_H) of FTOHs using IGS method. The influence of surface adsorption to the measurement was also investigated. K_H values obtained via IGS in this study were compared with those generated by modeling software and HS approach from references to better understand the molecular geometry of FTOHs.

Chapter 4 developed and demonstrated the efficiency, reliability, and detection limits of the thermal desorption – gas chromatography/mass spectrometry (TD–GC/MS) method for the quantitation of volatile PFASs including FTOHs, FOSAs, and FOSEs in indoor air. The applicability of the method for routine analysis of target PFASs in indoor air was also tested.

Chapter 5 investigated the interactions between sorbents and analytes in order to optimize the analytical protocol for airborne PFASs based on TD–GC/MS. The selected sorbent combination was further applied to investigate the temporal concentration profiles of target analytes in a local office building.

Chapter 6 compared two analytical methods for determination of volatile PFASs in the atmosphere of Singapore. The first was conventional method involving high-volume sample collection and solvent extraction. The second method included low-volume sample collection and thermal desorption. The performance of both methods in real samples was tested in the urban atmosphere of Singapore.

Appendix presents 1) analytes, acronyms, purity, and vendor information, 2) GC–PCIMS parameters, 3) GC chromatograms of blank experiments of TD

method, 4) optimized TD parameters for different tubes, and 5) calculation of indoor emission rate of 6:2 FTOH and air exchange rate.

Chapter 2

Literature review

2.1 PFASs – background, production, application and sources

Polyfluorinated alkyl substances (PFASs) are a large group of chemicals characterized by a hydrophobic perfluorinated alkyl chain and a hydrophilic end group with the general structure $F(CF_2)_nR$ (Prevedouros et al. 2006). The perfluorinated chain vary in lengths from $n = 4$ to 17 with the predominance of linear eight carbon. The hydrophilic end group is typically used to classify these compounds. PFASs comprise ionic compounds such as perfluoroalkyl sulfonates (PFASs, including perfluorooctane sulfonates, PFOS) and perfluoroalkyl carboxylates (PFCAs, Table 2-1), as well as neutral, volatile PFASs like fluorotelomer alcohols (FTOHs) and fluorooctane sulfonamides/-ethanols (FOSAs/FOSEs, Table 2-2), which are reported as precursors of ionic PFASs.

Table 2-1. Ionic PFAS, acronyms and structures.

Analytes	Acronyms	Structures
Perfluoroalkyl sulfonates (PFASs)		
C ₄ : Perfluorobutane sulfonate	PFBS	$F(CF_2)_4SO_3^-$
C ₆ : Perfluorohexane sulfonate	PFHxS	$F(CF_2)_6SO_3^-$
C ₈ : Perfluorooctane sulfonate	PFOS	$F(CF_2)_8SO_3^-$
C ₁₀ : Perfluorodecane sulfonate	PFDS	$F(CF_2)_{10}SO_3^-$
Perfluoroalkyl carboxylates (PFCAs)		
C ₅ : Perfluoropentanoate	PFPeA	$F(CF_2)_4CO_2^-$
C ₆ : Perfluorohexanoate	PFHxA	$F(CF_2)_5CO_2^-$
C ₇ : Perfluoroheptanoate	PFHpA	$F(CF_2)_6CO_2^-$
C ₈ : Perfluorooctanoate	PFOA	$F(CF_2)_7CO_2^-$
C ₉ : Perfluorononanoate	PFNA	$F(CF_2)_8CO_2^-$
C ₁₀ : Perfluorodecanoate	PFDA	$F(CF_2)_9CO_2^-$
C ₁₁ : Perfluoroundecanoate	PFUnA	$F(CF_2)_{10}CO_2^-$
C ₁₂ : Perfluorododecanoate	PFDoA	$F(CF_2)_{11}CO_2^-$

Table 2-2. Neutral PFAS, acronyms and structures.

Analytes	Acronyms	Structures
Fluorotelomer alcohols (FTOHs)		
C ₆ : 4:2 fluorotelomer alcohol	4:2 FTOH	F(CF ₂) ₄ CH ₂ CH ₂ OH
C ₈ : 6:2 fluorotelomer alcohol	6:2 FTOH	F(CF ₂) ₆ CH ₂ CH ₂ OH
C ₁₀ : 8:2 fluorotelomer alcohol	8:2 FTOH	F(CF ₂) ₈ CH ₂ CH ₂ OH
C ₁₂ : 10:2 fluorotelomer alcohol	10:2 FTOH	F(CF ₂) ₁₀ CH ₂ CH ₂ OH
Fluorooctane sulfonamides/ sulfonamidoethanols (FOSAs/FOSEs)		
N-methyl fluorooctane sulfonamide	NMeFOSA	F(CF ₂) ₈ SO ₂ N(CH ₃)H
N-ethyl fluorooctane sulfonamide	NEtFOSA	F(CF ₂) ₈ SO ₂ N(CH ₂ CH ₃)H
N-methyl fluorooctane	NMeFOSE	F(CF ₂) ₈ SO ₂ N(CH ₃)CH ₂ CH ₂ OH
N-ethyl fluorooctane sulfonamidoethanol	NEtFOSE	F(CF ₂) ₈ SO ₂ N(CH ₂ CH ₃)CH ₂ CH ₂ OH

Due to the high-energy carbon-fluorine bond, the ionic PFASs exhibit strong chemical stability as they resist hydrolysis, photolysis, biotic degradation and metabolism (Rayne and Forest 2009). They also show certain bioaccumulative and toxic properties, posing potential health hazard (Liu et al. 2011). Some of their precursors are volatile and can undergo long-range atmospheric transport (Ellis et al. 2004, Wallington et al. 2006). For this reason, certain PFASs can be classified as “emerging persistent organic pollutants”.

All PFASs with carbon chain lengths >2 are anthropogenic and have been produced for more than 60 years (Giesy and Kannan 2002). They are manufactured almost exclusively by one of the two manufacturing processes, namely electrochemical fluorination (ECF) and telomerization (TM) (Schultz et al. 2003, Lehmler 2005). ECF has been used by U.S. 3M since 1950s, which is the worldwide major producer of sulfonyl-based C₈ PFASs (Figure 2-1). This process yielded complex mixtures containing approximately 70% of linear and 30% of branched impurities as a result of the side reactions (Hans-Joachim 2008). TM was another commercial process used for synthesizing PFCAs and FTOH-based products, which initially developed by U.S. DuPont during 1970s (Figure 2-2).

Only linear and even-carbon chain length compounds are generated during the process (Prevedouros et al. 2006). The perfluorinated substances formed in these processes can be further processed to different derivatives and polymers.

Figure 2-1. Manufacturing process for production of fluorochemical products based on electrochemical fluorination (ECF). Reproduced from A. Jahnke (Jahnke 2007).

The fluorine moiety of PFASs provides extremely low surface tension and contributes to the unique hydrophobic and oleophobic nature of PFASs, making them ideal surfactants. They are used in many types of products where their capacity to form smooth oil, water and stain repellent surfaces is desirable. FOSAs/FOSEs are used in a variety of products for surface treatment (e.g. protector on carpets, leather, textiles and upholstery), paper, packaging protectors (e.g. food packaging), and performance chemicals (e.g. fire fighting foams, carpet spot cleaners) (3M 1999). FTOHs are used in similar applications, such as building blocks for the generation of polymeric fluorotelomer substances used in textile and

paper treatments, cleaning products and adhesives in both industrial and residential applications (Harjula 2006).

Figure 2-2. Manufacturing process for production of fluorochemical products based on telomerization (TM). Reproduced from A. Jahnke (Jahnke 2007).

Industrial production volumes of PFASs are difficult to point out. The United States Environmental Protection Agency (U.S. EPA) reported a total anticipated U.S. production volume for sulfonyl-based fluorinated chemicals at 3200 tons in 2000 based upon the estimation of 3M (U.S.EPA 2000). The estimates for the year of 2001 and 2002 were 500 tons and 200 tons, respectively (Jahnke 2007). Owing to environmental concerns, 3M voluntarily phased out the production of C_8 -PFAS by the end of the year 2000 and all production in the U.S. ceased in 2002. As such, it is believed that the majority of global PFAS production at this time is via TM method.

Recently, 3M is back to the market with perfluorobutyl-based products, which had much less bioconcentration potential and no known toxic effects. However, it is also worth to note that the production of sulfonyl-based C₈ fluorinated chemicals has grown by other producers in some developing countries such as China (Lim et al. 2011, Xie et al. 2013).

Fluorotelomer-based products have been manufactured since the 1970s (Prevedouros et al. 2006). Harrad cited the telomer research program with an estimation of global production of FTOHs at 5000 to 6500 tons per year from 2000 to 2002. After that, the production of FTOHs has increased approximately two fold, to an estimated 12,000 tons per year (Harrad 2010). Additional sources estimate that the production and use of FTOHs are in the order of 6000 tons per year (Harjula 2006).

Since PFASs has been manufactured and used for over 60 years, they have been released into the environment through their production, usage, and disposal. The global historical industry-wide emissions of total PFCAs from direct (manufacture, use, and consumer products) and indirect (PFCA impurities and precursors) sources were estimated to be 3200 – 7300 tons (Prevedouros et al. 2006). It was estimated that majority (~80%) of PFCAs have been released to the environment from fluoropolymer manufacture and use. For perfluorooctane sulfonyl fluoride, the global emissions were estimated to be 45,250 tons into air and water between 1970 and 2012, resulting in an estimated release of 450 – 2700 tons of PFOS into aquatic environment (Paul et al. 2009). Moreover, the reaction of FTOHs to make fluorotelomer-based products leaves 0.04 – 4 wt% unreacted residual FTOHs, which are present in the ultimate sales products (Dapremont-avignon et al. 1991, Washburn et al. 2005, Prevedouros et al. 2006). It is estimated that at least 100 tons of FTOHs is emitted from residuals annually (Renner 2006).

2.2 Human risks of PFASs

2.2.1 Toxic effects of ionic PFASs

The first observation of PFASs in human blood samples was reported by Taves in 1968 (Taves 1968). A lot of subsequent studies have been focusing on the investigation of the potential toxicity of ionic PFASs to animals and humans. In particular, the toxicology of PFOS and PFOA has been well studied and documented in the literature (Kennedy Jr et al. 2004, Lau et al. 2004). These two compounds are known to be very persistent as they are not metabolized and thus remain poorly eliminated (Renner 2001, Kennedy Jr et al. 2004, Lau et al. 2007). As the exceedingly effective surfactants with both lipophobic and hydrophobic properties, PFOS and PFOA do not preferentially accumulate in fats. Instead, they bind to blood proteins and distributed in the liver, kidney and gall bladder (Renner 2001). Therefore, most of the biomonitoring study reported PFASs detected in liver and blood samples (Lau et al. 2007). In addition, the rate of elimination of PFCAs and PFASs decreases with increasing length of the perfluorinated carbon chain (Lau et al. 2007).

Experimental animal tests suggested PFOA as a peroxisome proliferator (PPAR agonist) as early as 1987 (Pastoor et al. 1987), which was further confirmed in the following studies (Kennedy Jr et al. 2004). A similar profile of effects has been observed for PFOS (Sohlenius et al. 1992, Sohlenius et al. 1993). Exposure to peroxisome proliferators can result in a variety of toxic effects including increased β -oxidation of fatty acids, increase in several cytochrome P-450 (CYP450)-mediated reactions, inhibition of the secretion of very low-density lipoproteins and cholesterol from the liver, and induction of xenobiotic metabolizing enzymes such as aromatase (Biegel et al. 1995, Kennedy Jr et al. 2004).

PFASs and PFCAs were also found to inhibit gap junctional intercellular communication (GJIC) in *vitro* and *vivo* studies, and the inhibitory effect was determined by the length of fluorinated carbon chain instead of the functional group (Upham et al. 1998, Hu et al. 2002). GJIC is the major pathway for cells to send messages and exchange molecules and signals that improve their homeostatic

control (Bruzzzone et al. 1996). Disruption of GJIC results in abnormal cell growth and function, and could be further associated with tumor promotion (Trosko and Ruch 1998). Chronic disruption of GJIC could also lead to neurological, cardiovascular, reproductive, and endocrinological dysfunction (Trosko et al. 1998).

The toxicity of ionic PFASs found in animal studies has raised public concerns over their potential toxicity to humans. Recently, a positive correlation between attention deficit hyperactive disorder and the level of ionic PFASs in serum was found among children aged 12-15 in the U.S. (Hoffman et al. 2009). All these findings prompted further consideration of their relevance to human health risk. As both peroxisome proliferation and GJIC inhibition can result in tumor growth, U.S. EPA has proposed PFOA as a rodent carcinogen with potential relevance to humans (U.S.EPA 2006).

2.2.2 Toxic effects of neutral PFASs

A limited number of studies have investigated the toxicity of neutral PFASs such as FTOHs and FOSAs/FOSEs. An early study suggested the possibility that 8:2 FTOH could be converted into the ultimate metabolite PFOA in rats (Hagen et al. 1981). Later more evidence emerged showing FTOHs could undergo biodegradation to form the persistent PFCAs (Dinglasan et al. 2004, Kudo et al. 2005). FOSAs/FOSEs are known to be degraded metabolically to PFOS (Shipley et al. 2004, Lau et al. 2007). Therefore, these chemicals showed similar toxicological effects with PFOA and PFOS. For example, perfluorooctane sulfonamide (PFOSA) has been observed to inhibit GJIC (Hu et al. 2002). NEtFOSE was reported to exhibit developmental toxicology in mammals (Case et al. 2001), and the profile was quite similar to that of PFOS (Lau et al. 2003, Thibodeaux et al. 2003).

2.2.3 Human exposure

In recent years, PFAS have been reported at low parts per billion (ppb) concentrations in samples of human matrices collected worldwide as well as certain

wildlife samples (Giesy and Kannan 2001, Sottani and Minoia 2002, Martin et al. 2004). Concentrations of PFASs and PFCAS in human populations have been reviewed by Lau et al (Lau et al. 2007). In general, PFOS and PFOA are the predominant PFAS observed in human blood.

Human PFAS exposure occurs through different routes, including direct contact with treated consumer products or the intake of air, water, dust or contaminated food items (Lau et al. 2007). The potential human exposure to PFASs through consumer use of a variety of products treated with fluorinated polymers has been assessed, and the results indicated the exposure to PFOA during consumer use was not expected to be a significant source of contamination to the general public (Washburn et al. 2005, Trudel et al. 2008). In general, although the relative importance of the routes of human exposure to PFASs is not well established yet, it has been suggested that dietary exposure is probably the most important pathway of exposure to PFOS and PFOA, followed by the ingestion of dust and inhalation of air (Tittlemier et al. 2007, Trudel et al. 2008, Domingo 2012). However, most human exposure studies do not consider volatile precursor compounds that could be taken up and converted to PFOS or PFOA within human body.

The unbound FTOHs and FOSAs/FOSEs in the fluorinated polymers that are industrially applied and commercially available could be released as residuals to the environment (Dinglasan-Panlilio and Mabury 2006, Larsen et al. 2006). The decomposition of polymeric or nonpolymeric materials that incorporate FTOHs and FOSAs/FOSEs could be another source. The potential contribution could be substantial to the atmospheric burden of FTOHs as well as FOSAs/FOSEs. Inhalation of contaminated and subsequent metabolism of these volatile precursors would then lead to the PFCAs and PFASs detected in human matrices worldwide. Nilsson et al. found that a higher daily inhalation exposure of 8:2 FTOH led to the elevated blood levels of PFOA in ski wax technician compared to the general population (Nilsson et al. 2010). Furthermore, a significant correlation between 8:2 FTOH concentrations in air and PFOA concentrations in serum was reported recently (Fraser et al. 2012). Nevertheless, the significance of neutral PFASs

including FTOHs and FOSAs/FOSEs in human exposure is still far from understood.

2.3 Physicochemical properties of PFASs

Physicochemical properties of PFASs are strongly affected by the unique properties of the fluorine, which is the most electronegative element (Pauling 1989, Key et al. 1997). Due to the large difference in electronegativity between carbon and fluorine atoms, the carbon–fluorine bond is highly polarized and the strongest single bond in organic chemistry (Stock et al. 2004). The unusual strength of the carbon-fluorine bond and shielding effect of fluorine atoms contribute to the unique properties of fluorinated chemicals.

2.3.1 Vapor pressure

An important parameter governing a chemical's tendency for transport and dissemination in the environment is its vapor pressure. A few studies have measured vapor pressure of the neutral PFASs such as FTOHs (Kaiser et al. 2004, Lei et al. 2004, Stock et al. 2004, Krusic et al. 2005, Cobranchi et al. 2006). However, reported data exhibited significant variability, differing by several orders of magnitude. Generally, vapor pressures of FTOHs are influenced primarily by the length of perfluoroalkyl chain, which increase as the length of perfluoroalkyl chain decreases. Reported values of FTOHs are presented in Table 2-3.

In comparison with FTOHs, less information is available for vapor pressure of another group of neutral PFASs (FOSAs/FOSEs). Two studies investigated the values for NEtFOSA, NMeFOSE and NEtFOSE (Lei et al. 2004, Shoeib et al. 2004), which are also shown in Table 2-3. Similar to FTOHs, the reported vapor pressure of FOSAs/FOSEs showed great discrepancies at orders of magnitude. Increasing tendency of vapor pressure with decreasing molecular weight was also observed. Their vapor pressures appeared to be much lower than FTOHs with the

same length of perfluoroalkyl chain, which was probably due to the higher molecular weight of FOSAs/FOSEs.

Table 2-3. Physicochemical properties of PFASs.*

	FTOHs	FOSAs/FOSEs	PFSAs	PFCAs
Vapor Pressure	<u>4:2 FTOH</u>	<u>NEtFOSA</u>	<u>PFOS</u>	<u>PFOA</u>
(Pa, 25°C)	252 ^a	2.38 ^a	3.31×10 ⁻⁴ *	4.19 ⁱ
	992 ^b	<u>NMeFOSE</u>		4.1 ^j
	216 ^c	0.33 ^a		<u>PFNA</u>
	<u>6:2 FTOH</u>	2×10 ⁻³ ^c		1.27 ⁱ
	145.2 ^a	<u>NEtFOSE</u>		<u>PFDA</u>
	713 ^b	0.19 ^a		0.229 ⁱ
	44 ^c	8.6×10 ⁻³ ^c		<u>PFUnA</u>
	<u>8:2 FTOH</u>			0.105 ⁱ
	45.9 ^a			<u>PFDoA</u>
	254 ^b			8.03×10 ⁻³ ⁱ
	7 ^c			
	<u>10:2 FTOH</u>			
	144 ^b			
	13.27 ^a			
	0.2 ^c			
Water Solubility	<u>4:2 FTOH</u>	Not available	<u>PFOS</u>	<u>PFOA</u>
(25°C)	974 mg/L ^g		570 mg/L [*]	4.1 g/L (22°C) ⁿ
	<u>6:2 FTOH</u>			3.4 g/L ^p
	18.8 mg/L ^g			9.5 g/L ^q
	<u>8:2 FTOH</u>			<u>PFDA</u>
	137 µg/L ^d			5.1 g/L ^q
	194 µg/L ^r			
	<u>10:2 FTOH</u>			
	11 µg/L ^g			
Air-Water	<u>4:2 FTOH</u>	Not available	Not available	<u>PFOA</u>
Partitioning	2.09 ^a			0.4 ^k
Coefficient	1.87 ^f			0.49 ^m
log K_H (Pa m ³	<u>6:2 FTOH</u>			
mol ⁻¹ , 25°C)	1.92 ^a			
	2.83 ^f			

	<u>8:2 FTOH</u>			
	1.57 ^a			
	2.19 ^f			
Octanol-Air	<u>4:2 FTOH</u>	<u>NEtFOSA</u>	Not appropriate	Not appropriate
Partitioning	3.26 ^a	5.86 ^a		
Coefficient	4.8 ^f	<u>NMeFOSE</u>		
$\log K_{OA}$, 25°C	<u>6:2 FTOH</u>	6.78 ^a		
	3.56 ^a	20°C, 7.7 ^f		
	5.26 ^f	<u>NEtFOSE</u>		
	<u>8:2 FTOH</u>	7.09 ^a		
	4.17 ^a	20°C, 7.78 ^f		
	5.56 ^f			
	<u>10:2 FTOH</u>			
	4.83 ^a			
Soil Organic	<u>4:2 FTOH</u>	<u>PFOS</u>	<u>PFOA</u>	
Carbon-Water	0.65 ^g	2.68 ^s	2.11 ^s	
Partitioning	<u>6:2 FTOH</u>	<u>PFDS</u>	<u>PFNA</u>	
Coefficient	2.39 ^g	3.66 ^s	2.50 ^s	
$\log K_{OC}$ (L kg _{oc} ⁻¹)	<u>8:2 FTOH</u>		<u>PFDA</u>	
	4.13 ^r		2.92 ^s	
	<u>10:2 FTOH</u>		<u>PFUnA</u>	
	5.87 ^g		3.47 ^s	

* (Harrad 2010); ^a (Lei et al. 2004); ^b (Stock et al. 2004); ^c (Krusic et al. 2005); ^d (Kaiser et al. 2004); ^e (Shoeib et al. 2004); ^f (Goss et al. 2006); ^g (Liu and Lee 2007); ⁱ (Kaiser et al. 2005); ^j (Barton et al. 2008); ^k (Li et al. 2007); ^m (Kutsuna and Hori 2008); ⁿ (Prokop et al. 1989); ^p (U.S.EPA 2002); ^q (Kauck and Diesslin 1951); ^r (Liu and Lee 2005); ^s (Higgins and Luthy 2006).

Direct measurement of vapor pressures of ionic PFASs at ambient temperatures were also difficult due to their low volatility (Kaiser et al. 2005). Therefore, measurement are often conducted at elevated temperatures and extrapolated to lower temperatures. The reported vapor pressures of PFCAs were listed in Table 2-3 (Kaiser et al. 2005, Barton et al. 2008). For the PFSAs, only the vapor pressure of PFOS was reported at 20°C (Harrad 2010).

2.3.2 Water solubility

The extent of water solubility of PFASs ranges widely. In general, the neutral PFASs are poorly soluble in water (Table 2-3). It could be seen from the table that the water solubility of FTOHs decreases rapidly as the length of perfluoroalkyl chain increases, indicating the perfluorocarbon chain length was the dominant structural feature influencing their solubility. Measured water solubility of FOSAs/FOSEs has not been reported so far, but it is expected to be lower than FTOHs.

Water solubility of the ionic PFCAs is also present in Table 2-3 for PFOA, PFDA and PFOS, which are orders of magnitude higher than the neutral PFASs with the same length of perfluoroalkyl chain. Water solubility of PFOS is approximately one order of magnitude less water soluble than PFOA (Table 2-3). It is worth to note that these measurements are for the solubility of dissociated species instead of the free acid form, since PFSAs and PFCAs are completely dissociate in water. In order to determine the water solubility of free acid species, experiments are needed to be conducted in acidic solution to suppress dissociation. Although the water solubility of other PFCAs are currently not available, it is expected that their water solubility decrease with increasing chain length while maintained higher than the neutral PFASs with the same fluorinated carbon atoms. In addition, it is known that the surfactant character of PFSAs and PFCAs could result in these compounds forming molecular aggregated and micelle at low concentrations, which could dramatically increase their water solubility (Rayne and Forest 2009).

2.3.3 Air-water partitioning coefficient

The air-water partitioning coefficient, also known as Henry's law constant (K_H), plays a fundamental role in describing the environmental process which transport chemicals between gaseous and aqueous phases (Brutseart and Jirka 1984). To date, only two studies have been carried out for the determination of K_H of FTOHs, and results showed FTOHs presented predominantly in the gaseous phase. However,

apparent discrepancies were observed between different studies, which were probably due to the bias introduced by surface adsorption to the experimental setup, especially for the long-chained FTOHs (Goss et al. 2006). Unlike vapor pressure, the K_H of FTOHs generally increase with increasing length of perfluoroalkyl chain (Table 2-3). The reliability of widely used environmental models for the predication of K_H of FTOHs was also questioned in another study, since the predicated values differ by several orders of magnitude from experimental data (Arp et al. 2006). Although measured K_H values have not been available for FOSAs/FOSEs so far, it is widely accepted that FOSAs/FOSEs are inclined to partition into gas phase.

Difficulties are encountered in determining K_H for PFOA because PFOA forms aggregates and is ionized, surface-active, and sticky to walls of experimental apparatus (Rayne and Forest 2009). Two experimentally determined K_H at 25°C has been reported for the free acid form of PFOA (Li et al. 2007, Kutsuna and Hori 2008), which is one order of magnitude lower than 8:2 FTOH (Table 2-3). The measured K_H for PFSA and other PFCAs are currently not available. Furthermore, it is expected that K_H for the free acid species of PFSA and PFCAs will be higher than the K_H for the dissociated species, which are negligible (Prevedouros et al. 2006). Overall, PFSA and PFCAs are generally accepted to be predominant in aquatic phase in natural environment (Harrad 2010).

2.3.4 Octanol-air partitioning coefficient

Octanol-air partition coefficient (K_{OA}) is an important parameter used to describe the partitioning of organic compounds between the gaseous phase and a variety of natural organic substrates in soil, atmospheric particles and foliage (Xiao and Wania 2003). The K_{OA} of FTOHs have been reported in two studies (Lei et al. 2004, Goss et al. 2006) and shown in Table 2-3. It could be seen that K_{OA} of FTOHs increases with increasing chain length, indicating the tendency of partitioning into organic phase grows as perfluorocarbon chain increases. K_{OA} of FOSAs and FOSEs are also measured and exhibited in Table 2-3, which also exhibit increasing tendency with increasing molecular weight.

2.3.5 Soil organic carbon-water partitioning coefficient

The soil organic carbon normalized distribution coefficient (K_{OC}) is necessary in modeling and evaluating the fate of PFASs released to aqueous environment. Due to the unique hydrophobic and oleophobic property, PFASs are ideal surfactants that have a tendency to adsorb to a variety of surfaces including laboratory glassware and equipment (Kaiser et al. 2004, Arp et al. 2006). Therefore, it is expected that they will also exhibit sorption in the natural environment. Liu and Lee determined the log K_{OC} of 8:2 FTOH as 4.13, and the perfluorocarbon chain length appeared to be the dominant structural feature influencing the sorption, with each additional CF_2 moiety contributing 0.87 log units (Liu and Lee 2005, Liu and Lee 2007). The K_{OC} of ionic PFASs including PFSA and PFCA has also been investigated. Higgins and Luthy reported the sediment log K_{OC} value for PFOS and PFOA of 2.68 and 2.11 respectively (Higgins and Luthy 2006), both of which were lower than 8:2 FTOH. Increasing sorption of PFSA and PFCA to sediment with increasing length of perfluorocarbon chain was also observed. On average, the sediment sorption of PFSA was 1.7 times stronger than the PFCA analog.

2.4 Analysis of airborne PFASs

Trace analytical methods for determination of PFASs in air are addressed in this chapter, including both conventional methods and up-to-date protocols for sample collection, extraction and analysis of PFASs in air samples.

2.4.1 Sampling technique

The most widely used techniques for sampling of airborne neutral PFASs include high-volume air sampler and passive air sampler. Martin et al (Martin et al. 2002) firstly reported the application of high-volume sampler in enrichment of neutral PFASs in atmosphere. The analytical protocol was further optimized for the

collection, extraction and chromatographic analysis of FTOHs (4:2, 6:2, 8:2 and 10:2 FTOH) and FOSAs/FOSEs (NEtFOSA, NMeFOSA and NEtFOSE) through high-volume air sampling (500 – 1000 m³). The adsorptive enrichment of targeted PFASs was done on solid sorbents, including glass-fiber filters (GFFs) for particle phase and polyurethane foam (PUF)/XAD-2/PUF cartridge (65 mm I.D.) for gaseous phase. This technique was also used by other researchers and applied to some other airborne PFASs such as NMeFOSA, NMeFBSA and N-methyl perfluorooctane sulfonamidoethylacrylate (NMeFOSEA) et al (Shoeib et al. 2004, Piekarz et al. 2007). In addition, high-volume sampling was also employed in determination of PFOS in outdoor airborne particulate matter (Sasaki et al. 2003). However, the noise of high-volume air sampling has restricted its application in indoor environment. Breakthrough of the most volatile PFASs such as 4:2 and 6:2 FTOH on PUF/XAD/PUF cartridge was another widely reported problem (Barber et al. 2007, Jahnke et al. 2007a).

Shoeib et al (Shoeib et al. 2005) introduced passive sampler (140 mm I.D.) with XAD sorbent impregnated PUF disk (SIP) in sample collection of NMeFOSE and NEtFOSE as well as N-methyl perfluorooctane sulfonamidoethylacrylate (NMeFOSEA) in indoor and outdoor environment. Passive samplers were calibrated against low-volume air sampler at selected locations. Langer et al further employed passive sampler in the determination of indoor airborne PFASs including FTOHs, FOSAs/FOSEs as well as fluorotelomer acrylates (FTAs) (Langer et al. 2010). The major concern for passive sampler is the long sampling duration required (> 7 days), resulting in poor temporal resolution of concentration.

It is also worth to note that low-volume air sampler was recently developed and applied for the determination of volatile PFASs in gas phase. Jahnke et al developed the ISOLUTE ENV+ solid-phase extraction (SPE) cartridge filled with resin-based sorbents as low-volume air sampler for the adsorptive enrichment of FTOHs and FOSAs/FOSEs from indoor and outdoor air (Jahnke et al. 2007d). Sampling volume was in the range of 20 – 300 m³. The cartridge declared better retention for targeted PFASs in comparison with the conventional high-volume sampling cartridge due to the higher surface area of the sorbents employed.

2.4.2 Extraction methods

As the adsorptive enrichment of neutral PFASs in air is all based on solid adsorbents, all the reported sample extraction from the air sampling media is carried out through solvent extraction. Different solvent extraction systems were employed. Some researchers used the conventional Soxhlet extractor for continuous extraction (18 – 24 h) (Shoeib et al. 2008). Another widely used system is cold column elution, which extraction was done in multiple steps (2 – 4) of infusion involving about 300 – 500 mL of solvent in total. Extraction solvent included 1:1 mixture of acetone/methyl *tert*-butyl ether (MTBE) (Langer et al. 2010), 1:1 petroleum ether/acetone (Shoeib et al. 2004), methanol, ethyl acetate, etc. (Jahnke et al. 2007a). Moreover, it is worth to note that ethyl acetate was reported to lead to solvent-induced response enhancement and consequently result in unusually high recoveries of some PFASs with high molecular weight (> 400 g/mol) (Dreyer et al. 2008).

All extracts either from Soxhlet or cold column extraction were subsequently rotoevaporated to approximately 5 – 10 mL. Generally extracts are filtered prior to analysis. Some researchers have also included a clean-up step, e.g. Shoeib et al passed the PUF/XAD sample extracts through an alumina column and elute with dichloromethane in ethyl acetate prior to analysis of FTOHs and FOSAs/FOSEs (Shoeib et al. 2006). The extracts were then further concentrated to 500 – 1000 μ L with ethyl acetate as keeper under a gentle stream of high purity nitrogen.

The solvent extraction method is compatible with thermally unstable compounds and allows preconcentration of high volumes of air. However, it is widely known to prone to significant limitations. The major disadvantage is that the sample is diluted in solvent, of which 1 or 2 μ L is injected into the GC column using liquid injection. This could result in 1000-fold of reduction in limit of detection and necessitates the bulking of samples. Consequently, the method requires large volumes of sampled air and long sampling time. Furthermore, the evaporative loss in solvent reduction stage could result in low extraction recoveries, especially for some volatile organic compounds (Barber et al. 2007, Jahnke et al. 2007a). Other concerns of solvent

extraction include analytical interference brought by the solvent, intensive manual preparation required, and environmental health and safety issues.

2.4.3 Instrumental analysis

For the analysis of neutral, volatile PFASs, gas chromatography – mass spectrometry (GC–MS) is typically the method of choice. Martin et al (Martin et al. 2002) initially developed the GC–MS method for the analysis of FTOHs and FOSAs/FOSEs in atmospheric air samples. This method has been widely used and modified by other researchers (Shoeib et al. 2004, Stock et al. 2004, Jahnke et al. 2007a).

The separation of neutral PFASs was carried out on DB-WAX or equivalent column (Shoeib et al. 2006, Dreyer et al. 2008). These PFASs can be ionized using either electron or chemical ionization (Martin et al. 2002, Ellis and Mabury 2003). Electron ionization (EI) mode for the mass spectral identification and quantization of airborne PFASs proved to be problematic due to the lack of specific fragments of the analytes. Chemical ionization (CI), on the other hand, offers higher limit of detection and specificity as the lower energy involved in the process yields less fragmentation and abundant pseudo molecular ion ($[M+H]^+$ or $[M-H]^-$). Positive chemical ionization (PCI) usually produces a relative simple mass spectrum in comparison with the more elaborate spectra obtained through negative chemical ionization (NCI) (Ellis and Mabury 2003). Therefore, PCI is usually applied in the analysis of environmental samples since the low concentration levels of PFASs and high background interferences present at environmental air matrices. During analysis, the mass spectrometer is operated in single ion monitoring mode (SIM) with 2-3 ions monitored for each PFASs. Ions typically picked for qualification of FTOHs and FOSAs/FOSEs are presented in Table 2-4. As only one ion is monitored in the mass spectrum for NMeFOSA and NEtFOSA under PCI, the presence of these analytes is sometimes confirmed by NCI (Table 2-4).

Table 2-4. Ions monitored for GC–MS analysis of neutral, volatile PFASs in PCI and NCI mode.

Class	Analyte	PCI Ions monitored m/z	NCI
FTOHs	4:2 FTOH	227, 265 ^a	
	6:2 FTOH	327, 365 ^a , 393	
	8:2 FTOH	427, 465 ^a , 493	
	10:2 FTOH	527, 565 ^a , 593	
FOSAs	NMeFOSA	514 ^a	400, 483, 512
	NEtFOSA	528 ^a	400, 483, 526
FOSEs	NMeFOSE	540 ^a , 558	
	NEtFOSE	554 ^a , 572	

^aQuantitation ion

2.5 Environmental concentrations of PFASs

PFASs have been detected in a variety of environmental matrices in the global range, including surface waters, precipitation, air, sludge, soils, sediments, and ice caps. The reported concentration levels of PFASs in air (indoor and outdoor) samples are outlined in detail in this chapter. The concentrations of PFASs detected in aquatic phase are also presented.

2.5.1 PFAS levels in air

2.5.1.1 Indoor environment

Shoeib. et al firstly reported the indoor air concentrations of NMeFOSE (median 2589 pg/m³) and NEtFOSE (median 772 pg/m³) in one laboratory in North America, which were orders of magnitude higher than outdoor values (16.0 – 31.7 pg/m³ for NMeFOSE and 8.5 – 9.8 pg/m³ for NEtFOSE), indicating the potential existence of indoor sources of volatile PFASs (Shoeib et al. 2004). The follow-up study conducted by the same research group in 59 randomly selected homes in Ottawa, Canada revealed similar concentration levels of NMeFOSE (median 1970 pg/m³), NEtFOSE (median 1100 pg/m³) and NEtFOSA (median 59 pg/m³) (Shoeib et al.

2005). The first measurement of FTOHs in indoor air in North America was also conducted by Shoeib et al in 52 homes of Ottawa, with mean concentrations of 8:2 FTOH and 10:2 FTOH at 2070 pg/m³ and 890 pg/m³, respectively (Shoeib et al. 2008). Recently Fraser et al reported the concentration of FTOHs and FOSAs/FOSEs in office building in the Boston and Massachusetts area of U.S. (Fraser et al. 2012).

Barber et al firstly determined the concentrations of neutral PFASs in indoor air samples of residential houses in Norway, Europe, with total concentration ranging from 18,000 to 23,000 pg/m³ (Barber et al. 2007). The high contamination level was probably due to large amounts of textiles treated with PFASs used in private home. In comparison, the indoor air concentrations of FTOHs (1928 – 2329 pg/m³), FOSAs (158 – 188 pg/m³) and FOSEs (1032 – 1613 pg/m³) in the office of Germany were reported at lower levels (Jahnke et al. 2007d). Additionally, volatile PFASs in indoor air were also observed significantly higher than those of outdoor environment in these two studies, further confirming the release of these chemicals from indoor environment. Langer et al (Langer et al. 2010) investigated indoor air concentrations of volatile PFASs in residential and nonresidential indoor environments in Germany. Concentrations of total FTOHs and FOSAs/FOSEs were in the range of 3300 to 307,000 pg/m³ and 4400 to 148,000 pg/m³ respectively. Most elevated PFAS concentrations were detected in stores selling outdoor equipment, furniture and carpet, which were consistent with the application of PFASs in surface treatment products such as carpet, leather, and textile protection. The summary of reported indoor air concentrations of neutral PFASs are presented in Table 2-5. To date, there is no occurrence data on the concentration of volatile PFASs in the indoor environment of Singapore.

Table 2-5. Indoor air concentrations of neutral, volatile PFASs in gas phase at residential and nonresidential locations (pg/m³).^a

Location	FTOHs				FOSAs		FOSEs		Ref
	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	NMeFOSA	NEtFOSA	NMeFOSE	NEtFOSE	
Lab, Canada	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1698	1917	(Shoeib et al. 2004)
Residential houses, Canada	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1546-8315	289-1799	(Shoeib et al. 2004)
Residential houses, Ottawa,	n.a.	n.a.	n.a.	n.a.	n.a.	5.94-646	366-8190	227-7740	(Shoeib et al. 2005)
Residential houses, Ottawa,	n.a.	n.a.	261-28900	104-9210	n.a.	n.a.	n.a.	n.a.	(Shoeib et al. 2008)
Offices, U.S.	n.a.	n.d.-11000	283-70600	138-12600	5.93-162	n.d.-115	48.5-3880	n.d.-216	(Fraser et al. 2012)
Residential houses, Norway	114	2990	3424	3559	6608	6626	6018	5755	(Barber et al. 2007)
Office, Germany	n.d.	177-248	421-853	898-1660	n.d.	158-188	727-798	305-815	(Jahnke et al. 2007a)
Residential houses, Germany	800-1200	1100-2900	8100-17400	1900-5100	1000-1200	1200-1600	2700-3100	2100-2200	(Langer et al. 2010)
Offices, Germany	40-1100	3400-6000	4300-5500	1100-2400	600-800	1200-1500	2000-2300	1500-2100	(Langer et al. 2010)
Shops, Germany	n.d.-1000	100-37,000	1100-209,000	100-54,000	100-2400	100-1600	1000-10,000	700-12,000	(Langer et al. 2010)

^a n.a.- not available; n.d.- not detectable

2.5.1.2 Atmospheric environment

Martin et al firstly reported the concentrations of neutral, volatile PFASs (FTOHs and FOSAs/FOSEs) in atmosphere at two locations in Canada (Toronto, urban-long point, rural) (Martin et al. 2002). In Toronto, FOSEs exhibited highest levels (86 – 123 pg/m^3 for NMeFOSE and for 51 – 393 pg/m^3 for NEtFOSE), followed by FTOHs. 6:2 FTOH is the predominant compound of FTOHs, followed by 8:2 and 10:2 FTOH. In contrast, the concentrations at rural locations were significantly lower.

The follow-up study conducted by the same research group revealed the occurrence of volatile FTOHs in six North American cities (Stock et al. 2004). Results indicated FTOHs and FOSAs/FOSEs were widely distributed throughout the North American troposphere with mean concentrations ranging from 11 – 165 pg/m^3 and 22 – 403 pg/m^3 , respectively. Different distribution pattern of volatile PFASs were observed in specific sampling locations. High concentrations of NMeFOSE (359 pg/m^3) and NEtFOSE (199 pg/m^3) were identified in the sampling locations near carpet and paper manufacturing and treatment zone, indicating the probability of large point sources for the release of volatile PFASs in the environment. The concentrations of neutral PFASs in remote regions of U.S. (Mount Bachelor, Oregon) reported by Piekarz et al were significantly lower (Piekarz et al. 2007).

The first measurement of volatile PFASs in atmosphere outside of North America was from Germany, Europe (Jahnke et al. 2007a). Similar to that observed in North American atmosphere, elevated concentrations of volatile FTOHs were observed in the urban location (Hamburg, 221 pg/m^3) than the rural location (Waldhof, 150 pg/m^3). High concentrations of FOSAs/FOSEs detected in North America were not observed in Europe. It is also the first study to report the detection of NMeFOSA and 4:2 FTOH in the atmosphere. However, due to the reported low recoveries of 4:2 FTOH (< 30%) in the study, the concentration of 4:2 FTOH might be underestimated. The concentrations of volatile PFASs in other places of Germany including Bright North sea (rural) and Barsbuettel (urban) were also determined

(Dreyer and Ebinghaus 2009). Average total PFAS concentrations in Barsbüttel region (180 pg/m^3) were higher than those observed in German Bight (80 pg/m^3). FTOHs were the dominating class of compounds in the gas phase ($21 - 204 \text{ pg/m}^3$) with 8:2 FTOH in maximum proportions ($17 - 130 \text{ pg/m}^3$). Low PFAS concentrations were observed when air masses of marine origin were sampled in this study.

Barber et al reported the concentrations of neutral PFASs in four sites in Europe including UK, Ireland and Norway (Barber et al. 2007). 8:2 FTOH and 6:2 FTOH were the prevailing analytes found in gas phase, at $5 - 243$ and $5 - 189 \text{ pg/m}^3$, respectively. The predominant FOSAs/FOSEs was typically NMeFOSE ($36 - 54 \text{ pg/m}^3$), followed by NEtFOSE ($16 - 33 \text{ pg/m}^3$), NMeFOSA ($5 - 8 \text{ pg/m}^3$) and NEtFOSA ($5 - 10 \text{ pg/m}^3$). Generally, the concentrations of PFASs in air were declining with decreasing degree of urbanization.

Volatile PFASs have also been detected in arctic region. Shoeib et al reported the occurrence of 6:2, 8:2 and 10:2 FTOH, NMeFOSE and NEtFOSE at concentrations ranging from below detection limit (n.d.) to 31 pg/m^3 during the crossing of North Atlantic and Canadian Arctic Archipelago region (Shoeib et al. 2006). The highest concentrations of FTOHs were 8:2 FTOH ($5.8 - 26 \text{ pg/m}^3$), followed by 10:2 FTOH ($1.9 - 17 \text{ pg/m}^3$) and 6:2 FTOH (n.d. – 6 pg/m^3). FTOHs and FOSAs/FOSEs were also observed in the Canadian Arctic atmosphere with mean concentrations ranging from 2.8 to 29 pg/m^3 (Stock et al. 2007). These reported concentrations of volatile PFASs were on the same order of magnitude as concentrations observed in lower-latitude source regions discussed above, confirming the long-range atmosphere transport and wide distribution of volatile PFASs in global scale.

The first concentration data of airborne FTOH and FOSAs/FOSEs from south hemisphere was published in 2007 using air samples collected onboard a German research vessel (Jahnke et al. 2007c). A strongly decreasing concentration gradient from European continent toward less industrialized regions in South Africa was reported in the study, with the maximum level of 8:2 FTOH at 176 pg/m^3 in northern Europe compared to 3.1 pg/m^3 in southern Africa.

Volatile PFASs have been also detected in Asian atmosphere. Oono et al reported significantly higher concentrations of 6:2 FTOH (median 22 pg/m³), 8:2 FTOH (median 447 pg/m³) and 10:2 FTOH (median 56 pg/m³) in Keihan area of Japan in comparison with data published in North America and Europe, which was probably due to the different formulations for industrial applications (Oono et al. 2008). Jun Li et al also reported a general decline tendency in atmospheric PFAS concentrations from urban, rural, to remote locations in Asia (Li et al. 2011). However, no information regarding the PFAS concentrations in the atmospheric environment of Singapore is currently available. The summary of reported atmospheric air concentrations of neutral PFASs are presented in Table 2-6.

2.5.2 PFAS levels in water

The levels of PFASs have been determined in a wide variety of aqueous samples, including surface water, ground water, and precipitation. Concentrations of PFASs reported in aqueous phase cover a range of several orders of magnitude. The majority of studies of PFASs in waters have focused on PFOS and PFOA, in addition to other selected PFASs and PFCAs.

2.5.2.1 Surface water and ground water

Moody et al firstly report of ionic PFASs (PFCAs) in aqueous phase (ground water) impacted by fire-fighting activity in U.S. (Moody and Field 1999). Due to the application of PFASs in aqueous fire-fighting foams (AFFF) and extreme use of AFFF in fire-training activities in these sites, the total concentrations of PFHxA+PFHpA+PFOA ranged from 125 to 7090 µg/L, even after 7 – 10 years of inactivity.

Subsequent studies have observed ionic PFASs in a variety of surface waters including rivers, lakes, seas and oceans. Hanson et al observed PFOS and PFOA in the Tennessee River near a fluorochemical manufacturing plant in Decatur, Alabama,

Table 2-6. Concentrations of neutral, volatile PFASs in gas phase at urban, rural and remote atmosphere (pg/m³).

	Location	FTOHs				FOSAs		FOSEs		Ref
		4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	NMeFOSA	NEtFOSA	NMeFOSE	NEtFOSE	
urban	Toronto (Canada)	n.d.	30-196	9-123	7-46	n.a.	14	86-123	51-393	(Martin et al. 2002)
rural	Long Point (Canada)	n.d.	29	32	17	n.a.	n.a.	35	76	(Martin et al. 2002)
remote	Mount Bachelor, Oregon (U.S.)	n.a.	<0.4-16	<0.9-44	<1.0-42	n.a.	<0.4-1.9	<1-11	<1-3	(Piekarz et al. 2007)
urban	Hamburg (Germany)	30	55	108	28	7.0	2.5	18	3.5	(Jahnke et al. 2007a)
rural	Waldhof (Germany)	9.1	29	84	28	7.4	3.2	6.0	8.4	(Jahnke et al. 2007a)
rural	German Bright ^a	2.3	5.7	16	5.7	3.3	1.4	2.5	0.3	(Dreyer and Ebinghaus 2009)
urban	Barsbuettel ^b (Germany)	n.d.	38	127	34	2.1	2.7	3.8	0.8	(Dreyer and Ebinghaus 2009)
urban	Manchester (UK)	<16	61.2-187	237	61.8-65	<5.3-6.1	<3.7-9.6	<53.5	<2.2-6.4	(Barber et al. 2007)
semi-urban	Hazelrigg (UK)	26.3	31.5	66.5	21.2	<5.3	<3.7	<53.5	65.7	(Barber et al. 2007)
rural	Kjeller (Norway)	<0.1	11.7	34.4	17.2	5.5	5.0	48.9	29.5	(Barber et al. 2007)
rural	Mace Head (Ireland)	1.4	4.95	11.3	7.8	<4.9	<1.6	<79.6	<52.4	(Barber et al. 2007)
remote, ocean	Arctic region	n.a.	n.d.-6	5.8-26	1.9-17	n.a.	n.a.	2.6-31	n.d.-8.9	(Shoeib et al. 2006)
ocean	Northern Hemisphere		n.d.-157	13-176	2.9-46	0.6-3.8	<0.3-2.0	n.d.-19	n.d.-8.9	(Jahnke et al. 2007c)
ocean	Eastern Atlantic near South Africa	n.a.	n.d.	2.4-3.1	0.9-1.2	0.5-1.2	n.d.-1.3	n.d.	n.d.	(Jahnke et al. 2007c)
urban	Keihan area (Japan)	n.a.	n.d.-170	48-4,585	35-518	n.a.	n.a	n.a.	n.a	(Oono et al. 2008)
-	Japan	2.29-71.9	2.37-42.6	59.4-808	11.5-198	n.d.-10.2	n.d.-7.23	1.80-82.6	0.67-56.2	(Li et al. 2011)
-	India	2.21-235	n.d.-15.3	19.4-135	9.67-84.5	n.d.-13.1	n.d.-817	0.58-50.8	1.43-11.4	(Li et al. 2011)
-	China	n.d.-78.2	n.d.-292	14.4-498	6.45-285	1.27-12.5	n.d.-14.2	n.d.-18.5	n.d.-24.2	(Li et al. 2011)

U.S., with concentrations in the range of 16.8 to 144 ng/L and < 25 to 598 ng/L, respectively (Hansen et al. 2002). Increased concentrations of PFOS and PFOA were observed downstream of the fluorochemical manufacturing facility, indicating the industrial effluents were a likely source of PFASs to the river. Kannan et al observed of PFOS and PFOA in Raisin River and St.Clair River, which are two rivers in the Great Lakes system in North America (Kannan et al. 2005). Concentrations of PFOS and PFOA were at 1.9 – 3.9 ng/L and 4.4 – 14.7 ng/L, respectively.

Several studies have observed the ionic PFASs in the Great Lakes region in North America. Simcik et al measured the concentrations of ionic PFASs including PFCAs (C₆ to C₁₀) and PFOS in the Lake Michigan (Simcik and Dorweiler 2005). Concentrations of PFOS and PFOA from Lake Michigan were in the range of 0.93 – 3.1 and 0.28 – 3.4 ng/L. Scott et al observed a suite of PFCAs (C₂–C₈) in water samples collected from different depths of Lake Ontario (Scott et al. 2006a). PFCAs were detectable at all depths, with PFOA exhibiting mean concentration at 2.5 ng/L. Other PFCAs were observed at levels of about 1 ng/L. Sinclair et al reported the PFOS and PFOA in Lake Ontario and Lake Erie, with concentrations ranging from 2.8 to 30 and 13 to 34 ng/L, respectively (Sinclair et al. 2006). Myers et al reported the presence of PFCAs (C₆ – C₁₁, C₁₃) and PFSA (C₆, C₈, C₁₀) in Lake Ontario (Myers et al. 2012). PFOA was observed as the predominant compound.

Saito et al measured PFOS and PFOA in surface water samples collected from rivers in Japan, with concentrations ranging from 0.3 to 157 ng/L and 0.28 to 456 ng/L, respectively (Saito et al. 2003, Saito et al. 2004). Highest concentrations were observed in rivers near a public water disposal site and an airport, which were identified as the probable source of contamination. Seawater samples were also taken from various locations. At the sampling site of Tokyo Bay, concentrations of PFOS, PFHS and PFOA were between 3.3 to 192 ng/L. Their levels in offshore and open waters of the Pacific Ocean were three or four orders of magnitude lower. The ionic PFASs were still detectable in deep seawater samples collected at 1–4 km depth (< 0.2 – 117 pg/m³), with PFOA the predominant compound. Tseng et al monitored PFOA, PFOS and PFDA in surface water of two rivers in Taiwan at

concentration levels ranging from 4 to 181 ng/L (Tseng et al. 2006), which is similar to those observed in surface water of rivers in Japan. Nguyen et al reported the similar levels of PFCAs (C₇ – C₁₂) and PFSA (C₆ and C₈) in surface waters of Marina catchment in Singapore, with total concentrations at 9.7 – 119.2 and 2.1 – 223.2 ng/L (Nguyen et al. 2011).

Exner et al investigated the presence of a suite of PFCAs (n = 4 to 11) and PFSA (n = 4, 6 and 8) in the Rhine, Ruhr and Moehne River systems in Germany, Europe (Exner and Färber 2006). Concentrations of Σ PFSA + PFCAs in Rhine River (n.d – 178 ng/L) were much less than those detected in Moehne and Ruhr Rivers (n.d – 4385 ng/L and n.d. – 43348 ng/L, respectively). PFOA was the predominant compound in Ruhr and Moehne rivers (n.d. – 33900 ng/L). The application of contaminated organic wastes to the agricultural lands was assumed to be responsible for the pollution. Moreover, PFCAs and PFSA with total concentrations ranging from nondetectable values to 598 ng/L were detected in drinking water of the study.

2.5.2.2 Precipitation

In comparison with numerous reports on the concentrations of PFASs in surface waters, few reports have focused on the presence of PFASs in precipitation. Loewen et al reported fluorotelomer carboxylic acids and fluorotelomer unsaturated carboxylic acids in rainwater from Winnipeg, Canada (Loewen et al. 2005). These compounds are proposed to be oxidative products of FTOHs in atmosphere. Low levels were detected (< 1 ng/L), suggesting one possible pathway of removing FTOHs from atmosphere is through oxidation and wet deposition. Kim and Kannan reported ionic PFASs in rainwater from downtown of city Albany, U.S. (Kim and Kannan 2007). Sum of PFCAs (C₆ to C₁₂), PFSA (C₆, C₈, C₁₂) and fluorotelomer sulfonates were between 0.91 – 13.2 ng/L. PFOA was the predominant compound. Levels of PFOA in rainwater were lower than the concentrations determined in the lake water at the same site, implying the contribution of wet deposition to PFOA contamination in urban lakes within the studied area was relatively small. Scott et al

detected the C₂ and C₈ PFCAs in precipitation samples taken at different sites in Canada (Scott et al. 2006a). The levels of C₄ to C₈ PFCAs were between < 0.5 and 3.2 ng/L. The same group investigated a suite of PFCAs (C₂ to C₁₂) in precipitation samples from 9 sites in North America (Scott et al. 2006b). The concentrations of C₂ to C₉ PFCAs were significantly higher than C₁₀ to C₁₂ PFCAs, with concentrations of PFOA ranging from < 0.1 to 89 ng/L. Excluding trifluoroacetate (TFA, *n* = 2) and perfluoropropanoate (PFPrA, *n* = 3), PFOA was the predominant PFCA observed in most sampling locations.

Dreyer et al determined the PFCAs (C₄ to C₁₂) and PFSA (C₄ and C₈) in rainwater from northern Germany (Dreyer et al. 2010). Total concentrations of ionic PFASs were between 1.6 to 48.6 ng/L. PFOA and PFBA were usually observed in highest concentrations (1.8 and 2.5 ng/L on average). PFOS concentrations in precipitation were around 1 ng/L. Generally the reported concentrations of PFASs in precipitation samples were lower than those in surface waters discussed above.

2.6 Atmospheric chemistry of volatile PFASs

The detection of ionic PFASs in remote regions was surprising at first, as these chemicals are nonvolatile and only moderately water-soluble. Long-range atmospheric transport appeared quite unlikely for these compounds. In order to explain the observations, a theory was proposed that volatile PFAS precursors could undergo long-range transportation to remote regions via atmosphere and be degraded in situ to form the persistent PFSA and PFCAs. Ellis et al firstly studied the kinetics of reactions of Cl atoms and OH radicals with FTOHs and found out the length of carbon chain had no discernible impact in the reactivity of the molecule (Ellis et al. 2003). They concluded that the atmospheric lifetime of FTOHs was determined by reaction with OH radicals and was approximately 20 days, which was sufficient to allow for a widespread distribution in the environment. In the follow-up study, the same group determined the atmospheric chemistry of 4:2 FTOH (Hurley et al. 2004). The Cl atom initiated atmospheric oxidation yielded the small, but discernible amounts of PFCAs.

The smog chamber studies presented by the same group indicated that FTOHs can degrade in the atmosphere to yield a homologous series of PFCAs through reaction with OH radicals and Cl atoms (Ellis et al. 2004). Therefore, the long range transport and in situ atmospheric degradation of FTOHs is likely to contribute to the wide spread occurrence of PFCAs in environment and explain the presence of long-chained PFCAs in arctic animals. The wet deposition is expected to be more probable for the atmospheric intermediates of FTOHs (PFCAs) due to their higher water solubility and low vapor pressure.

The low volatility of FOSAs/FOSEs has hampered the smog chamber experiments due to the insufficient introduced quantities. Instead, Martin et al conducted smog chamber experiments to investigate atmospheric chemistry of N-ethyl perfluorobutane sulfonamide (NEtFBSA) (Martin et al. 2006). As for FTOHs, the OH-initiated oxidation is the dominant degradation mechanism of NEtFBSA in troposphere. The estimated atmospheric lifetime of NEtFBSA is 20 – 50 days, thus allowing long-range atmospheric transport. C₂ – C₄ PFCAs identified as degradation products were observed in all samples with a proposed yield of 45%. The results suggested that FOSAs/FOSEs were likely to contribute to the PFCA burden in remote regions.

D'Eon et al investigated the atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanols (NMeFBSE) (D'Eon et al. 2006). The atmospheric lifetime of NMeFBSE is determined by reaction with OH radicals and is approximately 2 days. Degradation products included N-methyl perfluorobutane sulfonamide (NMeFBSA), perfluorobutane sulfonate (PFBS), and C₂ – C₄ PFCAs et al. Given the estimation that NMeFBSA has an atmospheric lifetime of > 20 days, NMeFOSE may also contribute to the ubiquity of PFSA and PFCAs in the environment.

2.7 Summary

The extensive use of PFASs in both commercial and industrial applications has prompted research into the environmental behavior, occurrence and impact of this class of compounds in recent years. FTOHs and FOSAs/FOSEs are important

subgroups of PFASs, which have been recognized as the volatile precursors of the persistent PFCAs and PFSA. Recently a significant correlation between FTOH concentrations and PFOA concentration in human serum has been reported, increasing their toxicological concerns to public health. A limited number of studies have investigated the air-water partitioning coefficient of FTOHs, but the reported values show great discrepancies, making the predication of their environmental behavior difficult. Furthermore, although FTOHs and FOSAs/FOSEs are widely detected in indoor and ambient air of Europe and North America, no published concentration data of FTOHs and FOSAs/FOSEs in the air of Singapore is available, and a highly sensitive analytical method which can achieve both satisfying temporal resolution and high accuracy for determination of neutral, volatile PFASs in gas phase has not been developed yet.

Chapter 3

The effect of surface adsorption and molecular geometry on the determination of Henry's law constants for fluorotelomer alcohols

3.1 Introduction

Fluorotelomer alcohols (FTOHs) are neutral, volatile PFASs with the general structure $F(CF_2)_nCH_2CH_2OH$, where n is an even number. The FTOHs are often referred to as $X:Y$ FTOH based upon number of fluorinated carbon atoms (X) and hydrogenated carbon atoms (Y). Their occurrence in atmosphere has been widely reported in global range including arctic region (Stock et al. 2004, Jahnke et al. 2007d, Dreyer and Ebinghaus 2009). In addition, FTOHs could undergo biodegradation or oxidation to yield perfluorocarboxylic acids (PFCAs), which persist in the environment and accumulate in the body of human and wildlife (Ellis et al. 2004).

Henry's law constant (K_H), which describes the equilibrium partitioning between gaseous and aqueous phases, is essential to predict the environmental behavior, transport and fate of many classes of organic chemicals (Brutseart and Jirka 1984). In this study, the K_H is expressed as the ratio of vapor pressure P_g to its aqueous concentration C_w . The K_H can also take the dimensionless form (K_{AW}), which is related to K_H by

$$K_{AW} = \frac{C_A}{C_w} = \frac{K_H}{RT} \quad 3.1$$

Where C_A is the concentration of the compound in the gas phase; R is the ideal gas constant; and T is the thermodynamic temperature.

Enthalpy ΔH and entropy ΔS of phase change from dissolved phase to gas phase were calculated using slope and intercept values by plotting $\ln K_{AW}$ against the reciprocal of absolute temperature.

$$\ln K_{AW} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad 3.2$$

Where ΔH represents the energy required to overcome the intermolecular interaction in transferring molecules between the two phases. ΔS is the associated entropy change. This expression assumes that ΔH and ΔS are temperature independent, which is a reasonable assumption over a small temperature range in this Chapter from 36.6 to 61.2 °C.

Despite numerous reports on environmental concentrations and treatment methods about FTOHs (Renner 2006, Shoeib et al. 2006, Jahnke et al. 2007b), very little experimental information is available on their physicochemical properties. Several studies (Lei et al. 2004, Arp et al. 2006, Goss et al. 2006) have used equilibrium headspace gas chromatography (HS) approach to determine K_H of 4:2, 6:2 and 8:2 FTOH, which measures the equilibrium headspace concentration in closed glass vials with typical sizes of 10 or 20 mL (Lei et al. 2004, Goss et al. 2006). This approach is relatively reliable and straight forward in the experiment processes. However, the adsorption of FTOHs to the glass wall at equilibrium might lead to an underestimation of K_H , as reported by Goss et al (Goss et al. 2006).

This Chapter measured K_H values for 4:2, 6:2, 8:2 and 10:2 FTOH from 36.6 to 61.2 °C using integrated gas-stripping (IGS) method. To our knowledge, the current study is the first to employ IGS to determine K_H of FTOHs. Surface adsorption, which was suspected as an potential influencing factor to the measurement in IGS, were also investigated by batch experiments employing glass and stainless steel vials. K_H values obtained via IGS in this study were compared with K_H generated by modeling software (EPI Suite and SPARC) and HS approach from references to better understand the molecular geometry of FTOHs, as well as the advantages and potential flaws in these approaches.

3.2 Experimental section

3.2.1 Chemicals

All standards and solvents used in this study were analytical grade purchasing from various suppliers. 1H,1H,2H,2H-Perfluoro-1-hexanol (4:2 FTOH; 97%, CAS No.: 2043-47-2) was obtained from ABCR, Germany. 1H,1H,2H,2H-perfluoro-1-octanol (6:2 FTOH; 97%, CAS No.: 647-42-7) and 1H,1H,2H,2H-perfluoro-1-decanol (8:2 FTOH; 97%, CAS No.: 678-39-7) were from Sigma-Aldrich, U.S. 1H,1H,2H,2H-perfluoro-1-dodecanol (10:2 FTOH; 96%, CAS No.: 865-86-1) were obtained from Lancaster Synthesis, U.K. $^{13}\text{C}_2\text{d}_2$ -8:2 FTOH with concentration of 50 $\mu\text{g/mL}$ in methanol (mass-labelled surrogate standard for FTOHs) were from Wellington Laboratories, Canada. Internal standards 1H,1H-perfluoro-1-octanol (7:1 FA; 98%, CAS No.: 307-30-2) and 1H,1H-perfluoro-1-dodecanol (11:1 FA; 90%, CAS No.: 423-65-4) were from Lancaster Synthesis, U.K.

Ethyl acetate (ETOAc, for gas chromatography Suprasolv, $\geq 99.8\%$, CAS No.: 141-78-6) was obtained from Merck, Germany. Methyl *tert*-butyl ether (MTBE, puriss. p.a., $\geq 99.5\%$, CAS No.: 1634-04-4) was from Sigma-Aldrich, U.S. Acetone ($\geq 99.8\%$, CAS No.: 67-64-1) was purchased from Fisher Scientific, UK.

3.2.2 Apparatus

The IGS method employed the gas-stripping apparatus similar to that described by Mackay et al. (Mackay and Shiu 1981). Two stripping vessels in similar size were fabricated respectively using stainless steel (SUS304) and glass (90 cm high with 5.5 cm I.D.). Each set up consists of two columns fused together in the bottom. The outer column, filled with circulated water, served as water jacket for temperature control; while the inner column was used for gas stripping measurements with four sampling ports installed at different positions.

Preparation of the aqueous solution is an important factor in IGS experiments. It is noteworthy that the existence of organic solvent in the solution might potentially

affect the experimental results for FTOHs, though Ten Hulscher et al. has demonstrated a negligible solvent effect on measurement of K_H for some hydrophobic organic compounds by IGS (Ten Hulscher et al. 1992). However, in order to minimize the loss of FTOHs during chemical dissolving process and achieve complete dissolution, this study followed the similar approaches with other studies using IGS method (Bamford et al. 2000, Miyano et al. 2010). The solution was prepared using Milli-Q water in a 2 L volumetric flask and spiked with 1 mL mixed standards of 4:2, 6:2 and 8:2 FTOH in methanol, equivalent to 200 μg for each compound. 1 mL of solution containing 40 μg of 10:2 FTOH in methanol was spiked separately due to its low solubility (Liu and Lee 2007).

The flask was covered with aluminum foil and stirred with a magnetic bar for one day. Measured aqueous concentration of FTOHs in the flask was lower than the reported or estimated saturation level of each compound (Liu and Lee 2007). Then the solution was transferred to the vessel and allowed to sit in the thermostatted column overnight prior to gas stripping experiment in order to reach equilibrium with the apparatus. Nitrogen stream (99.9995%, Air Liquide, Singapore) generated from the gas cylinder was used as stripping gas with an in-line mass flow controller (FMA5512, OMEGA Instrument, U.S.) maintaining a constant flow rate at 50 mL/min. To minimize the water partitioning effect during the experiment, the nitrogen stream was saturated with water by passing through tandem 500 mL gas-washing bottles before entering the column. Bubbling was carried out through an air stone with pore size in the range of 40 to 50 μm . Temperature control was done by using water jacket circulated through outer column to maintain the isothermal condition of the stripping system.

Both concentrations in the aqueous solution and the existing gas were monitored during each run. No statistical difference in aqueous concentrations collected from different sampling ports was discernable, indicating a homogeneous distribution of FTOHs within the vessel. Therefore, 6 mL aqueous sample was withdrawn from the middle section of the column every 0.5 h in the subsequent experiments. The FTOHs in the exiting gas stream (50 mL/min) were collected by the 13-mm diameter of OSHA Versatile Sampler (OVS) tubes (SKC, U.S.) for 0.5 h during a

total 3 h sampling period after an initial 1 h purging of the system. The sorbent tubes were then spiked with 50 ng of mass-labeled 8:2 FTOH in methanol prior to sampling for recovery calculation and data quality monitoring.

To investigate the adsorption of FTOHs onto different material surfaces, another set of batch experiments were conducted using 10 mL vials (60 mm high with 16 mm i.d.) made by stainless steel and glass respectively. Duplicate sets of vials were filled with 10 mL aqueous solution containing 100 ng of each FTOH with minimal headspace remained. Duplicate samples were kept in water bath under different temperatures and time durations. The aqueous solution was removed at the end of the experiments for concentration measurement, and then the remaining FTOHs absorbed to the surfaces were recovered by MTBE. Results showed adsorption of all FTOHs within the vial equilibrated for 6 h. Therefore, to ensure equilibrium had been reached, 8 h was chosen for the adsorption experiments.

3.2.3 Sample treatment and quality control

For the gas samples collected in IGS, the filter with the front section of XAD-2 resin in the OVS tube were transferred to a 4 mL vial and solvent-extracted with 3 mL mixture of acetone and MTBE in equal proportions by volume. The vial was immersed approximately 15 mm in an ultrasonic bath for 30 minutes. The extracts were filtered through a 0.45 μ m nylon syringe filter (Acrodisc, Pall Gelman) into the 15 mL centrifuge tubes. The back sections of XAD-2 resin were also analyzed to ensure no breakthrough during the sampling period. The volume of the extracts was reduced with ETOAc as keeper to 500 μ L by gentle stream of high purity nitrogen. 10 μ L of internal standard containing 2000 ng of 7:1 FA and 11:1 FA in ETOAc was added prior to the analysis for volume correction. For the water samples, 50 ng of mass-labeled 8:2 FTOH in methanol was spiked in before extraction. Then the aqueous samples were solvent extracted three times with 1 mL MTBE in 15 mL centrifuge tubes, and the combined extracts were reduced to about 500 μ L in ETOAc. 10 μ L internal standard was added prior to the analysis.

All glassware was baked at 400 °C for 2 h before each experiment to minimize contamination. Procedural blanks were run with each batch of aqueous and gaseous samples to detect background contamination during the experimental process. All samples were extracted immediately upon collection.

Results showed none of the target compound in the blank was higher than the detection limit. Therefore, the experimental contamination could be neglected in data analysis. The average recovery rates of mass-labeled 8:2 FTOH for 112 water and 52 air samples are $(89 \pm 12)\%$ and $(100 \pm 13)\%$, respectively, indicating high credibility of the data obtained in this experiment.

3.2.4 Instrumental analysis

Sample quantitation was conducted using a GC–MS system (Agilent 6890N – 5973, U.S.) working in electron ionization (EI) mode. Gas inlet parameters include: inlet temperature of 240 °C; 2 µL splitless injection; purge flow of 50 mL/min at 1 min. Chromatographic separation of FTOHs was performed on 60 m HP-INNOWAX column (0.25 mm I.D., 0.25 µm film thickness, J & W Scientific, U.S.) using helium as the carrier gas (1.2 mL/min). The oven temperature program was set at 50 °C for 2 min, 3 °C/min to 80 °C, hold for 0 min, then 10 °C/min until 230 °C with another hold for 5 min..

Quantitation was based on area integration of the target ion of each compound. Two more ions were picked to assist qualification of the interest compound. 7:1 FA served as the internal standard for all analyses except 10:2 FTOH, which used 11:1 FA instead. A National Institute for Occupational Safety and Health (NIOSH) procedure (Kennedy et al. 1995) was employed to determine the instrumental limit of detection (IDL) and instrumental limit of quantitation (IQL) for each target compound, as indicated in Table 3-1.

Table 3-1. Instrumental detection limits (IDL), instrumental quantitation limits (IQL) of FTOHs calculated using NIOSH method (Kennedy et al. 1995), and ions monitored by GC–MS working in EI mode.

Compound	IDL/pg	IQL/pg	EI Ions monitored m/z
4:2 FTOH	1.20	3.98	31 ^a , 95, 244
6:2 FTOH	2.52	8.38	31 ^a , 95, 344
8:2 FTOH	0.88	2.96	31 ^a , 95, 405
10:2 FTOH	1.48	4.92	31 ^a , 95, 505
¹³ C ₂ , d ₂ -8:2 FTOH ^b	-	-	34 ^a , 96, 415
7:1 FA ^c	-	-	31, 100, 131
11:1 FA ^c	-	-	31, 119, 131

^aQuantitation ion^bMass-labeled surrogate standard^cInternal standard

3.2.5 K_H measurement

The IGS approach involves measurement of declining aqueous and air concentration as the water solution is purged with a flow of gas. K_H could be calculated as the ratio of time-integrated gas phase concentration (C_A) over the average of the two aqueous concentrations which were measured at the start ($C_{w(n)}$) and end ($C_{w(n+1)}$) of each air samples.

$$K_{AW} = \frac{C_A}{(C_{w(n)} + C_{w(n+1)}) / 2} \quad 3.3$$

Comparing to small glass vials in HS method, IGS requires larger vessel volume, typically in the range of liters, for gas stripping. This leads to a much lower surface-to-volume ratio than that in HS. As the long-chained FTOHs had been reported to have significant surface adsorption, IGS has the advantage to minimize the artifact in this regard. Furthermore, IGS method allows repeated measurements of K_H in one experimental run, which improves the data quality control.

3.2.6 General partitioning models

Sparc Performs Automated Reasoning in Chemistry (SPARC) is a general purpose calculator developed by University of Georgia (Hilal et al. 2007, Hilal et al. 2008). It is widely used in situations where suitable measured values are not available. SPARC calculates various physicochemical parameters from molecular structure and basic environmental information. In most cases, SPARC only requires the input of simplified molecular input line entry specification (SMILES string), which is used for describing the structure of chemical molecules, to predict a parameter.

Estimation programs interface (EPI) suite is another widely used software developed by U.S. Environmental Protection Agency to predict physicochemical properties of organic compounds (U.S.EPA 2011). The Henrywin v3.20 integrated inside EPI suite v4.10 is employed to estimate the Henry's law constant through the group contribution and bond contribution methods.

3.3 Results and discussion

3.3.1 Adsorption of FTOHs on glass and stainless steel surface

Due to air stripping in IGS, the aqueous concentrations of FTOHs were expected to decrease with time. Preliminary results indicated a stable declining tendency of 4:2 FTOH in glass vessel. However, greater fluctuations were observed for longer-chained compounds including 6:2, 8:2 and 10:2 FTOH. This indicated the measurement of air-water partitioning coefficient of FTOHs in glass vessel was biased by some other factors, which was suspected to be surface adsorption. FTOHs, as the strong surfactants, have been reported to exhibit adsorption tendency to surfaces including laboratory glassware and equipment (Kaiser et al. 2004, Arp et al. 2006, Goss et al. 2006), and the sorptive abilities were observed to increase with increasing length of fluorinated carbon chain (Liu and Lee 2005, Arp et al. 2006). In addition, some studies investigating K_H of other hydrophobic organic compounds

using IGS method had also suggested that the adsorption to glass surface might be an important factor leading to this phenomenon (Bamford et al. 1999, Bamford et al. 2000).

Measurements of K_H by IGS were also conducted using stainless steel vessel. Compared with glass vessel, the data from stainless steel showed more consistent declining trends in aqueous concentrations. In order to better understand the adsorption of FTOHs to the stainless steel and glass surfaces, another set of batch experiments were conducted in small glass and stainless steel vials.

Figure 3-1 shows the wall adsorption ratio in glass and stainless steel at 40 °C (Figure 3-1a) and 50 °C (Figure 3-1b). The y axis indicates the ratio of the amount of FTOHs recovered from the vial surface to the total amount of FTOHs injected to the vial. It can be observed that the shorter FTOHs (4:2 and 6:2) exhibited little or slight adsorption on both stainless steel and glass surfaces. In contrast, the surface adsorption increased significantly for two longer-chained FTOHs (8:2 and 10:2) on glass surface, while stainless steel only displayed a modest adsorption for 10:2 FTOH compared with glass surface.

Temperature was observed as another important factor, other than the fabricating material, which could also affect the wall adsorption of FTOHs, especially for longer FTOHs (8:2 and 10:2). As indicated in Figure 3-1, the adsorption ratio of 10:2 FTOH was reduced by half when the temperature increased from 40 to 50°C for both surfaces. Therefore, the results of the small vial experiment provided a sound evidence for the presence of surface adsorption of FTOHs, which could be an important source of fluctuating aqueous concentrations in glass vessel discussed above.

Due to the fluctuating aqueous concentrations, no consistency was observed for calculated K_H of 6:2, 8:2 and 10:2 FTOH in IGS experiment using glass vessel, with relative standard deviations of K_H occasionally higher than 0.5. In addition, although polypropylene was reported to be a good material for PFCs with relatively low adsorption, the temperature control in PP vessel would be an issue due to its

poor thermal conductivity. Therefore, stainless steel vessel was employed instead of the widely-used glass column for K_H measurement by IGS in this study.

(a)

(b)

Figure 3-1. Adsorption ratio of FTOHs to the vial surface made of different materials. $M_{adsorbed}$, amount of FTOHs adsorbed to the vial surface; M_{tot} , total amount of FTOHs injected into the vial; ■, stainless steel; □, glass; (a) at 40 °C; (b) at 50 °C.

Furthermore, the loss of chemical from aqueous phase during IGS can also be attributed to chemical adsorbing on the air bubble surface, in addition to the chemical partitioning to air phase and chemical adsorbing to reactor wall. While wall adsorption effect was discussed above, the air bubble surface effect was controlled by the adsorption coefficient of FTOHs on the water surface from the water side and surface-to-volume ratio of air bubbles. Upon the bursting of air bubbles, the FTOHs absorbed on gas bubbles surfaces will transfer to the headspace of the reactor and lead to the overestimation of the K_H . Detailed quantitation of the influence of air bubble adsorption effect in IGS requires further study. A comparison with parallel experiments using HS and IGS with stainless steel containers might be helpful to better understand the impact of the air bubble effect.

3.3.2 Results of Henry's law constant

To measure Henry's law constant, it is essential to ensure equilibrium was achieved between gaseous and aqueous phases within the stripping vessel. Initial tests were conducted to measure the K_H values obtained at purge heights of 40, 67 and 84 cm under 50 °C. Results showed that K_H values of FTOHs obtained at 67 and 84 cm yield similar values with relative standard deviation less than 0.1, indicating the equilibrium was reached at the height above 67 cm. To further ensure equilibrium conditions, all experiments were conservatively conducted at the height of 84 cm in this study.

Table 3-2 shows measured Henry's law constants of FTOHs with a confidence interval of 0.95 at each temperature. The estimates of uncertainties, with a coverage factor $k = 2$, were compliant with the NIST method of reporting (Taylor and Kuyatt 1994). The measured dimensionless K_{AW} revealed the propensity of FTOHs to partition into air and the tendency generally increased with increasing molecular weight and temperature. All the measured K_H values were analyzed using linear regression of $\ln K_{AW}$ versus the reciprocal of temperature to predict the K_H values (Figure 3-2). The r^2 values for the linear regression analysis of all FTOHs ranged from 0.92 to 0.99, validating the assumption that enthalpy ΔS and entropy ΔH were

invariant over the investigated temperature range (eq 3.2). This finding allowed the K_H of FTOHs to be reasonably extrapolated to 25 °C with estimates of uncertainties, as shown in Table 3-3. Calculated enthalpy ΔS and entropy ΔH of phase change based on the slope and intercept of the lines were also included in Table 3-3. It is noteworthy that, unlike the results obtained by Lei et al. (Lei et al. 2004), no linear increase of both ΔS and ΔH with each additional $-\text{CF}_2-\text{CF}_2-$ unit was observed in this study. However, the extrapolated K_H of 8:2 FTOH at 25 °C by Lei et al. (Lei et al. 2004), using their ΔH and ΔS would be lower than that of 4:2 FTOH, which was inconsistent with the results reported in this study and other groups (Krusic et al. 2005, Goss et al. 2006).

Table 3-2. Henry's law constants of FTOHs measured in the 36.6 to 61.2 °C temperature range. ^a

Compound	$T/^\circ\text{C}$	K_{AW}	$K_H/\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$	$\log (K_H/\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1})$
4:2 FTOH	36.6	0.11 ± 0.01	280 ± 30	2.45 ± 0.04
	41.5	0.12 ± 0.01	310 ± 30	2.50 ± 0.05
	46.6	0.15 ± 0.02	400 ± 50	2.60 ± 0.05
	50	0.18 ± 0.02	480 ± 50	2.68 ± 0.05
	57	0.23 ± 0.02	630 ± 60	2.80 ± 0.04
	61.2	0.29 ± 0.01	810 ± 30	2.91 ± 0.02
6:2 FTOH	36.6	2.82 ± 0.42	7260 ± 1080	3.86 ± 0.07
	41.5	3.60 ± 0.54	9410 ± 1410	3.97 ± 0.07
	46.6	4.10 ± 0.32	10890 ± 850	4.04 ± 0.04
	50	4.27 ± 0.82	11470 ± 2200	4.06 ± 0.09
	57	4.54 ± 0.42	12460 ± 1150	4.10 ± 0.04
	61.2	5.15 ± 0.84	14310 ± 2330	4.16 ± 0.08
8:2 FTOH	36.6	2.95 ± 0.22	7590 ± 570	3.88 ± 0.03
	41.5	3.27 ± 0.54	8550 ± 1410	3.93 ± 0.08
	46.6	3.86 ± 0.22	10260 ± 590	4.01 ± 0.03
	50	4.29 ± 0.50	11520 ± 1340	4.06 ± 0.05
10:2 FTOH	36.6	3.88 ± 0.40	9990 ± 1030	4.00 ± 0.05
	41.5	4.95 ± 0.56	12940 ± 1460	4.11 ± 0.05
	46.6	5.69 ± 1.62	15120 ± 4310	4.18 ± 0.15
	50	6.03 ± 0.68	16190 ± 1830	4.21 ± 0.05
	57	6.65 ± 1.46	18250 ± 4010	4.26 ± 0.11
	61.2	7.05 ± 0.72	19590 ± 2000	4.29 ± 0.05

^a 0.95 confidence intervals (± 2 standard deviation) (Taylor and Kuyatt 1994)

Table 3-3. Henry's law constants extrapolated to 25 °C (298 K) for FTOHs ^{a,b} along with calculated entropy ΔH^c and enthalpy ΔS^d .

FTOHs	K_H /Pa·m ³ ·mol ⁻¹	ΔH /kJ·mol ⁻¹	ΔS /J·K ⁻¹ ·mol ⁻¹
4:2 FTOH	150 ± 30	34.6 ± 6.4	92.9 ± 19.9
6:2 FTOH	5730 ± 1220	18.6 ± 7.6	69.4 ± 23.8
8:2 FTOH	5040 ± 1030	23.5 ± 18.1	84.9 ± 19.6
10:2 FTOH	7780 ± 1610	19.6 ± 7.4	75.2 ± 23.1

^a Derived Henry's law constants from the linear regression analysis of measured $\ln K_{AW}$ versus the reciprocal temperature. ^b Working–Hotelling 0.95 confidence band. ^c 0.95 confidence interval ($\pm t$ critical $\times$ standard errors of the slope). ^d 0.95 confidence interval ($\pm t$ critical $\times$ standard errors of the intercept).

As indicated in Table 3-2, the K_H values of FTOHs generally increase with the increasing fluorinated carbon chain and temperature. However, the values of K_H for 6:2 and 8:2 FTOH show little difference. Generally speaking, if analogue group possess a similar structure, their K_H and molar enthalpy of phase change should increase with increasing molecular weight (Ong and Lion 1991). This trend was not observed in the current study. Similarly, Lei et al. and Goss et al. (Lei et al. 2004, Goss et al. 2006) using HS reported a slight reduction of K_H for 8:2 FTOH compared with 6:2 FTOH. Goss et al. (Goss et al. 2006) attributed the lower value of K_H of 8:2 FTOH to the extensive adsorption of FTOHs to the glass surface. In addition, we expect these unusual phenomena may also indicate the influence of the molecular structure of FTOHs to their physicochemical properties, since all experimental K_H data of FTOHs displayed similar trends.

It is reported that unlike hydrocarbons, the geometry of fluorocarbons changes as the chain length increases to minimize the steric hindrance due to the larger van der waals radius of fluorine than hydrogen. If the CF₂ units are less than eight, the fluorocarbon segments mainly form a planar and flexible zigzag conformation; while more than eight CF₂ units, slight distortion at each CF₂ leads to helix conformation, which the tendency increases strongly with increasing number of CF₂ units (Bunn and Howells 1954, Wang and Ober 1999). The change of molecular

geometry with increasing fluorocarbon chain would impact electron density distribution within molecules and the free energy of thermodynamic process. Wang et al. (Wang and Ober 1999) reported the melting enthalpy of a series of semifluorinated 1-bromoalkane decrease when the number of CF_2 group increased from 8 to 12.

Hydrogen bonding might also serve as another important factor. In addition to the intermolecular hydrogen bonding, multiple fluorination of alkanol also results in intramolecular hydrogen bonding within FTOHs. The X-ray crystallographic study (Bamford et al. 1999) suggested a hex-shaped intramolecular bonding with hydrocarbon functional group of FTOHs at the end of the carbon chain folding back on top of fluorinated portion, as illustrated in Figure 3-3. The competition between intramolecular and intermolecular hydrogen bonding would affect relative physicochemical properties of FTOHs.

Figure 3-2. Measured dimensionless Henry's law constant K_{AW} of FTOHs as a function of temperature from 36.6 to 61.2 °C. ●, 4:2 FTOH; ○, 6:2 FTOH; ▼, 8:2 FTOH; △, 10:2 FTOH.

Figure 3-3. Molecular geometries of FTOHs. (a) Intramolecularly hydrogen bonded; (b) Unbonded

This hex-cyclic intramolecular hydrogen bonding and intermolecular hydrogen bonding in FTOHs, coupled with the twisting and stiffening effect of carbon segments discussed above, might further complicate the physicochemical properties, especially for longer-chained compounds such as 8:2 and 10:2 FTOH. Furthermore, all these factors could interactively influence one another. For example, as the gradually twisted and stiffened fluorocarbon segment tends to become poorly compatible with the flexible hydrocarbon tail with increasing hydrophobic carbon chain length, the polarization of -OH functional group was enhanced. Consequently, the hydrogen segment of longer FTOHs would be easier to establish intermolecular molecular hydrogen bonding with other FTOHs or water molecules in aqueous phase. This could compensate the effects resulting from increasing chain length, making the longer FTOHs less volatile than expected. This effect could be illustrated as the observed vapor pressures of FTOHs were higher than their hydrocarbon counterparts, which was believed mainly due to the masking of -OH functional group by intramolecular hydrogen bonding (Lei et al. 2004, Stock et al. 2004, Krusic et al. 2005). The K_H values of FTOHs are also approximately 1 to 2 orders of magnitude higher than those of nonsubstituted alcohols (Mackay 1993).

Therefore, the slight difference of K_H value between 6:2, 8:2 and 10:2 FTOH in this study might be due to the combined effects of conformation change and hydrogen bonding as discussed above, making their physicochemical properties quite different from those of their hydrocarbon counterparts.

3.3.3 Comparison between experimental and modeling results

Plots of extrapolated experimental K_H of FTOHs at 25 °C (298 K) from various studies via different experimental approaches versus number of fluorinated carbon atoms are illustrated in Figure 3-4, including values obtained by current study using IGS method, Goss et al. (Goss et al. 2006) using HS methods, Lei et al. (Lei et al. 2004) using HS method, as well as values of short-chained fluorinated alcohols $\text{CF}_3\text{CH}_2\text{OH}$ and $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$ reported by Chen et al. (Chen et al. 2003) using absolute calibration method. It could be seen that K_H values were mainly influenced

Figure 3-4. Plots of reported experimental Henry's law constants of FTOHs at 25 °C versus number of fluorinated carbon atoms. ■, this work using integrated gas-stripping method (IGS); ○, Goss et al. (Goss et al. 2006) using headspace method (HS); ●, Lei et al. (Lei et al. 2004) using HS; △, Chen et al. (Chen et al. 2003) using absolute calibration method for short-chained fluorinated alcohols $\text{CF}_3\text{CH}_2\text{OH}$ and $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$.

by the number of fluorinated carbon atoms except the reversed trend reported by Lei et al. (Lei et al. 2004), which might be erroneous. It is also clear that all extrapolated values of $\log K_H$ of FTOHs by HS method are lower than those by IGS method. This discrepancy might be mainly attributed to the different extent of surface adsorption of FTOHs to the wall due to different surface-to-volume ratio and fabrication materials in IGS and HS. The equilibrium between bulk phase (water, air) and vessel surface in the closed container of HS method would lead to the reduction in sampled gaseous concentration. This has been confirmed by Goss et al. (Goss et al. 2006), who reported a slightly higher K_H value of 8:2 FTOH by using silanized glass vial. IGS, which employs a much larger vessel than HS, will suffer less from the interface adsorption effect due to the relatively lower surface-to-volume ratio.

Table 3-4 lists the values of $\log K_H$ at 25 °C obtained in this study, calculated from vapor pressure (P) and water solubility (S), (Krusic et al. 2005, Liu and Lee 2007) and modeling results generated by the latest versions of EPI and SPARC (EPI suite v4.10 and SPARC Sep, 2009). It is clear that the estimated partitioning coefficients by EPI and SPARC differ considerably. Through comparison with experimental values, the group method of EPI suite v4.10 is probably not a suitable method for predicting the partitioning behavior of FTOHs as it overestimates the value by up to 6 orders of magnitude. In contrast, EPI bond method performed relatively better, but still reported higher K_H values for longer-chained FTOHs by up to 4 orders of magnitude. Compared with EPI suite, the latest SPARC gave a closer estimation for all FTOHs except 10:2 FTOH.

To sum up, significant discrepancies were observed between experimental values and modeling predictions, which was in accordance with our expectations. Both SPARC and EPI suite require only the input of basic structure of molecule to predict a parameter, resulting in large uncertainty in their predication due to lack of compensation for geometrical features of FTOHs. The existence of cyclic intramolecular hydrogen bonding and conformation distortion also lead to the conclusion that all physicochemical properties of FTOHs governed by molecular geometry will be significantly affected, as the novel geometry will impact the

Table 3-4. $\log (K_H/\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1})$ of FTOHs at 25 °C (298 K) generated in this study (IGS)^a, and calculated from vapor pressure(*P*) and solubility(*S*)^b, as well as values predicted by modeling software (EPI Suite and SPARC).

Compound	$\log (K_H/\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1})$				
	IGS (Current Study)	<i>P/S</i>	EPI Suite v4.10 Bond method	EPI Suite v4.10 Group method	SPARC Sep, 2009
4:2 FTOH	2.18 ± 0.09	1.77	2.74	3.23	1.02
6:2 FTOH	3.76 ± 0.10	2.54	4.18	5.23	2.4
8:2 FTOH	3.70 ± 0.08	4.10	5.62	7.23	4.31
10:2 FTOH	3.89 ± 0.10	4.01	7.06	9.23	6.71

^a Working-Hotelling 0.95 confidence band for linearly predicted Henry's law constants. ^b

4:2 FTOH: 216 Pa (Krusic et al. 2005), 974000 µg/L (Liu and Lee 2007); 6:2 FTOH: 18 Pa (Krusic et al. 2005), 18800 µg/L (Liu and Lee 2007); 8:2 FTOH: 4 Pa (Krusic et al. 2005), 148 µg/L (Ellis et al. 2003, Kaiser et al. 2004, Liu and Lee 2005); 10:2 FTOH: 0.2 Pa (Krusic et al. 2005), 11 µg/L (Liu and Lee 2007).

electron density distribution and free energy of thermodynamic process. Furthermore, the changes of molecule's geometry with increasing chain length of FTOHs would result in difficulty in the predication of these properties, based on differences between experimental and modeling values observed in this study.

3.4 Conclusions

The Henry's law constants of 4:2, 6:2, 8:2 and 10:2 FTOH were determined using IGS method at various temperatures from 36.6 to 61.2 °C. Results revealed the propensity of this class compounds to partition into air. Great fluctuation in calculated K_H values in IGS employing glass vessel was observed, especially for FTOHs with longer fluorocarbon chains. In contrast, a set of stable K_H values were observed by stainless steel vessel. The adsorption of FTOHs to vessel surface was suspected to be the main influencing factor for this phenomenon and was investigated by batch experiment employing stainless steel and glass vials. A strong adsorption of long-chained FTOHs, 8:2 and 10:2, to the glass surface than stainless

steel was observed. Furthermore, unlike their hydrocarbon counterparts, the linear dependence of K_H on molecular weight was not observed for FTOHs, which was consistent with the results by other researchers using HS approach. The unique geometry of FTOHs with hydrogen bonding and conformation distortion was believed to contribute to the unusual physicochemical properties of FTOHs reported in experiments. It also increased the difficulties in predication by modeling software such as SPARC and EPI Suite. In addition, various extent of deviations between IGS-generated and HS-generated values for different FTOHs were observed, which might be mainly attributed to the differences in surface adsorption of FTOHs due to different surface-to-volume ratio and fabrication materials in IGS and HS methods.

Chapter 4

Development of analysis of volatile polyfluorinated alkyl substances in indoor air using thermal desorption – gas chromatography – mass spectrometry

4.1 Introduction

In recent years, several ionic PFASs including PFCAs and PFSAAs, have drawn great attention, since they are persistent and could pose potential adverse effects to human health (Ellis et al. 2004, Prevedouros et al. 2006, Kannan 2011). The long-range atmospheric transport and subsequent oxidation of volatile precursor PFASs, including FTOHs and perfluorooctane sulfonamides/ethanols (FOSAs/FOSEs), is considered as the major contributor to the ubiquitous environmental occurrence of ionic PFASs (Ellis et al. 2004, Wallington et al. 2006).

FTOHs are a class of linear polyfluorinated alcohols which are often used in the production of fluorotelomer-based substances to provide oil and water repellent properties. FOSAs and FOSEs are produced and used in similar application as FTOHs. The volatile PFASs may be released into environment from products that incorporate the volatile PFASs or contain residual PFASs during product use or disposal (Dapremont-avignon et al. 1991, Washburn et al. 2005, Sinclair et al. 2007). Volatile PFASs have been widely detected in environment with significantly higher concentrations in indoor air (Jahnke et al. 2007b, Jahnke et al. 2007d, Dreyer and Ebinghaus 2009). FTOHs are usually the predominant group of targeted PFASs observed in indoor air (200 – 20000 pg/m³), followed by FOSEs (120 – 12000 pg/m³) and FOSAs (50 – 12000 pg/m³) (Shoeib et al. 2004, Langer et al. 2010).

Most of published sample collection of indoor airborne targeted PFASs were conducted using passive sampler (Langer et al. 2010) or high-volume sampler

(Stock et al. 2004, Dreyer and Ebinghaus 2009), which has been introduced in literature review. Recently the solid-phase extraction (SPE) cartridge was introduced as low-volume air sampler (Jahnke et al. 2007d). However, these sampling setups suffer from a lot of drawbacks including low temporal resolution, high noise, analyte breakthrough or low recovery (Barber et al. 2007, Jahnke et al. 2007d, Shoeib et al. 2008). The extraction of target compounds from these samplers was all solvent-based, which is also prone to significant limitations such as sample dilution (Diaby et al. 2009) and evaporative losses of analytes (Barber et al. 2007, Jahnke et al. 2007a).

In comparison with other existing methods involving large diameter samplers and solvent-based extraction, the thermal desorption (TD) method used in this study coupled standard stainless steel tubes (5 mm I.D.) for air sampling and solvent-free extraction (Bates et al. 2008). Appropriate selection of sorbents could ensure good retention of analytes of interest while keeping the size sampling tubes much smaller than those used in existing methods (Woolfenden 2010a, Woolfenden 2010b). The small size of the sorbent tube can facilitate the process of cleaning, sampling and transport. The following two-stage gas extraction process in TD method, which could lead to significant concentration enhancement with 100% transfer of desorbed analytes into the GC column if required, makes the request of sampling volume significantly lower than other existing methods (Ramírez et al. 2010). It also eliminates the multi-step sample pretreatment stage, reducing the risk of sample loss and contamination before quantitation. However, the application of TD to analysis of targeted PFASs (FTOHs, FOSAs, and FOSEs) in indoor air has not been reported so far.

Therefore, the main objective of this Chapter is to develop and demonstrate the efficiency, reliability, and detection limits of the TD method for the quantitation of volatile PFASs including FTOHs, FOSAs, and FOSEs in indoor air. Furthermore, the applicability of the method for routine analysis of FTOHs, FOSAs, and FOSEs in indoor air is presented.

4.2 Experimental section

4.2.1 Chemicals

The standards of FTOHs, 7:1 FA and 11:1 FA used in this chapter were the same with those in Chapter 3. N-methyl perfluorooctane sulfonamide (NMeFOSA; >98%), N-ethyl perfluorooctane sulfonamide (NEtFOSA; > 98%), N-methyl perfluorooctane sulfonamidoethanol (NMeFOSE; > 98%), and N-ethyl perfluorooctane sulfonamidoethanol (NEtFOSE; > 98%) were purchased from Wellington Laboratories, Canada. Isotopically-labeled compounds of > 98% purity used as surrogate standards for quality control purposes were obtained from Wellington Laboratories, Canada: d₄-4:2 FTOH, ¹³C₂, d₂-6:2 FTOH, ¹³C₂, d₂-8:2 FTOH, ¹³C₂, d₂-10:2 FTOH, d₃-NMeFOSA and d₇-NMeFOSE. All surrogate standards were spiked before sampling to monitor analyte losses during sampling and extraction. Internal standards (7:1 FA and 11:1 FA) were added to the sorbent tube before instrumental analysis to correct for signal suppression/enhancement during determination.

Optima grade methanol was purchased from Fisher Scientific, U.K. All standards and solvents were used as received. Nitrogen of > 99.999% purity was from Air Liquide, Singapore.

4.2.2 Sorbent tubes

89 mm standard stainless steel tube (6.4 mm O.D., Markes international, U.K.) were used for sample collection in this study. Two sorbent materials were tested in this study. Tenax TA is an inert macroporous polymer sorbent with reported specific surface area of 35 m²/g, while Carbograph 1TD is the fine-grained non-porous graphitized carbon black with specific surface area of 100 m²/g. Each tube was packed with 150 mg of Tenax TA (35/60 mesh, Markes international, U.K.) followed by 200 mg of Carbograph 1TD (40/60 mesh, Markes international, U.K.). Each tube was thoroughly conditioned at 335 °C and sealed tightly prior to usage.

4.2.3 Calibration

The calibration solution was introduced into the tubes through a calibration solution loading rig (CSLRTM, Markes international, U.K.). 1 to 5 μL of standard mixtures in methanol was spiked into the tube using a standard Agilent GC syringe. The liquid vaporized in the flow of carrier gas and reached the sorbent bed in vapor phase. 250 mL of high purity nitrogen set at 50 mL/min was allowed to pass the cartridge to purge the solvent out of the tube and ensure analytes were well-retained on the sorbents.

4.2.4 Instrumentation

The analytical system included a TD-100TM high capacity thermal desorber (Markes International, U.K.) interfaced by a heated and deactivated fused-silica transfer line to a GC-MS (Agilent 7890A-5975C, U.S.) working in positive chemical ionization (PCI) mode. The two-stage TD comprised an autosampler and a desorption oven connected to a sorbent-packed cold-trapping system. The sample tubes placed in the oven were firstly thermally desorbed in a flow of helium to extract target analytes from the sorbent (primary desorption). The desorbed analytes from the sample were re-focused on the electrically-cooled sorbent trap (cold trap) and released subsequently during a rapid heating cycle of the trap (secondary desorption). The plug of sample gas stream was then introduced to the GC-MS system through the transfer line.

Separation of analytes was performed on 60 m HP-INNOWAX column (0.25 mm I.D., 0.25 μm film thickness, J & W Scientific, U.S.) using helium as the carrier gas (1.6 mL/min). The oven temperature program was set at 50 °C for 2 min, 2 °C/min to 80 °C, hold for 0 min, then 10 °C/min until 230 °C followed by a 5 min hold. The mass spectrometer was operated in selective ion monitoring (SIM) mode, where methane was set at 0.8 mL/min. Quantitation was based on area integration of the target ion of each compound. One or two more ions were picked to assist qualification of each analyte based on the corresponding mass spectra with the

exception of NMeFOSA and NEtFOSA, where only one ion was present in each mass spectrum. Detailed GC–MS parameters could be found in appendix.

4.2.5 Breakthrough and recovery experiments

The retention of analytes in sampling was investigated in breakthrough experiment using the multibed sorbent cartridge Tenax/Carbograph 1TD. Overall performance of TD method in retention and extraction efficiency was studied in method recovery experiments. In the breakthrough experiments, two Tenax/Carbograph 1TD tubes were coupled in series by inert metal connectors. The front tubes were spiked with 500 pg of analyte mixture and 200 pg of isotopically labeled standards. Duplicate sets were collocated to conduct sampling simultaneously. Three different sampling periods (4, 8, and 16 h) were conducted at a fixed flow rate of 0.009 m³/h. Generally, breakthrough is confirmed if the loss of analyte is higher than 5% of the analyte entering the tube.

The method recovery experiments were performed in triplicate at two spiking levels, 60 and 500 pg, which correspond to the typical daytime and nighttime indoor concentrations in the office buildings in Singapore. Different volumes of air (0.036–0.144 m³) were drawn through the tubes at flow rate of 0.009 m³/h. The spiked tubes were subsequently treated like real samples. The quantitation of analytes was calculated internally using seven-point calibration curve (10 – 1000 pg).

4.2.6 Validation study and quality control

Blank experiments, including instrumental blank and sorbent tube blank, were carried out through analyzing stainless steel tube without and with adsorbents, respectively. Extraction and determination were done as real samples.

The limits of detection (LOD) and quantitation (LOQ) of targeted PFASs were determined based on the mass of analytes needed to generate a peak with signal to

noise ratios of 3 and 10 respectively, which were calculated through spiking standard solutions to blank sorbent tubes at very low amount (0.2 – 5 pg). The linearity of calibration curve was determined on seven points between 10 to 1000 pg by loading the tube with different amounts of targeted PFASs. Repeatability was expressed by the relative standard deviation (RSD%) at two levels (20 and 200 pg). Accuracy was evaluated by analyzing the results of repeatability experiment with a Student's *t*-test.

4.2.7 Indoor air sampling

Indoor air samples were collected at one laboratory and three offices including one 7-seat carpeted office and two 35-seat noncarpeted student offices during May–June 2011. All sampling locations were equipped with heating, ventilation and air conditioning (HVAC) system maintaining constant temperature (22 – 25 °C) and relative humidity (50 – 60%) during daytime. Each tube was first spiked with 2 µL standard solution of mass labeled standards containing d₄-4:2 FTOH, ¹³C₂, d₂-6:2 FTOH, ¹³C₂, d₂-8:2 FTOH, ¹³C₂, d₂-10:2 FTOH, d₃-NMeFOSA, and d₅-NEtFOSA (100 pg/µL) to monitor analyte losses during sample collection and extraction. The sorbent tube were then connected to calibrated portable pump (AirChek XR 5000, SKC, U.S. and Gilian Gilibrator-2 Air Flow Calibrator, SENSIDYNE, U.S.) with sampling end placed approximately one meter high above the ground. Sampling duration was 8 h at flow rate of 0.009 m³/h. A total of four sets of duplicate indoor samples were collected during daytime. Another three indoor air samples were collected at the same three offices during nighttime while central air-conditioner was shut off. Three field blanks were taken by placing an open sorbent tube at sampling sites during sampling in order to monitor possible background contamination. At the end of sampling period, the tube was disconnected, tightly sealed and stored in a metal container at 4 °C prior to analysis. All samples were analyzed within one week and internally quantified through the same calibration curve used in recovery experiments.

4.3 Results and discussion

4.3.1 Optimization of TD parameters

High extraction efficiency in primary and secondary desorption were among the key requirements for complete extraction of the analytes retained on sorbent tubes in the two-stage TD system. Primary desorption temperature was evaluated for Tenax/Carbograph 1TD tube. Figure 4-1 shows the dependence of analyte recovery on thermal desorption temperature from 220 to 330 °C. Results indicated lower desorption efficiency at 220 and 250 °C, but no significant difference above 280 °C. This is probably due to the incomplete desorption of the analytes from the adsorbent. Given the recommended desorption temperature range for Tenax (up to 325 °C), 320 °C was selected to as primary desorption temperature.

Figure 4-1. Dependence of analyte recovery (200 pg) on primary thermal desorption temperature for Tenax/Carbograph 1TD tube. The peak area was normalized to the maximum value of each compound. ●, 4:2 FTOH; ○, 6:2 FTOH; ▼, 8:2 FTOH; △, 10:2 FTOH; ■, NMeFOSA; □, NEtFOSA; ◆, NMeFOSE. Other TD parameters were set the same (Table 4-1).

Table 4-1. Optimized parameters of thermal desorption and GC–MS system for the analysis of Tenax/Carbograph 1TD sorbent tube.

Parameter	Value
<i>Primary desorption (sorbent tube)</i>	
Temperature	320 °C
Time	10 min
Gas flow	40 mL/min
Split	Off
<i>Secondary desorption (cold trap)^a</i>	
Packing	
Temperature	335 °C
Time	5 min
Split	5 mL/min
GC Column flow	1.6 mL/min
Transfer line	220 °C
<i>GC-MS instrument parameters</i>	
Auxiliary temperature	250 °C
Source temperature	300 °C
GC cycle time	32 min

^a One general purpose cold trap was used in this study (graphitized carbon, U-T11GPC-2S, Markes international, UK).

The secondary desorption temperature (cold trap system) were also optimized. Two temperatures at 335 and 350 °C were tested for different intervals (3 – 5 min). Results shows similar responses were obtained for the two temperatures from 3 min onwards. Optimized parameters of TD for targeted PFASs are listed in Table 4-1. In order to minimize the carry over, the flow path temperature was set at maximum value of 220 °C, and one empty tube was desorbed at 360 °C after each run of actual sample. Results indicated analytes were either undetectable or at very low residue levels (< 5%) in the second desorption cycle for the same tube, as illustrated in Figure 4-2.

Figure 4-2. Total ion chromatogram (TIC) of a cartridge spiked with 500 pg of targeted PFASs and 2000 pg of internal standards (IS) in the first and the second thermal desorption cycle.

4.3.2 Breakthrough experiment results

The results of breakthrough experiments indicated a good enrichment of analytes of interest on the dual-stage tube Tenax/Carbograph 1TD at flow rate of 0.009 m³/h for sampling duration between 4 and 16 h. The amount of most volatile 4:2 FTOH on the back-up tube was below detection limit. The losses of other FTOHs from the front tube were less than 4.7%, and no breakthrough was found for FOSAs and FOSEs at all air sample volumes (0.036 – 0.144 m³).

In comparison, the high-volume sampling with conventional PUF/XAD/PUF cartridge always exhibited breakthrough for the most volatile 4:2 FTOH (> 50%) and 6:2 FTOH (> 10%) (Barber et al. 2007, Jahnke et al. 2007a), while the low-volume sampling through SPE cartridge reported comparable retention efficiency with our study (Jahnke et al. 2007d). However, the proposed method exhibited better recovery than that of SPE cartridge. The major differences between these samplers are outlined in Table 4-2. Adsorption is a surface phenomenon and mainly dependent upon the surface area of sorbent as well as the strength of interaction between sorbent and analyte. The total surface area of XAD-2 resin in the

PUF/XAD/PUF cartridge (3000 – 7500 m²) was much higher than that of Tenax (5.2 m²) and Carbograph 1TD (20 m²) in this study. However, the reported breakthrough from the literature revealed that, despite the high surface area, the sorbent-sorbate affinity between targeted PFASs and PUF/XAD/PUF cartridge was not strong enough to retain the most volatile PFASs at high sample volumes (50 – 200 m³). The Tenax/Carbograph 1TD tube, on the other hand, proved to have sufficient sorptive capacity for targeted PFASs at significantly lower sample volumes (0.036 – 0.072 m³).

Table 4-2. Sampling parameters of different samplers for targeted PFASs in gaseous phase, including stainless steel tubes in this study and solid-phase extraction (SPE) cartridge for low-volume air sampling (LVS), as well as XAD-2 resin sandwiched between two polyurethane plug (PUF/XAD/PUF) for high-volume air sampling (HVS).

Sampling	Cartridge	Rate	Duration	Volume
LVS ^a	Stainless steel tube	0.009 m ³ /h	4–8 h	0.36–0.72 m ³
LVS ^b	SPE cartridge	1.1 m ³ /h	20–100 h	20–100 m ³
HVS ^c	PUF/XAD/PUF column	12–24 m ³ /h	3–6 h	50–200 m ³

^a this study. ^b (Jahnke et al. 2007d). ^c (Jahnke et al. 2007d) and (Barber et al. 2007)

4.3.3 Analytical performance of the method

4.3.3.1 Blank experiment

The chromatograms of instrumental blank and sorbent tube blank are shown in appendix. Only NMeFOSE was detected in instrumental blank, corresponding to absolute amounts of 1.9 – 6.8 pg. Similar results were observed in blank sorbent tubes, in which most of the targeted PFASs and IS were not detectable except NMeFOSE (1.9 – 7.4 pg). The residues were probably from the thermal desorption instrument as NMeFOSE were not detected in blank GC–MS analysis. Based on an average sample volume of 0.072 m³, the results imply a maximum background

contamination of 102 pg/m³ for NMeFOSE, which was below its detection limit (166 pg/m³). Given the low blank levels, no blank correction was made for real samples.

4.3.3.2 Method recovery experiment results

The method recoveries displayed the overall performance of proposed TD method, including retention capacity with extraction efficiency. Figure 4-3 exhibits the results of method recovery experiments at spiking level of 60 pg (a) and 500 pg (b) of analytes. For the FTOHs, the TD method demonstrated comparable recoveries at the two spiking levels, ranging from 88% (4:2 FTOH) to 119% (8:2 FTOH). Decreasing method recoveries with increasing volatility of the FTOHs, which widely presented in other existing methods (Table 4-3), was not observed in this study. Regarding FOSAs, the recoveries were within the acceptable range of 86 and 138%. The results demonstrated high efficiency in retention and extraction of TD method. In comparison, the conventional method using PUF/XAD/PUF sampler revealed very poor method recoveries for 4:2 and 6:2 FTOH (Table 4-3), which was attributed to the analyte breakthrough during sample collection and evaporative losses during solvent-based sample extraction (Barber et al. 2007). Even the latter factor itself could significantly compromise the method recoveries of SPE method (Table 4-3), which declared no breakthrough of analytes during sample collection step (Jahnke et al. 2007d). The good method recoveries of FTOHs and FOSAs in this study indicated the straightforward, leak-proof gas extraction process used in TD method could minimize the evaporative loss of analytes that usually occurs in conventional solvent extraction.

However, the recoveries of FOSEs (140 – 210%) were apparently higher than other analytes in this study (Figure 4-3). Similar signal enhancement of FOSEs was also reported by other researchers (Table 4-3) (Barber et al. 2007, Jahnke et al. 2007a, Jahnke et al. 2007d). This is probably attributed to the difference in adsorption–desorption behavior of FOSEs and IS, as IS (7:1 FA) are structurally more similar to FTOHs. It was expected to be remediated by the application of isotopically labeled standards as IS for each FOSE.

(a)

(b)

Figure 4-3. Average method recoveries ($n=3$) of analytes using Tenax/Carbograph 1TD tube at spiking level of 60 pg (a) and 500 pg (b), followed by sampling of 0.036, 0.072 and 0.144 m³ of air; Error bars are standard deviations.

Table 4-3. Method recovery (%) of thermal desorption (TD) method (60 pg spike, sampling volume: 0.072 m³), solid-phase extraction (SPE) method (200 ng spike, sampling volume: 50 m³), and high-volume (HV) method (5 µg spike, sampling volume: 1000 m³).

Compound	Method recoveries (%)		
	TD ^a	SPE ^b	HV ^c
4:2 FTOH	120 ± 20	33	6
6:2 FTOH	94 ± 12	46	37
8:2 FTOH	117 ± 13	69	80
10:2 FTOH	105 ± 6	168	73
NMeFOSA	95 ± 10	200	76
NEtFOSA	103 ± 15	217	79
NMeFOSE	183 ± 12	148	133
NEtFOSE	166 ± 9	183	143

^a this study. ^b from Jahnke, A. et al (Jahnke et al. 2007d). ^c from Barber, J. L. et al (Barber et al. 2007).

Additionally, increasing recoveries with increasing sample volume were observed for FOSAs and FOSEs at lower spiking level (Figure 4-3). This was probably due to the so-called matrix enhancement effects where the coextracted matrix constituents contained in real samples blocked the active sites within the TD–GC/MS system (Erney et al. 1993). The influence of the effect was probably limited and more pronounced at low spiking level, as such phenomenon was not observed at high spiking level (Figure 4-3). Referring to the recoveries of mass labeled standards, the values generally met the requirement of (80 – 120)% criteria, indicating high credibility of results.

Overall, the results of method recoveries for TD method indicated high efficiency in retention and extraction of PFASs of interest, and showed great improvement compared with the conventional method (Barber et al. 2007) or the SPE method (Jahnke et al. 2007d). High recoveries were also observed for FOSEs, which could probably result in the overestimation of these analytes in real samples of this study.

4.3.3.3 Limits of detection, limits of quantitation, method detection limit and linearity

Table 4-4 exhibits LOD and LOQ of targeted PFASs. The LOQ ranged from 1.4 pg (NEtFOSA) to 7.2 pg (4:2 FTOH), with the majority of PFASs below 3.5 pg. The low detection limit for short-chained FTOHs (4:2 and 6:2) was understandable since the baseline interference were always higher at low mass ions for GC–MS system. Comparable values were also reported in other studies (Dreyer and Ebinghaus 2009).

Determination of method detection limits (MDLs) was based upon the variability between eight replicates run at identical concentrations for FTOHs, FOSAs, and NEtFOSE, where blank contamination was not found (Ripp 1996). Briefly the eight replicates of sorbent cartridge were prepared and each cartridge was spiked with 20 pg of PFASs. The MDL was calculated as sample standard deviation times Student's *t*-value (Table 4-4). The MDL of NMeFOSE, on the other hand, was calculated as mean blank plus three times standard deviation as it was detected in blank. All calculated MDLs were converted to a concentration basis through dividing by a sampling volume of 0.072 m³, resulting in concentration in the range of 45 pg/m³ (NEtFOSA) to 166 pg/m³ (NMeFOSE).

Table 4-4. Limits of detection (LOD), limits of quantitation (LOQ), method detection limits (MDL), and correlation coefficient (r^2) of the calibration curve (10–1000 pg) for analytes of interest.

Compound	LOD (pg)	LOQ (pg)	MDL (pg/m ³)	r^2
4:2 FTOH	2.9	7.2	67	0.998
6:2 FTOH	1.9	5.3	56	0.997
8:2 FTOH	0.7	2.7	61	0.994
10:2 FTOH	0.7	2.6	56	0.999
NMeFOSA	0.4	1.6	51	0.997
NEtFOSA	0.4	1.4	45	0.999
NMeFOSE	0.8	3.5	166	0.998
NEtFOSE	0.8	3	65	0.999

The linearity was determined in the range of 10 to 1000 pg. As indicated in Table 4-4, the seven points calibration curve showed good linearity with correlation coefficients (r^2) higher than 0.990 for all analytes.

4.3.3.4 Repeatability and accuracy

Repeatability was evaluated at two levels (20 and 200 pg) with eight replicates at each level. Table 4-5 shows the results expressed in RSD%, which ranged from 3.7% (NMeFOSA) to 8.6% (NEtFOSE) at the level of 20 pg. Better results were obtained at 200 pg level in the range of 1.6% (6:2 FTOH) to 4.3% (NEtFOSE). Overall, the RSD% were less than 10% for all compounds, indicating good reliability of the method.

Table 4-5. Repeatability of the proposed method expressed in relative standard deviation (RSD%) and calculated t -statistic using Student's t -test ($n - 1 = 7$ degrees of freedom) at spiking levels of 20 and 200 pg.

	20 pg RSD%	t - statistic	200 pg RSD%	t - statistic
4:2 FTOH	7.5	-1.53	3.9	-1.33
6:2 FTOH	7.5	-2.06	1.6	-2.02
8:2 FTOH	7.7	-0.43	3.8	-1.07
10:2 FTOH	5.3	1.07	3.5	2.26
NMeFOSA	3.7	-1.65	3.2	-0.59
NEtFOSA	5.1	-1.83	4.3	0.07
NMeFOSE	8.1	2.53	3.8	0.51
NEtFOSE	8.6	0.72	3.9	0.31

Generally a method is considered accurate if the difference between the experimental results and the reference values is not statistically significant. Therefore, accuracy was evaluated at two levels (20 and 200 pg) by analyzing the results of repeatability experiment with a Student's t -test. For a 95% confidence interval with $(n - 1) = 7$ degrees of freedom, the t -critical value is 2.365 (two-

tailed). The calculated Student's *t*-statistic values for PFASs in this study are presented in Table 4-5, and they are all lower than the *t*-critical except NMeFOSE. The *t*-statistic of NMeFOSE (2.53) was slightly higher than the *t*-critical at the level of 20 pg, which might be mainly attributed to the influence of blank contamination at levels near to the quantitation limit of this compound. The bias became less significant with increasing spiking levels as an improved *t*-statistic was observed at 200 pg level for NMeFOSE.

4.3.4 Quantitation of PFASs in indoor air

One of the main advantages of this optimized method is the considerably shortened sampling time, which makes it possible to achieve high temporal resolution, as the passive sampling method can only represent the average concentration over a long period (e.g. 1 week or longer for passive samplers). The application of TD method for routine quantitation of volatile PFAS in indoor air was verified. A total of 8 daytime and 3 nighttime samples were collected from three offices and one laboratory on campus in Singapore. Figure 4-4 shows chromatogram of the environmental sample, in which all targeted PFASs were detected except 4:2 FTOH. The RSD% obtained from the parallel samples were in the range of 1.5 to 17% except NMeFOSE, which had higher variation between parallel samples (7.2 – 25.3%). This was probably due to the interference of background contamination of this compound, which had been discussed above. The recoveries of isotopically labeled compounds were in the range of 80.3 to 115.7%. Results of field blanks did not show any of target analytes above their respective MDLs. Few interference peaks were present in real sample analysis. The results indicated that this methodology was highly reliable when applied to real samples.

Figure 4-4. Total ion chromatogram (gray line) and extracted ion chromatogram (black line) of TD extracts of targeted PFASs in the real sample spiked with 200 pg of mass labeled standards and 2000 pg of internal standards.

All analytes were detected in indoor air except for 4:2 FTOH (Table 4-6). FTOHs, which are widely used in stain repellents on carpets, cleaning products, and adhesives, were the most abundant class of compounds. The group accounted for 72 to 89% of total targeted PFASs, followed by FOSEs (7 – 17%) and FOSAs (2 – 12%). For the composition of FTOHs, 8:2 FTOH generally exhibited highest indoor air concentration, followed by 10:2 FTOH and 6:2 FTOH (Table 4-6). The distribution was consistent with the observations reported by other researchers (Barber et al. 2007, Jahnke et al. 2007c, Jahnke et al. 2007d). Apparently higher concentrations of FTOHs were observed in carpeted offices, indicating the carpet might be sources of targeted PFASs in indoor air.

Unlike FTOHs, the concentrations of FOSAs and FOSEs were observed at comparable levels in different locations, indicating that they may arise from different sources (Table 4-6). Furthermore, it could be seen that the indoor air concentrations of PFASs collected at night (ventilation system off) were significantly higher than that collected during daytime (ventilation system on), clearly indicating existence of indoor sources of targeted PFASs.

Table 4-6. Indoor air concentrations of volatile PFASs on campus in Singapore (pg/m³). Each data indicates four sets of parallel samples during the daytime (average $\pm$ SD, $n = 2$), and three during nighttime.^a

Compound	Laboratory	Carpeted Office		Student Office 1		Student Office 2	
	Day	Day	Night	Day	Night	Day	Night
4:2 FTOH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2 FTOH	420 $\pm$ 30	310 $\pm$ 40	840	160 $\pm$ 20	600	200 $\pm$ 10	290
8:2 FTOH	2590 $\pm$ 40	4130 $\pm$ 130	10460	1130 $\pm$ 20	5110	1490 $\pm$ 90	2320
10:2 FTOH	610 $\pm$ 60	1260 $\pm$ 30	3310	460 $\pm$ 40	2190	650 $\pm$ 50	910
NMeFOSA	80 $\pm$ 13	120 $\pm$ 10	210	140 $\pm$ 7	230	140 $\pm$ 20	140
NEtFOSA	140 $\pm$ 6	140 $\pm$ 6	180	150 $\pm$ 20	240	160 $\pm$ 10	170
NMeFOSE	370 $\pm$ 60	240 $\pm$ 60	850	210 $\pm$ 30	800	230 $\pm$ 20	260
NEtFOSE	200 $\pm$ 20	220 $\pm$ 10	990	170 $\pm$ 30	930	220 $\pm$ 10	220
Σ FTOHs	3620	5700	14610	1750	7900	2340	3520
Σ FOSAs	220	260	390	290	470	300	310
Σ FOSEs	570	460	1840	380	1730	450	480
Σ PFASs	4410	6420	16840	2420	10100	3090	4310

^a n.d.: not detected

To sum up, the indoor concentrations of PFASs were in the range of 2420 to 16840 pg/m³, with FTOHs the dominant compounds. More importantly, the significantly shortened sampling time required in TD method allowed the variations of concentrations of PFASs within different periods of a day to be reported in this study for rooms of various sizes, which was limited in other existing methods due to extended sampling duration or large sample volume requirement. The concentration tendency data could be essential in optimizing energy use in building design.

4.4. Conclusion

The TD method has been developed and successfully applied to the determination of indoor airborne volatile PFASs in this Chapter. The Tenax/Carbograph 1TD

sampling tube exhibited significantly improved retention of analytes over the conventional PUF/XAD/PUF sampler with minimal breakthrough in sampling period. The two-stage gas extraction in TD method proved to prevent the evaporative loss of analytes occurring in conventional solvent-based extraction. The high efficiency of TD method in sample collection and extraction guaranteed good method recoveries for FTOHs and FOSAs. For the first time, the long-term problem of low method recoveries of 4:2 and 6:2 FTOH was solved in analysis of airborne PFASs. The TD method also demonstrated high accuracy and reproducibility. The detection limit of the method is low enough for routine quantitation of volatile PFASs in indoor air. The significantly shortened sampling time of TD method help to achieve satisfactory time resolution for indoor air concentrations of targeted PFASs compared to other existing methods.

Chapter 5

Airborne polyfluorinated alkyl substances in indoor office environment of Singapore

5.1 Introduction

FTOHs and FOSAs/FOSEs are among the most commonly reported volatile PFASs in indoor air, which was probably due to their extensive application in commercial products (Prevedouros et al. 2006, Jahnke et al. 2007b, Dreyer and Ebinghaus 2009, Langer et al. 2010). Recently PFCAs in the serum were found significantly correlated with the indoor air levels of FTOHs (Fraser et al. 2012).

FTOHs have been manufactured through telomerisation since 1970s by telomer makers such as DuPont (Prevedouros et al. 2006) and continue to be produced in increasing amounts in recent years (Harrad 2010). FOSAs and FOSEs have been produced through electrochemical fluorination since 1950s by 3M (3M 1999), which has phased out the production of sulfonyl-based C₈ fluorinated compounds by 2000.

Quantitation of volatile PFASs in indoor environment is challenging due to the complexity and heterogeneity of air matrix, as well as their low concentration levels (typically in pg/m³). Air sampling using solid sorbents followed by thermal desorption and chromatographic analysis offers a number of advantages in comparison with the conventional analytical methods, which has been described in Chapter 4. The thermal desorption method has many air monitoring applications, and a wide variety of commercial sorbents to select (Woolfenden 2010a, Woolfenden 2010b).

In the process of sampling and analysis of a diversity of compounds using thermal desorption technique, it is necessary to make a characterization of the potency of the

individual sorbents in the trapping and releasing of target analytes. This is important for a better sorbent selection and a more accurate quantitative determination. Referring to the determination of airborne FTOHs and FOSAs/FOSEs in indoor environment, a thermal desorption method using a commercial multi-sorbent tube has been developed in Chapter 4. However, the contribution of each type of sorbent to the trapping and desorption of targeted PFASs from air remains unknown.

The aim of Chapter 5 was to optimise and validate a highly accurate and sensitive analytical method for the determination of indoor airborne PFASs including FTOHs, FOSAs and FOSEs. The analytical protocol developed in Chapter 4 was adapted and further optimised. The adsorptive enrichment and thermal desorption performance of different adsorbents and their combinations were investigated for targeted PFASs. The optimum sorbent tube was proposed. Finally, the applicability of customized tubes was shown in indoor air samples collected at a local office building by means of an innovative air sampling strategy. The source strength of PFASs and performance of building air handling units were evaluated based on the data obtained through a well-mixed indoor air box model.

5.2 Experimental Section

5.2.1 Chemicals

All standards and solvents used were the same with those employed in Chapter 4.

5.2.2 Sampling media

Selection of appropriate sorbents is critical in thermal desorption method since analytical detection limit and precision are largely determined by sampling efficiency, desorption efficiency and interference levels of sorbents (Dettmer and Engewald 2002, Woolfenden 2010b). Commercially available sorbents for thermal desorption application can be divided into four categories: porous organic polymers,

graphitized carbon blacks, molecular sieves and other non-carbon sorbents. However, the sorbent strength of molecular sieves is apparently too strong for targeted PFASs, whose molecular weight ranged from 264 to 571. The non-carbon sorbents such as silica gel, quartz beads and glass wool are also not suitable for PFAS enrichment during sampling. Therefore, these two categories of sorbents were excluded in the preparation of sampling media. Regarding the porous polymers, one weak strength sorbent, named Tenax TA (35/60 mesh, Markes international, U.K.), was selected as it was a general purpose sorbent most widely used in air monitoring among porous polymers (Clément et al. 2000, Dettmer and Engewald 2002). The stronger porous polymers such as Chromosorb and PoraPak series, were not selected due to their low temperature limit ($< 250^{\circ}\text{C}$) and high inherent artifact levels. Referring to the graphitized carbon blacks, one very weak strength sorbent (Carbograph 2TD, 40/60 mesh, Markes international, U.K.) and one weak/medium strength sorbent (Carbograph 1TD, 40/60 mesh, Markes international, U.K.) were selected, both of which were widely applied for trace-level air analysis (Wu et al. 2003, Woolfenden 2010b). Information of the selected three sorbents was presented in Table 5-1.

Table 5-1. Specific surface area and structure of selected adsorbent.

Type of adsorbent	Name	Specific surface area (m^2/g)	Surface model
Macroporous polymer of 2,6-diphenylphenylene- oxide	Tenax TA	35
Nonporous graphitized carbon blacks	Carbograph 2TD	10
Nonporous graphitized carbon blacks	Carbograph 1TD	100	

The sorbents were packed into the 89 mm standard stainless steel sorbent tubes (Markes international, U.K.). A total of five kinds of sorbent tubes, including three single-sorbent and two multi-sorbent tubes, were prepared in this Chapter. The single-sorbent tubes were packed with 150 mg of Tenax, Carbograph 2TD, and Carbograph 1TD, respectively. The multi-sorbent tubes were packed with 150 mg of Tenax followed by 200 mg of Carbograph 1TD or Carbograph 2TD to examine the combination effects. Each tube was thoroughly conditioned and sealed tightly prior to usage.

5.2.3 Instrumentation

The analytical system included a TD-100TM high capacity thermal desorber (Markes International, U.K.) interfaced by a heated and deactivated fused-silica transfer line to a GC-MS (Agilent 7890A-5975C) working in PCI mode. 7:1 FA served as IS for all analyses except 10:2 FTOH, which used 11:1 FA instead. Detailed information regarding instrumentation could be found in chapter 4 and appendix.

5.2.4 Investigation of different adsorbent materials

5.2.4.1 Breakthrough experiments

The performances of different sorbents on the adsorptive enrichment of analytes in air sampling was investigated in the breakthrough experiment. Two adsorbent tubes were coupled in series by inert metal connectors (Markes International, U.K.). The front tube was the single-sorbent tube packed with the sorbent that would be investigated, while the back was the Tenax/Carbograph 1TD tube to capture the breakthrough analyte. All front tubes were spiked with 500 pg of analyte mixture and 200 pg of isotopically labeled standards. Two duplicate sets were collocated to conduct the breakthrough experiment concurrently in a relatively clean indoor environment (temperature: 24 – 25 °C; relative humidity: 50 – 53 %), where the

preliminary sampling results indicated the background levels of targeted PFASs was low ($< 200 \text{ pg/m}^3$). Three different sampling periods (4, 8 and 16h) were conducted at a fixed flow rate of $0.009 \text{ m}^3/\text{h}$.

5.2.4.2 Recovery experiments

The ability of sorbent tubes in trapping and analysis of targeted PFASs was studied in method recovery experiment. It was conducted in triplicate at two spiking levels (60 and 500 pg), which correspond to the typical daytime and nighttime indoor concentrations in the local office buildings. Two different volumes of air ($0.036 - 0.072 \text{ m}^3$) were drawn through the sorbent tubes at flow rate of $0.009 \text{ m}^3/\text{h}$ at the same indoor environment with breakthrough experiments. The spiked tubes were subsequently treated as real samples. The quantitation of analytes was calculated internally using seven-point calibration curve ($10 - 1000 \text{ pg}$).

5.2.5 Indoor air sampling

In order to investigate the indoor source strength of targeted PFASs, a highly original air sampling was conducted in a 6-day period (28, March to 2, April 2012) at a 300 m^3 public lobby of a seven-story office building equipped with heating, ventilation and air conditioning (HVAC) system. The HVAC system was shut off from 7pm to 6am of the next day during the weekdays, and kept off over weekend from Friday 7pm to 6am of the following Monday. The temperature and relative humidity in the building were $22 - 25 \text{ }^\circ\text{C}$ and $50 - 60\%$ with HVAC system on, which increased to $30 \text{ }^\circ\text{C}$ and $70 - 80\%$ when HVAC system remained off. Sampling time was set at 4 h at flow rate of $0.009 \text{ m}^3/\text{h}$ by the calibrated portable pump (AirChek XR 5000, SKC, U.S.). The indoor air was sampled in three cycles: (1) during HVAC system operation, (2) during short-term shut down of HVAC system ($< 12 \text{ h}$), (3) when the HVAC system remained off for a longer term ($> 48 \text{ h}$). Samplings under cycle (1) were conducted on normal working days in the morning

(8am – 12 noon) and afternoon section (2pm – 6pm). Under cycle (2), the samplings were conducted in the nighttime (8pm – 12 midnight) and early morning (2am – 6am) of working days. Samplings under cycle (3) were conducted on weekend at all time sessions in cycle (1) and (2). In addition to the indoor air sampling, three outdoor air samples were collected on campus with sampling duration set at 12h and flow rate at 0.009 m³/h.

Each tube was firstly spiked with 100 pg of standard solution of mass labeled standards containing d₄-4:2 FTOH, ¹³C₂, d₂-6:2 FTOH, ¹³C₂, d₂-8:2 FTOH, ¹³C₂, d₂-10:2 FTOH, d₃-NMeFOSA, and d₅-NEtFOSA to monitor analyte losses during sampling and extraction. The sampling inlet was placed approximately one meter high above the ground. Three field blanks were also taken by placing open adsorbent tubes at sampling sites during sampling in order to monitor possible diffusive background contamination. At the end of the sampling period, the tube was tightly sealed and stored in a metal container. A total of 14 sets of duplicate indoor air samples and three outdoor air samples were collected. All samples were stored at 4 °C and analyzed within three days.

5.3 Results and discussion

5.3.1 Breakthrough analysis

One of the most important aspects in selecting the proper sorbent is to choose the one that can retain the specific group of analytes at designed sample volume, which was tested in breakthrough experiment. Figure 5-1a shows the results of breakthrough experiments conducted on sampling tubes packed with Tenax. Breakthrough occurred for the more volatile PFASs. 4:2 FTOH, which has the lowest molecular weight, exhibited the highest breakthrough. The breakthrough percentages tended to decrease with increasing molecular weight (6:2 and 8:2 FTOH). Internal standard 7:1 FA also exhibited high breakthrough due to its low molecular weight. Increasing breakthrough ratios with increasing sample volume

was also observed. PFASs with high molecular weights (10:2 FTOH, FOSAs and FOSEs) were well-retained by Tenax.

Figure 5-1. Proportions (%) of PFASs measured from the front Tenax cartridge spiked with 500 pg of standard mixture and 200 pg of internal standards in breakthrough experiments ($n = 2$). Relative recoveries based on “front cartridge” + “back cartridge” = 100%. All cartridges were quantified externally; (a) Tenax TA; (b) Carbograph 2TD.

The adsorption of PFASs on sorbent surface was predominated by physical adsorption, where the attractive forces (Van der Waals forces) consist of London dispersion forces, dipole–dipole interactions as well as hydrogen bonding forces. Tenax is a macroporous polymer of 2,6-diphenylphenylene-oxide with polar bonds and nonuniform charge distribution, where the charge is essentially localized on the oxygen atoms (Table 5-1). Given the presence of high moisture in surrounding air (50 – 53% humidity), the capacity of hydrogen bonding between the hydroxyl hydrogen atom of FTOHs (–OH) and oxygen atom of Tenax was expected to be minimized. The dominance of dispersion interactions and dipole–dipole interactions were anticipated. Dispersion force, resulting from temporary dipole-induced dipole interactions, is present between all molecules and usually makes the biggest contribution to Van der Waals bonding. The strength normally increases in order of increasing sizes of molecules, which is consistent with the our findings (Figure 1a).

Results of breakthrough experiments conducted on Carbograph 2TD tubes are shown in Figure 5-1b, which only moderate breakthrough (15%) for 4:2 FTOH was observed at sample volume of 0.144 m³. For the stronger Carbograph 1TD, no breakthrough of target analytes was observed. In comparison with Tenax, graphitized carbon blacks are nonporous aggregates of small polyhedral particles, where carbon atoms are organized in planes of symmetrical hexagons (Table 5-1). The higher the degree of graphitization, the lower the specific surface area of the material is (Dettmer and Engewald 2002). Carbograph 2TD was normally considered as a weaker adsorbent than Tenax due to its lower specific surface area (Table 5-1). However, the results suggested Carbograph 2TD was actually more retentive than Tenax for targeted PFASs. This observation clearly indicated that, although the specific surface area was usually considered as the most influential factor in the adsorption process, the surface characteristics of sorbent were critical in this case. The surface of graphitized carbon black consists of graphite crystals with uniform charge distribution over all carbon atom centers, which has little polarity compared with Tenax (Table 5-1). Consequently, the surface interactions on graphitized carbon black depend mainly on dispersion forces. Due to the high concentration of carbon atoms on the basal face of graphite, the energy of

nonspecific interactions with graphitized carbon blacks are reported to be relatively higher than the non-specific adsorption on other adsorbents (Engewald and Pörschmann 1991). This probably resulted in the observed higher trapping efficiency of graphitized carbon blacks on PFASs. Moreover, the breakthrough of isotopically-labeled standards was generally in accordance with the trend of native analytes.

To sum up, the graphitized carbon blacks showed higher trapping efficiency of targeted PFASs compared with the porous polymer Tenax in air sampling. In contrast, the traditional high-volume sampling cartridges containing XAD resin and polyurethane foam (PUF) plugs (PUF/XAD/PUF) always exhibited breakthrough for the most volatile 4:2 FTOH (> 50%) and 6:2 FTOH (> 10%) (Barber et al. 2007, Jahnke et al. 2007a).

5.3.2 Recovery analysis

The appropriate sorbent must be sufficiently strong to efficiently trap the analytes of interest from the air sampled and then weak enough to release them as efficiently as possible in thermal extraction (Dettmer and Engewald 2002). These capacities were demonstrated in the recovery experiment, which exhibited the overall performance of the sorbent in trapping and desorption of analytes, and the chromatographic analysis. The analytes was quantified internally through the individual calibration curve (10 – 1000 pg) created for the each kind of sorbent tubes tested. However, difficulty was encountered in the preparation of calibration curve for FOSEs using Carbograph 1TD and Carbograph 2TD tube. No explanation has been found for this phenomenon yet. Instead, the calibration curve obtained from Tenax/Carbograph 1TD tube was employed to quantify FOSEs for these two tubes.

Figure 5-2 indicates the results of recovery experiments using graphitized carbon black tubes at sample volume of 0.036 m³. Carbograph 1TD revealed poor and unsteady recoveries for FOSAs and FOSEs, while Carbograph 2TD exhibited a

better, but not satisfactory performance. Temperature-caused incomplete desorption was unlikely as the analytes exhibited very low residue levels ($< 3\%$) when the sample tubes were analyzed in the second adsorption cycle at a higher temperature ($380\text{ }^{\circ}\text{C}$). Therefore, it was likely attributed to the irreversible adsorption of FOSAs and FOSEs on graphitized carbon blacks, as high energy of nonspecific interactions were expected due to their high molecular masses. The observation indicated that although graphitized carbon blacks could retain the targeted PFASs for the specified sample volume, they could not be able to release all of them efficiently during the desorption process. This might affect the long-term repeatability and result in carry over.

Figure 5-2. Average analyte recoveries ($n = 3$) of single-stage Carbograph 2TD and Carbograph 1TD tube at spiking level of 60 and 500 pg, followed by sampling 0.036 m^3 of air; Error bars are standard deviations.

Since none of the single-sorbent tubes could demonstrate a satisfactory recovery performance, the multi-sorbent tubes with the weaker Tenax bed placed in front of the graphitized carbon black were prepared in the hope of remediating the analyte

breakthrough and incomplete desorption observed on individual sorbents. In comparison with the single-sorbent tubes, the multi-sorbent tubes have higher sampling resistance and shorter sample storage times. The operation temperature should not exceed the temperature limit of any other sorbent in the tube (Woolfenden 2010a, Woolfenden 2010b). As discussed in the breakthrough experiment, Tenax had difficulty in retaining those volatile analytes (4:2 FTOH, 6:2 FTOH, 8:2 FTOH and 7:1 FA), but demonstrated good capability in PFASs with larger molecule sizes. When it was combined with Carbograph in the multi-sorbent tubes, some of the volatile PFASs that broke through the weaker front sorbent Tenax could be captured by the stronger sorbent Carbograph behind, and the higher boiling FOSAs/FOSEs would be retained and desorbed from the Tenax without coming into contact with the Carbograph. Figure 5-3 shows the results of recovery experiments of multi-sorbent tubes Tenax/Carbograph 2TD and Tenax/Carbograph 1TD at sample volume 0.036 m³. Both of them demonstrated significantly improved recoveries of FTOHs in comparison with the single-sorbent Carbograph tube. The poor recovery of FOSAs and FOSEs were not observed as well; even they were desorbed at a lower temperature (320 °C). This is likely due to the lower adsorption energy on Tenax surface compared with graphitized carbon blacks as discussed above.

In general, the customized Tenax/Carbograph 2TD tube exhibited a better and satisfactory recovery performance at designed sample volume in comparison with the commercially available Tenax/Carbograph 1TD, especially for FOSAs and FOSEs (76 – 127% vs. 86 – 163%). The tube also showed less variation of recovery at different spiking levels. The result was within our expectation as the single-sorbent Carbograph 2TD tube showed better recovery performances than Carbograph 1TD (Figure 5-2). Therefore, the Tenax/Carbograph 2TD was proposed as the optimum sorbent combination in the sampling and analysis of indoor airborne volatile OFASs in this Chapter.

In sum, the specially customized multi-sorbent Tenax/Carbograph 2TD tube exhibited the best recovery of analytes among all the tubes prepared. This optimised

method also showed advantages over other existing methods (Barber et al. 2007, Jahnke et al. 2007d).

Figure 5-3. Average analyte recoveries ($n = 3$) of Tenax/Carbograph 2TD and Tenax/Carbograph 1TD tube at spiking level of 60 and 500 pg, followed by sampling of 0.036 m^3 of air; Error bars are standard deviations.

5.3.3 Analysis of PFASs in indoor environment

One of the main advantages of this optimized method is the considerably shortened sampling time (4 h), which makes it possible to achieve high temporal resolution, as the typical methods can only represent the average concentration over a long period (e.g. 1 week or longer for passive samplers). The applicability of the optimised analytical method was tested in indoor air sampling at a local office building using an original sampling strategy. The indoor air concentrations of the targeted PFASs are also listed in Table 5-2. The recoveries of isotopically labeled compounds were in the range of 77.5 – 131.2%. Results of the field blanks did not show any of target analytes exceeding their respective method detection limits. Few interference peaks were present in the real sample analysis. Most analytes were

detected in this indoor environment except 4:2 FTOH and NEtFOSE. FTOHs, which are widely used in stain repellents and adhesives, appeared to be the most abundant class of compounds.

Figure 5-4 exhibits the concentrations of selected targeted PFASs against time during the 6-day period. It could be seen clearly the indoor FTOH concentrations were closely correlated, implying the possible common origin of these three analytes and similar behaviors in indoor environment. Furthermore, the concentration variation of PFASs appeared to be directly affected by the operation of HVAC system. The lowest concentrations during the weekdays happened in the afternoon (2 pm - 6 pm section), while the highest concentrations appeared in the early morning (2 am - 6 am section) due to the night time accumulation effect when the HVAC system were off. The morning concentrations (8 am - 12 noon section) dropped down significantly when the HVAC system turned on at 6 am in the morning. When the HVAC system was kept off during the weekend, the accumulation of analytes in indoor environment was very significant.

As the proposed method can provide high temporal resolution that cannot be achieved before, one can derive a rough estimation on the indoor source strength using a simplified well-mixed box model as shown in eq 5.1. We assumed that the mass generation rate from a specific area was a constant with time, and the concentration of PFASs in the incoming air (outdoor) was constant. The model is described mathematically as:

$$C_t = \frac{G + (I + k)VC_{Ain}}{(I + k)V} (1 - e^{-(I+k)t}) + C_0 (e^{-(I+k)t}) \quad 5.1$$

where C_t = indoor concentration of targeted PFASs at time t (pg m⁻³); G = emission rate (pg h⁻¹); I = air exchange rate (h⁻¹); k = first order loss rate constant through other mechanisms (h⁻¹); V = volume of air in the lobby (m³); C_{Ain} = concentration of targeted PFASs in the incoming air (outdoor) (pg m⁻³); C_0 = indoor concentration of targeted PFASs from preceding time (pg m⁻³).

Table 5-2. Indoor air concentrations of volatile PFASs in Singapore (pg/m³) at different periods of time from 28, March (Wed) to 2, April (Monday) 2012 (average $\pm$ range, $n=2$).^a

Time		4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	NMeFOSA	NEtFOSA	NMeFOSE	NEtFOSE
Wed	20:00-24:00	n.d.	4210 $\pm$ 160	6990 $\pm$ 420	2220 $\pm$ 150	348 $\pm$ 7	192 $\pm$ 7	1980 $\pm$ 50	n.d.
Thurs	02:00-06:00	n.d.	5680 $\pm$ 140	9520 $\pm$ 90	2760 $\pm$ 40	412 $\pm$ 4	200 $\pm$ 8	3380 $\pm$ 80	n.d.
	08:00-12:00	n.d.	3570 $\pm$ 30	6250 $\pm$ 30	1730 $\pm$ 30	343 $\pm$ 21	194 $\pm$ 4	1810 $\pm$ 80	n.d.
	14:00-18:00	n.d.	3210 $\pm$ 280	5520 $\pm$ 110	1560 $\pm$ 80	327 $\pm$ 14	190 $\pm$ 3	1660 $\pm$ 10	n.d.
	20:00-24:00	n.d.	4090 $\pm$ 210	6630 $\pm$ 250	2250 $\pm$ 90	383 $\pm$ 25	196 $\pm$ 3	2540 $\pm$ 10	n.d.
Fri	02:00-06:00	n.d.	5620 $\pm$ 150	9120 $\pm$ 290	2660 $\pm$ 200	445 $\pm$ 23	206 $\pm$ 1	3350 $\pm$ 100	n.d.
	08:00-12:00	n.d.	3800 $\pm$ 290	6190 $\pm$ 20	1840 $\pm$ 120	344 $\pm$ 4	193 $\pm$ 1	1860 $\pm$ 70	n.d.
	14:00-18:00	n.d.	3560 $\pm$ 110	5410 $\pm$ 510	1650 $\pm$ 230	332 $\pm$ 13	192 $\pm$ 8	1460 $\pm$ 50	n.d.
	20:00-24:00	n.d.	4280 $\pm$ 40	7580 $\pm$ 70	2290 $\pm$ 80	393 $\pm$ 25	199 $\pm$ 5	2500 $\pm$ 140	n.d.
Sat	14:00-18:00	n.d.	4390 $\pm$ 120	8820 $\pm$ 130	2530 $\pm$ 20	389 $\pm$ 36	194 $\pm$ 5	2850 $\pm$ 180	n.d.
Sun	08:00-12:00	n.d.	6470 $\pm$ 70	12060 $\pm$ 110	3420 $\pm$ 400	444 $\pm$ 37	202 $\pm$ 2	3290 $\pm$ 240	150 $\pm$ 10
Mon	02:00-06:00	n.d.	8030 $\pm$ 210	13640 $\pm$ 260	4260 $\pm$ 160	539 $\pm$ 49	216 $\pm$ 2	4150 $\pm$ 200	170 $\pm$ 20
	08:00-12:00	n.d.	4390 $\pm$ 180	7060 $\pm$ 300	2130 $\pm$ 100	334 $\pm$ 2	194 $\pm$ 3	1610 $\pm$ 2	n.d.
	14:00-18:00	n.d.	3640 $\pm$ 20	5420 $\pm$ 260	1640 $\pm$ 170	321 $\pm$ 24	190 $\pm$ 11	1370 $\pm$ 140	n.d.

^a n.d.- not detected.

Figure 5-4. Indoor air concentrations of selected targeted PFASs collected at different periods of time from 28, March (Wednesday) to 2, April (Monday), 2012. ●, 6:2 FTOH; ○, 8:2 FTOH; ▼, 10:2 FTOH.

The concentration data obtained at the nighttime periods during the weekdays can provide a good estimation on the emission source strength because the I and k terms are relatively small or stable. The HVAC system was off and the infiltration/loss due to the human activities, e.g. door openings, were minimal. The major removal mechanism during the nighttime is the loss through the building leakage, which is equivalent to I at $0.05 \text{ (h}^{-1}\text{)}$ based on previous experiences (Laussmann and Helm 2011). The loss through other mechanisms was considered negligible ($k = 0$). By using the C_{Ain} obtained from the outdoor air samples (Table 5-3), the emission rate G can be calculated. To obtain a generic idea on the source strength from the surface (mass emitted per surface area per time), the emission rate was then normalized by the effective surface area of the lobby (235 m^2). The values of the four most abundant analytes (6:2 FTOH, 8:2 FTOH, 10:2 FTOH and NMeFOSE) are presented in Table 5-3. The rest were not included since they were either not

detected or presented at low concentrations in indoor environment. Detailed data fitting process can be found in appendix.

Table 5-3. Calculated emission rate per effective surface area (average $\pm$ range, $n = 2$) and outdoor air supply (average $\pm$ SD, $n = 3$) of the public lobby (Volume: 300 m³; Surface area: 235 m²; Floor area: 68 m²), as well as measured concentration of targeted PFASs in the incoming air (C_{Ain}).

Compound	Emission rate per m ² effective surface area (pg m ⁻² h ⁻¹)	Outdoor air supply m ³ /h per m ² floor area	C_{Ain} (pg/m ³)
6:2 FTOH	623 $\pm$ 5	0.71 $\pm$ 0.04	150
8:2 FTOH	1038 $\pm$ 23	0.75 $\pm$ 0.04	200
10:2 FTOH	253 $\pm$ 20	0.71 $\pm$ 0.05	90
NMeFOSE	415 $\pm$ 76	1.04 $\pm$ 0.08	0

It could be seen from Table 5-3 that the calculated area-specific emission rate showed little variation for each compound, indicating the steady release of targeted PFASs from the indoor environment. The calculated emission rate was further employed to predict the concentration accumulation during weekend based on eq 5.1 using the same value of I and k . It turned out the modeling results were more than 10% higher than the on-site sampling data. The discrepancies were probably due to the underestimated I and k terms for the weekend. For example, sunlight-induced degradation was expected to happen during the daytime in the weekend, and further promoting the decay mechanism (Ellis et al. 2003). In addition, higher air exchange rate I was also expected during the daytime in the weekend due to the possible human activities in comparison with nighttime in weekday.

The estimated emission rate was also employed to calculate air exchange rate I maintained by HAVC system during daytime in the weekday. The results are converted to outdoor air supply rate and presented in Table 5-3. The exchange rates calculated based on the data of FTOHs display a good consistency, while the value derived from concentrations of NMeFOSE appears to be higher. This discrepancy might be resulted from the different environmental behavior of the semi-volatile NMeFOSE. It can sorb onto the indoor surfaces or dust, and may thus result in

further decrease in gas-phase concentration and overestimation of air exchange rate (Shoeib et al. 2004). Furthermore, the average of calculated outdoor air supply ($0.81 \text{ m}^3/\text{h}$ per m^2 floor area) provided by the HVAC system in this study is slightly lower than the minimum outdoor air supply requirement in Singapore standard SS 553 for lobbies ($1.1 \text{ m}^3/\text{h}$ per m^2 floor area). This highlights an important concern in the industry practice. Since it is often difficult to monitor the fresh air intake using automatic sensors, most of local HVAC management systems currently rely on the CO_2 , relative humidity, and temperature sensors to control the damper opening, which indirectly represents the fresh air intake. It is very common to see such discrepancies when the management system tries to achieve a satisfactory operation based on the indirect management approach, but lead to an unsatisfactory result in the end.

To sum up, the application of the optimised analytical method proved to be highly sensitive and accurate in the determination of volatile PFASs in the indoor environment. The concentrations of indoor airborne PFASs with high temporal resolution were measured, enabling the quantitation of indoor source strength of target analytes, as well as the estimation of interactions between the airborne PFASs and building HVAC operation. This could help to overcome the major hindrance to implement more effective source control measures and thus prevent “sick building syndrome”. Furthermore, the measurement would be very useful in a lot of other research, such as the determination of sources and transport mechanisms, health effects studies and setting of regulatory limits.

5.4 Conclusion

The analytical method developed in Chapter 4 for the determination of volatile PFASs through low-volume air sampling was further optimised in this Chapter. Adsorptive enrichment and thermal desorption of airborne PFASs on several commercial available sorbents have been investigated by means of breakthrough and recovery experiments. The graphitized carbon blacks demonstrated a higher trapping property in air sampling even with a low specific surface area in

comparison with the porous polymer Tenax, indicating the importance of the surface characteristics of sorbents. However, incomplete desorption of FOSAs/FOSEs on graphitized carbon blacks was observed. As none of single sorbent tubes were found highly efficient in both trapping and releasing of targeted PFASs, the eventual need for a combination of sorbents in a single tube was determined. The sorbent combination was further optimised to achieve a satisfactory method recovery. Finally the proposed sorbent tube Tenax/Carbograph 2TD was applied in the high-resolution temporal analysis of indoor air samples using an innovative sampling strategy. The source strength of PFASs in indoor environment was estimated, and the performance of building air handlings was evaluated, which could help building operation engineers and human exposure scientists to implement more effective and energy-efficient source control measures. The further application of the optimised method to other research areas included the determination of sources and transport mechanisms, health effects studies, regulatory limits setting, etc.

Chapter 6

Comparative study of solvent extraction and thermal desorption methods for analysis of volatile polyfluorinated alkyl substances in the atmosphere of Singapore

6.1 Introduction

Neutral, volatile PFASs including FTOHs and FOSAs/FOSEs are widespread atmospheric pollutants (Jahnke et al. 2007b, Dreyer and Ebinghaus 2009, Kannan 2011). Due to the complexity of environmental air matrix and low concentration levels of volatile PFASs in ambient air (typically in pg/m^3), the determination of volatile PFASs requires highly sensitive and efficient sample collection, extraction and analysis techniques. The choice of air sampling technique and type of sorbent is directly affected by the extraction technique applied.

Solvent extraction is the oldest and the most commonly used method of desorption, and most often XAD resin and polyurethane foam (PUF) are used as sorbent (Shoeib et al. 2006, Barber et al. 2007). However, this technique has significant limitations, which have been described in Chapter 3. Thermal desorption (TD) is a highly sensitive alternative to conventional solvent extraction (Woolfenden 2010a, Woolfenden 2010b). However, the applicability and engineering aspect of thermal desorption in the analysis of targeted PFASs (FTOHs, FOSAs and FOSEs) in outdoor urban environment has not been reported so far.

The aim of this Chapter was to conduct a comparative investigation of performance and applicability of two methods for determination of volatile PFASs commonly found in urban ambient air. The first was the classic method with high-volume air sampling (HVS) and solvent extraction (method A). The second one included low-volume air sampling (LVS) and thermal desorption (method B). The

findings can provide insight into the planning of proper outdoor air monitoring strategies for volatile PFASs.

6.2 Experimental section

6.2.1 Chemicals

All standards and solvents used were the same with those in Chapter 3 and 4.

6.2.2 Sampling media preparation and sample extraction

6.2.2.1 Method A. HVS – Solvent extraction

The sampling cartridges are glass tubes containing a 50-mm and a 25-mm section of PUF plugs (65 mm O.D., Tisch Environmental, U.S.), with a section of 25 g amberlite XAD-2 resin (Sigma-Aldrich, U.S.) sandwiched between the two PUF layers (PUF/XAD/PUF cartridge). Preparation of the XAD resin and PUF plugs consisted of 80-90 cycles of Soxhlet extraction with acetone followed by another 80-90 cycles of extraction with hexane (four cycles per hour). The wet XAD resin and PUF plugs were then dried under a flow of high-purity nitrogen (99.9995%, Air Liquide, Singapore). The circular quartz fiber filters (QFF; 432 μm thick, 102 mm dia., Tisch Environmental, U.S.) were baked at 400 °C for 2 h and individually wrapped in methanol-rinsed aluminum foil sleeves. The packed cartridges were stored in screw-capped jars before installation on the sampler.

The extraction of analytes was solvent-based. The QFF, PUF plug and XAD resin were extracted separately with mixture of 1:1 acetone and MTBE (v:v) twice. The solvent was allowed to soak into the materials for 1 h (extraction step 1) and ½ h (extraction step 2). All extracts were subsequently rotoevaporated (Heidolph Laborota 4000 efficient, Germany) to approximately 5 mL, filtered through 0.45 μm nylon syringe filters (Acrodisc, Pall Gelman) and concentrated to 500 – 1000 μL with ethyl acetate as keeper under a gentle stream of high purity nitrogen. 10 μL of IS (200 ng/ μL) was added prior to analysis for volume correction and signal

intensity normalization. The quantitation of analytes was performed using an eight-point calibration curve (2 – 500 pg/ μ L).

6.2.2.2 Method B. LVS – Thermal desorption

The customized dual-stage sorbent tube developed in Chapter 5 was used for sample collection. Each tube (89 mm standard stainless steel tube, Markes international, U.K.) was packed with 150 mg of Tenax TA (35/60 mesh, Markes international, U.K.) followed by 200 mg of Carbograph 2TD (40/60 mesh, Markes international, U.K.). All tubes were thoroughly conditioned at 335 °C under a helium flow at 100 mL/min for 30 min and sealed tightly prior to usage.

The thermal desorption of analytes from the sampling tube was carried out on a TD-100TM high capacity thermal desorber (Markes International, U.K.). 1 μ L of IS (2 ng/ μ L) was introduced into the tubes prior to analysis using a stream of high purity nitrogen. Details about the system were given in Chapter 4. Quantitation of analytes was performed using a seven-point calibration curve (5 – 500 pg). The main differences between method A and B are outlined in Table 6-1.

Table 6-1. Major differences between HVS – solvent extraction (method A) and LVS – thermal desorption (method B).

	Method A	Method B
Sorbent	GFF for particulate phase PUF/XAD/PUF for gaseous phase	Tenax and Carbograph 2TD
Extraction media	Ethyl acetate	Helium
Sample volume (m ³)	400-500	0.1
Sampling rate (m ³ /h)	6-7	0.009
Sample split ratio (%) ^a	0.4	24.2
Unit weight (kg)	7	0.5
Noise level (dBA)	77	54
Power supply during sampling	Required	Optional

^a The sample split ratio represents the ratio of the mass of analytes reaching the detector of GC–MS system to the total mass of analytes collected in the sample tube.

6.2.3 Breakthrough experiment

6.2.3.1 Method A

The retention efficiency of two kinds of PUF/XAD/PUF cartridges, which were loaded with 10 and 25 g of XAD resin respectively, were compared in breakthrough experiment. The glass tube was loaded with a front PUF (50 mm), first section of resin (10 or 25 g), middle PUF, second section of 5 g resin and a back PUF. 200 ng of solution containing standards was spiked on the top PUF using a standard 100 μL GC syringe (Hamilton, U.S.), and the pre-calibrated high-volume air sampler (CF-1002BRL-DGT, HI-Q, U.S.) was started immediately at approximately 0.1 m^3/min for different sampling duration (6 – 120 h). The front PUF and XAD were extracted separately, while the middle PUF and second XAD resin were extracted together to examine the breakthrough of analytes. As the preliminary experiment indicated the target analytes retained in the back PUF plug were below detection limit, the back plug was not included in the extraction process.

6.2.3.2 Method B

Two Tenax/Carbograph 2TD tubes were coupled in series by inert metal connectors. The front tubes were spiked with 500 pg of analyte mixture. Duplicate sets were collocated to conduct breakthrough experiment simultaneously. Three different sampling periods (4, 8 and 16 h) were conducted at a fixed flow rate of 0.009 m^3/h by the personal air sampling pump (AirChek XR 5000, SKC, U.S.). The tubes were subsequently treated as real samples.

6.2.4 Outdoor air sampling

6.2.4.1 Method A

Comparison of the performance in real samples was carried out by sampling atmospheric air over 12 days at a four-story high open platform extending from a

lecture building on campus. Prior to sampling, 100 μL standard solution of isotopically labeled standards (500 $\text{pg}/\mu\text{L}$) was spiked to the cartridge to monitor analyte losses during sample collection and extraction. The high-volume pump was started immediately at flow rate of 0.1 m^3/min . Approximately 450 m^3 of air was drawn through the filter and sorbent cartridge during the 72 h sampling period. A total of 4 outdoor samples were collected. Field blanks ($n = 3$) were also collected by placing an open PUF/XAD/PUF cartridge at sampling site for 48 h in order to monitor possible background contamination. Samples were sealed air tight and stored at 4 $^{\circ}\text{C}$ until analysis. All samples were extracted and concentrated to 500 μL in ethyl acetate within 3 days after collection.

6.2.4.2 Method B

Each tube was spiked with 1 μL standard solution of isotopically labeled standards (100 $\text{pg}/\mu\text{L}$) and connected to the personal air sampling pump with sampling end approximately one meter high above the ground. Sampling duration was 12 h at flow rate of 0.009 m^3/h , resulting in a sampling volume at 0.108 m^3 . A total of 24 sets of duplicate outdoor samples were collected. Three field blanks were also taken by placing an open sorbent tube at sampling site for 12 h. Two background samples were collected at the edge of a wild forest in the west region of Singapore using the same sampling parameters. At the end of sampling period, the tube was disconnected, tightly sealed and stored in a metal container at 4 $^{\circ}\text{C}$ prior to analysis. All samples were analyzed within three days. Meteorological parameters including ambient temperature and relative humidity were recorded throughout the sampling period.

6.2.5 Chromatographic conditions

Sample separation and detection of both methods were conducted on a GC–MS (Agilent 7890A–5975C, U.S.) working in PCI mode. Separation of analytes was performed on 60 m HP-INNOWAX column (0.25 mm I.D., 0.25 μm film thickness,

J & W Scientific, U.S.) using helium as the carrier gas (1.6 mL/min). For method A, the analytes were introduced into the column through injecting 2 μ L of 500 – 100 μ L extracts to front inlet at 240 °C in splitless mode. For method B, the heater of interface (back inlet) between the thermal desorption system and GC column was set off. The samples were introduced in splitless mode as well.

The GC oven temperature program was the same for both methods and could be found in Chapter 4. The auxiliary temperature (GC–MS interface) was set at 250 °C for both methods. The mass spectrometer was operated in SIM mode, where methane was used as reagent gas with flow rate set at 20%. Quantitation was based on area integration of the target ion of each compound. Detailed GC–MS parameters could be found in appendix.

6.3 Results and discussion

The two methods were firstly evaluated for the retention efficiency of sampling tube, followed by the comparison of analytical performances. Finally the applicability of each method was tested and compared in the urban environment.

6.3.1 Breakthrough of analytes

6.3.1.1 Method A

Unlike other trace organic pollutants such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), the standardized method for the measurement of PFASs in ambient air is still lacking, and a variety of solid sorbent cartridges, were employed in studies using method A (Shoeib et al. 2004, Stock et al. 2004, Jahnke et al. 2007d, Cai et al. 2012). Our preliminary experiment indicated that the commercial 75 mm PUF cartridge could not retain targeted PFASs, although it had been widely used for other airborne organic pollutants (Mari et al. 2008). The low retention efficiency was probably due to the low total surface area of PUF ($< 1 \text{ m}^2$) and high volatility of targeted PFASs.

The majority of researchers chose the PUF/XAD-2/PUF cartridge (Stock et al. 2004, Dreyer and Ebinghaus 2009). XAD-2 resin is a porous hydrophobic copolymer with large surface area ($300 \text{ m}^2/\text{g}$). However, the loaded amount of XAD resin varied among different groups. Some researchers used the pre-assembled PUF/XAD (10g)/PUF tubes (Shoeib et al. 2006, Dreyer and Ebinghaus 2009), which were recommend by US EPA 600/8-80-038 method for air sampling of organic pesticides, while others inclined to load the tubes with 25g resin or more based on specially customized formula (Stock et al. 2004, Barber et al. 2007, Jahnke et al. 2007d, Cai et al. 2012). Breakthrough of 6:2, 8:2 and 10:2 FTOH was observed for the PUF/XAD (10g)/PUF cartridge even at low sampling volume in this Chapter (Figure 6-1a), while the PUF/XAD (25g)/PUF cartridge exhibited greatly improved retention efficiency (Figure 6-1b). FOSAs and FOSEs were well retained by both cartridges. Moreover, although the breakthrough of 4:2 FTOH was not found, the recovery of spiked mass was very low for both cartridges ($< 5\%$), indicating the compound was too volatile to retain.

Overall, the results suggest that the common high-volume sampling tubes obtained from commercial sources, including the 75 mm PUF tube and PUF/XAD (10 g)/PUF tube, are not suitable for high-volume sampling of targeted PFASs in tropical regions. The cartridge should be embedded with at least 25 g XAD-2 resin to ensure retention efficiency. Therefore, all the following experiments were conducted using the PUF/XAD (25 g)/PUF cartridge.

6.3.1.2 Method B

The results of breakthrough experiments on method B using the dual-stage tube of Tenax/Carbograph 2TD indicated better enrichment of analytes of interest in comparison with method A. The losses of all targeted PFASs from the front tube were less than 5% at flow rate of $0.009 \text{ m}^3/\text{h}$ for sampling duration between 4 and 16 h, which were consistent with the findings in Chapter 4.

(a)

(b)

Figure 6-1. Breakthrough percentage of certain targeted PFASs from the PUF/XAD/PUF cartridge loaded with different amounts of XAD resin; (a) 10 g; (b) 25 g.

6.3.2 Comparison of the analytical performances

Table 6-2 exhibits the repeatability of both methods, which was calculated as the relative standard deviation (%RSD) between five replicates of 100 pg standard mixture of analytes. As method A and B had different sample split ratios (Table 6-1), different mass of PFASs was spiked into the sampling tube of each method in order to achieve the same injection amount to GC column. For method A, the tube was spiked with 50 ng of standard mixture and extracted immediately. 2 μ L out of 1000 μ L extracts was analyzed. The method B tube was spiked with 400 pg of standard solution and thermal desorbed. Repeatability of method A were in the range of 5.9% (8:2 FTOH) to 11.6% (4:2 FTOH), which was generally higher than those of method B (2.0% for NEtFOSA to 10.4% for NEtFOSE). No RSD exceed the 25% criteria recommend by U.S. EPA (U.S.EPA 1999), indicating good reliability of both methods.

Table 6-2. Repeatability (%RSD, $n = 5$), recovery (average $\pm$ SD, $n = 3$) as well as method detection limits (MDLs) and method quantitation limits (MQLs) of method A and method B.

	Repeatability (%)		Recovery (%)		MDL(pg/m ³)		MQL(pg/m ³)	
	A	B	A	B	A	B	A	B
4:2 FTOH	11.6	8.1	4 $\pm$ 1	90 $\pm$ 8	2.2	26.9	11.1	92.6
6:2 FTOH	6.9	3.3	77 $\pm$ 7	92 $\pm$ 4	2.6	17.6	4.4	46.3
8:2 FTOH	5.9	6.8	111 $\pm$ 9	95 $\pm$ 3	4.6	6.5	11.1	46.3
10:2 FTOH	6.7	4.2	95 $\pm$ 4	94 $\pm$ 4	6.5	6.5	11.1	46.3
NMeFOSA	8.1	3.1	68 $\pm$ 3	100 $\pm$ 3	0.4	3.7	2.2	46.3
NEtFOSA	7.8	2.0	79 $\pm$ 4	99 $\pm$ 2	0.3	3.7	2.2	46.3
NMeFOSE	6.6	10.2	138 $\pm$ 3	95 $\pm$ 9	0.9	110.4	4.4	185.2
NEtFOSE	10.4	10.4	142 $\pm$ 5	91 $\pm$ 7	1.8	7.4	4.4	92.6

The method recovery experiments were performed in triplicates through the analysis of 400 pg of analytes using method A and method B. The method A tube was spiked with 200 ng of each analyte and the high volume pump was started immediately for 72-h air sampling (0.1 m³/min). The samples were extracted and concentrated to 1000 μ L in ethyl acetate, of which 2 μ L were injected and analyzed. Method B tube was spiked with 1600 pg of analytes, sampled for 12 h (150

mL/min), and then analyzed. The chromatograms of spiked air samples are shown in Figure 6-2. Recovery values are presented in Table 6-2. For method A, the values appeared to be acceptable for targeted PFASs except the most volatile 4:2 FTOH. However, it is noteworthy that given the high sampling volume (approximately 450 m³) and concentration ranges of 6:2, 8:2 and 10:2 FTOH in environment air obtained in preliminary experiments ($> 50 \text{ pg/m}^3$), the real method recoveries of these three analytes were expected lower. This was supported by the recoveries of their isotopically labeled analogues, which were $61 \pm 4\%$, $86 \pm 6\%$, $80 \pm 3\%$, respectively. FOSEs had too high recoveries, suggesting that they were subject to a matrix enhancement fact (Jahnke et al. 2007d). For method B, the recoveries of targeted analytes were all above 89%, and those of isotopically labeled analogues were between 92 and 107%, indicating high retention and extraction efficiency of the method.

The method detection limits (MDLs) were calculated as mean blank plus three times standard deviation if the analyte was detected in blank. For analytes did not present a signal in the blank, the MDLs were determined as the mass of analytes needed to generate a peak with signal to noise ratios of 3. Method quantitation limits (MQLs) of all analytes were fixed as the lowest calibration level. All calculated MDLs and MQLs were converted to a concentration basis through dividing by a sampling volume of 450 m³ and 0.108 m³ for method A and method B, respectively. The MDLs and MQLs of both methods are presented in Table 6-2. The MDLs for method A are between 0.3 pg/m³ (NEtFOSA) and 6.5 pg/m³ (10:2 FTOH), which are lower than those of method B (3.7 pg/m³ for NEtFOSA to 110.4 pg/m³ for NMeFOSE). Similarly, the MQLs of method A are substantially lower. The result does not agree with those reported in the literature, which compared the two methods for some volatile organic compounds such as benzene, toluene, ethylbenzene, xylene etc (Czaplicka and Klejnowski 2002, Ramírez et al. 2010), and showed higher MDLs of method A. The differences are mainly due to the considerably higher sampling volume employed in this study for method A (450 m³ vs. 0.01 – 0.720 m³).

(a)

(b)

Figure 6-2. Total ion chromatograms of spiked air samples obtained in the recovery experiments by method A. HVS – Solvent extraction (a) and by method B. LVS – Thermal desorption (b).

6.3.3 Comparison of the performance in real samples

6.3.3.1 Measurement of concentration

Results of both methods in real samples were compared. The typical extract ion chromatograms of FTOHs detected in the environmental samples are presented in Figure 6-3, and the average concentrations of analytes are given in Table 6-3. Method A quantified 7 of 8 analytes while only 6:2, 8:2 and 10:2 FTOH were detected by method B. Targeted PFASs were not detected in the background samples of method B, indicating the occurrence was source-related. As all PFASs with carbon chain lengths >2 are anthropogenic, their concentrations in the ambient air decline with decreasing degree of urbanization due to the existence of point and diffuse sources at urban sites (Piekarz et al. 2007, Jahnke et al. 2007a). Based upon the published data, the levels of PFASs observed in rural and remote ambient air were typically in the range of single-digit and double-digit picogram per cubic meter, while the levels in urban ambient air were usually one order of magnitude higher (Martin et al. 2002, Dreyer and Ebinghaus 2009). Given the reported MDLs in the previous section of this Chapter, method B appeared to be less suitable for determination of PFASs in remote or rural regions.

Figure 6-3. Typical extracted ion chromatogram (EIC) of real environmental samples for 6:2 FTOH, 8:2 FTOH and 10:2 FTOH using method A (a) and method B (b).

Table 6-3. Average concentrations of volatile PFASs in environmental air of Singapore determined by method A and method B, respectively (pg/m³).^a

	Day 1-3		Day 3-6		Day 6-9		Day 9-12	
	A	B	A	B	A	B	A	B
4:2 FTOH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2 FTOH	118	281	144	264	89	307	109	223
8:2 FTOH	250	304	232	312	144	279	112	216
10:2 FTOH	69	127	57	151	62	139	48	99
NMeFOSA	7	n.d.	7	n.d.	6	n.d.	6	n.d.
NEtFOSA	7	n.d.	4	n.d.	4	n.d.	3	n.d.
NMeFOSE	20	n.d.	18	n.d.	18	n.d.	16	n.d.
NEtFOSE	18	n.d.	19	n.d.	17	n.d.	16	n.d.

^a n.d.: not detected

Furthermore, it could be seen from the table that the concentrations measured by method A were generally lower than those obtained from method B, which was most likely due to the analyte losses in analytical process. The speculation was supported by the recoveries of isotopically labeled analogues in the real samples of method A (51 – 89%) and method B (77 – 113%). As a result, the concentrations of FTOHs might be underestimated by method A.

The 4 samples collected via method A were compared with the 24 samples measured by method B (Figure 6-4). The tendency of concentrations measured by method B does not correspond well to those of method A for 6:2 and 10:2 FTOH. However, the decreasing concentration trend of 8:2 FTOH was detected by both methods. The discrepancy might be due to the difference in method recovery and normal measurement errors. Moreover, method B displayed a higher temporal resolution than method A. Although the resolution of method A might be increased through shortening sampling time, the improvement would be limited due to the low concentrations of FOSAs/FOSEs (Table 6-3). It is also not feasible in this study to perform extra concentration of samples to less than 100 μ L extracts for improving MDLs of method A. The over-concentrated environmental samples, which contain a lot of organic contaminants, would result in excessive backgrounds and serious contamination to the GC column and mass selective detector (MSD).

(a)

(b)

(c)

Figure 6-4. Concentrations (pg/m³) of FTOHs detected by method A and method B (average $\pm$ range $n = 2$): 6:2 FTOH (a); 8:2 FTOH (b); 10:2 FTOH (c).

6.3.3.2 Outdoor air quality implications

The concentrations of FTOHs obtained at daytime and nighttime by method B were compared, and daytime levels were generally higher or close to those collected at the followed nighttime. This was against our expectation since FTOHs were reported to undergo UV-induced degradation in atmosphere during daytime (Ellis et al. 2004), which would result in lower concentrations. The contradiction suggested the situation might be complicated by many other factors, making the predication of outdoor air concentration tendency difficult. E.g., PFASs released from nearby indoor sources, which has been indicated in Chapter 4 and 5. The strong correlation between PFAS concentrations and ambient temperature (Jahnke et al. 2007b) was not observed, which was probably due to the relatively lower temperature variability in Singapore. In addition, significant decrease of FTOH concentrations was not observed during rain events, indicating wet deposition might not be a

significant sink for these analytes from ambient air. This was consistent with our findings in Chapter 3 and literature for their low water solubility and high tendency to partition into gaseous phase (Goss et al. 2006).

PFASs detected in this Chapter confirmed their widespread distribution in global scale, although it appeared to be different in areas with different land-use characteristics. FTOHs were the most abundant class of compounds detected in this study and their concentration levels were generally on the same order of magnitude as those determined in the urban atmosphere of European and North American regions, but significantly lower than those of urban areas in Japan and Taiwan (Oono et al. 2008, Li et al. 2011). The levels of FOSAs/FOSEs were considerably lower than those of FTOHs in this study and comparable to the concentrations of European urban regions (Barber et al. 2007, Jahnke et al. 2007b). High concentrations of FOSAs/FOSEs detected in some of North American sites (Martin et al. 2002, Stock et al. 2004) were not observed in Singapore, which might be due to the phase-out of sulfonate-based C₈ chemicals since 2000. In sum, the results of our study were more in line with the European pattern and might indicate an increasing tendency toward using FTOHs in these regions.

6.3.3.3 Method applicability in urban environment

One important aspect of the tested methods is the applicability in the urban environment of Singapore, which is an island city with high population density. The concentrations of PFASs in air can fluctuate in both time and space, and a good method should be able to accommodate these fluctuations and provide the result which can be used for the intended purpose. The sampling equipment of method A weights more than 7 kg and requires power supply throughout the sampling process (Table 6-1). The sampling noise (77 dBA) has exceeded the maximum permissible levels near hospital, school and residential buildings in Singapore set by National Environmental Agency (NEA). All these limitations restrict its portability and application in highly populated regions. It is more often to be installed for long-term ambient air monitoring at specific sampling sites, which usually avoid public areas

and residential buildings. In comparison, the pocket-sized personal air sampling pump used in method B is less than 0.6 kg with internal battery, which operates quietly and eliminates the risk of power failure encountered in method A (Stock et al. 2004). With these advantages the samplers could be easily located in the field and easily adjusted to accommodate changing needs and priorities. These features could facilitate the multi-point sampling at areas with concentrated point and variable diffusive sources, e.g. big cities, industry zones, etc. Method B can also serve as a pre-survey screening tool to establish whether a major intensive study is necessary.

Furthermore, the accurate, automated thermal desorption method avoids the intensive manual pretreatment procedures and sample handling errors. It is with these advantages in mind that we recommend method B as a more proper technique for quantifiable analysis of airborne PFASs in the high-density urban environment. It can be applied to the studies of other trace organic pollutants in the ambient air of heavily-polluted areas as well.

6.4 Conclusion

Statistical evaluation showed that the method using low volume sampling system and thermal desorption (method B) exhibited better repeatability and recovery, and higher temporal resolution in comparison with the classic high volume sampling – solvent extraction (method A). Method B can also operate with battery assisted pump and has low noise level, making it easy to use in both laboratory and field measurements. Application of method B in determining urban air pollution allows for the assessment of PFAS concentration variations and source apportionment analysis. The major concern of this method is the relatively higher detection limit, which is not suitable for rural or background baseline monitoring. Further research can focus on exploring the maximum flow rate and breakthrough volumes of method B to improve its MDLs.

Chapter 7

Conclusions and recommendations

The air-water partitioning behavior and occurrence of neutral, volatile PFASs in Singapore was investigated. A novel trace analytical method has been developed for the determination of these analytes in the environment. The major findings and conclusions are summarized as:

- 1) The Henry's law constants of FTOHs were determined using IGS method. Results revealed the propensity of this class of compounds to partition into air, leading to the expectation that FTOHs might be predominant in gaseous phase in natural environment. The linear dependence of K_H of FTOHs on molecular weight was not observed, which was probably attributed to their unique geometry with hydrogen bonding and conformation distortion. The unique properties of FTOHs might also increase the difficulties in predication of K_H by modeling software.
- 2) A new trace analytical method employing TD and GC-MS technique has been developed and successfully applied to the determination of indoor airborne volatile PFASs. The new method achieves high accuracy and temporal resolution as well as good recovery, exhibiting significant improvement compared with other existing air sampling methods.
- 3) The TD method has been successfully applied to routine quantitation of volatile PFASs in indoor environment. The dynamic changes of PFASs in indoor environment was observed, enabling the estimation of their indoor source strength and assessment of the effect of building air handlings. This could help building operation engineers and human exposure scientists to implement more effective and energy-efficient source control measures.
- 4) When applied to the measurement of target PFASs in the atmospheric environment, TD method indicates a higher time resolution, high portability

and low noise level in comparison with the conventional solvent extraction method. These advantages make it more suitable in the monitoring of volatile PFASs in highly urbanized regions for source apportionment analysis and assessment of their concentration variations. The findings could assist air quality researchers, regulation authority and industry with background information and insight into the planning of proper outdoor air monitoring strategies for volatile PFASs.

In order to obtain further understanding of neutral, volatile PFASs, the following work is suggested:

- 1) A complete investigation of the occurrences of PFASs in indoor and outdoor air of Singapore. The presence of neutral, volatile PFASs in indoor and outdoor environment of Singapore has been confirmed, but the levels and distribution pattern across Singapore have not been systematically measured.
- 2) A systematic study of the source identification of airborne PFASs in indoor environment. The existence of indoor sources for volatile PFASs has been proved. A further investigation towards identification of potential indoor sources of PFASs such as carpet, furniture and paint etc. is necessary.
- 3) Development of an indoor emission model for the target PFASs at various temperatures. The emissions of target PFASs from indoor environment have been studied. However, the fundamental mechanisms governing the release of PFASs from polymer materials have not been elucidated.
- 4) Development of a screening-level exposure assessment approach for neutral, volatile PFASs based upon the emission model and measured concentration. This could be very helpful in predicting human exposure mainly via inhalation to volatile PFASs.

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Appendix

Section A

Chemicals

Table A.1. Analytes, acronyms, purity, and vendor information.

Analyte	Acronym	Purity	Vendor
H,1H,2H,2H-Perfluoro-1-hexanol	4:2 FTOH	97%	ABCR, Germany
1H,1H,2H,2H-Perfluoro-1-octanol	6:2 FTOH	97%	Sigma-Aldrich, U.S.
1H,1H,2H,2H-Perfluoro-1-decanol	8:2 FTOH	97%	Sigma-Aldrich, U.S.
1H,1H,2H,2H-Perfluoro-1-dodecanol	10:2 FTOH	96%	Lancaster Synthesis, U.K.
N-methylperfluoro-1-octanesulfonamide	NMeFOSA	> 98%	Wellington Laboratories, Canada
N-ethylperfluoro-1-octanesulfonamide	NEtFOSA	> 98%	Wellington Laboratories, Canada
N-methylperfluoro-1-octanesulfonamido-ethanol	NMeFOSE	> 98%	Wellington Laboratories, Canada
N-ethylperfluoro-1-octanesulfonamido-ethanol	NEtFOSE	> 98%	Wellington Laboratories, Canada
2-perfluorobutyl-[1,1,2,2- ² H ₄]-ethanol	d ₄ -4:2 FTOH	> 98%	Wellington Laboratories, Canada
2-perfluorohexyl-[1,1- ² H ₂]-[1,2- ¹³ C ₂]-ethanol	¹³ C ₂ , d ₂ -6:2 FTOH	> 98%	Wellington Laboratories, Canada
2-perfluorooctyl-[1,1- ² H ₂]-[1,2- ¹³ C ₂]-ethanol	¹³ C ₂ , d ₂ -8:2 FTOH	> 98%	Wellington Laboratories, Canada
2-perfluorodecyl-[1,1- ² H ₂]-[1,2- ¹³ C ₂]-ethanol	¹³ C ₂ , d ₂ -10:2 FTOH	> 98%	Wellington Laboratories, Canada
N-methyl-d ₃ -perfluoro-1-octanesulfonamide	d ₃ -NMeFOSA	> 98%	Wellington Laboratories, Canada
N-ethyl-d ₅ -perfluoro-1-octanesulfonamide	d ₅ -NEtFOSA	> 98%	Wellington Laboratories, Canada
1H,1H-Perfluoro-1-octanol ^a	7:1 FA	98 %	Lancaster Synthesis, U.K.

APPENDIX

1H,1H-Perfluoro-1-dodecanol ^a	11:1 FA	90 %	Lancaster Synthesis, U.K.
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^a Internal standard

Section B

GC–MS parameters

Figure B.1. Retention times (on a 60m HP-INNOWAX column) and molecular weights of targeted PFASs, as well as ions monitored by GC–MS working in PCI mode.

Analyte	Retention time (min)	Molecular weight	PCI Ions monitored m/z
4:2 FTOH	13.6	264	227, 265 ^a
6:2 FTOH	15.5	364	327, 365 ^a , 393
8:2 FTOH	17.3	464	427, 465 ^a , 493
10:2 FTOH	18.7	564	527, 565 ^a , 593
NMeFOSA	24.5	513	514 ^a
NEtFOSA	23.8	527	528 ^a
NMeFOSE	26	557	540 ^a , 558
NEtFOSE	26.1	571	554 ^a , 572
d ₄ -4:2 FTOH ^b	13.3	268	230, 269 ^a
¹³ C ₂ , d ₂ -6:2 FTOH ^b	15.4	368	331, 369 ^a , 397
¹³ C ₂ , d ₂ -8:2 FTOH ^b	17.2	468	431, 469 ^a , 496
¹³ C ₂ , d ₂ -10:2 FTOH ^b	18.8	568	531, 569 ^a , 597
d ₃ -NMeFOSA ^b	24.4	516	517 ^a
d ₅ -NEtFOSA ^b	23.7	532	533 ^a
7:1 FA ^c	16.6	400	381, 401
11:1 FA ^c	19.6	600	581, 601

^a Quantitation Ion

^b Mass-labeled Surrogate Standard

^c Internal Standard

Section C

Blank experiments of TD method

Figure C.1. Total ion chromatogram of instrument blank (stainless steel tube without sorbents).

Figure C.2. Total ion chromatogram of the sorbent tube blank (Tenax/Carbograph 1TD).

Section D

Optimized Instrumentation parameters for different tubes

Table D.1. Optimized parameters of thermal desorption system (TD).

Parameter	Value
<i>Adsorbent tube desorption</i>	
Temperature	320 °C ^a ; 360 °C ^b
Time	10 min
Gas flow	40 mL/min
Split	Off
<i>Cold trap desorption</i>	
Packing	
Temperature	335 °C ^a ; 375 °C ^b
Time	5 min
Split	5 mL/min
Column flow	1.6 mL/min
Transfer line	220 °C
<i>GC-PCIMS instrument parameters</i>	
Auxiliary temperature	250 °C
Source temperature	300 °C
GC cycle time	32 min

^a For thermal desorption of single-stage adsorbent tube of Tenax, dual-stage tube of Tenax/Carbograph 2TD and Tenax/Carbograph 1TD. ^b For thermal desorption of single-stage adsorbent tube of Carbograph 2TD and Carbograph 1TD.

Section E**Calculation of indoor emission rate of 6:2 FTOH and air exchange rate using a well-mixed indoor air box model**

$$C_t = \frac{G + (I + k)VC_{Ain}}{(I + k)V} (1 - e^{-(I+k)t}) + C_0 (e^{-(I+k)t}) \quad \text{eq 5.1}$$

1. Calculation of area specific emission rate

1.1) For the concentrations of 6:2 FTOH collected at weekday night (Wednesday midnight and Thursday morning, table 5-2),

$$C_0 = 4210 \text{ pg m}^{-3}; C_t = 5680 \text{ pg m}^{-3}; C_{Ain} = 150 \text{ pg m}^{-3};$$

$$I = 0.05 \text{ h}^{-1}; k = 0; t = 6 \text{ h}; V = 300 \text{ m}^3, \text{ using eq 5.1}$$

$$\Rightarrow G = 145700 \text{ pg h}^{-1}$$

As Surface area equal to 235 m^2 , the area specific emission rate is $145700/235 = 620 \text{ pg m}^{-2} \text{ h}^{-1}$.

1.2) For the concentrations of 6:2 FTOH collected at weekday night (Thursday midnight and Friday morning, table 5-2),

$$C_0 = 4090 \text{ pg m}^{-3}; C_t = 5620 \text{ pg m}^{-3}; C_{Ain} = 150 \text{ pg m}^{-3};$$

$$I = 0.05 \text{ h}^{-1}; k = 0; t = 6 \text{ h}; V = 300 \text{ m}^3, \text{ using eq 5.1}$$

$$\Rightarrow G = 147240 \text{ pg h}^{-1}$$

The area specific emission rate is $147240/235 = 626 \text{ pg m}^{-2} \text{ h}^{-1}$.

1.3) Therefore, the specific indoor emission rate of 6:2 FTOH is 623 ± 5 (average $\pm$ range).

2. Calculation of air exchange rate

2.1) For the concentrations of 6:2 FTOH collected at weekday daytime (Thursday, table 5-2),

$$G = 146000 \text{ pg h}^{-1}; C_{\text{Ain}} = 150 \text{ pg m}^{-3}; C_0 = 3570 \text{ pg m}^{-3}; C_t = 3210 \text{ pg m}^{-3};$$

$$k = 0; t = 6 \text{ h}; V = 300 \text{ m}^3, \text{ using eq 5.1}$$

$$\Rightarrow I = 0.17 \text{ h}^{-1}$$

2.2) For the concentrations of 6:2 FTOH collected at weekday daytime (Friday, table 5-2),

$$G = 146000 \text{ pg h}^{-1}; C_{\text{Ain}} = 150 \text{ pg m}^{-3}; C_0 = 3800 \text{ pg m}^{-3}; C_t = 3560 \text{ pg m}^{-3};$$

$$k = 0; t = 6 \text{ h}; V = 300 \text{ m}^3, \text{ using eq 5.1}$$

$$\Rightarrow I = 0.15 \text{ h}^{-1}$$

2.3) For the concentrations of 6:2 FTOH collected at weekday daytime (Monday, table 5-2),

$$G = 146000 \text{ pg h}^{-1}; C_{\text{Ain}} = 150 \text{ pg m}^{-3}; C_0 = 4390 \text{ pg m}^{-3}; C_t = 3640 \text{ pg m}^{-3};$$

$$k = 0; t = 6 \text{ h}; V = 300 \text{ m}^3, \text{ using eq 5.1}$$

$$\Rightarrow I = 0.16 \text{ h}^{-1}$$

2.4) The average air exchange $I = 0.16 \pm 0.01 \text{ h}^{-1}$.

As the floor area is 68 m^2 , the outdoor air supply per floor area is $0.16 \cdot 300 / 68 = 0.71 \text{ m}^3/\text{h}$ per m^2 floor area.