GKSS
FORSCHUNGSZENTRUM
in der HELMHOLTZ-GEMEINSCHAFT

Determination of Indoor Air Concentrations of Polyfluorinated Compounds with Passive Samplers

(Von der Fakultät III: Umwelt und Technik Institut für Ökologie und Umweltchemie der Leuphana Universität Lüneburg als Diplomarbeit angenommene Arbeit)

Authoress:
V. Langer

ISSN 0344-9629

HELMHOLTZ
| GEMEINSCHAFT

wissen
schafft
nutzen

GKSS 2010/4

GKSS 2010/4

Determination of Indoor Air Concentrations of Polyfluorinated Compounds with Passive Samplers

(Von der Fakultät III: Umwelt und Technik Institut für Ökologie und Umweltchemie der Leuphana Universität Lüneburg als Diplomarbeit angenommene Arbeit)

Authoress:

V. Langer

(Institute of Coastal Research)

GKSS-Forschungszentrum Geesthacht GmbH · Geesthacht · 2010

Die Berichte der GKSS werden kostenlos abgegeben.
The delivery of the GKSS reports is free of charge.

Anforderungen/Requests:

GKSS-Forschungszentrum Geesthacht GmbH
Bibliothek/Library
Postfach 11 60
21494 Geesthacht
Germany
Fax.: +49 4152 87-17 17

Als Manuskript vervielfältigt.

ISSN 0344-9629

GKSS-Forschungszentrum Geesthacht GmbH · Telefon (04152) 87-0
Max-Planck-Straße 1 · 21502 Geesthacht / Postfach 11 60 · 21494 Geesthacht

GKSS 2010/4

Determination of Indoor Air Concentrations of Polyfluorinated Compounds with Passive Samplers

(Von der Fakultät III: Umwelt und Technik Institut für Ökologie und Umweltchemie der Leuphana Universität Lüneburg als Diplomarbeit angenommene Arbeit)

Vera Langer

85 pages with 21 figures and 24 tables

Abstract

In this study indoor air concentrations of fifteen volatile per- and polyfluorinated compounds (PFC) (five fluorotelomer alcohols (FTOH), three fluorotelomer acrylates (FTA), three perfluorinated sulfonamido ethanols (FASE) and three perfluorinated sulfonamides (FASA)) were determined in residential and non-residential buildings. Sampling locations were two residential homes, two offices, two furniture shops, two outdoor gear shops, one electroplating service, one coating service, one auto body shop and one carpet shop. Air samples were taken with passive samplers, consisting of XAD – 4 impregnated polyurethane-foam (PUF) disks in a steel housing. Prior to taking real samples, an optimized sampling and extraction method was developed. This included a field calibration of samplers to determine different uptake phases of all analytes. A sampling period of 14 days was chosen. Samplers were deployed in duplicate in all sites. PUF disks were extracted with fluidized bed extraction (FBE) using Methyl *tert*-butyl ether (MTBE):acetone (1:1) as solvent followed by quantitative analysis using gas chromatography-mass spectrometry (GC-MS). Total PFC concentrations ranged from 8.2 ng m^{-3} - 458 ng m^{-3}. Individual PFC concentrations were between 42 pg m^{-3} (6:2 FTA) and 209 ng m^{-3} (8:2 FTOH). Sum concentrations for the substance groups ranged from 0.2 ng m^{-3} - 152 ng m^{-3} (FTA), from 3.3 ng m^{-3} - 307 ng m^{-3} (FTOH) and from 4.4 ng m^{-3} to 148 ng m^{-3} (FASA, FASE). On the basis of the contamination level and statistical analysis (cluster analysis and Pearson correlation coefficients), low and high contamination sites were determined. Elevated individual, group and total PFC concentrations were detected in both outdoor gear shops, one furniture shop and the carpet shop. A daily intake scenario of some of this study's analytes contribution to the burden of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in humans was calculated. Results were between 0.01 ng kg^{-1} d^{-1} and 0.97 ng kg^{-1} d^{-1} for PFOS and between 0.04 ng kg^{-1} d^{-1} and 0.19 ng kg^{-1} d^{-1} intake for PFOA.

Bestimmung von Innenraumluftkonzentrationen von Polyfluorierten Verbindungen mit Passivsammlern

Zusammenfassung

In dieser Studie wurden Innenraumluftkonzentrationen von fünfzehn volatilen per- und polyfluorierten Verbindungen (PFC) (fünf Fluortelomeralkohole (FTOH), drei Fluortelomeracrylate (FTA), drei Perfluorsulfonamide (FASA) und drei Perfluorsulfonamidoethanole (FASE)) in Wohnhäusern und anderen Gebäuden bestimmt. Die Probenahmeorte waren zwei Wohnhäuser, zwei Büros, zwei Möbelläden, zwei Outdoor - Ausstatter, ein Galvanotechnik Betrieb, ein Beschichtungsservice, eine Autolackiererei und ein Teppichladen. Die Luftproben wurden mit Passivsammlern genommen. Diese bestanden aus XAD-4 imprägnierten Scheiben aus Polyurethanschaum (PUF) in einem Stahlgehäuse. Vor den Probenahmen wurde eine optimierte Sampling- und Extraktionsmethode entwickelt. Diese beinhaltete eine Feldkalibration der Sammler um die verschiedenen Aufnahmestadien der Analyte zu untersuchen. Auf den Resultaten basierend wurde eine Probenahmedauer von 14 Tagen bestimmt. Die Sammler wurden als Parallelproben in allen Probenahmestellen aufgehängt. Die PUF Scheiben wurden mittels Wirbelschicht mit Methyl *tert*-butyl Ether (MTBE):Aceton (1:1) als Lösungsmittel extrahiert und anschließend mit Gaschromatographie – Massenspektrometrie (GC-MS) quantitativ analysiert. Gesamt PFC-Konzentrationen lagen zwischen 8.2 ng m^{-3} und 458 ng m^{-3}. Analytenkonzentrationen lagen zwischen 42 pg m^{-3} (6:2 FTA) und 209 ng m^{-3} (8:2 FTOH). Die Konzentrationen der Substanzgruppen waren 0.2 ng m^{-3} bis 152 ng m^{-3} (FTA), 3.3 ng m^{-3} bis 307 ng m^{-3} (FTOH) und 4.4 ng m^{-3} bis 148 ng m^{-3} (FASA und FASE). Aufgrund der individuellen Kontaminationslevel und einer statistischen Auswertung (Cluster Analyse und Pearson Korrelationskoeffizienten) wurden die Probenahmeorte in niedrig- und hochbelastete Innenräume eingeteilt. Erhöhte Gesamt-Substanzgruppen- und Analytenkonzentrationen wurden bei den Outdoor Ausstattern, einem Möbelladen und dem Teppichladen nachgewiesen. Ein Daily-Intake-Scenario für den Anteil einiger Analyte dieser Studie zur Belastung von Menschen durch Perfluoroktansulfonat (PFOS) und Perfluoroktanoat (PFOA) wurde erstellt. Die Ergebnisse lagen zwischen 0.01 ng kg^{-1} d^{-1} - 0.97 ng kg^{-1} d^{-1} für PFOS und zwischen 0.04 ng kg^{-1} d^{-1} - 0.19 ng kg^{-1} für PFOA.

Manuscript received / Manuskripteingang in TFP: 28. Juni 2010

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

10:2 FTA	perfluorodecyl ethylacrylate
10:2 FTOH ^{13}C	2-Perfluorodecyl-(1,1-^{2}H2)-(1,2-13C2)-ethanol
10:2 FTOH	perfluorodecyl ethanol
12:2 FTOH	perfluorododecyl ethanol
^{13}C3 TCB ^{13}C3	trichlorobenzene
4:2 FTOH ^{13}C	2-perfluorobutyl-[1,1-2H2, 1,2-13C2] ethanol
4:2 FTOH	perfluorobutyl ethanol
6:2 FTA	perfluorohexyl ethylacrylate
6:2 FTOH	perfluorohexyl ethanol
6:2 FTOH ^{13}C	2-perfluorohexyl-[1,1-2H2, 1,2-13C2] ethanol
8:2 FTA	perfluorooctyl ethylacrylate
8:2 FTOH ^{13}C	2-perfluorooctyl-(1,1-^{2}H2)-(1,2-13C2)-ethanol
8:2 FTOH	perfluorooctyl ethanol
ABS	auto body shop
BaA	benzo(a)anthracene
BaP	benzo(a)pyrene
BghiP	benzo(ghi)perylen
CAS	carpet shop
COS	coating service
CRY	chrysene
DCM	dichloromethane
DDT	dichlorodiphenyltrichloroethane
ECF	electro-chemical-fluorination
EP	electroplating service
EtFOSA D_5	n-ethyl-d5-perfluoro-1-octanesulfonamide
EtFOSA	n-ethyl perfluorooctane sulfonamide
EtFOSE D_9	2-(n-deuterioethylperfluoro-1-octanesulfonemanido)-1,1,2,2,-tetradeuterioethanol
EtFOSE	n-ethyl perfluorooctanesulfonamido ethanol
FASA	perfluorinated sulfonamides
FASE	perfluorinated sulfonamido ethanols
FBE	fluidized bed extraction
FS1	furniture shop 1
FS2	furniture shop 2
FTA	fluorotelomer acrylates
FTOH	fluorotelomer alcohols
FTUCA	unsaturated telomer acid

GC	gas chromatography
H1	residential house 1
H2	residential house 2
HCB	hexachlorobenzene
IND	indeno(1,2,3-cd)pyrene
K_{AW}	air-water-partition coefficient
K_{OA}	octanol-air-partition-coefficient
LDPE	low-density polyethylene
LOD	instrumental limits of detection
LOQ	instrumental limits of quantification
MeFBSA	n-methyl perfluorobutane sulfonamide
MeFBSE	n-methyl perfluorobutanesulfonamido ethanol
MeFOSA D_3	n-methyl-d3-perfluoro-1-octanesulfonamide
MeFOSA	n-methyl perfluorooctane sulfonamide
MeFOSE D_7	2-(n-deuteriomethylperfluoro-1-octanesulfonemanido)-1,1,2,2,-tetradeuterioethanol
MeFOSE	n-methyl perfluorooctanesulfonamido ethanol
MS	mass spectrometry
MTBE	methyl *tert*-butyl ether
MTC	mass transfer coefficient
N.A	not analysed
N.D	not detected
NGO	non-governmental organization
OF1	office 1
OF2	office 2
OH	hydroxyl
OS1	outdoor gear shop 1
OS2a	outdoor gear shop 2a
OS2b	outdoor gear shops 2b
PAH	polyaromatic hydrocarbons
PBDE	polybrominated diphenyl ethers
PCB	polychlorinated biphenyles
PCC	Pearson Correlation Coefficients
PCI	positive chemical ionization mode
PFAA	perfluoroalkyl acids
PFBS	perfluorobutane sulfonate
PFC	per- and polyfluorinated compounds
PFCA	perfluoroalkyl carboxylates
PFO	perflouro – n – octane

PFOA	perfluorooctanoate
PFOS	perfluorooctane sulfonate
PFSA	perfluoroalkyl sulfonates
POPs	persistent organic pollutants
POSF	perfluorooctanesulfonyl fluoride
PSM	passive sampling medium
R	recovery rate
SD	standard deviation
SIM	selected ion monitoring
SIP	sorbent impregnated
SXL	soxhlet extraction
SMPD	semi-permeable membrane devices
SPME	solid-phase micro extraction
TFE	tetrafluorethylene
TM	telomerization
TWA	time-weighted average
TWK	Drinking Water Commission
US	ultrasonication
V	volt
WWTP	wastewater treatment plants

I. INTRODUCTION

1.1. CHEMISTRY OF POLY- AND PERFLUORINATED COMPOUNDS (PFC)

1.1.1. General Information

Although several plants, fungi and micro organisms are able to produce fluorinated organic molecules in low concentrations (such as mono-fluoroacetic acid), long-chain perfluorinated compounds do not occur in the environment. PFC are a class of molecules that are strictly anthropogenic to todays knowledge. (Giesy and Kannan 2002). PFC are molecules that consist of an alkyl chain (usually between 4 and 12 carbon atoms), whose hydrogen atoms are completely ("perfluorinated") or almost completely ("polyfluorinated") replaced by fluorine. Each molecule includes a functional moiety at the end of the alkyl chain, which makes the compound more reactive. Functional moieties include carboxylic, sulphonic, hydroxyl, sulfonamido or acrylic groups. They can be either neutral, positively or negatively charged, so that the whole molecule is either non-ionic or has cationic or anionic charge (EFSA 2008). The combination of the hydrophobic alkyl chain and the lipophobic functional moiety makes the PFC molecule amphiphilic. Therefore polyfluorinated surfactants have beneficial properties; they are both water and oil repellent (Jensen et al. 2008). The carbon - fluorine bond is very strong (about 460 kJ/mol) (Kissa 2001) which makes perfluoroalkyl sulfonates (PFSA) and carboxylates (PFCA) resistant to UV radiation, heat, chemical degradation and metabolic processes (Schultz et al. 2003). Moreover, the nonbonding electrons of the fluorine atoms shield the molecule from outer influences (Giesy and Kannan 2002). Overall several hundreds of PFC molecules are known today. They can be divided into two groups. The first group consists of ionic perfluorinated molecules that are persistent and toxic and have moderate to high water solubilities and low vapour pressures. The two most popular PFC of this group, perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) are depicted in figures 1 and 2. The second group contains neutral per- and polyfluorinated molecules that are volatile and not persistent. However, these PFC are finally broken down to persistent PFC of the first group (Ellis et al. 2003; Stock et al. 2004b). All analytes determined in this study belong to the second group. Their chemical structures are given in table 1. Analytes of this study include fluorotelomer alcohols (FTOH), fluorotelomer acrylates (FTA), perfluorosulfonamides (FASA) and perfluorosulfonamido ethanols (FASE). FTOH and FTA are polyfluorinated chemicals that consist of an even-numbered perfluorinated alkyl chain, a

$(CH_2)_2$ – group and an ethanol (FTOH) or acrylate (FTA) moiety. They are named after their way of production (Telomerization). FASA and FASE are perfluorinated compounds that consist of an alkyl chain with usually either four or eight carbon atoms. FASA include a sulfonamido moiety. The chemical structures of FASE are very similar to FASA, as they only have an additional ethanol moiety attached to the sulfonamido moiety.

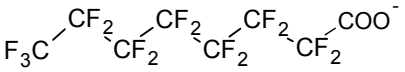


Figure 1: Chemical structure of perfluorooctanoate (PFOA).

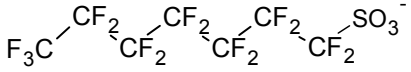
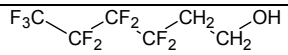
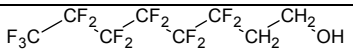
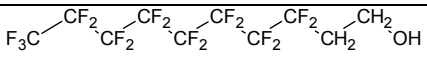
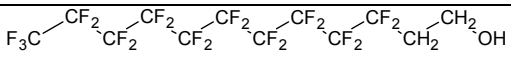
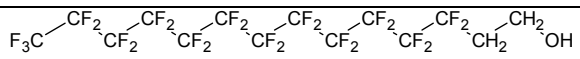
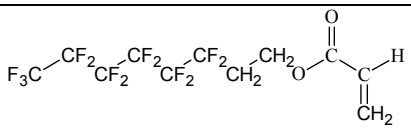
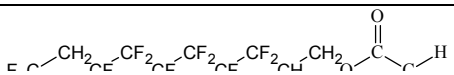
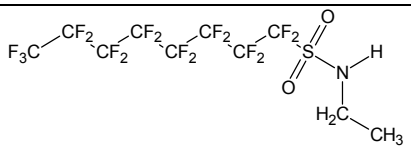
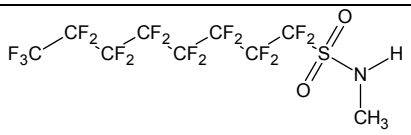
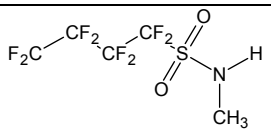
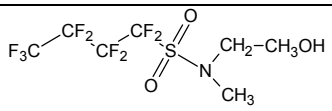
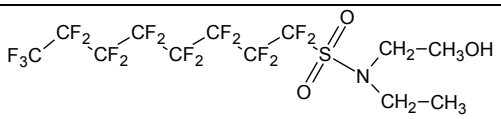
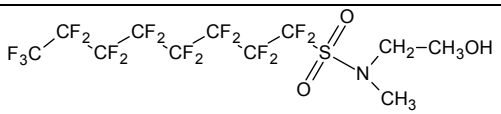


Figure 2: Chemical structure of perfluorooctane sulfonate (PFOS).

Table 1: Chemical structures of analytes determined in this study.

Analyte	Chemical Structure
FLUOROTELOMER ALCOHOLS	
perfluorobutyl ethanol (4:2 FTOH)	
perfluorohexyl ethanol (6:2 FTOH)	
perfluorooctyl ethanol (8:2 FTOH)	
perfluorodecyl ethanol (10:2 FTOH)	
perfluorododecyl ethanol (12:2 FTOH)	
FLUOROTELOMER ACRYLATES	
perfluorohexyl ethylacrylate (6:2 FTA)	
perfluorooctyl ethylacrylate (8:2 FTA)	
perfluorodecyl ethylacrylate (10:2 FTA)	

PERFLUOROALKYL SULFONAMIDES	
n-ethyl perfluorooctane sulfonamide (EtFOSA)	
n-methyl perfluorooctane sulfonamide (MeFOSA)	
n-methyl perfluorobutane sulfonamide (MeFBSA)	
PERFLUOROALKYLSULFONAMIDO ETHANOLS	
n-methyl perfluorobutanesulfonamido ethanol (MeFBSE)	
n-ethyl perfluorooctanesulfonamido ethanol (EtFOSE)	
n-methyl perfluorooctanesulfonamido ethanol (MeFOSE)	

1.1.2 Physico- chemical properties of PFC

Ionic and neutral PFC have different physico-chemical profiles and therefore have different partition behaviours and ways of transport in the environment. Ionic PFC have low vapour pressures. Values for vapour pressure are 3.31 x 10^{-4} Pa at 20°C for PFOS (OECD 2002) and 4.2 Pa at 25°C for PFOA (USEPA 2002a). Water solubilities for ionic PFC are moderate to high (depending on chain length). In pure water, the solubility of PFOS is 519 mg L^{-1} at 20°C (OECD 2002) and that of PFOA is 4.1 g L^{-1} at 22°C (USEPA 2002a). Hence, ionic PFC are mostly found in aqueous phases in the environment. In contrast to this, neutral PFC are very volatile. Published values for the vapour pressure of FTOH and FASA/E at 25°C are given in table 2. FTOH are several orders of magnitude more volatile than FASA/E. This is probably caused by different polarities within the molecules. The polarities of the sulfonamides moieties of FASA/E increase intermolecular interactions and thus lower the vapour pressure (Lei et al. 2004). Vapour pressures of FTOH and FASA/E are more than 1000-fold higher than that of PFOS. Vapour pressures for FTA have not been published. It is assumed that the

values are in the same order of magnitude as those of FTOH as both classes of substances have similar chemical structures.

Table 2: Vapour pressures of FTOH and FASA/E at 20°C. n.a. not analysed.
[a] Lei et al. 2004, [b] Stock et al. 2004a.

Analyte	Vapour pressure (Pa)	
4:2 FTOH	1670[a]	992[b]
6:2 FTOH	876[a]	713[b]
8:2 FTOH	227[a]	254[b]
10:2 FTOH	53[a]	144[b]
EtFOSA	7[a]	n.a.
MeFOSE	0.7[a]	n.a.
EtFOSE	0.35[a]	n.a.

The partition behaviour of a substance between an organic and a gaseous phase is described by its octanol-air-partition-coefficient (K_{OA}). In the environment, this coefficient determines whether a substance preferentially partitions to an organic phase (such as organic films on aerosols, organic carbon in soil or lipid portions of vegetation) or the atmosphere. Log K_{OA} values for most analytes of this study are presented in table 3. Log K_{OA} values for MeFBSE and MEFBSA have not been published. It is assumed that they are slightly lower than those of MeFOSA and MeFOSE due to the similar chemical structures of the molecules but shorter chain length. The octanol-air partition coefficients of FASA/E, FTOH and FTA increase linearly with reciprocal absolute temperature (Thuens et al. 2008; Dreyer et al. 2009a). This means that the substances preferably partition to organic phases at colder temperatures. In the environment FTOH, FTA and FASA/E are likely to partition to the atmosphere (Thuens et al. 2008; Dreyer et al. 2009a; Lei et al. 2004). The partition behaviour of a substance between the air and aqueous phases is described by the air-water-partition coefficient (K_{AW}). Reported log K_{AW} values for FTOH at 25°C are 1.4 for 4:2 FTOH, 1.47 for 6:2 FTOH and 1.82 for 8:2 FTOH (Lei et al. 2004). Reported water solubilities for analytes of this study are low. The water solubility of 8:2 FTOH is 137µg L^{-1} at 25°C. Water solubilities of FTOH decrease with increasing alkyl chain length (Kaiser et al. 2006; Liu and Lee 2007). The Water solubility of EtFOSA (< 1mg L^{-1}) is more than 500-fold lower than that of PFOS (Giesy and Kannan 2002). Given the low water solubilities, high vapour pressures, high air-water-partition coefficients and low octanol-air-partition coefficients, the analytes of this study are likely to be in the atmosphere in the environment.

Table 3: Octanol-air-partition coefficients (K_{OA}) of FTOH, FTA and FASA/E at 25°C.
[a] Thuens et al. 2008, [b] Dreyer et al. 2009a.

Analyte	log K_{OA}
4:2 FTOH	4.6[a]
6:2 FTOH	4.8[a]
8:2 FTOH	5.6[a]
10:2 FTOH	5.7[a]
12:2 FTOH	6.2[a]
6:2 FTA	4.4 [b]
8:2 FTA	5.2[b]
10:2 FTA	5.7[b]
MeFOSA	6.3[b]
MeFOSE	6.4[b]
EtFOSA	6.6[b]
EtFOSE	6.7[b]

1.2 SYNTHESIS OF PFC

Organofluorine chemistry started in the late 19th century when F. Swarts developed a method to add fluorine atoms to organic compounds (Audenaert et al. 1999). Later, Simons developed the Electro-Chemical-Fluorination (ECF) process, which is used to produce PFC today (3M 1999). Large scale production of PFC began in the 1940s. Companies like the American conglomerate 3M started to produce perfluorinated compounds using ECF processes (Prevedouros et al. 2006). Initially PFC were used as multipurpose oil- and water- repellents. In 1953 well-known fluorinated stain repellent Scotchgard® was discovered by accident, when a lab worker spilled some experimental compound on his shoes, keeping them clean. This incident led to the development of a new product market of impregnating agents (Renner 2006).

As elemental fluorine is very aggressive and hard to handle, direct fluorination of organic compounds is not very suitable for industrial synthesis of PFC. Today there are two major ways for the synthesis of PFC: Electrochemical Fluorination (ECF) and Telomerization (TM). Besides ECF and TM there are other ways of producing PFC like oligomerization, but these are not commonly used on a for industrial production (Kissa 2001).

1.2.1 Electrochemical Fluorination

An organic substance that is to be fluorinated is dissolved or dispersed in liquid hydrogen fluoride. An electric current between five and seven volt is passed through the solution. The hydrogen atoms are evolved at the cathode and the organic substance is fluorinated. All hydrogen atoms in the molecule are replaced except for hydrogen in functional groups (Kissa 2001). For industrial synthesis, octanesulfonal fluoride is usually the compound to be fluorinated during the ECF process. This results in perfluorooctanesulfonyl fluoride (POSF) after ECF (figure 3).

$$2\ C_8H_{17}SO_2F + 34\ HF \xrightarrow{4.5 - 7.0\ V} 2\ C_8F_{17}SO_2F + 17\ H_2$$

Figure 3: Synthesis of POSF by electrochemical fluorination (ECF). V = volt.

PFOS is the result of the chemical or enzymatic hydrolysis of POSF. Chemically, it cannot be further broken down. However, the ECF process of POFS is not completely efficient. It yields about 35 % - 40 % linear chain POSF and a mixture of different byproducts (e.g. higher and lower straight-chain homologs, branched and cyclic perfluoroalkanes). The commercialized POSF derived products are a mixture of about 70 % linear POSF and 30 % branched impurities (3M 1999). In the past, volatile byproducts created during ECF production steps were emitted to the atmosphere. These days they are destroyed by thermal oxidation. Less volatile byproducts are incinerated, discharged to wastewater treatment systems or recycled back into the ECF process. Although POSF is a commercially usable product, it was primarily used as an intermediate for the production of other PFC. There are two major production steps following the synthesis of POSF to create various poly- and perfluorinated compounds. For the first reaction step, POSF is reacted with methyl or ethyl amine to synthesise mainly MeFOSA or EtFOSA, but also fluorinated amides, silanes or carboxylates. Subsequently, MeFOSA and EtFOSA further react with ethylene carbonate to create MeFOSE or EtFOSE, and also polyfluorinated alcohols, urethanes, copolymers or phosphate esters. However, these substances are not pure. There are varying amounts of fluorinated residuals (unreacted or partly reacted starting materials or intermediates) in the final products (3M 1999; Dinglasan-Panlilio and Mabury 2006). A reaction tree of ECF-based production of PFC depicting all relevant intermediates and final products is given in figure 4.

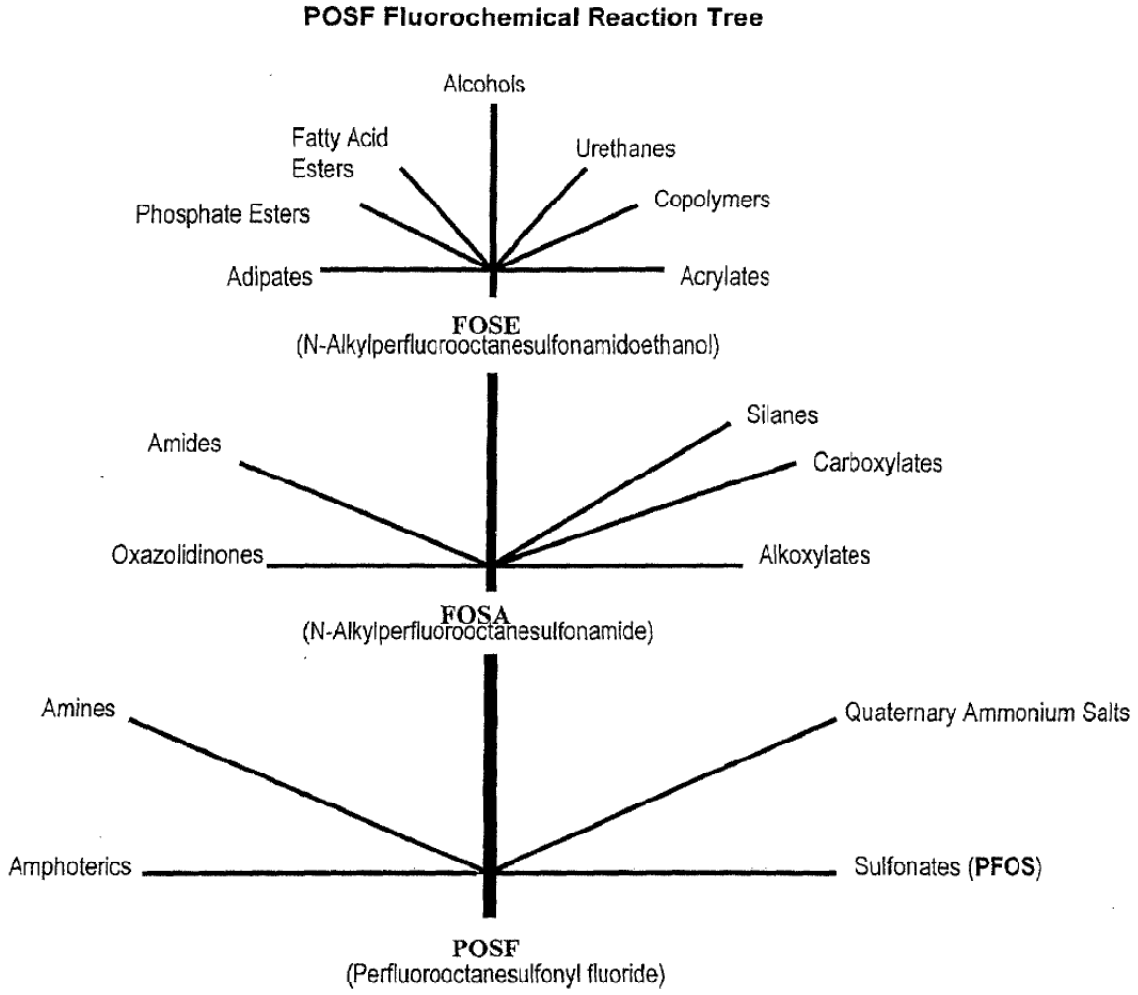


Figure 4: POSF-chemical reaction tree (3M 1999)

1.2.2 Telomerization

The process of telomerization requires one molecule (telogen) and at least two ethylenically unsaturated molecules (taxogens). The reaction of a telogen and taxogens is called telomerization. The general procedure of this type of process is depicted in figure 5. For commercial telomerization of PFC, the first step is the fluoroiodination of tetrafluorethylene (TFE), resulting in pentafluoroiodo ethane. In the second reaction, this product is used as the telogen and is reacted with TFE (taxogen) to produce a mixture of perfluoroalkyl iodides, which, after repeatedly reacted with TFE yields the intermediate perfluoroalkylethyl iodode. When producing PFC by telomerization, only linear fluoroalkyl chains with even numbers of fluorinated carbon atoms are produced. Perfluoroalkylethyl iodode can easily be converted to intermediates such as perfluoroethyl alcohols, olefins, thiols or sulfonyl chlorides. These intermediates can be reacted to obtain different final products. Fluorotelomer alcohols are

yielded by the hydrolysis of perfluoroalkyl iodides. There are different patents applying a variety of solvents e.g. nonoxidizing acids. Copper salts are used to catalyze the hydrolysis (Kissa 2001; Schultz et al. 2003).

$$\underset{\text{Telogen}}{YZ} + \underset{\text{Taxogen}}{nA} \rightarrow \underset{\text{Telomer}}{Y\text{-}(A)_n\text{-}Z}$$

Figure 5: Telomerization.

1.3 PRODUCTION, APPLICATION AND EMISSIONS OF PFC

Today the most important fields of application of PFC are carpet protection, paper and board protection, textile protection, leather protection, fire-fighting foams, specialty surfactants and polymerisation aids (Hekster 2002). POSF-based substances are used for metal plating, photographic and photolithographic uses, semiconductor industries, hydraulic fluids, aqueous fire fighting foams (Paul et al. 2009). FASA/E are predominantly applied as intermediates in the production of other POSF-based PFC or as add-ons in polymers or other substances (3M 1999; Kissa 2001). FTOH are mainly used for paper coatings, food packaging and carpet treatments (Kissa 2001; Dinglasan et al. 2004) and have been detected in microwave popcorn bags (Begley et al. 2005; Sinclair et al. 2007) and non-stick cookware (Sinclair et al. 2007). FTA are monomers used in the manufacture of FTOH-based polymers (Butt et al. 2009). Most producers of PFC are located in the Northern hemisphere. Known producers include 3M company (United States), DuPont (United States), PCR Inc. (United States), Exfluor Research Corporation (United States), Clariant (Germany), Hoechst (Germany), Dyneon (Germany), Asahi Glass (Japan), Daikin (Japan), Miteni S.p.a. (Italy), EniChem Synthesis S.p.a. (Italy) and Shanhai 3F New Materials Co., Ltd. (China) (USEPA 2002). 3M has been characterized as the dominant global producer of PFC with a total production of 85 percent of PFOS worldwide. Established brands include aforementioned Scotchgard®, Gore-Tex®, Zonyl® or Stainmaster® (USEPA 2002).

Although estimaties about usage, application and production of PFC are given for few countries, specific data on PFC production and consumption in most countries is not published or does not exist. Today the world production of PFC is estimated to be 10 000 t per year (Jensen et al. 2008). The total historical worldwide production of POSF was estimated to be 122 500 t (including unsuable waste) between 1970-2002 (Paul et al. 2009)

resulting in a global release of 45 250 t PFC to air and water between 1970 – 2012 (Paul et al. 2009). Although production of POSF using ECF started in 1949 (3M 1999), it has been assumed that POSF-production was low pre-1970 (Paul et al. 2009). From 1970 to 1990 the total global POSF-production increased from 500 t to 4 500 t per year. This production volume remained constant in the 1990s, until in 2000 3M decided to phase-out POSF-based products (Paul et al. 2009). POSF-production from 2002 onward is likely to be about 1 000 t per year (Paul et al. 2009). Estimated emissions of PFOS-related substances and PFOS-polymers in the EU for the year 2000 were 174 tonnes, with the highest emissions being caused by fabrics service life into the water compartment (101 800 kg) (Jensen et al. 2008). In 2003 20-60 tonnes of PFOS-related substances were produced in Germany (Scientific Committee on Health and Environmental Risks 2004). Fluorotelomer-based products such as FTOH and FTA are produced by a series of steps, beginning with Telomer A (Prevedouros et al. 2006). Global Telomer A production in the years 2000 and 2002 was 5 000 t and 6 000 t per year (USEPA 2002b). Other estimates assume that worldwide production of FTOH during the years 2000 and 2002 was 5 000 t per year, 40 % of which was produced in North America (Ellis et al. 2003) and has increased to currently 11 000 t – 14 000 t per year (Dinglasan et Mabury 2006).

1.4. RELEASE OF VOLATILE PFC INTO THE ENVIRONMENT

The sources of volatile PFC have not yet been completely identified. However, assumptions about release pathways have been made. Volatile PFC (including FTOH, FTA, FASA/E) may be released during production of PFC (direct emissions) or be released from final products either as impurities or components (indirect emissions) (Dinglasan-Panlilio and Mabury 2006). Possible sources for the release of FASA and FASE from the production of POSF-based PFC are given in figure 4, which depicts the different stages of POSF-based PFC synthesis (FOSE= FASE, FOSA = FASA). It becomes evident that there are intermediates such as FASA and FASE resulting from the different steps or production, which may remain in the final product as residuals. The residuals can be released into the environment later on. Global direct emissions of volatile PFC to the air caused during production of POSF-based PFC have been estimated to be 435 – 575 t between 1970 and 2002 (Paul et al. 2009). Indirect emissions of volatile PFC are made up by losses from consumer products during use and disposal (85 %) and release from secondary industrial applications, such as treatment of paper or carpets with PFC-containing impregnating agents (15 %) (Paul et al. 2009). Global release

of volatile POSF-based PFC from consumer products to air was estimated to be 235 t between 1970 - 2002. Global release of volatile POSF-based PFC from secondary applications was estimated to be 56 t between 1970 -2002 (Paul et al. 2009).

About 80 % of all fluorotelomer compounds are used in polymers (USEPA 2002b). FTOH are attached to polymers by ester, amide, urethane or ether bonding (Moody 2000). It has been reported that FTOH and FASA/E are present in polymers as residual materials and can be released from the polymer surface by cleavage of covalent bonding in FASA/E or FTOH – based polymers (Wang et al. 2005). This was confirmed by detection of free FTOH and FASA/E molecules in several fluorinated materials, such as carpet protector (Dinglasan-Panlilio and Mabury 2006). 8:2 FTOH was found in the highest abundance. A potential way of 8:2 FTOH release from a fluorinated polymer is given in figure 6. One hundred tonnes of FTOH have been reported to be residual in the total global manufacture of fluorotelomer products from 2000 to 2002 (Prevedouros et al. 2006). FTA are significant residuals in FTA-based polymers and can be released into the atmosphere from these products in a manner similar to that of FTOH (Dinglasan-Panlilio and Mabury 2006).

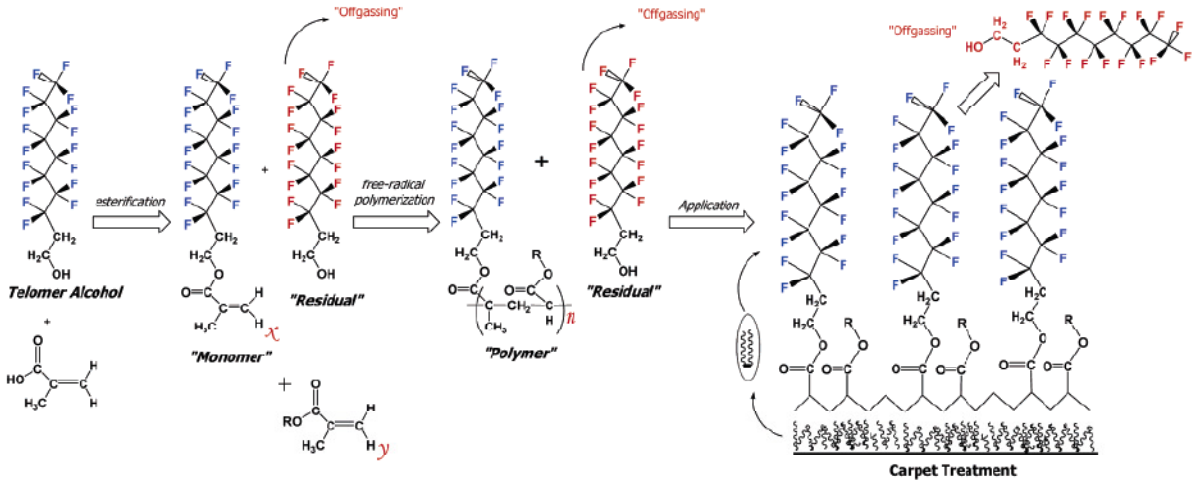


Figure 6: Outline of the production steps of a polymer containing 8:2 FTOH. Potential sources of offgassing of residual FTOH are depicted (Dinglasan-Panlilio and Mabury 2006).

Furthermore, volatile PFC may be released to the atmosphere from wastewater treatment plants (WWTP). Ionic PFC have been detected in wastewater at significant concentrations (Herzke et al. 2008; Ahrens et al. 2009). Wastewater of many different branches of the industry is stored in WWTP. Besides, possible PFC contaminations from common households are discharged into WWTP via domestic wastewater. This results in an increased PFC

concentration in WWTP and makes them a source for off-gasing of volatile PFC (Umweltbundesamt 2009). Investigation is underway in a separate diploma thesis (Weinberg).

1.5 PFC IN THE ENVIRONMENT

Contamination by individual PFC have been observed in many environmental compartments, biota and humans across the globe (Giesy and Kannan 2001; Kannan et al. 2001; Giesy and Kannan 2002; Yamashita et al. 2005; Falandysz et al. 2007; Ahrens et al. 2008). PFC contamination in the environment originates from direct in indirect anthropogenic sources. Direct sources include manufacture and use of perfluoroalkylated acids (PFAA), whereas indirect sources are represented by PFAA as product impurities and production of chemicals that may degrade to PFAA (Prevedouros et al. 2006).

1.5.1 Transport of PFC

PFC are transported by two main mechanisms in the environment (Armitage et al. 2006; Prevedouros et al. 2006; Dinglasan-Panlilio and Mabury 2006; Ellis et al. 2004; Stock et al. 2004b; Yamashita et al. 2005). As PFAA preferably enter aquatic phases in the environment (USEPA 2002a; OECD 2002), they are likely to travel long distances by transport with oceanic currents (Armitage et al. 2006). Due to their persistence and hydrophilicy they can be transported over long distances in large water bodies to remote regions (e.g. the Arctic) (Yamashita et al. 2005; Lau et al. 2007). This was confirmed by detections of ionic PFC in Arctic mammals (Giesy and Kannan 2001). Furthermore, PFAA concentrations in the level of pg L^{-1} have been detected in surface waters from several locations, including the Atlantic and Pacific Ocean (Yamashita et al. 2005; Armitage et al. 2006; Ahrens et al. 2008). Traces of PFOA and PFOS have also been detected in deep sea water (Yamashita et al. 2005). Applying a model, it has been estimated that there was a net ocean transport flux of perflouro – n – octane (PFO) to the arctic of 8-23 tons in 2005 (Armitage et al. 2006).

Secondly, non-persistent, volatile and neutral PFC ("precursors") in the atmosphere can be transported by air masses over long distances before or while they are degraded to persistent PFAA such as PFOA and PFOS (Ellis et al. 2004; Stock et al. 2004b). Precursors include FTOH, FTA and FASA/E (Dinglasan-Panlilio and Mabury 2006; Ellis et al. 2004; Butt et al. 2009). The individual atmospheric lifetimes of precursors are long enough to ensure long range transport, starting from their releasing locations to remote regions of the earth (section

1.5.2), where they are degraded to PFCA/PFSA and accumulated via wet deposition (Ellis et al. 2004). Sources of these volatile PFC are not well known, but it was assumed that they are released from fluorinated polymer production, as intermediates from ECF or TM production steps or as residuals from final products (Dinglasan-Panlilio and Mabury 2006) (section 1.4).

1.5.2 Degradation of precursors

Experiments investigating abiotic or biotic degradation of FTOH, FASA/E and FTA have recently been carried out (Dinglasan-Panlilio and Mabury 2006; Prevedouros et al. 2006; Ellis et al. 2004; Butt et al. 2009). Smog chamber experiments have demonstrated that FTOH may degrade to PFCA by OH-radical initiated oxidation (Ellis et al. 2004). These reactions are likely to occur at environmental conditions in the atmosphere (Ellis et al. 2004). Dinglasan et al. (2004) observed that 8:2 FTOH can be degraded to the 8:2 fluorotelomer unsaturated carboxylate (8:2 FTUCA) by microbial activity. Although definite biotransformation processes cannot be determined yet, PFOA production significantly correlated to the amount of 8:2 FTUCA produced by 8:2 FTOH degradation seemed to occur (Dinglasan et al. 2004). This confirms previous observations (Hagen et al. 1981; Lange 2002). The atmospheric lifetimes of FTOH are about 20 days (Ellis et al. 2003). It is estimated that atmospheric degradation of FTOH yields a PFCA flux to the Arctic in the range of 1-100 t per year (Ellis et al. 2004). Wallington et al. (2006) calculated that the atmospheric PFOA deposition flux to the Arctic caused by FTOH degradation is about 0.4 tonnes per year. This is in a similar order of magnitude as the annual arctic loadings of POPs from the atmosphere such as hexachlorobenzene (HCB) which is about 1.8 tonnes year per year (Wallington et al. 2006). It is estimated that FASE undergo reactions with OH-radicals in the atmosphere, resulting in FASA (D'eon et al. 2006). These can be further broken down to PFOA and shorter-chained PFCAs by cleavage of the sulfonamido group (D'eon et al. 2006). The estimated atmospheric lifetime of individual FASE is two days (D'Eon et al. 2006). Produced FASA are supposed to have lifetimes ranging around 20-50 days (D'Eon et al. 2006). Furthermore, EtFOSE has been reported to undergo aerobic biodegradation processes in wastewater treatment sludge, yielding both PFOA and PFOS in small amounts (Lange 2000; Rhoads et al. 2008). It has been assumed that there is a flux of PFOA yielded by degradations of FASA/E into the Arctic in a similar order of magnitude as FTOH (Schenker et al. 2008). So far there is only one published study on the atmospheric chemistry of FTA. Conducted smog chamber experiments by Butt et al. (2009) revealed that 4:2 FTA can be oxidized by OH-radicals and Cl-radicals.

The lifetime of 4:2 FTA in the atmosphere in urban areas is about 9 days (Butt et al. 2009). Atmospheric oxidation of FTA is expected to lead to a 1-10% molar yield of PFCA (Butt et al. 2009). Figure 7 depicts degradation schemes of FTOH, FTA and FASA/E in air.

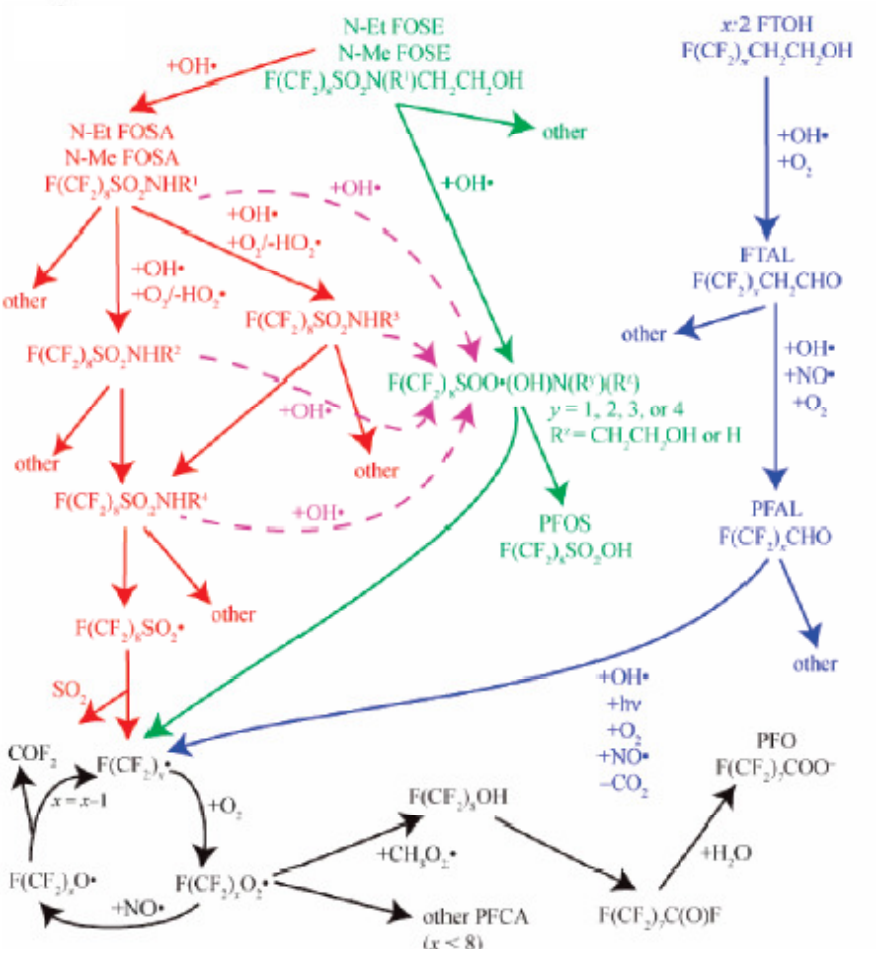


Figure 7: Degradation scheme of EtFOSE, MeFOSE and FTOH into PFO in air (Schenker et al. 2008).

1.5.3 Volatile PFC in indoor and outdoor air

In past years PFC have been determined in air of different regions across the earth. PFC contamination detected in the Arctic atmosphere drew a lot of scientific interest (Renner 2005; Shoeib et al. 2006; Stock et al. 2007). PFC air sampling focused on precursor PFC (Shoeib et al. 2004; Stock et al. 2004b; Jahnke et al. 2007c; Dreyer et al. 2009b). Applying high volume air sampling, analytes are enriched on a cartridge containing a PUF - XAD2 – PUF sandwich (polymer resin and polyurethane foam). A glass-fibre filter fixed on top of the cartridge collects air particles. Cartridges are usually extracted by cold extraction applying

acetone:MTBE (1:1) (Dreyer et al. 2009c), methanol or ethyl acetate as solvent (Stock et al. 2007; Barber et al. 2007; Jahnke et al. 2007d). Using passive air sampling, analytes are trapped on PUF-disks that are placed in a steel housing (Shoeib and Harner 2002).

Detected marine background precursor PFC concentrations in the northern hemisphere were between 2 pg m^{-3} and 11 pg m^{-3} in the Canadian Arctic (Shoeib et al. 2006) and up to 40 pg m^{-3} in air masses from the Atlantic ocean (Jahnke et al. 2007b; Dreyer et al. 2009c). They were one order of magnitude lower than concentrations from populated parts of the northern hemisphere, which were up to 972 pg m^{-3} (Dreyer et al. 2009b) and 243 pg m^{-3} (Barber et al. 2007) in Central Europe, 26 pg m^{-3} (Piekarz et al. 2007) and 2466 pg m^{-3} (Oono et al. 2008) in Asia and 403 pg m^{-3} (Stock et al. 2004b) in Northern America. PFC concentrations determined in rural Northwest Europe ranged from 0 to 50 pg m^{-3} (Barber et al. 2007) and 12 – 300 pg m^{-3} (Jahnke et al. 2007a) Concentrations of FTOH and FASA/E were higher in urban than in rural regions. Varying individual predominant FASA/E and FTOH were observed in different sites. However, 8:2 FTOH was the dominating fluorotelomer alcohol in most sampling locations. Spatial distribution of precursors was observed to be inhomogeneous (Stock et al. 2004b; Barber et al. 2007; Jahnke et al. 2007). Dreyer et al. (2009d) observed significant variations of airborne PFC concentrations over the year, depending on air masses origin and the presence of local sources.

Although only few measurements of volatile PFC in indoor air have been carried out so far, determined indoor air concentrations of PFC were significantly higher than PFC outdoor air concentrations. Published indoor air PFC concentrations from residential homes are sumarized in table 4. Further indoor air PFC contamination was detected in non-residential buildings. Jahnke et al. (2007c) observed elevated concentrations of FTOH and FASA/E in office air. Concentrations were 20 – 300 pg m^{-3} for individual FTOH and 20 - 200 pg m^{-3} for individual FASA/E. Shoeib et al. (2004, 2008) observed individual FTOH, FASA and FASE in indoor air of a library and laboratories. Concentrations in the library were 982 – 4790 pg m^{-3} (FTOH) and 67 – 395 pg m^{-3} (FASA/E). FASE concentrations in the laboratories were 10 – 1900 pg m^{-3}. MeFOSA, MeFOSE, EtFOSA and EtFOSE were also detected in dust from residential houses at concentrations up to 590 ng g^{-1} (Kato et al. 2008).

Table 4: PFC indoor air concentration in residential houses reported in the literature. Concentrations are given as arithmetic means (pg m^{-3}). n.a. not analysed.

analyte	sampling location			
	Tromsø, Norway 2005 High Volume sampler (Barber et al. 2007)	Ottawa, Canada 2002/2003 Passive Sampler (Shoeib et al. 2005)	Northern Norway 2008 High Volume Sampler (Huber 2008)	Canada 2001/2003 High Volume Sampler (Shoeib et al. 2004)
4:2 FTOH	114	n.a.	24	n.a.
6:2 FTOH	2 990	n.a.	9 830	n.a.
8:2 FTOH	3 424	n.a.	11 100	n.a.
10:2 FTOH	3 559	n.a.	6 000	n.a.
12:2 FTOH	n.a.	n.a.	n.a.	n.a.
MeFOSA	6 600	35	200	5 – 283
MeFOSE	6 018	1 970	1300	667-8 300
EtFOSA	6 626	59	150	n.a.
EtFOSE	5 755	1 100	320	289-1 800

1.6 TOXICOLOGY OF PFC

Several PFC are bioaccumulative and are assumed to biomagnify, as they have mainly been detected in biota of higher trophic levels (Giesy and Kannan 2002; Muir et al. 2006). The bioaccumulation potential of PFC is directly connected to the carbon chain length (Muir et al. 2006). PFC with a chain shorter than eight or longer than twelve carbon atoms are not bioaccumulative (Conder et al. 2007; Muir et al. 2006). Bioaccumulation increases proportionally to the increasing length of the PFC carbon chain (Muir et al. 2006). Unlike most persistent organic pollutants (POPs), PFC do not accumulate in the fatty tissues of humans and animals, as they are not only lipophilic, but also hydrophilic. Being proteophilic, they are stored in the liver, gall bladder or bind to blood proteins (Renner 2001; Conder et al. 2008). It has been examined *in vitro* that 6:2 FTOH and 8:2 FTOH are xenoestrogens which support cell proliferation (Maras et al. 2006). In laboratory tests with animals it has been demonstrated that only one percent of the FTOH intake is metabolised to PFOA (Ladics et al. 2005). FTOH were not observed to be genotoxic or carcinogenic (Ladics et al. 2005). However, they do have effects on reproduction. Reduced progeny and skeletal mutations in the foetus have been detected in rats that were fed with FTOH (Mylchreest et al. 2005). No

observed effect levels (NOEL) of FTOH in rats was 5 mg kg^{-1} bodyweight day^{-1} (Wölfle 2006). NOEL of FTA in rats were 1000 mg kg^{-1} d^{-1} for FTA copolymers and polymers and 50 mg kg^{-1} d^{-1} for FTA urethane polymers (Wölfle 2006).

Considering the precursor role of FTOH, FASA/E and FTA, the toxicology of their atmospheric and biological degradation products PFOA and PFOS has to be taken into account as well (Dinglasan et al. 2004). The half-life of PFOS in humans is about four years (OECD 2002). Toxicity tests with rats have demonstrated that PFOS has acute and subchronic lethal effects with discoloration of the liver and lung (OECD 2002). Chronic effects included liver and bladder cancer (USEPA 2002a). PFOS acts as an endocrine disruptor (OECD 2002). The mean half-life for PFOA in humans is 4.3 years (USEPA 2002a). Acute lethal effects were observed in rats given oral doses of PFOA (USEPA 2002a). Subchronic effects in rats included hepatotoxicity and histopathologic effects and death at concentrations higher than 10,000 ppm (USEPA 2002a). On a chronic level PFOA causes liver, pancreatic, leydig cell and mammary gland cancer (USEPA 2002a).

1.7 POLITICAL SITUATION

Recently, increasing attention has been paid to PFC by Non-Governmental Organizations (NGOs) but also by governmental agencies (Umweltbundesamt 2007). Several extensive hazard assessment reports on individual PFC have been published in the last years. The OECD released a hazard assessment of PFOS in 2002 (OECD 2002) and the USEPA published a report on PFOA in 2002 (USEPA 2002a). The Australian government issued a report on perfluorobutane sulfonate (PFBS) in 2005 (NICNAS 2005). More specific reports have been released very recently, such as a scientific opinion on PFOS and PFOA in the food chain (EFSA 2008) or the presence of PFC in consumer articles (Jensen et al. 2008).

Industry reacted to research observations indicating that several PFC are bioaccumulative toxic and persistent. In 2000 the American conglomerate 3M announced they were going to voluntarily phase out their POFS-based products. The phase-out was completed in 2002. POFS-based products have been replaced by shorter-chained PFC which are supposed to be less bioaccumulative, toxic and persistent (USEPA 2000; Renner 2006). In 2006 a "PFOA, PFOS and fluorinated telomers" stewardship program was launched by the USEPA. Eight major PFC producers (Arkema, Asahi, Ciba, Clariant, Daikin, 3M, DuPont, Solvay Solexis) committed to reduce their production of respective PFC by 95% until 2010 from the baseline year 2000. Until 2015 PFOA production is supposed to be completely eliminated. Annual

progress reports by each company are published by the USEPA (USEPA 2008b). Reports for the years 2006 and 2007 demonstrated that precursor emissions have already been reduced by 96 % by individual companies (USEPA 2008a; USEPA 2008b).

Only recently, on May 9th 2009, PFOS has been added to the Annex B of the Stockholm Convention. This is regarded as a remarkable step towards global effort to minimize the impact of this substance, also representing the entire class of PFC, on the environment and on human health (COP4 2009; Wang et al. 2009).

In terms of national regulations, the tolerable daily intake (TDI) of PFOS and PFOA in drinking water in Germany is 100 ng kg^{-1} bodyweight (Fromme et al. 2009a). In 2006, the Drinking Water Commission (TWK) of the German Ministry of Health at the Federal Environment Agency passed a health based guide value for lifelong exposure of 0.3 μg L^{-1} for both PFOS and PFOA in drinking water (Trinkwasserkommission 2006). There are no regulations regarding other media in Germany (Wang et al. 2009).

1.8 PASSIVE SAMPLING

1.8.1 Theory of Passive Sampling

Passive sampling is a sampling technique which is based on the free flow of the analyte molecules from the sampling medium onto the passive sampling (collecting) medium as result of different chemical potentials of the analyte towards the different media (Gorecki and Namiesnik 2002). Uptake occurs until the capacities of the sampler are completely occupied by the analyte, i.e. the chemical potential of the analyte on the collective medium and in the matrix are equal. This proceeds in three steps. First, when majority of capacities on the sampler are unoccupied, the uptake is linear. As the chemical is building up more on the sampler, the uptake becomes curvilinear. Eventually there will be an equilibrium between the concentration of the analyte on the sampler and in the sampling medium and a plateau is reached (figure 8) (Shoeib and Harner 2002; Bartkow et al. 2005). Ideally, a sampling is performed in the linear uptake phase. However, it must be assured that the sampling rate remains constant throughout the sampling duration (Hazrati and Harrad 2007).

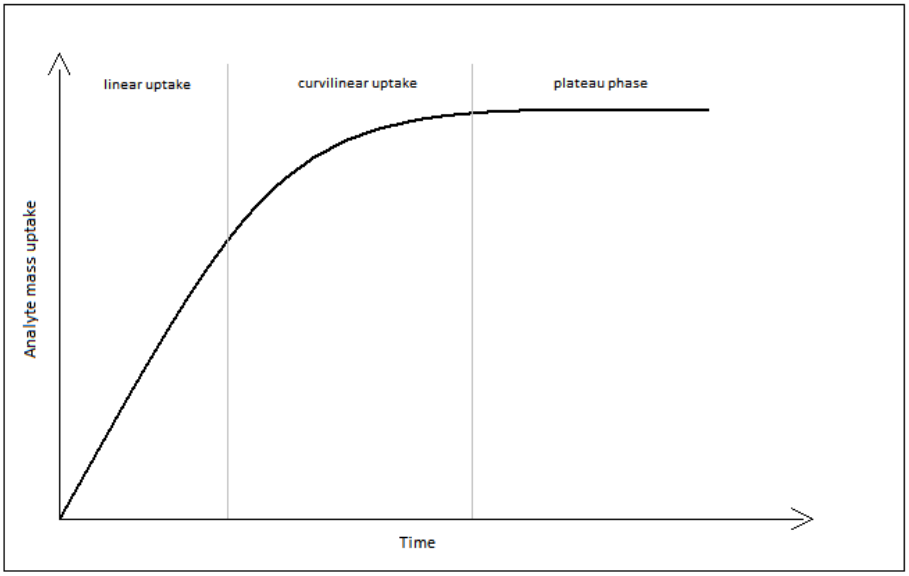


Figure 8: Uptake stages of the passive sampler.

1.8.2 Calculation of concentrations of analytes in the sampled medium

Analysis of samples collected by passive sampling delivers concentrations of analytes trapped on the sampling medium (e.g. PUF disk). To draw conclusions about respective concentrations of analytes in the sampled medium (e.g. air, soil, water), calculations have to be made. Applying the Whitman two-film approach (Whitman 1923), the passive sampling medium (PSM) is a porous compartment into which the analyte can diffuse. The velocity of the mass-transfer of the analyte from the surrounding matrix into the PSM is defined by the addition of resistances towards the analyte in the boundary layer of the respective matrix and the PSM. In terms of air sampling, the overall mass transfer coefficient (MTC) can be derived as described in the following equation:

$$1/k = 1/k_A + 1/(k_{PSM} * K_{PSM\text{-}A}) \quad (1)$$

where k_A is the airside MTC, k_{PSM} is the PSM-side MTC and $K_{PSM\text{-}A}$ is the PSM-air partition coefficient. $K_{PSM\text{-}A}$ has approximately the same magnitude as the octanol-air partition coefficient (K_{OA}) of the respective chemical. The accumulation of a substance on the PSM equals the uptake of the chemical on the PSM minus the loss and can be described as followed:

$$V_{PSM}\,(dC_{PSM}/dt) = k_A * A_{PSM}\,(C_A - C_{PSM}/K_{PSM\text{-}A}) \quad (2)$$

where V_{PSM} is the volume of the PSM, C_{PSM} and C_A are concentrations of the chemical on the PSM and in the air and, respectively, A_{PSM} is the planar area of the PSM. Initially, in the linear uptake phase, C_{PSM} is small and the term $C_{PSM}/K_{PSM\text{-}A}$ is insignificant. Uptake is then governed by k_A, A_{PSM} and C_A. Therefore, the equation applied to calculate concentrations for linear uptake is:

$$M = k_A * A_{PSM} * C_A * \Delta t \quad (3)$$

where M is the total mass of analyte sequestered on the PSM and Δt is the deployment time of the sampler. As the concentration of the chemical on the PSM increases, the term $C_{PSM}/K_{PSM\text{-}A}$ becomes more important. During this curvilinear phase the uptake is reduced. Finally, C_{PSM} becomes constant and the equilibrium is reached. This means that C_A equals the term $C_{PSM}/K_{PSM\text{-}A}$ and there is no more net uptake (Gorecki et Namiesnik 2002; Hazrati et Harrad 2007; Seethapathy et al. 2008; Shoeib et Harner 2002).

1.8.3 Types of Passive Air Samplers

There are different types of passive air samplers. Solid-phase micro extraction (SPME) samplers are tube-type designed and consist of a stationary phase (such as triolein) coated on a fibre inside of a stainless steel or polyethylene gauged needle. Analyte collection begins when the stationary phase is exposed to the matrix by pushing the fibre out of the needle (Gorecki and Namiesnik 2002; Shoeib and Harner 2002; Seethapathy 2008). Semi-permeable membrane devices (SPMD) comprise membranes made of low-density polyethylene tubes (LDPE) filled with high-molecular weight lipids, usually triolein. The membrane is solely transient for molecules or particles with a size smaller than 1 nm. This excludes large molecules or substances adsorbed to colloids or humic acids. Organic compounds with octanol-water-partition coefficients log $K_{OW} > 3$ diffuse into the sampler and are trapped by the triolein filling. SPMD are most commonly used for passive sampling of organic compounds (Vrana et al. 2005) and have been recently applied for PFC air sampling (Fiedler et al. *in press*). Polyurethane foam (PUF) passive air samplers consist of a PUF disk which is placed inside of a stainless steel housing (figure 9). Two major gaps between the upper and lower bowl of the steel housing and holes in the lower bowl assure sufficient air circulation

within the sampler. Airborne analytes adsorb on the PUF disk and can be extracted after sampling. PUF disks can be optionally impregnated with sorbent to improve the sorption capacities for certain analytes in the air (Pozo et al. 2006; Shoeib et al. 2008). PUF passive air samplers have been used widely for environmental monitoring (Harner et al. 2006; Hazrati and Harrad 2007; Chaemfa et al. 2008). PUF and sorbent impregnated PUF disks have already been applied for PFC air sampling (Shoeib et al. 2008).

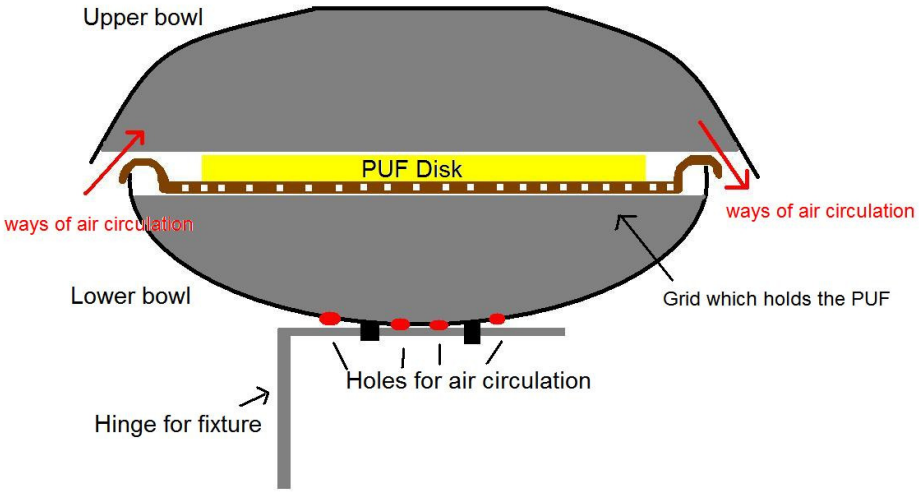


Figure 9: Schematic design of a PUF passive air sampler.

1.8.4 Why Passive Sampling?

Concentrations of analytes in air can be determined sampling the medium either by passive or active sampling. Active air sampling is usually designed as a sampling device that is fixed to a high or low volume pump. This approach allows controlling the flow or volume of the air and is appropriate for high-resolution measurements where a high sampling volume is required to collect a sufficient amount of analytes. However, active air sampling equipment is very expensive, bulky and heavy, resulting in high financial and logistic effort for sampling campaigns. Furthermore, active air samplers require electricity to work and cause noises and fumes, making them inappropriate for indoor air measuring.

Compared to active air samplers, passive air samplers are very cheap. Their small size and low weight makes them easy to transport. Passive air samplers do not require electricity. They are not noisy nor do they produce fumes. This makes them the ideal sampling device for indoor air sampling campaigns, but also for long-term outdoor air monitoring campaigns in remote areas where there is no access to electricity. As there is no sampling volume control, passive air sampling is appropriate to determine time-weighted average (TWA)

concentrations of analytes in air. Thus passive air samplers are the ideal sampling device for long-term monitoring studies (Hazrati and Harrad 2007).

II. OBJECTIVES OF THIS STUDY

There are still many unknowns regarding the sources of volatile PFC in the environment. Particular shops, households and certain branches of the industry have been reported to produce, sell, or apply PFC-containing products. However, limited data is available about PFC indoor air contamination levels of these locations. Therefore the overall goal of this study is determining PFC indoor air concentrations in places that are regarded as being possible sources for the release of volatile PFC.

Specifically the objectives are:

1. The assessment of indoor air contamination. What are the levels of PFC indoor air concentrations in different shops producing or selling PFC-containing products? Are there differences in the PFC indoor air concentration levels of residential and non-residential houses?

2. The evaluation of indoor air. Is indoor air a significant source for the release of volatile PFC into the environment?

3. The investigation of potential human exposure towards PFC indoor air contaminations. How do indoor air contaminations of precursors contribute to the daily intake of persistent PFC?

4. The evaluation of passive samplers as devices for indoor air sampling. Are passive samplers an appropriate, cost-efficient device for indoor air PFC sampling?

5. The optimization of a sampling and extraction method for indoor air passive sampling of volatile PFC.

III. METHOD DEVELOPMENT

3.1 EXPERIMENTAL

3.1.1 Chemicals

Solvents used in this study were acetone (Picograde, Promochem, Wesel, Germany), dichloromethane (DCM) (Picograde, Promochem, Wesel, Germany), hexane (Picograde, Promochem, Wesel, Germany) and methyl *tert*-butyl ether (MTBE) (SupraSolv, Merck, Darmstadt, Germany).

Native analytes used were 4:2 FTOH (3,3,4,4,5,5,6,6,6-Nonafluoro-1-hexanol, Sigma Aldrich, Steinheim, 97%), 6:2 FTOH (1H, 1H, 2H, 2H Perfluorooctanol, Fluorochem, Glossop, England, 97%), 8:2 FTOH (1H, 1H, 2H, 2H Perfluoro-1-decanol, Fluorochem, Glossop, England, 97%), 10:2 FTOH (1H, 1H, 2H, 2H Perfluoro-1-dodecanol, Fluorochem, Glossop, England, 97%), 12:2 FTOH (2-Perfluorododecylethanol, Fluorochem, Glossop, England, 97%), 6:2 FTA (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctylacrylate, Sigma Aldrich, Steinheim, Germany, 97%), 8:2 FTA (2-(Perfluorooctyl)ethylacrylate, Fluorochem, Glossop, England, 97%), 10:2 FTA (2-(Perfluorodecyl)ethylacrylate, Fluorochem, Glossop, England, 97%), MeFBSA (N-methylperfluorobutanesulfonamid, 3M, Stockport, England, >95%), MeFBSE (N-methylperfluorobutanesulfonamidoethanol, 3M, Stockport, England, >99%), MeFOSA (N-Methylperfluorooctanesulfonamide, Campro Scientific, Berlin, Germany, 97%), MeFOSE (N-Methylperfluorooctanesulfonamidoethanol, 3M, Stockport, England, 98%), EtFOSA (N-Ethylperfluorooctanesulfonamide, ABCR, Karlsruhe, Germany, 95%) and EtFOSE (N-Ethylperfluorooctanesulfonamidoethanol, 3M, Stockport, England, 98%).

The following mass- labelled standards were used: 4:2 FTOH ^{13}C (2-perfluorobutyl-[1,1-H2, 1,2-13C2] ethanol, Campro Scientific, Berlin, Germany, >98%), 6:2 FTOH ^{13}C (2-perfluorohexyl-[1,1-2H2, 1,2-13C2] ethanol, Campro Scientific, Berlin, Germany, >98%), 8:2 FTOH ^{13}C (2-Perfluorooctyl-(1,1-^{2}H2)-(1,2-13C2)-ethanol, Campro Scientific, Berlin, Germany, >98%), 10:2 FTOH ^{13}C (2-Perfluorodecyl-(1,1-^{2}H2)-(1,2-13C2)-ethanol, Campro Scientific, Berlin, Germany, >98%), EtFOSA D_5 (N-Ethyl-d5-perfluoro-1-octanesulfonamide, Campro Scientific, Berlin, Germany, >98%), MeFOSA D_3 (N-Methyl-d3-perfluoro-1-octanesulfonamide, Campro Scientific, Berlin, Germany, >98%), MeFOSE D_7 (2-(N-deuteriomethylperfluoro-1-octanesulfonemanido)-1,1,2,2,-tetradeuterioethanol, Campro Scientific, Berlin, Germany, >98%) and EtFOSE D_9 (2-(N-deuterioethylperfluoro-1-

octanesulfonemanido)-1,1,2,2,-tetradeuterioethanol, Campro Scientific, Berlin, Germany, >98%). ^{13}C3 TCB (^{13}C3 trichlorobenzene; Dr. Ehrenstorfer GmbH, Augsburg, Germany, 97%) was used as injection standard for GC-MS analysis.

3.1.2 Preparation of sampling equipment

PUF disks (14 cm x 1.35 cm, surface area 365 cm^{-2}, mass 4.40 g, density 0.00213 g cm^{-3}, Tisch Environmental, Cleves, Ohia, USA) were cleaned by ultrasonication with acetone for three consecutive times, dried in a clean lab and stored in glass jars. Amberlite XAD-4 polymeric resin (GFS chemicals, Powell, Ohia, USA) was grinded in a ball mill (Retsch, Haan, Germany) and cleaned with acetone and dichloromethane for each 24 hours using Soxhlet extraction. 6.5 g of the powdered XAD-4 was suspended in 1L of hexane and was thoroughly stirred. This suspension was used to impregnate a set of ten PUF-disks. Each disk was dipped and pivoted in the suspension for three times, then dried in a clean lab and stored in Petri dishes. The sorbent impregnated (SIP) disks were weighted before and after impregnating to make sure the XAD-4 powder was distributed uniformly to all disks. Each disk was impregnated with an average XAD-4 mass of 450 mg ± 87 mg.
Passive samplers (Tisch Environmental, Cleves, Ohia, USA) used for this study consisted of a stainless steel housing (diameter 25 cm) with a stainless steel grid to hold the PUF disk inside. Air circulation within the samplers was assured by a gap between the upper and the lower bowl and several holes in the bottom. Prior to deployment, passive samplers were cleaned in a washer, manually wiped with acetone and stored in a clean lab.

3.1.3 Recovery rates of spiked solvent

Triplicate volumes of 250 mL solvent (acetone/MTBE 1:1) were spiked with 80 µL of a solution containing the following mass-labelled substances: 4:2 FTOH ^{13}C, 6:2 FTOH ^{13}C, 8:2 FTOH ^{13}C, 10:2 FTOH ^{13}C, EtFOSA D_5, MeFOSA D_3, MeFOSE D_7 and EtFOSE D_9 (750 µg mL^{-1}). Solvent was reduced to 10 mL using rotary evaporators (Büchi, Flawil, Switzerland) at a pressure of 420 mbar and a temperature of 30°C. Solvent was further reduced under a gentle stream of preheated nitrogen to a volume of 150 µL (Nitrogen evaporator, Barkey, Leopoldshöhe, Germany). Samples were transferred to amber glass vials and 50µL of injection standard ^{13}C3 TCB (400 pg μL^{-1}) were added. All vials were stored in a freezer at -20°C until gas chromatography – mass spectrometry (GC-MS) analysis.

3.1.4 Extraction tests

3.1.4.1 Fluidized-bed extraction (FBE)

Three SIP disks were spiked with 80 µL of a solution (750 µg mL^{-1}) containing the following mass-labelled substances: 4:2 FTOH ^{13}C, 6:2 FTOH ^{13}C, 8:2 FTOH ^{13}C, 10:2 FTOH ^{13}C, EtFOSA D_5, MeFOSA D_3, MeFOSE D_7 and EtFOSE D_9 and 80 µl of a solution (750 µg mL^{-1}) containing the following native substances: 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 6:2 FTA, 8:2 FTA, 10:2 FTA, MeFBSA, MeFBSE, MeFOSA, MeFOSE, EtFOSA and EtFOSE. SIP disks were extracted by fluidized-bed-extraction (FBE) (IKA-Werke, Staufen, Germany) using 200 mL of a 1:1 blend of acetone and MTBE as solvent. Samples were extracted in three consecutive heating and cooling cycles. For each cycle samples were heated up and kept at 70°C for 30 minutes and then cooled down to 30°C. After extraction solvent was reduced to 10 mL using rotary evaporators at a pressure of 420 mbar and a temperature of 30°C. Solvent was further reduced under a gentle stream of preheated nitrogen to a volume of 150 µL. Samples were transferred to amber vials and 50µL of injection standard $^{13}C3$ TCB (400 pg μL^{-1}) were added. All vials were stored in a freezer at -20°C until GC-MS analysis.

3.1.4.2 Soxhlet extraction (SXL)

Three SIP disks were spiked with 80 µL of a solution (750 µg mL^{-1}) containing the following mass-labelled substances: 4:2 FTOH ^{13}C, 6:2 FTOH ^{13}C, 8:2 FTOH ^{13}C, 10:2 FTOH ^{13}C, EtFOSA D_5, MeFOSA D_3, MeFOSE D_7 and EtFOSE D_9 and 80 µL of a solution (750 µg mL^{-1}) containing the following native substances: 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 6:2 FTA, 8:2 FTA, 10:2 FTA, MeFBSA, MeFBSE, MeFOSA, MeFOSE, EtFOSA and EtFOSE. SIP disks were extracted with Soxhlet extraction. Each sample was extracted twice (with fresh solvent each) for 24 hours at 70°C with 500 mL acetone/MTBE (1:1) as solvent. After extraction the volumes of the sample extract fractions were reduced to 5 mL each using rotary evaporators at 420mbar and 30°C. Matching extract fractions of each SIP disk were unified in polyethylene centrifuge tubes. Tubes were centrigfugated for 15 minutes at 3000U (Universal 320 centrifuge, max. RCF = 21,382, Hettich Zentrifugen, Tuttlingen, Germany) to separate remaining XAD-4-powder from the solvent. Samples were transferred into 10 mL glass vials and solvent was reduced to 150 µL under a gentle stream of preheated nitrogen, then all samples were transferred to amber vials. 50 µL of injection

standard ^{13}C3 TCB (400 pg μL^{-1}) were added. All vials were stored at -20°C until GC-MS analysis.

3.1.4.3 Ultrasonic extraction (US)

Three SIP disks were spiked with 80 µL of a solution (750 µg mL^{-1}) containing the following mass-labelled substances: 4:2 FTOH ^{13}C, 6:2 FTOH ^{13}C, 8:2 FTOH ^{13}C, 10:2 FTOH ^{13}C, EtFOSA D_5, MeFOSA D_3, MeFOSE D_7 and EtFOSE D_9 and 80 µL of a solution (750 µg mL^{-1}) containing the following native substances: 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 6:2 FTA, 8:2 FTA, 10:2 FTA, MeFBSA, MeFBSE, MeFOSA, MeFOSE, EtFOSA and EtFOSE. Each SIP disk was placed in a 250 mL glass flask and 200 mL of acetone/MTBE (1:1) as solvent were added. Flasks were covered with aluminium foil and extracted with ultrasonication thrice (Sonorex, Bandelin, Mörfelden-Walldorf, Germany) with fresh solvent each for 60 minutes at 25°C. After extraction the volumes of the sample extract fractions were reduced to 5 mL each using rotary evaporators at 420 mbar and 30°C. Matching extract fractions of each SIP disk were unified in polyethylene centrifuge tubes. Tubes were centrigfugated for 15 minutes at 3000U to separate remaining XAD-4-powder from the sample. Samples were transferred into 10 mL glass vials and solvent was reduced to 150 µL under a gentle stream of preheated nitrogen, then all samples were transferred to amber vials. 50 µL of injection standard ^{13}C3 TCB (400 pg μL^{-1}) were added. All vials were stored at -20°C until GC-MS analysis.

3.1.5 Comparison of impregnated and unimpregnated sampling media

To compare the extraction efficiencies of analytes spiked to unimpregnated PUF disks and sorbent- impregnated SIP disks, triplicate unimpregnated PUF disks and triplicate SIP disks were spiked with each 80 µL of a solution (750 µg mL^{-1}) containing the following mass-labelled substances: 4:2 FTOH ^{13}C, 6:2 FTOH ^{13}C, 8:2 FTOH ^{13}C, 10:2 FTOH ^{13}C, EtFOSA D_5, MeFOSA D_3, MeFOSE D_7 and EtFOSE D_9. Samples were extracted with FBE and further worked up as described in section 3.1.4.1.

3.1.6 Uptake study

To determine the uptake behaviour of PFC for this study, an uptake study was carried out during which seven passive samplers were deployed in a building with the highest PFC air contaminations of this study. The temperature was 25°C. All samplers were deployed at the same starting time and harvested individually after 1, 5, 7, 14, 18, 22 and 25 days. Prior to FBE extraction and further laboratory work up as described in section 3.1.4.1, samples were spiked with 80 µL of a solution containing the following surrogates to check recovery rates (4:2 FTOH ^{13}C, 6:2 FTOH ^{13}C, 8:2 FTOH ^{13}C, 10:2 FTOH ^{13}C, EtFOSA D_5, MeFOSA D_3, MeFOSE D_7, EtFOSE D_9; 750 µg mL^{-1}).

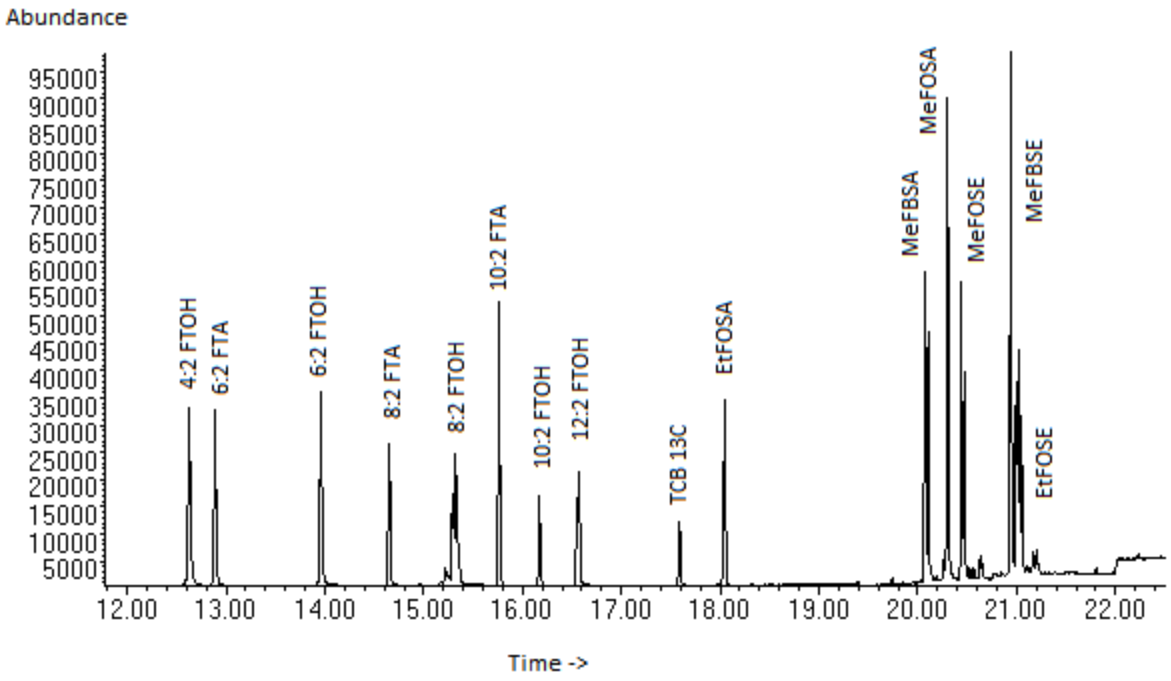
3.1.7 Separation and Detection

Analytes were separated by gas chromatography (GC) and detected by mass spectrometry (MS) in positive chemical ionization mode (PCI). For chromatographic separation and analysis an Agilent 6890N GC and Agilent 5975 MSD (Agilent Technologies, Waldbronn, Germany) were used. The following parameters were used for analysis:
COLUMN: Supelco Wax10 capillary column (60m length, 250.0 µm diameter, 0.25 µm film thickness, Sigma-Aldrich, Steinheim, Germany), constant column flow at 1.5 mL min^{-1} ; carrier gas: helium (5.5, Linde AG, Pullach, Germany); INLET: injection volume: 2 µl; pulsed splitless injection mode; initial inlet temperature: 60°C, final inlet temperature 275°C, heating rate: 400 °C min^{-1} to 270 °C (hold for 20 min), pulsed splitless injection (40 psi); OVEN: Initial oven temperature 50°C hold for 2 min, 3°C min^{-1} to 70°C hold for 0 min, 10°C min^{-1} to 130°C hold for 0 min, 20°C min^{-1} to 220°C hold for 0 min, 120°C min^{-1} to 275°C hold for 5 min, 10°C min^{-1} to 270°C hold for 10 min, run time: 35.13 min; MS: transfer line temperature: 250°C, ion source temperature: 300°C, reactant gas: methane (Messer Group GmbH, Krefeld, Germany), quadruple temperature: 150°C. All samples were detected in selected ion monitoring (SIM) mode. Parameters are given in table 5.

Table 5: mass fragments of compounds analysed in this study. m/z: mass to charge ratio.

Analyte	m/z quantifier	m/z qualifier 1	m/z qualifier 2
4:2 FTOH	265	227	293
6:2 FTOH	365	327	393
8:2 FTOH	465	427	493
10:2 FTOH	565	527	593
12:2 FTOH	665	627	693
6:2 FTA	418	447	-
8:2 FTA	518	547	-
10:2 FTA	618	647	-
MeFBSA	314	294	292
MeFBSE	340	358	293
MeFOSA	514	-	-
MeFOSE	540	540	-
EtFOSA	528	-	-
EtFOSE	572	554	-
4:2 FTOH ^{13}C	268	269	231
6:2 FTOH ^{13}C	368	369	331
8:2 FTOH ^{13}C	468	469	431
10:2 FTOH ^{13}C	568	569	531
MeFOSA D_3	516	517	-
MeFOSE D_7	564	547	565
EtFOSA D_5	532	533	-
EtFOSE D_9	580	563	581

Concentrations of analytes were determined using a seven-point calibration including all native analytes (10 pg μL^{-1} to 200 pg μL^{-1}). Concentrations of native analytes were corrected by the peak areas of the injection standard ($^{13}C3$ TCB). Instrumental limits of detection (LOD) and instrumental limits of quantification (LOQ) were adapted from Dreyer et al. (2008). They were less than 1 pg μL^{-1} (LOD) and less than 1.2 pg μL^{-1} (LOQ) for all analytes determined in this study (Dreyer et al. 2008). A SIM chromatogram of all native analytes determined in this study is given in figure 10.


Abundance
95000
90000
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
4:2 FTOH
6:2 FTA
6:2 FTOH
8:2 FTA
8:2 FTOH
10:2 FTA
10:2 FTOH
12:2 FTOH
TCB 13C
EtFOSA
MeFBSA
MeFOSA
MeFOSE
MeFBSE
EtFOSE
12.00
13.00
14.00
15.00
16.00
17.00
18.00
19.00
20.00
21.00
22.00
Time ->
Figure 10: SIM chromatogram of injection standard and native PFC determined in this study.

3.2 RESULTS

3.2.1 Recovery rates of spiked solvent

Results for the laboratory-work up and analysis of spiked solvent are given in table 6. Recovery rates (R) ± relative standard deviation (SD) were between 36 % ± 4.1 % (4:2 FTOH ^{13}C) and 78 % ± 2.6 % (MeFOSE D_7).

Table 6: Recovery rates (R) for spiked solvent (acetone/MTBE 1:1). SD standard deviation.

Analyte	R (%) ± SD (%)
4:2 FTOH ^{13}C	36 ± 4.1
6:2 FTOH ^{13}C	41 ± 5.0
8:2 FTOH ^{13}C	46 ± 4.5
10:2 FTOH ^{13}C	53 ± 3.9
MeFOSA D_3	56 ± 2.2
MeFOSE D_7	78 ± 2.6
EtFOSA D_5	58 ± 2.7
EtFOSE D_9	68 ± 1.9

3.2.2 Extraction tests

Results for the extraction tests are given in table 7. Recovery rates ± relative standard deviations were between 14 % ± 3 % (4:2 FTOH) and 64 % 13 % (MeFOSE D_7) for FBE extraction, between 1.2 % ± 2.5 % (10:2 FTOH ^{13}C) and 53 % ± 26 % (8:2 FTOH) for Soxhlet extraction and between 7.1 % ± 2.0 % (4:2 FTOH ^{13}C) and 46 % ± 13 % (MeFOSE D_7) for ultrasonic extraction.

Table 7: Average recovery rates for extraction tests of native and mass-labelled standards used in this study. FBE: fluidized bed extraction, SXL: soxhlet extraction, US: ultrasonic extraction. *low values may be due to analytical problems.

Analyte	FBE R (%) ± SD (%)	SXL R (%) ± SD (%)	US R (%) ± SD (%)
4:2 FTOH	14 ± 3.0	22 ± 15	7.3 ± 2.7
6:2 FTOH	15 ± 3.0	24 ± 14	8.5 ± 3.0
8:2 FTOH	26 ± 4.7	53 ± 26	16 ± 4.3
10:2 FTOH	25 ± 2.9	7 ± 11*	13 ± 9.4
12:2 FTOH	29 ± 4.2	39 ± 16	25 ± 8.3
6:2 FTA	14 ± 1.9	16 ± 10	9.9 ± 4.1
8:2 FTA	15 ± 3.1	17 ± 11	12 ± 3.6
10:2 FTA	16 ± 3.1	12 ± 11	14 ± 3.1
MeFBSA	31 ± 1.2	46 ± 13	29 ± 8.5
MeFBSE	41 ± 3.9	39 ± 9.3	32 ± 9.3
MeFOSA	31 ± 2.3	33 ± 9.0	26 ± 7.7
MeFOSE	58 ± 10	49 ± 14	42 ± 16
EtFOSA	38 ± 2.7	43 ± 12	33 ± 10
EtFOSE	59 ± 11	48 ± 13	41 ± 16
4:2 FTOH ^{13}C	13 ± 3.1	20 ± 13	7.1 ± 2.0
6:2 FTOH ^{13}C	15 ± 5.7	23 ± 19	6.3 ± 2.3
8:2 FTOH ^{13}C	17 ± 3.5	27 ± 14	12 ± 2.4
10:2 FTOH ^{13}C	14 ± 4.7	1.2 ± 2.5*	8.3 ± 9.3
MeFOSA D_3	37 ± 3.2	39 ± 11	32 ± 6.3
MeFOSE D_7	64 ± 13	52 ± 14	46 ± 13
EtFOSA D_5	37 ± 2.8	40 ± 10	32 ± 6.4
EtFOSE D_9	57 ± 12	46 ± 13	40 ± 13

3.2.3 Comparison of impregnated and unimpregnated sampling media

Results for the FBE extraction of PUF disks and SIP disks are presented in table 8. Recovery rates ± relative standard deviation were between 12 % ± 0.2 % (4:2 FTOH ^{13}C) and 33 % ± 2.7 % (MeFOSE D_7) for PUF disks and between 13 % ± 3.1 % (4:2 FTOH ^{13}C) and 64 % ± 12.8 % (MeFOSE D_7) for SIP disks.

Table 8: Recovery rates for the extraction of PUF disks and SIP disks.

Analyte	PUF disks R (%) ± SD (%)	SIP disks R (%) ± SD (%)
4:2 FTOH ^{13}C	12 ± 0.2	13 ± 3.1
6:2 FTOH ^{13}C	13 ± 0.2	15 ± 5.7
8:2 FTOH ^{13}C	14 ± 0.1	17 ± 3.5
10:2 FTOH ^{13}C	14 ± 0.4	16 ± 4.7
MeFOSA D_3	29 ± 1.2	37 ± 3.2
MeFOSE D_7	33 ± 2.7	64 ± 13
EtFOSA D_5	29 ± 1.0	37 ± 2.8
EtFOSE D_9	30 ± 3.3	57 ± 12

3.2.4 Uptake study

The results for the uptake study of FTA, FTOH and FASA/E are presented in figures 11, 12 and 13. Uptake profiles of individual analytes are depicted as a plot of the total mass of analyte sequestered on the SIP disk against the deployment time of the passive sampler. Days given on the x-axis captions represent the days on which individual samplers were harvested.

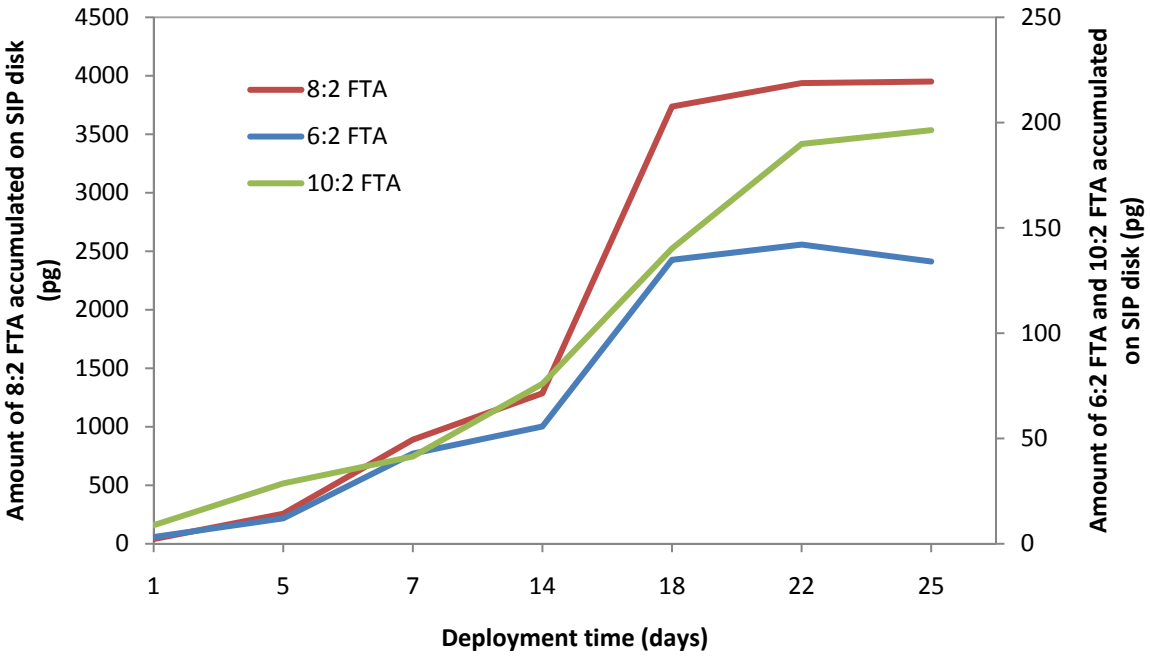


Figure 11: SIP uptake of FTA over the deployment time of 25 days.

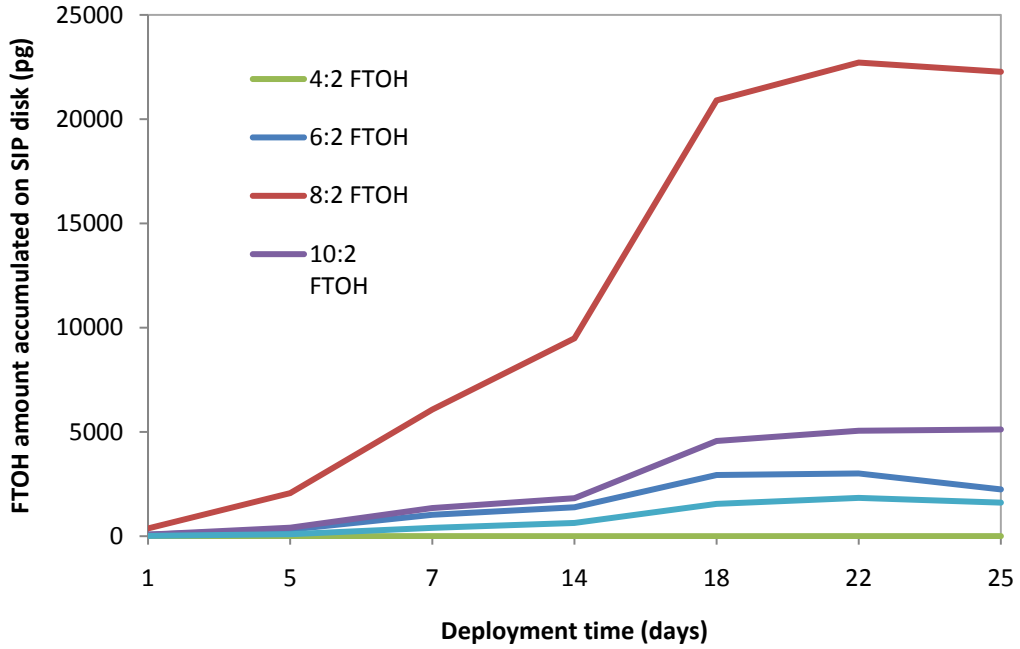


Figure 12: SIP uptake of FTOH over the deployment time of 25 days.

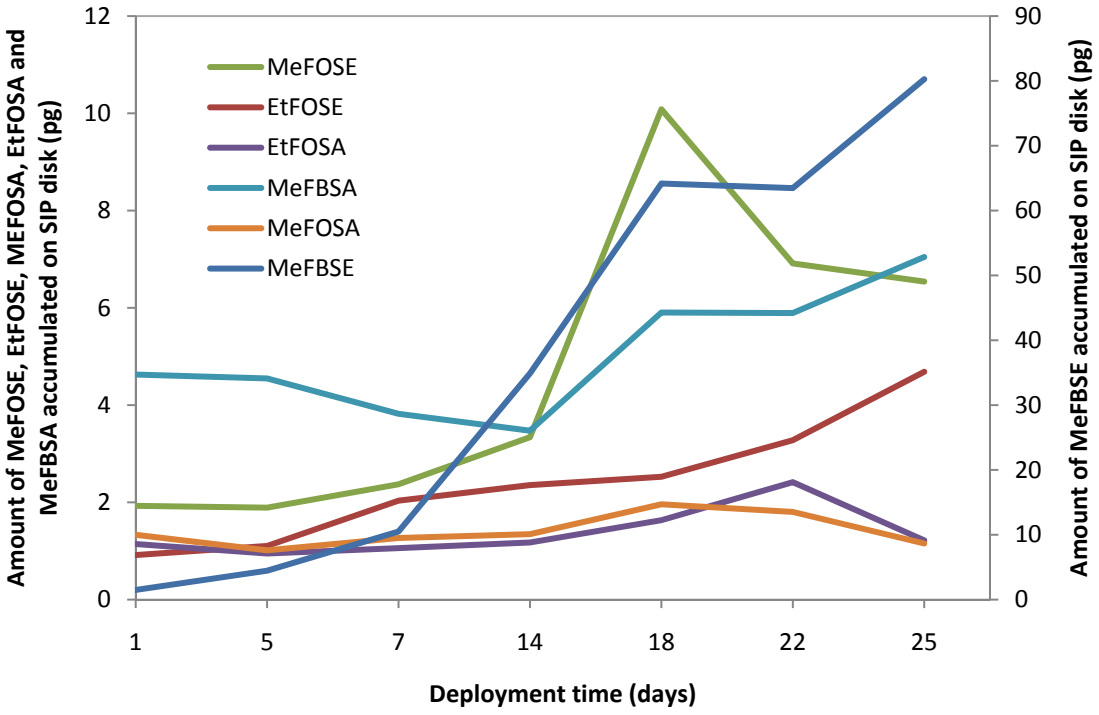


Figure 13: SIP uptake of FASA and FASE over the deployment time of 25 days.

3.3 DISCUSSION

3.3.1 Recovery rates of spiked solvent

Recovery rates of analyte groups increased in the order FTOH < FASA < FASE. Individual recovery rates of FTOH increased with addition of CF_2- groups to the molecule. This is likely to be caused by the increased volatility of shorter-chained FTOH (table 2). The higher recovery rates of FASA and FASE compared to FTOH can also be explained by the lower volatilities of FASA and FASE in relation to FTOH (table 2). Therefore losses of analytes during laboratory work-up are assumed to be mainly caused by high volatilities of individual PFC. This is confirmed by previous observations (Jahnke et al. 2007b).

3.3.2 Extraction tests

Ultrasonication yielded the lowest recovery rates for most analytes. Results for FBE and Soxhlet extraction were very similar. Recovery rates determined by FBE had the lowest standard deviations for most analytes, followed by ultrasonication and Soxhlet extraction. FBE extraction required about 250 mL solvent for each sample. Soxhlet extraction required about 500 mL solvent and Ultrasonication required 600 mL solvent per sample. Therefore FBE was the most cost efficient method. Overall, Soxhlet extraction took 48 hours, ultrasonication took 4 hours and FBE extraction took 3 hours. Soxhlet and ultrasonic extracted samples had to be centrifuged to separate XAD-4 remains from the extract, while the FBE method contained filtration with a cellulose filter which separated the XAD-4 powder from the solvent. Comparing the determined recovery rates, the time and cost efficiency as well as the general effort of each method, FBE was chosen as the most suited extraction method for indoor air sampling with SIP disks.

In contrast to the recovery rates observed in this study, Shoeib et al. (2008) determined recovery rates for the Soxhlet extraction of SIP disks that were significantly higher (table 9). However, it remains unclear whether the values of Shoeib et al. represent realistic conditions.

Table 9: Recovery rates (R) for the extraction of SIP disks from different studies. S.D. standard deviation.

Analyte	Shoeib et al. (2008) Soxhlet extraction R (%) ± SD (%)	This study Soxhlet extraction R (%) ± SD (%)
8:2 FTOH ^{13}C	87 ± 15	53 ± 26
MeFOSA D_3	86 ± 21	33 ± 9.0
MeFOSE D_7	126 ± 50	49 ± 14

The analytes determined in this study are very volatile and have low K_{OA} values (tables 2 and 3). It is therefore possible that crucial losses of analytes occurred during the analytical procedure in the laboratory due to evaporation processes of the analytes. During FBE extraction, analytes are exposed to a maximum temperature of 70°C and a temperature span of 40°C. Given the high vapour pressures of the analytes, it can be estimated that losses of analytes were caused mainly by off-gasing processes during work-up. Furthermore, low recovery rates of this study were supported by solvent recovery tests described in sections 3.1.1 and 3.2.1. Recovery rates of PFC for the extraction of PUF and XAD-2 resin from other studies were in the same order of magnitude as the ones from this study (Jahnke et al. 2007b; Dreyer et al. 2009c). Therefore it can be assumed that the recovery rates of this study represent reasonable values. The high recovery rates of PFC observed by Shoeib et al. might be caused by signal enhancement of analytes during GC-MS analysis due to matrix effects. This effect has been previously described for PFC (Jahnke et al. 2007b) and intensively elucidated by Dreyer et al. (2008).

3.3.3 Comparison of impregnated and unimpregnated sampling media

Recovery rates for the FBE extraction of SIP disks were higher compared to those of PUF disks. It has been observed that SIP disks have enhanced sorption capacities for volatile PFC than unimpregnated PUF disks (Shoeib et al. 2008). However, as demonstrated in this study, this does not result in lower recovery rates for the extraction of SIP disks compared to those of PUF disks. Therefore SIP disks were chosen as the sampling medium for indoor air sampling in this study.

3.3.4 Uptake study

Uptake profiles for FTA and FTOH (figures 11 and 12) clearly demonstrate that these analytes reached the equilibrium stage somewhere between 17 and 22 days under the sampling conditions of this study. The indoor air temperature remained constant (25°C) throughout the whole sampling duration. Samples were taken in a non-air-conditioned, windowless room. Significant gains or losses of the mass of 4:2 FTOH sequestered on the SIP disk over the whole sampling deployment period of 25 days were not observed. It is assumed that only a very small amount of 4:2 FTOH can be sequestered on the SIP disk due to the very high volatility and low K_{OA} value of this analyte (tables 2 and 3). Uptake patterns for FASA and FASE cannot clearly be derived from the uptake study (figure 13). Although

concentrations for individual FASA/E generally seem to increase from day 1 to day 25, no obvious trend can be observed as for FTOH and FTA. Individual masses of FASA (7 pg) and FASE (less than 80 pg) sequestered on the SIP disks were close to the instrumental LOD and LOQ. Therefore inaccuracies during the quantification of those analytes may have occurred. The results of the uptake study are confirmed by previous observations about uptake behaviour of PFC for SIP indoor air sampling. Shoeib et al. (2008) determined linear uptake to be roughly 21 days for FTOH and to be more than 80 days for FASA and FASE (Shoeib et al. 2008). Hence it is assumed that the uptake results for FASA and FASE of this study represent linear uptake. A deployment period significantly longer than 25 days is needed to determine more accurate uptake patterns for FASA and FASE. The duration for the deployment of all real samples of this study was chosen to be 14 days. This length of time is appropriate to assure all analytes are sequestered on the SIP disks during linear uptake.

3.3.5 Applicability of SIP-disk passive air samplers for PFC samples

PUF-disk passive air samplers used for this study were bought for about 85 Euro per unit (including 1 PUF disk and 1 passive sampler). Solvent and XAD-4 used for the impregnation cost about 200 euro to impregnate 50 PUF-disks. This is rather cheap compared to high-volume sampling equipment. Passive samplers are very easy to transport to the sampling locations as they weighted less than 500g per sampler. Set-up of the samplers was simple. At the sampling location samplers were easy to fix at any detached bar or pipe by using cable ties. The small size and the fact that the samplers did not require and electricity to sample and did not produce any noises or fumes made them very suited at any indoor location. Work-up of the samples in the labatory took about the same time as work-up of other samples (for example extraction of cartridges from high volume active air sampling) takes. However, extraction of SIP disks requires only half as much solvent (250 mL) as extraction of cartridges used for high volume sampling (500 mL) (Dreyer et al. 2008). Sampler housings can be reutilised several times as they consist of stainless steel and can easily be cleaned. PUF-disks need to be exchanged for every new sampling but they are very cheap (about 5 Euro each). A problem that occurred during method development were the low recovery rates for extraction of some analytes. This was probably due to the high volatilities of the analytes. It would be helpful to further optimize a method so that recovery rates for the extraction could possibly be improved. Summarizing, SIP-type passive samplers are appropriate for PFC indoor air sampling and recommendable for future sampling campaigns.

IV. STUDY

4.1 METHOD

4.1.2 Sites

Samples were taken in the following locations which have been described as potential sources for the release of PFC in the literature (Kissa 2001; Prevedouros et al. 2006; Jensen et al. 2008; Paul et al. 2009):

- 2 furniture shops (= “FS1”, “FS2”).
- 1 carpet shop (= “CAS”)
- 1 electroplating service (= “EP”)
- 1 coating service (=”COS”)
- 1 auto body shop (=”ABS”)
- 2 outdoor gear shops (=OS1”, “OS2a”, “OS2b”)

The furniture shops were selling different items. Furniture shop 1 was a three-storey building mainly selling upholstery. Furniture shop 2 consisted of only one salesroom and was selling mainly wooden furniture. Outdoor gear shop 1 was smaller than outdoor gear shop 2. Samplers in outdoor gear shop 1 and 2a were fixed in storage rooms that had higher densities of selling items than the salesrooms. The sampler in outdoor gear shop 2b was fixed in the salesroom adjacent to the storage room of outdoor gear shop2. Furthermore, samples were taken in the bedrooms of two residential homes (“H1”, “H2”) both non-carpeted and in one newly painted office (“OF1”) and one newly carpeted (“OF2”) office of the same building.

4.1.3 Sampling

Sampling equipment was prepared as described in section 3.1.2. SIP disks were transported in air tight sealed petri dishes to the sampling locations to avoid contamination during transport. At the sampling location SIP disks were placed inside of the sampler after wiping the grid with acetone. Samplers were deployed in duplicate in each sampling location for fourteen days. It was avoided to fix the samplers next to windows, ventilation shafts or direct sun light. Figure 14 depicts a picture of a set of samplers deployed in a sampling location. Samplers

were deployed for 14 days. After sampling SIP disks were taken out of the passive samplers and put in clean Petri disks during transport, then sealed air tight and stored in a cooling chamber at -20°C until extraction.

Figure 14: Passive samplers in a sampling location

4.1.4 Extraction

SIP disks were extracted with FBE using 200 mL of acetone/MTBE (1:1) as solvent. Prior to extraction, SIP disks were spiked with 80 µL of a solution containing the following surrogates to check recovery rates: 4:2 FTOH ^{13}C, 6:2 FTOH ^{13}C, 8:2 FTOH ^{13}C, 10:2 FTOH ^{13}C, EtFOSA D_5, MeFOSA D_3, MeFOSE D_7 and EtFOSE D_9 (750 µg mL^{-1}). The volume of the solvent was reduced to 150 µL and 50µL of injection standard $^{13}C3$ TCB (400 pg μL^{-1}) were added. Details on extraction and further analytical procedure are given in chapter 3.1.4.1.

4.1.5 Detection

Analytes were separated by gas chromatography and detected by mass spectrometry (GC-MS) in positive chemical ionization mode (PCI). For chromatographic separation and analysis an Agilent 6890N GC and Agilent 5975 MSD (Agilent Technologies, Waldbronn, Germany) were used. Details are given in chapter 3.1.7.

4.1.6 Calculation of indoor air PFC concentrations

Indoor air PFC concentrations were calculated applying the following equation:

$$C\ (A) = \frac{M}{k(A) * A(SIP) * d\ (t)}$$

where C(A) is the relative indoor air contamination of the analyte (pg m^{-3}), M is the total mass of analyte sequestered on the SIP disk (pg), k(A) is the airside mass transfer coefficient of the analyte (m d^{-1}), A(SIP) is the surface of the SIP disk (0.0365 m^2) and d (t) is the deployment time (14 days). Shoeib et al. (2008) published k(A) values for some analytes of this study (table 10). On the basis of these values and log K_{OA} values reported in the literature (table 3), k(A) values of remaining analytes of this study were estimated. 7.04 * 10^1 was used for MeFOSA and MeFBSA and 4.06 * 10^1 was used for MeFOSE. Values for FTOH were extrapolated to 1.26 * 10^2 (6:2 FTOH) and 1.28 * 10^2 (4:2 FTOH). 1.26 * 10^2 was used for 6:2 FTA, 1.24 * 10^2 was used for 8:2 FTA and 1.22 * 10^2 was used for 10:2 FTA.

Table 10: Airside mass transfer coefficients k(A) for FTOH and FASA/E (Shoeib et al. 2008).

Analyte	k(A) (m d^{-1})
8:2 FTOH	1.24 * 10^2
10:2 FTOH	1.22 * 10^2
MeFOSE	4.06 * 10^1
EtFOSA	7.04 * 10^1
EtFOSE	3.79 * 10^1

4.1.7 Statistical analysis

Statistical analysis was performed with Winstat version 2007. The Kolmogorov- Smirnov-Test was applied to determine if analyte concentrations and analyte compositions were normal – distributed. Cluster analysis applying the WARD agglomeration method was performed on normal-distributed PFC compositions. The number of clusters was determined according to the elbow – criterion. Concentrations of normal – distributed PFC were correlated using Pearson correlation. Correlation coefficients were determined for normal – distributed analyte concentrations of those sites assigned to previously determined individual clusters and also of sites of paired clusters. Furthermore, correlation coefficients were determined for all sites compared to each other.

4.1.8 Quality assurance and control

All experiments were carried out in a clean lab (class 10,000). Per- and polyfluorinated materials and polymers were avoided during all laboratory work steps and GC-MS analysis. Glassware and passive samplers were cleaned in a dish washer and dried at 250°C for 12 hours, then rinsed with solvent before use. Non-glassware materials were cleaned with acetone by ultrasonication twice and stored at 60°C until use. PUF-disks and XAD-4 were cleaned thrice by ultrasonication with acetone. After impregnation, SIP disks were stored in glass jars until use. All standards were used at room temperature. Internal and injection standards were used to correct for losses during laboratory work-up and GC-MS analysis. 4:2 FTOH ^{13}C was used to correct for 4:2 FTOH; 6:2 FTOH ^{13}C was used to correct for 6:2 FTOH and 8:2 FTA; 8:2 FTOH ^{13}C was used to correct for 8:2 FTOH; 10:2 FTOH ^{13}C was used to correct for 10:2 FTA, 10:2 FTOH and 12:2 FTOH. EtFOSA D_5 was used to correct for EtFOSA; MeFOSA D_3 was used to correct for MeFOSA and MeFBSA; MeFOSE D_7 was used to correct for MeFOSE and MeFBSE; EtFOSE D_9 was used to correct for EtFOSE. Average recovery rates were between 4.0% ± 0.1% (4:2 FTOH ^{13}C, outdoor shop2a) and 74% ± 14% (MeFOSE D_7, auto body shop). Details on recovery rates are given in the supporting information (table S6). A seven-point calibration (10 pg mL^{-1} to 200 pg mL^{-1}) was used for quantification of the analytes. Linearity was checked before each measurement. For GC-MS analysis, qualifier ions were chosen for every analyte when possible. Field and laboratory blanks were taken. Contamination, when detected, was insignificant. Details on blanks are given in the supporting information (table S7). SIP disks were stored and transported to the sampling locations in air tight sealed Petri dishes to avoid contamination. Duplicate samples were taken at each site. Combined and expanded measurement uncertainties according to ISO 20988 were calculated for average concentrations of all low contamination sites (H1, H2, OF1, OF2, COS, ABS, EP, FS1) and all high contamination sites (FS2, CAS, OS1, OS2a, OS2b). Combined uncertainty ranged from 5.5 % (MeFOSE) to 74 % (6:2 FTOH) in the low contamination sites and from 6.5 % (MeFOSE) to 151 % (4:2 FTOH) in the high contamination sites. Expanded uncertainty ranged from 12 % (MeFOSE) to 162 % (6:2 FTOH) in the low contamination sites and from 14 % (MeFOSE) to 328 % (4:2 FTOH) in the high contamination sites. Details are given in the supporting information (table S8).

4.2 RESULTS

4.2.1 Indoor air PFC concentrations

An overview of all concentrations of volatile PFC in indoor air is given in table 11. Figures 15 and 16 depict the total PFC indoor air concentrations and composition at all sites. Total PFC concentrations ranged from 8.2 ng m^{-3} (ABS) to 458 ng m^{-3} (OS1). Sum concentrations for FTA ranged from 0.2 ng m^{-3} (EP) to 152 ng m^{-3} (OS1), for FTOH from 3.3 ng m^{-3} (ABS) to 307 ng m^{-3} (OS2a) and for FASA/E from 4.4 ng m^{-3} (ABS) to 148 ng m^{-3} (FS2). Individual PFC indoor air contaminations determined in this study ranged from 42 pg m^{-3} (6:2 FTA, H1) to 209 ng m^{-3} (8:2 FTOH, OS1). FTOH were the dominating analyte group in most of the samples. 8:2 FTOH was mostly found in highest concentrations.. MeFBSE was observed in highest proportion at 72% (CAS), followed by 8:2 FTOH at 47% (OS2a).

Table 11: PFC indoor air concentrations (ng m^{-3}). n.d. not detected.

	H1	H2	OF1	OF2	COS	ABS	EP	FS1	FS2	CAS	OS1	OS2a	OS2b
4:2 FTOH	0.8	1.2	n.d.	1.1	n.d.	n.d.	1.0	n.d.	n.d.	n.d.	0.2	n.d.	n.d.
6:2 FTOH	1.1	2.9	3.4	6.0	1.1	0.6	0.1	1.3	33	9.9	20	37	13
8:2 FTOH	8.1	17	55	4.3	2.3	1.9	1.1	3.0	164	15	209	196	79
10:2 FTOH	1.9	5.1	2.4	1.1	0.8	0.5	0.1	0.9	44	4.1	48.1	54	28
12:2 FTOH	0.8	1.7	1.5	0.5	0.5	0.2	1.1	0.4	16	16	17.0	19	10
6:2 FTA	0.0	0.2	3.4	0.2	0.1	0.2	0.1	0.1	1.8	0.2	2.9	2.5	1.0
8:2 FTA	0.2	1.5	7.5	2.6	0.6	0.3	0.1	0.6	67	0.9	132	86	23
10:2 FTA	0.7	1.1	2.1	0.5	0.1	0.1	0.1	0.1	8.4	1.6	16	11	5.9
EtFOSA	1.2	1.6	1.5	1.2	0.8	0.8	1.2	1.1	1.5	0.5	1.0	1.6	1.0
MeFBSA	n.d.	n.d.	0.4	n.d.	0.6	0.4	1.0	0.8	1.2	2.8	0.8	1.4	0.6
MeFOSA	1.0	1.2	0.6	0.8	0.5	0.5	1.2	1.1	1.5	0.7	0.8	1.6	0.9
MeFOSE	2.7	3.1	2.0	2.3	1.0	1.1	1.3	1.6	1.3	2.0	1.2	1.2	1.6
MeFBSE	2.4	2.6	1.5	3.5	1.0	0.6	2.6	6.3	4.2	141	7.1	4.0	4.2
EtFOSE	2.1	2.2	1.5	2.1	1.2	0.9	1.7	1.4	2.0	0.7	1.0	1.9	9.0
Σ FTA	0.9	2.8	13	3.3	0.7	0.6	0.2	0.8	77	2.7	152	100	30
Σ FTOH	13	28	13	13	4.7	3.3	3.4	5.7	257	45	294	307	130
∑ FASA/E	9.4	11	7.6	9.8	5.0	4.4	9.0	12	12	148	12	12	17
Σ PFC	23	42	34	26	10	8	13	19	346	196	458	418	177

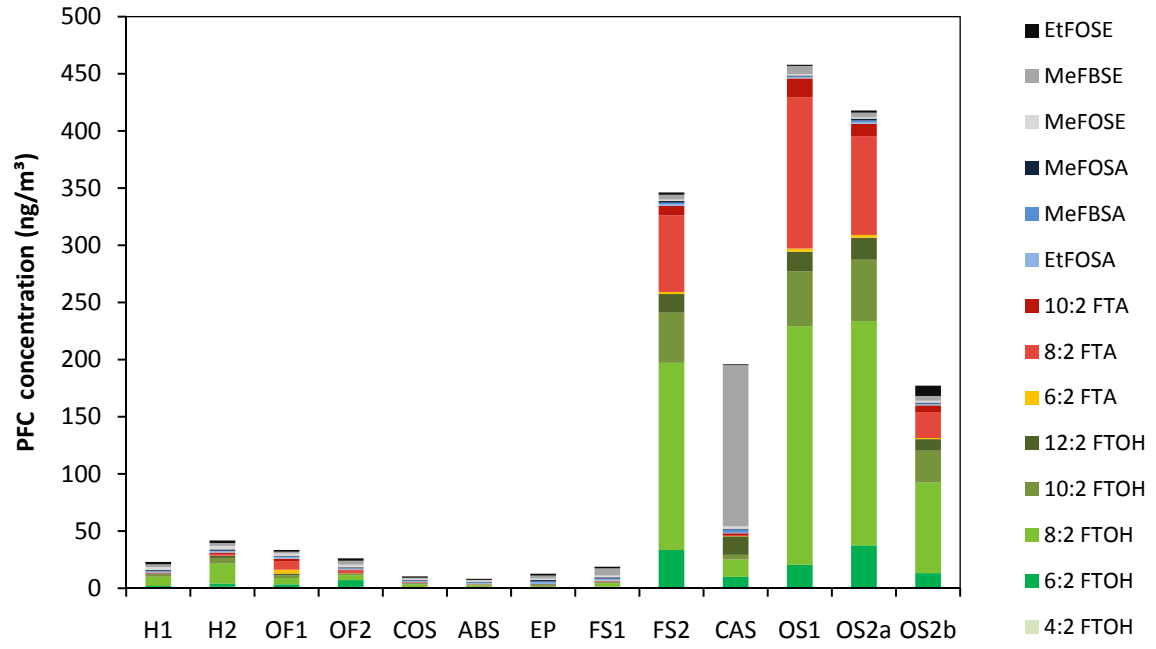


Figure 15: PFC concentrations in indoor air

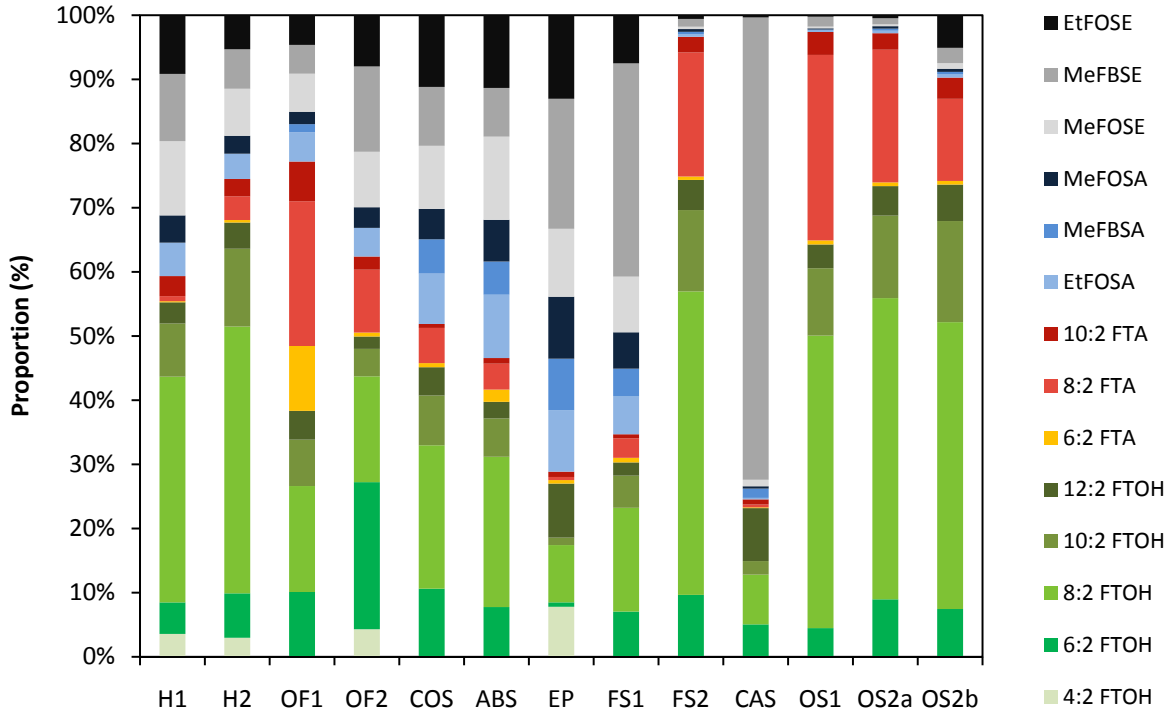


Figure 16: PFC composition in indoor air

2.2 Statistical analysis

The results of the cluster analysis are given in figure 17. According to their composition, sites can be divided into the following four clusters: cluster 1 (H1, H2, OF1, and OF2), cluster 2 (COS, ABS, FS1 and EP) cluster 3 (FS2, OS1, OS2a and OS2b) and cluster 4 (CAS).

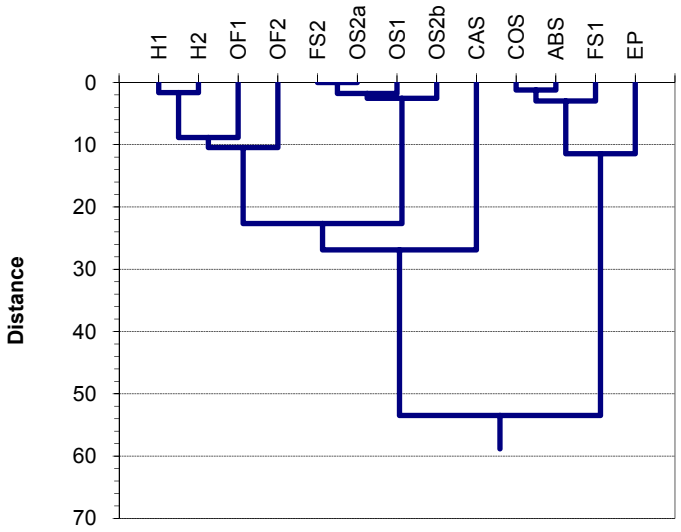


Figure 17: Cluster analysis on the basis of the analyte composition at all sites.

Pearson correlation coefficients (PCC) of all sites compared to each other are given in table 12. Pearson correlation coefficients of all analytes at all sites are given in table 13. Pearson correlation coefficients of all analytes in all determined clusters are given in the supporting information (tables S12 – S16).

From the PCC of all sites compared to each other, it can be observed that except for OF1, EP and CAS, which were significantly correlated to few sites, most of the other sites were significantly correlated to a large number of other sites (table 12). Both houses, both offices, both furniture shops and all outdoor gear shops were significantly correlated (table 12). For the PCC of all analytes in all sites, all FTOH (except 4:2 FTOH) and all FTA were significantly correlated to each other (table 13). For other analytes, only few individual correlations could be observed (table 13). For the PCC of paired clusters 3 and 4 (FS2, CAS, OS1, OS2a, OS2b), correlations between several FFA and FTOH were detected (table S9). Most FASA/E and 4:2 FTOH were significantly correlated to none or few other analytes (table S9). Similar correlations were observed for the PCC of all analytes in all sites of cluster 3 (FS2, OS1, OS2a, OS2b). Correlations for FTOH and FTA were slightly fewer,

while correlations for FASA/E were slightly higher (table S10). For the PCC of all sites of clusters 1 and 2 (H1, H2, OF1, OF2, COS, ABS, EP, FS1), some correlations within the FTOH/FTA groups were observed (table S11). 8:2 FTOH was also significantly correlated to some FASA/E (table S11). Few correlations were detected within individual FASA/E (table S11). There were less correlations after separating these clusters. Within the PCC of the analytes in the sites of cluster 1 (table S12) (H1, H2, OF1, OF2) there were no obvious correlations between FTOH and FTA as observed for the analytes of other individual and paired clusters. Most analytes of cluster 1 were significantly correlated to only few other analytes. MeFBSA was significantly correlated to all FTA (table S12). Similar observations were made for the PCC of the analytes in the sites of cluster 2 (table S13) (COS, ABS, EP, FS1). 10:2 FTA was significantly correlated to most other analytes. All FASA were significantly correlated to each other. Few correlations were detected between other analytes (table S13).

Table 12: Pearson correlation coefficients for all sites of this study. [a] ($p < 0.05$), [b] ($p < 0.01$).

	H1	H2	OF1	OF2	COS	ABS	EP	FS1	FS2	CAS	OS1	OS2a
H2	0.96[b]											
OF1	0.31	0.45										
OF2	0.52[a]	0.51[a]	0.46[a]									
COS	0.88[b]	0.85[b]	0.38	0.69[b]								
ABS	0.89[b]	0.82[b]	0.31	0.56[a]	0.96[b]							
EP	0.32	0.09	-0.44	0.10	0.33	0.37						
FS1	0.52[a]	0.38	0.04	0.53[a]	0.56[a]	0.50[a]	0.72[b]					
FS2	0.78[b]	0.91[b]	0.73[b]	0.51[a]	0.73[b]	0.65[b]	-0.18	0.21[a]				
CAS	0.19	0.06	-0.09	0.33	0.18	0.08	0.65[b]	0.90[b]	-0.04			
OS1	0.69[b]	0.82[b]	0.81[b]	0.44	0.63[b]	0.57[a]	-0.20	0.18	0.97[b]	-0.05		
OS2a	0.77[b]	0.90[b]	0.74[b]	0.50[a]	0.71[b]	0.64[b]	-0.19	0.20	1.00[b]	-0.05	0.98[b]	
OS2b	0.84[b]	0.95[b]	0.63[b]	0.48[a]	0.77[b]	0.70[b]	-0.11	0.25	0.98[b]	-0.02	0.93[b]	0.98[b]

Table 13: Pearson correlation coefficients for all analytes in all sites. a ($p < 0.05$), b ($p < 0.01$).

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTA	8:2 FTA	10:2 FTA	EtFOSA	MeFBSA	MeFOSA
6:2 FTOH	-0.37										
8:2 FTOH	-0.33	0.92[b]									
10:2 FTOH	-0.36	0.94[b]	0.99[b]								
12:2 FTOH	-0.44	0.89[b]	0.85[b]	0.86[b]							
6:2 FTA	-0.43	0.61[a]	0.68[b]	0.67[b]	0.55[a]						
8:2 FTA	-0.29	0.80[b]	0.97[b]	0.93[b]	0.78[b]	0.72[b]					
10:2 FTA	-0.32	0.81[b]	0.97[b]	0.94[b]	0.82[b]	0.74[b]	0.99[b]				
EtFOSA	0.33	0.32	0.28	0.30	-0.02	0.42	0.22	0.19			
MeFBSA	-0.48[a]	0.40	0.25	0.26	0.67[b]	0.10	0.19	0.21	-0.42		
MeFOSA	0.18	0.65[b]	0.53[a]	0.56[a]	0.43	0.19	0.39	0.37	0.67[b]	0.16	
MeFOSE	0.67[b]	-0.36	-0.40	-0.40	-0.32	-0.26	-0.41	-0.36	0.30	-0.33	0.04

4.3 DISCUSSION

4.3.1 Overall PFC contamination

Of the sites investigated in this study high and low contamination locations became obvious (figure 12). Sites of low PFC air contamination are H1, H2, OF1, OF2, COS, ABS, EP and FS1. Sites of high PFC air contamination are FS2, CAS, OS1, OS2a and OS2b. On average these sites' total PFC concentrations differ by a factor of fifty. Individual analyte concentrations are up to twothousand-fold higher in high contamination sites (132 ng m^{-3} of 8:2 FTA in OS1) compared to low contamination sites (0.06 ng m^{-3} of 8:2 FTA in EP). The results of the cluster analysis (figure 14) supported the separation of sampling locations into low and high PFC contamination sites. Clusters 1 and 2 consist of low contamination sites. Clusters 3 and 4 are composed of high contamination sites.

4.3.2 High contamination sites

Total PFC concentrations in the highly contaminated sites ranged from 177 ng m^{-3} (OS2b) to 458 ng m^{-3} (OS1). Similar composition of analytes was observed in all sites of cluster 3 (FS2, OS1, OS2a and OS2b). These samples were dominated by FTOH and FTA (> 90 %), with 8:2 FTOH and 8:2 FTA having the highest concentrations. Contribution of FASA/E to the overall PFC contamination were less than 10 % in these sites.

Both outdoor gear shops sampled in this study were selling a similar range of products (sleeping bags, tents, waterproof shoes and clothing). Both storage rooms had no windows and no air conditioning. Ventilation was enabled by the exchange of air through the doors to adjacent selling rooms. The determined concentrations of all analytes in the storage rooms of both locations were very similar, although the air volume of the storage room of OS1 was only about one fourth of that of OS2a. However, the ratio of the volume of selling products related to the indoor air volume was similar in both OS1 and OS2a. This indicates that the relation of PFC-releasing products to indoor air volume is more crucial for the magnitude of PFC indoor air concentrations than the size of the indoor air volume itself. Thus a room with a bigger volume does not necessarily have higher PFC indoor air concentrations compared to a room with a smaller air volume. This is confirmed by the ratio of PFC concentrations in the storage room of outdoor shop2 (OS2a) and in the sales room of the same location (OS2b). Both rooms contained similar products. The room volume of the sales room was about 3 times larger than that of the storing room. However, the density of products in the storage room was

much higher than that in the sales room. Resulting from this, determined PFC air concentrations in the storage room are more than twice as high as those from the sales room, with the composition of analytes being almost identical in OS2a and OS2b (figure 13). Product-wise, both outdoor shops were selling similar items. Hence it can be concluded that items available from outdoor gear shops (such as tents, clothes or shoes) are impregnated with 8:2 FTOH or 8:2 FTA - containing agents to a high degree. FASA/E impregnations are less often used.

Surprisingly, furniture shop2 has almost the same composition of analytes as both outdoor shops. FS2 was mainly selling wooden items, unlike the other furniture shop which containted a broad spectrum of furniture (e.g. sofas, beds, tables, etc. made of different materials). This may indicate that FS2 was selling products that had been impregnated with similar agents as those sold in the outdoor gear shops. This is also supported by significant correlations of 8:2 FTOH to 10:2 FTOH, 12:2 FTOH, 6:2 FTA and 8:2 FTA in all sites of cluster 3 (FS2, OS1, OS2a, OS2b) (table S10). FASA/E concentrations observed in the outdoor shops and FS2 were in the same order of magnitude as those detected in the low contaminated sites. Thus, the high PFC contaminations of FS2, OS1, OS2a and OS2b are due to strongly elevated FTOH and FTA concentrations.

In contrast to the remaining high contamination sites, the carpeting shop was characterized by different analyte composition. The contribution of FASA/E was about 75 % of the entire PFC contamination. The different proportions are reflected by cluster 4, which only containted this site. With about 25 %, proportions of FTOH were much lower than the proportion average. Although FTA concentrations were still up to 5 to 10 times higher than at low contaminated sites, their contribution at the carpet shop was insignificant compared to the remaining PFC classes. This location is characterized by a remarkable contamination with MeFBSE (141 ng m^{-3}) which is more than twentyfold higher than the concentrations determined at the other sampling locations. It appears that the shorter-chained substitutes have been applied for carpet impregnating agents in this location. This has not been observed in any other sampling location of this study. Being a C4-chained PFC, MeFBSE is used as a replacement molecule for the longer-chained PFC ($C \geq 8$) substances.

4.3.3 Low contamination sites

Total PFC concentrations of low contamination sites were less than 50 ng m^{-3}. They ranged from 8 ng m^{-3} (ABS) to 42 ng m^{-3} (H2). Except for 4:2 FTOH and MeFBSA in individual samples, all analytes were detected. As indicated by the cluster analysis, the low contamination sites can be further distinguished. The sites of cluster 1 (H1, H2, OF1 and OF2) represent residential homes and regular working environments. They were characterized by different proportions compared to the sites of cluster 2 (COS, ABS, FS1 and EP), which represent industrial locations. The sites of cluster 1 were dominated by elevated FTOH/FTA concentrations, whereas elevated FASA/E concentrations were detected in the sites of cluster 2. In comparison to the other low contaminated sites, H1 and H2 contained elevated FTOH (especially 8:2 FTOH) concentrations. This may be due to the application of household impregnating items such as shoe-spray or the existence of impregnated jackets and shoes in both households. There were no carpets in either of the houses. Hence carpet impregnating agents were no source for volatile PFC in these locations. H1, H2 and OF2 had very similar proportions of analytes. Elevated FTA concentrations of about 40 % were detected in OF1. This may be due to certain ingredients of paint, as the office had been freshly painted. Only few correlations between individual analytes of cluster 1 could be observed (table S12). This indicates that although the proportions and concentrations of analytes were similar for the sites of cluster 1, they were not caused by the same range of products. However, significant correlations between 8:2 FTOH and 10:2 FTOH, as well as MeFBSA, 6:2 FTA, 8:2 FTA and 10:2 FTA were detected. This may indicate that PFC-containing products (such as paint) that included aforementioned analytes were used in all sites.

At the sites of cluster 2 (COS, ABS, FS1 and EP), which represents the lowest PFC-contaminated sites of this study, FASA/E concentrations were observed to be higher than FTOH concentrations. Except for the carpet shop, this was not observed in any other site of this study. The coating service and the auto body shop were characterized by similar composition of analytes. This was possibly caused by the application of similar varnishes or coatings in both shops. A similar proportion of analytes as in the high contaminated CAS was observed in FS1, with FASA/E being the dominating analyte group. This may be due to the predominance of upholstery in the furniture shop. This suggests that carpets and upholstery are rather impregnated with FASA/E-containing products, whereas wooden furniture as sold in the high contaminated FS2 may be rather impregnated with FTOH and FTA-containing products.

Few correlations between individual FTOH and FTA as well as correlations between 10:2 FTA and several FASA/E were observed in the sites of cluster 2 (table S13). However, as the types of sites of cluster 4 differ significantly, it is not assumed that similar PFC-containing products were used at any of the sites.

4.3.4 Comparison of residual and non-residual PFC air contaminations

The two residential homes that were sampled in this study belong to the low contaminated sites. PFC indoor air concentrations of residential homes that have been previously published were in the same order of magnitude as the PFC air concentrations in the houses that were determined in this study (table 4) (Barber et al. 2007; Shoeib et al. 2004; Fromme et al. 2009a). However, not only the residential houses, but also most of the indoor air samples of this study were characterized by low PFC air concentrations. Therefore residential houses do not necessarily contain lower PFC air concentrations than buildings in which PFC-containing goods may potentially be applied or sold. Yet, all highly contaminated sites of this study were non-residential. Therefore it can be concluded that houses are potentially low PFC-contaminated and non-residential sites can be either low or high contaminated, depending on the amount/density and type of PFC-containing products in the location. To further investigate this assumption, the number of samples taken at both residential and non-residential houses need to increased.

4.3.5 Comparison to PFC previously determined indoor and outdoor air

Individual PFC concentrations and compositions are consistent with previous findings in indoor and outdoor air (Barber et al. 2007; Jahnke et al. 2007d; Shoeib et al. 2008; Dreyer et al. 2009c). FTOH and FASA/E indoor air concentrations have been previously determined in residential houses (Barber et al. 2007; Shoeib et al. 2008). PFC air concentrations determined in these studies were in the same order of magnitude as in the low contaminated sites of this study (table 11). FTA have not been determined in indoor air so far. FTOH concentrations of this studies' high contamination sites of were up to fiftyfold higher than those published in previous studies. Comparison indicates that there is widespread application and use of PFC containing products by consumers/households and industry. This potentially results in low-level PFC contamination of indoor air that is characterized by similar substance composition. Elevated PFC concentrations as observed in this study (e.g. MeFBSE concentration in CAS) were likely caused by specialized application using particular substances.

Determined individual indoor air PFC concentrations of this study are several orders of magnitude higher than published individual outdoor air PFC concentrations. Marine PFC background concentrations range around 1.5 pg m^{-3} for FTA (Dreyer et al. 2009c), 10 – 20 pg m^{-3} for FTOH (Shoeib et al. 2006; Dreyer et al. 2009c) and 2 – 3 pg m^{-3} for FASA/E (Dreyer et al. 2009c). Total PFC air concentrations in urban and semi-urban areas were usually less than 1000 pg m^{-3} (Barber et al. 2007; Dreyer et al. 2009d), with maximum PFC group concentrations ranging around 120 pg m^{-3} for FTOH, 50 pg m^{-3} for FTA and 80 pg m^{-3} for FASA/E (Dreyer et al. 2009d). Outdoor air PFC samples are characterized by proportions of more than 80% of FTOH followed by FASE, FTA, and FASA (Barber et al. 2007; Jahnke et al. 2007d; Dreyer et al. 2009d). Results of this study demonstrate that there were different composition patterns for indoor air PFC. Most of the high contamination sites of this study were composed by FTOH > FTA > FASA/E (FS2, OS1, OS2a, OS2b) or FASE > FTOH > FASA > FTA (CAS). Although there was no general composition pattern for the low contamination sites of this study, FTOH were the dominant PFC group in the sites of cluster 1 (H1, H2, OF1, OF2). This indicates that although there may be differences in the composition of analytes, it is likely that FTOH are detected in highest abundance in indoor and outdoor air. Besides, it is possible that due to lower vapour pressures and slightly higher log K_{OA} values of FASA/E compared to FTOH and FTA (tables 2 and 3), FASA/E may also adsorb to particulate matter in air masses which was not analysed in this study.

FTOH composition can be further expressed as concentration ratios of 6:2 FTOH to 8:2 FTOH to 10:2 FTOH relative to the FTOH of lowest concentration, as suggested by Piekarz et al (Piekarz et al. 2007). Average 6:2 FTOH : 8:2 FTOH : 10:2 FTOH concentration ratios were between 1.0 : 2.3 : 1.6 and 2.8 : 3.3 : 1.0 in rural Europe (Barber et al. 2007; Jahnke et al. 2007d), and between 1.0 : 2.3 : 1.2 and 2.0 : 3.8 : 1.0 in urban areas of Europe and Canada (Barber et al. 2007; Shoeib et al. 2008). FTOH ratios calculated from air samples of the Atlantic Ocean suggest that there was an overall decrease of 6:2 FTOH contributions and an increase of 10:2 FTOH from the north toward the south, while the 8:2FTOH contribution increased from its potential source region in temperate regions toward the north and the south (Dreyer et al. 2009c). Indoor air FTOH ratios were 1.0 : 2.0 : 1.0 and 1.0 : 1.1 : 1.2 in residential houses (Barber et al. 2007; Shoeib et al. 2008). As indicated by statistical analysis, correlations between all FTOH were detected (table 13). FTOH ratios of all sites of this study are given in table 14. They were between 1.4 : 2.3 : 1.0 (OF1) and 1.0 : 13.0 : 1.7 (EP) in the low contamination sites and between 1.0 : 4.9 : 1.3 (FS2) and

1.0 : 10.3 : 2.4 (OS1) in the high contamination sites. This demonstrates that an increased 8:2 FTOH ratio is detected at individual low and high contamination sites. The FTOH ratios of the samples taken in residential houses of this study are different to those previously published. Contribution of 8:2 FTOH was much higher in the residential houses of this study. Some of the FTOH ratios of sites of this study are very similar (e.g. OF1, COS, ABS, FS1 or OS2a and OS2b). This may indicate that PFC-containing products of similar FTOH composition products were used in those sites. On the other hand FTOH ratios of all sites of this study are variable. There does not seem to be a general trend for FTOH ratios in indoor air. This is likely due to the different product application patterns in the individual locations. Similar product application patterns may result in similar FTOH ratios. Summarizing, in terms of magnitude most FTOH ratios of this study were only slightly different to previously observed outdoor air FTOH ratios. Only few striking differences were detected.

Table 14: FTOH ratios

	6:2 FTOH	8:2 FTOH	10:2 FTOH
H1	1.0	7.2	1.7
H2	1.0	6.0	1.8
OF1	1.4	2.3	1.0
OF2	5.3	3.8	1.0
COS	1.4	2.9	1.0
ABS	1.3	3.9	1.0
EP	1.0	13.0	1.7
FS1	1.4	3.2	1.0
FS2	1.0	4.9	1.3
CAS	2.4	3.7	1.0
OS1	1.0	10.3	2.4
OS2a	1.0	5.2	1.4
OS2b	1.0	6.0	2.1

4.3.6 Are buildings potential sources for the release of volatile PFC into the atmosphere?

Natural sources for PFC are not known (Giesy and Kannan 2002). Therefore PFC detected in the environment must originate from anthropogenic point sources. Neutral PFC can be degraded by OH-radical oxidation processes (Ellis et al. 2003; Dinglasan et al. 2004). As OH-radicals are not produced indoors, there is no source for the degradation of neutral PFC in indoor air. As there are ventilation processes in residential and non-residential houses, neutral PFC in indoor air can be easily vented to the atmosphere. Furthermore, it has been observed that PFC concentrations in outdoor air from densely populous and industrialized areas are

significantly higher than those in outdoor air from rural areas (Barber et al. 2007; Dreyer et al. 2009d). Therefore buildings can be regarded as potential sources for the release of volatile PFC into the atmosphere.

4.3.7 Comparison to other organic pollutants determined in indoor air

In the past decades, an increasing number of organic pollutants have been detected in indoor air, including classic POPs like dichlorodiphenyltrichloroethane (DDT) or polychlorinated biphenyles (PCB) but also modern anthropogenic organic pollutants like polybrominated diphenyl ethers (PBDE). Determined air concentrations in residential houses were 3 – 340 pg m^{-3} for DDT (Bohlin et al. 2008) and 20 – 890 pg m^{-3} for hexachloro benzene (HCB) (Bohlin et al. 2008). Polyaromatic hydrocarbons (PAH) indoor air concentrations were less than 1 ng m^{-3} for benzo(a)anthracene (BaA) and less than 6 ng m^{-3} for chrysene (CRY), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IND) and benzo(ghi)perylen (BghiP) (Menichini et al. 2007). Polychlorinated biphenyles (PCB) have been detected at Σ 413 ng m^{-3} for six standard PCB (Heinzow et al. 2007). PBDE were observed at 55 pg m^{-3} (Takigami et al. 2009) and 8 to 477 pg m^{-3} (Fromme et al. 2009b). PFC sum indoor air concentrations in this study ranged from 8 ng m^{-3} (ABS) to 458 ng m^{-3} (OS1) and for individual PFC from 42 pg m^{-3} (6:2 FTA, H1) to 209 ng m^{-3} (8:2 FTOH, OS1). Total PFC concentrations of the high contamination sites of this study were in the same order of magnitude as detected Σ PCB concentrations. PFC concentrations in the low contamination sites were in the same order of magnitude as previously published DDT, HCB, BaA, IND, BghiP and PBDE concentrations.

4.3.8 Daily intake scenario

There are different pathways for the exposure of humans to persistent and toxic ionic PFC like PFOA and PFOS. Direct exposure of humans to ionic PFC occurs orally via intake of contaminated food and water or dermally via the appliance of PFC-containing products (Trudel et al. 2008; Vestergren et al. 2008). Exposure to precursor PFC occurs via inhalation of contaminated dust or air (Trudel et al. 2008). Analytes determined in this study can be metabolized to persistent PFC in the human body (Lange 2000; Vestergren et al. 2008) and therefore need to be taken into account in estimates of the daily human exposure to ionic PFC. It has been suggested that the intake of contaminated food and water is the main pathway leading to exposure to PFOS (91 %) and PFOA (99 %) (Fromme et al. 2009a, Vestergren et al. 2008).Vestergren et al. (2008) proposed that the contribution of precursors (FTOH and

FASA/E; FTA were not considered) in general consumer exposure to PFOS and PFOA is less than 1% for low-exposure scenarios, around 5% for intermediate scenarios and between 60 % - 80 % (PFOS) and 20 % - 60 % (PFOA) for high-exposure scenarios (Vestergren et al. 2008). Inhalation of precursors in indoor air is expected not to contribute significantly to the exposure to PFOS and PFOA in a low-exposure scenario, while it contributes at 1.6 – 3.5 % in an intermediate scenario and at 10 – 19 % in a high-exposure scenario (Vestergren et al. 2008). Overall, precursors are expected to cause a minor contribution to the daily intake doses of PFOS and PFOA (Fromme et al. 2009a, Trudel et al. 2008; Vestergren et al. 2008). Total daily intake of PFOS and PFOA (low-exposure to high-exposure) in humans of a general population of an industrialized country is estimated to range from 4 – 520 ng kg^{-1} d^{-1} (Vestergren et al. 2008) or 3 – 220 ng kg^{-1} d^{-1} (Trudel et al. 2008) for PFOS and 0.3 – 140 ng kg^{-1} d^{-1} (Vestergren et al. 2008) or 0.4 – 130 ng kg^{-1} d^{-1} (Trudel et al. 2008) for PFOA. Fromme et al. (2009a) suggested lower values, ranging between 1.6 - 8.8 ng kg^{-1} d^{-1} for PFOS and 2.9 – 12.6 ng kg^{-1} d^{-1} for PFOA (Fromme et al. 2009a).

On the basis of several studies investigating the conversion of precursors to PFCA and PFSA, Fromme et al. (2009a) estimated the conversion rates of FTOH to PFCA to be 5% and those of FASA/E to PFSA to be 20 % (Fromme et al. 2009a). Values for FTA have not been published, hence conversion rates of FTOH will be adopted for FTA. The total daily intake rate of air is assumed to be 13.3 m^3 (USEPA 1997). Fromme et al. (2009a) assumed that people generally spend 90 % of their daytime indoors and 10 % outdoors, resulting in a daily inhalation of 12 m^3 indoor air and 1.3 m^3 outdoor air (Fromme et al 2009a). In this study we estimate that people generally spend one third of their daytime at work and two thirds of their daytime at home. Subtracting the time they spend outdoors, this results in a total daily 4 m^3 indoor air inhaled at work and 8 m^3 indoor air inhaled at home. From these values a simple daily intake worst-case scenario (c = 100 %) determining the contribution of precursors (chain length = 8) to the daily intake of PFOA and PFOS for a person with a bodyweight of 70 kg can be made for the analytes of this study (table 15). Metabolism of other ionic PFC and elimination rates were not considered.

The results demonstrate that indoor air PFC contamination results in a daily PFOA intake between 0.01 ng kg^{-1} d^{-1} and 0.97 ng kg^{-1} d^{-1} at individual sites of this study. PFOS intake is between 0.04 ng kg^{-1} d^{-1} and 0.19 ng kg^{-1} d^{-1} at individual sites. Results for both PFOA and PFOS production are consistent with intermediate exposure estimates made by Trudel et al. (2008), Vestergren et al (2008) and Fromme et al (2009a). However, is has to be noted that the calculations made in this study are very simple and large uncertainties are remaining. For

more exact results it is suggested to collect further information about the uptake and metabolism rates of individual precursors and to take into consideration factors like elimination rates, bodyweight span or differences in air inhalation volumes.

Table 15: Calculations of the daily human intake of PFOS and PFOA produced by the metabolism of volatile precursors inhalated from indoor air.
[a] values copied from table 11. [b] Σ MeFOSA, EtFOSA, MEFOSE, EtFOSE. [c] values for intake rates calculated according to USEPA (1997) and Fromme et al. (2009a). [d] values calculated using conversion rates of 5% for FTOH and FTA and 20% for FASA/E (Fromme et al. 2009a) and a bodyweight of 70 kg.

Sampling location	Indoor air concentration (ng/m³)			Intake rate	Daily amount of PFOA produced	Daily amount of PFOS produced
	8:2 FTA[a]	8:2 FTOH[a]	Σ FASA/E[a,b]	(m^3 d^{-1})[c]	(ng kg^{-1} d^{-1})[d]	(ng kg^{-1} d^{-1})[d]
H1	0.2	8.1	6.9	8	0.05	0.16
H2	1.5	17	8.1	8	0.11	0.19
OF1	7.5	5.5	5.7	4	0.04	0.07
OF2	2.6	4.3	6.4	4	0.02	0.07
COS	0.6	2.3	3.5	4	0.01	0.04
ABS	0.3	1.9	3.3	4	0.01	0.04
EP	0.1	1.1	5.4	4	0.00	0.06
FS1	0.6	3.0	5.2	4	0.01	0.06
FS2	67	164	6.2	4	0.66	0.07
CAS	0.9	15	3.8	4	0.05	0.04
OS1	132	209	4.1	4	0.97	0.05
OS2a	86	196	6.4	4	0.81	0.07
OS2b	23	79	12.4	4	0.29	0.14

V. CONCLUSIONS AND OUTLOOK

In this study volatile PFC were detected in indoor air of residential houses and non-residential buildings like carpeting or outdoor gear shops, an electroplating service or an auto body shop. An optimized sampling and extraction method for PUF disk passive air sampling was developed which was regarded to be appropriate for indoor air PFC sampling. Among the sites sampled in this study, low and high PFC contamination sites were observed. While most high contamination sites were characterized by similar PFC composition, different PFC profiles were detected in the low contamination sites. At the carpet shop an increased amount of MeFBSE was detected. This suggests that this substance may have been used as a short-chain replacement for PFC with a chain length ≥ 8 which are assumed to be toxic. A daily intake scenario for the contribution of some of this study's analytes to the total daily intake of PFOS and PFOA was made. PFOS and PFOA intake via metabolism of inhaled precursors was calculated to be less than 1 ng kg^{-1} d^{-1} for both substances.

It would be desirable to further improve the PUF disk passive air sampling method, as the recovery rates for some analytes of this study were very low. Besides, the number of sites has to be considerably increased to collect more specific data on PFC indoor air contamination. Furthermore, it would be helpful to sample sites more than once to possibly collect data on temporal variations of PFC in indoor air or to link increase of PFC concentrations to certain events (e.g. delivery of new goods in a shop).

Resulting on the findings of this study, open questions remain. For example, it would be interesting to analyse product samples from shops and compare their PFC composition to respective indoor air PFC profiles. Yield and velocity rates for PFC release off products could be determined. PFC outdoor air samples could be taken next to sampled indoor air sites to observe possible concentration correlations. It would be of interest to determine possible losses of indoor air PFC concentrations due to ventilation processes. Summarizing, there are still many unknowns regarding PFC in indoor air which could be minimized by a lot of future research.

LITERATURE

3M "The science of organic fluorochemistry" US EPA Public docket OPPT AR226-0547 **1999**.

Ahrens, L.; Xie, Z. et al. *Poster presentation SETAC*: Warsaw, **2008**.

Ahrens, L.; Felizeter, S. et al. *Marine Pollution Bulletin* **2009,** 58, 1326-1333

Armitage, J.; Cousins, I.T. et al. *Environmental Science & Technology* **2006,** 40, 6969-6975.

Audenaert, F.; Lens, H.; Rolly, a.D. et al. *Journal of the Textile Institute* **1999,** 90, 76-94.

Barber, J. L.; Berger, U.et al. *Journal of Environmental Monitoring* **2007**, *9*, 530-541.

Bartkow, M.; Booij, E.K., et al. *Chemosphere* **2005,** 60, 170-176.

Begley, T.H.; White, K. et al. *Food Additives and Contaminations* **2005,** 22, 1023-1031

Bohlin, B.; Jones, K.C. et al. *Atmospheric Environment* **2008**, 42, 7234–7241.

Butt, C. M.; Young, C.J. et al. *Journal of Physical Chemistry* **2009,** 113, 3155-3161.

Chaemfa, C.; Barber, J.L. et al. *Environmental Pollution* **2008,** 156, 1290-1297.

Conder, J.M.; Hoke, R.A. et al. *Environmental Science &Technology* **2008**, *40*, 995-1003.

COP4, Press release COP4, Geneva, 9th May **2009**.

D'Eon, J. C. Hurley, M.D. et al. *Environmental Science &Technology* **2006**, *40*, 1862-1868.

Dinglasan-Panlilio, M. J. A. and Mabury, S.A: *Environmental Science & Technology* **2006,** 40, 1447-1453.

Dinglasan, M. J. A.; Ye, Y.; et al. *Environmental Science & Technology* **2004**, *38*, 2857-2864.

Dreyer, A.; Langer, V. et al *Journal of Chemical & Engeneering Data* **2009a,** in press.

Dreyer A.; Weinberg I. et al. *Environmental Science & Technology* **2009c,** 43, 6507–6514.

Dreyer, A.; Temme, C.; et al. *Journal of Chromatography A* **2008**, *1178*, 199-205.

Dreyer A.; Matthias, V. et al. *Environmental Science & Technology* **2009d**, 43, 4029-4036.

Dreyer, A.; and Ebinghaus, R. *Atmospheric Environment* **2009b,** 43, 1527-1535.

European Food Safety Authority (EFSA) *The EFSA Journal* **2008,** 653, 1-131.

Ellis, D. A.; Martin, J. W. et al. *Environmental Science & Technology* **2004**, *38*, 3316-3321.

Ellis, D. A.; Martin, J. W.; et al. *Environmental Science & Technology* **2003**, *37*, 3816-3820.

Falandysz, J.; Taniyasu, S. et al. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* **2007,** 42, 715-719.

Fiedler, S. et al. *Environmental Science & Pollution Research*, **in press.**

Fromme, H.; Korner, W. et al. *Environment International* **2009b,** 35, 1125-35.

Fromme, H.; Tittlemier, S. A.; et al. *International Journal of Hygiene and Environmental Health* **2009a,** 212, 239-270.

Giesy, J. P. and Kannan, K. *Environmental Science & Technology* **2001,** 35, 1339-1342.

Giesy, J. P. and Kannan, K. *Environmental Science & Technology* **2002,** 36, 146A-152A.

Gorecki, T. and J. *Namiesnik Trac-Trends in Analytical Chemistry* **2002,** 21, 276-291.

Hagen, D.F.; Johnson, B.J. et al. *Analytical Biochemistry* **1981,** 118, 336-343.

Harner, T.; Shoeib, M. et al. *Chemosphere* **2006,** 64, 262-267.

Hazrati, S. and Harrad, S. *Chemosphere* **2007,** 67, 448-455.

Heinzow, B.; Mohr, S. *Chemosphere* **2007,** 67, 1746–1753.

Hekster, F. M. "Perfluoroalkylated substances," University of Amsterdam, **2002**.

Herzke, D., Schlabach. M. et al. *Organohalogen Compounds,* **2008,** 70, 381-385.

Huber, S.; Smastuen, H.L. et al. *Organohalogen Compounds,* **2008,** 70, 394-397.

International Standard Organisation (ISO), Air Quality - Gudelines for estimating measurement incertainty. ISO 20988, **2007.**

Jahnke, A.; Ahrens, L. et al. *Analytical and Bioanalytical Chemistry* **2007b,** 387, 965-975.

Jahnke, A.; Ahrens, L. et al. C. *Environmental Science &Technology* **2007d**, *41*, 745-752.

Jahnke, A.; Berger, U. et al. *Environmental Science &Technology* **2007a**, *41*, 3055-3061.

Jahnke, A.; Huberc, S. et al. *Journal of Chromatography A* **2007c**, *1164*, 1-9.

Jensen, A. A.; Poulsen, P.B. et al. *Survey of Chemical Substances in Consumer Products* **2008,** 99.

Kaiser, M.; Barton C,A. et al. *Organohalogen Compound* **2006,** 68, 675-678.

Kannan, K.; Koistinen, J.; et al. *Environmental Science & Technology* **2001**, *35*, 1593-1598.

Kato, K.; Calafat, K.M. et al. *Organohalogen Compounds* **2008,** 70, 618-621.

Kissa, E. *Fluorinated surfactants and repellents. Second Edition revised and expanded.* New York, Marcel Dekker **2001.**

Ladics, G. S.; Stadler, J.C. et al. *Drug and Chemical Toxicology* **2005,** 28, 135-158.

Lange, C. C. "The Aerobic Biodegradation of N-EtFOSE Alcohol by the Microbial Activity Present in Municipal Wastewater Treatment Sludge", Biodegradation Study Report, 3M Project ID: LIMS E00-2252, **2000.**

Lange, C. C. "Biodegradation screen study for telomer type alcohols", U.S. EPA Public Docket AR-226-0555 **2002.**

Lau, C.A., Hodes, K. et al. *Toxicological Science* **2007,** 99, 366-394.

Lei, Y. D.; Wania, F. et al. *Journal of Chemical and Engineering Data* **2004,** 49, 1013-1022.

Liu, J. X. and L. S. Lee, L.S. *Environmental Science & Technology* **2007,** 41, 5357-5362.

Maras, M.; Vanparys, C., et al. *Environmental Health Perspectives* **2006,** 114, 100-105.

Menichini, E.; Iacovella, M. et al. *Atmospheric Environment* **2007,** 41, 9518–9529.

Moody, R. "After-treatment method for imparting oil- and water-reppelency to fabric", **2000.**

Muir, D. C. G. and Howards, P.H. *Environmental Science & Technology* **2006,** 40, 7157-7166.

Mylchreest, E., Ladics, G.S., et al. *Drug and Chemical Toxicology* **2005,** 28, 159-175.

NICNAS "Potassium perfluorobutane sulphonate". National Industrial Chemicals Notification and Assessment Scheme (NICNAS), **2005.**

OECD "Co-operation on existing chemicals hazard assessment of perluorooctance sulfonat (PFOS) and its salts", **2002.**

Oono, S.; Matsubara, E.; et al. *Bulletin of Environmental Contamination & Toxicology* **2008**, *80*, 102–106.

Paul, A. G.; K. C. Jones, et al. *Environmental Science & Technology* **2009,** 43, 386-392.

Piekarz, A. M.; Primbs, T.et al. *Environmental Science & Technology* **2007**, *41*, 8248-8255.

Pozo, K., Harner, T. et al *Environmental Science & Technology* **2006**, *40*, 4967 - 4973.

Prevedouros, K.; Cousins, I. T. et al. *Environmental Science & Technology* **2006**, *40*, 32-44.

Renner, R. *Environmental Science & Technology* **2001**, *35*, 154A-160A.

Renner, R. *Environmental Science & Technology* **2005,** *39*, 56A-57A.

Renner, R. *Environmental Science & Technology* **2006,** *40*, 12A-13A.

Rhoads, K. R.; Janssen E. M. L. et al. *Environmental Science & Technology* **2008**, *42*, 32873 - 2878.

Schenker, U.; Scheringer, M.; et al. *Environmental Science & Technology* **2008**, *42*, 3710-3716.

Schultz, M. M.; D. F. Barofsky, et al. *Environmental Engineering Science* **2003,** 20, 487-501.

Scientific Committee on Health and Environmental Risks, S. Opinion on RPA's report "Perfluorooctane Sulfonates Risk reduction strategy and analysis of advantages and drawbacks", **2004.**

Seethapathy, S.; Gorecki, T., et al. *Journal of Chromatography A* **2008,** 1184, 234-253.

Shoeib, M. and T. Harner *Environmental Science & Technology* **2002**, *36*, 4142-4151.

Shoeib, M.; T. Harner, et al. *Environmental Science & Technology* **2004**, *38*, 1313-1320.

Shoeib, M.; T. Harner, et al. *Analytical Chemistry* **2008,** 80, 675-682.

Shoeib, M.; Harner, T. et al. *Environmental Science & Technology* **2006**, *40*, 7577-7583.

Shoeib, M.; Harner, T. et al. *Environmental Science & Technology* **2005,** 39, 6599-6606.

Sinclair, E.; Kim, S.E. et al. *Environmental Science & Technology* **2007,** 41, 1180-1185.

Stock N.L.; L. F. K., et al. *Environmental Science & Technology* **2004a,** 38, 991-996.

Stock, N. L.; Furdui, V. I.; Muir, D. C. G.; Mabury, S. A. *Environmental Science & Technology* **2007**, 41, 3529-3536.

Takigami, H.; Suzuki, G. et al. *Chemosphere* **2009,** 76, 270–277.

Thuens, S.; Dreyer, A.et al. *Journal of Chemical and Enineering Data* **2009,** 54, 3022–3025.

Trinkwasserkommission, Bundesministerium für Gesundheit "Provisional evaluation of PFT in drinking water with the guide substances perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) as examples, **2006.**

Trudel, D., Horowitz, L. et al. *Organohalogen Compounds* **2008,** 70, 726 - 729.

Umweltbundesamt "Perfluorinated compounds: False alarm or justified concern?", **2009.**

Umweltbundesamt "Do without per- and polyfluorinated chemicals and prevent their discharge into the environment", Umweltbundesamt, UBA, **2009.**

USEPA, U. E. P. A. Public Docket AR226-629, **2000.**

USEPA, US Environmental Protection Agency, Revised draft: Hazard assessment of pefluoroctanoic acid and its salts, **2002a.**

USEPA, US Environmental Protection Agency, Telomer Research Program, USEPA, **2002b.**

USEPA, US Environmental Protection Agency, EPA's Summary Tables for 2008 Company Progress Report, **2008a.**

USEPA, US Environmental Protection Agency "2010/2015 Stewardship Program Homepage." from http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html, **2008b.**

Vestergren, R.; Cousins, I.T. et al. *Chemosphere* **2008,** 73, 1617–1624.

Vestergren, R. and Cousins, I.T. *Environmental Science & Technology* **2009,** 43, 5565-5575.

Vrana, B.; Mills, G.A. et al. *Trends in Analytical Chemistry* **2005,** 24, 854 - 868.

Wallington, T. J.; Hurley, M.D. et al. *Environmental Science & Technology* **2006,** 40, 924-930.

Walters, A. and Santillo, D. *Greenpeace Research Laboratories Technical Note* **2006.**

Wang, N.; Szostek, B. et al. *Environmental Science & Technology* **2005,** 39, 7516-7528.

Wang, T.; Wang, Y.W. et al. *Environmental Science & Technology* **2009,** 43, 5171-5175.

Whitman, W.G. *Chemical and Metallurgical Engineering* **1923,** 29, 146–150 .

Wölfle, D. "Fluortelomere - unerkanntes Risiko?" Bundesinstitut für Risikobewertung **2006.**

Yamashita, N.; Kannan, K.; et al. *Marine Pollution Bulletin* **2005,** 52, 658-668.

SUPPORTING INFORMATION

Figure S1: Samplers deployed in a sampling location

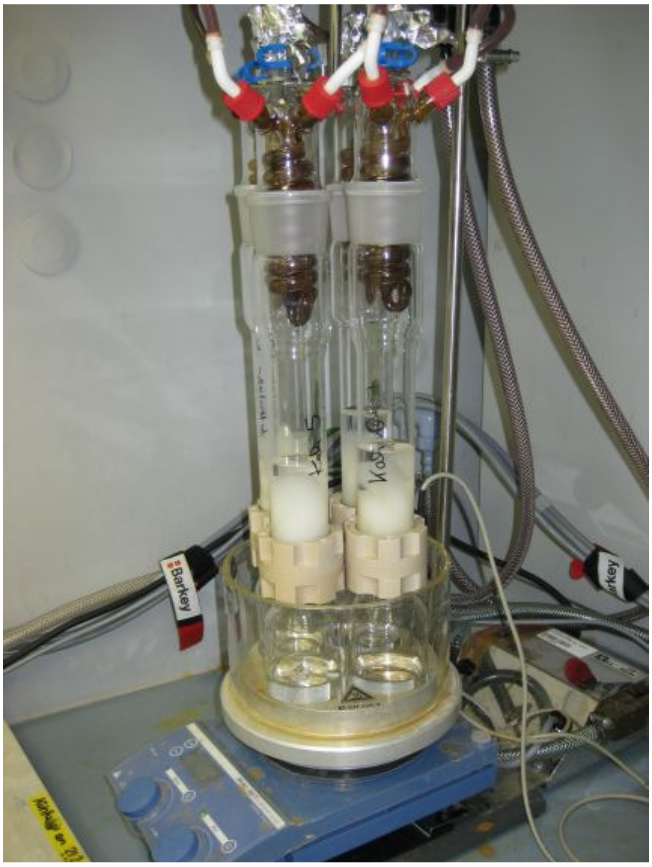


Figure S2: Fluidized bed extraction

Figure S3: Nitrogen evaporator

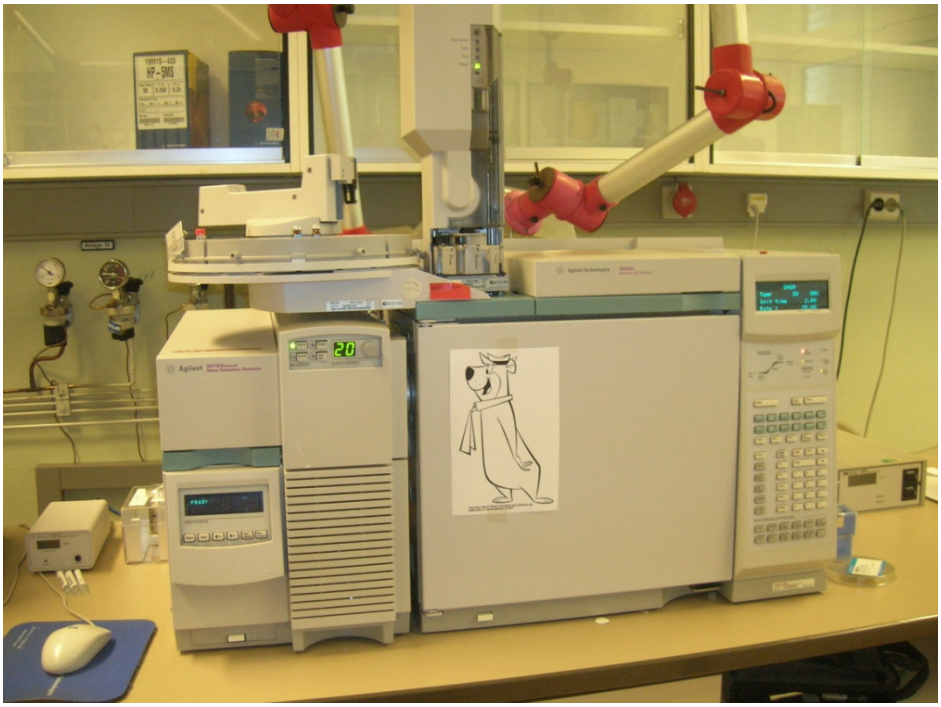


Figure S4: Gaschromatography – Massspectrometry

Table S5: Indoor air concentrations of PFC (pg m^{-3}) from duplicate samples. [a] sample b was lost during laboratory work-up. n.d. not detected.

	6:2 FTA	4:2 FTOH	6:2 FTOH	8:2 FTA	8:2 FTOH	10:2 FTA	10:2 FTOH	12:2 FTOH	EtFOSA	MeFBSA	MeFOSA	MeFOSE	MeFBSE	EtFOSE
H1 a	n.d.	559	1 430	15	9 597	838	2 436	855	1 333	n.d.	1 100	2 926	2 594	2 277
H1 b	88	1 154	926	366	7 288	666	1 543	727	1 171	n.d.	939	2 622	2 436	2 111
H2 a	164	1 437	3 319	1 673	17 739	1 364	5 369	2 051	1 816	n.d.	1 331	3 325	2 813	2 459
H2 b	176	1 152	2 715	1 578	18 508	995	5 199	1 509	1 618	n.d.	1 111	3 061	2 554	2 167
OF1 [a]	3 560	n.d.	1 069	7 923	5 764	2 168	2 526	1 568	1 594	437	677	2 071	1 571	1 615
OF2 a	159	1 122	11 535	5 026	4 990	522	1 348	500	1 287	n.d.	895	2 413	3 755	2 315
OF2 b	185	1 224	962	352	4 003	599	990	548	1 148	n.d.	861	2 302	3 500	2 035
COS a	60	n.d.	1 514	781	1 828	49	703	399	1 028	739	596	1 204	1 349	1 382
COS b	81	n.d.	779	410	3 001	83	973	553	667	417	422	923	627	1 030
ABS a	n.d.	n.d.	622	326	1 903	67	465	241	870	461	559	1 216	724	1 066
ABS b	330	n.d.	709	372	2 117	80	559	204	823	426	559	1 005	582	883
EP a	146	590	181	128	481	n.d.	308	180	1 449	1 137	1 454	1 578	3 133	1 917
EP b	n.d.	1 480	n.d.	n.d.	1 886	221	n.d.	2 051	1 090	985	1 107	1 227	2 245	1 529
FS1 a	149	n.d.	1 464	688	3 558	171	1 265	497	858	437	738	1 548	6 245	991
FS1 b	136	n.d.	1 309	510	2 798	80	706	313	1 484	1 242	1 493	1 860	6 816	1 949
FS2 a	3 476	n.d.	65 588	136 893	324 747	17 257	88 361	32 609	1 333	1 190	1 403	1 377	6 194	2 100
FS2 b	398	n.d.	4 150	3 660	16 754	398	3 192	1 296	1 710	1 353	1 717	1 287	2 531	2 068
CAS a	275	n.d.	8 798	829	13 598	1 328	3 627	9881	609	1 586	772	1 860	116 204	689
CAS b	249	n.d.	11 876	974	18 065	1 954	5 005	23 837	348	4 309	738	2 282	178 184	700
OS1 a	2 598	437	13 210	143 782	180 546	10 552	36 236	14 714	1 241	962	1 230	1 216	7 122	1 238
OS1 b	3 447	n.d.	29 109	134 108	254 803	23 720	64 025	20 735	852	630	509	1 367	7 663	862
OS2a a	486	n.d.	4 150	3 713	16603	371	3 299	1320	1 496	1 341	1 476	1 096	2 082	1 378
OS2a b	4 687	n.d.	74 004	177 683	392 597	22 098	108 769	38 721	1 873	1 528	1 862	1 448	6 173	2 671
OS2b a	1 050	n.d.	14 956	24 019	89 207	6 765	32 459	11 303	1 189	711	1 057	1 478	1 714	17 888
OS2b b	1 053	n.d.	12 582	23 614	76 040	5 487	25 764	9 714	858	513	755	1 800	7 061	905

Table S6: Recovery rates of internal standards (%) ± standard deviation (%).

	6:2 FTOH 13C	8:2 FTOH 13C	10:2 FTOH 13C	EtFOSA D5	MeFOSA D3	MeFOSE D7	EtFOSE D9	4:2 FTOH 13C
H1	6.6 ± 0.9	7.5 ± 0.6	9.9 ± 1.7	28 ± 2.8	28 ± 2.8	36 ± 0.8	31 ± 0.6	9.8 ± 4.8
H2	8.0 ± 1.7	8.2 ± 0.9	10 ± 2.7	25 ± 2.1	26 ± 2.2	35 ± 1.9	35 ± 2.5	6.9 ± 1.1
OF1	6.8 ± 0.0	10 ± 0.0	12 ± 0.0	44 ± 0.0	44 ± 0.0	43 ± 0.0	38 ± 0.0	5.7 ± 0.0
OF2	4.1 ± 4.5	14 ± 1.8	20 ± 2.9	44 ± 1.4	45 ± 0.7	49 ± 1.2	41 ± 3.8	9.1 ± 0.1
COS	4.8 ± 2.6	6.6 ± 1.9	14 ± 0.4	38 ± 15	37 ± 14	67 ± 24	51 ± 19	7.1 ± 0.0
ABS	6.3 ± 2.5	7.8 ± 5.1	15 ± 2.4	44 ± 2.0	41 ± 0.4	74 ± 14	67 ± 9.4	3.8 ± 1.0
EP	7.2 ± 0.6	14 ± 7.7	8.5 ± 8.3	48 ± 9.7	45 ± 9.5	48 ± 8.9	43 ± 6.9	5.5 ± 0.2
FS1	11 ± 3.1	13 ± 2.4	17 ± 5.4	43 ± 4.9	42 ± 6.2	43 ± 11	41 ± 5.6	11 ± 1.9
FS2	6.3 ± 0.2	7.1 ± 0.5	10 ± 0.2	40 ± 6.6	36 ± 5.3	54 ± 4.4	35 ± 0.3	5.8 ± 0.5
CAS	12 ± 0.7	18 ± 2.7	4,5 ± 0.7	52 ± 6.2	49 ± 7.3	67 ± 6.8	68 ± 5.7	8.9 ± 4.1
OS1	5.9 ± 0.3	8.1 ± 0.3	11 ± 1.7	46 ± 4.8	43 ± 3.3	69 ± 4.5	65 ± 9.1	6.3 ± 0.9
OS2a	4.3 ± 0.2	5.2 ± 0.2	7.6 ± 0.7	36 ± 5.7	34 ± 5.6	62 ± 14	43 ± 19	4.0 ± 0.1
OS2b	9.7 ± 1.1	12 ± 1.4	14 ± 2.6	41 ± 9.6	39 ± 9.7	57 ± 5.9	26 ± 33	8.7 ± 0.8

Table S7: Blank contamination (pg μL^{-1}). SB = Solvent blank. FB = Field blank.

	6:2 FTA	4:2 FTOH	6:2 FTOH	8:2 FTA	8:2 FTOH	10:2 FTA	10:2 FTOH	12:2 FTOH	EtFOSA	MeFBSA	MeFOSA	MeFOSE	MeFBSE	EtFOSE
SB 1	n.d.	n.d.	n.d.	1.6	6.8	n.d.	5.0	3.4	4.4	8.0	8.5	10	4.7	8.6
SB 2	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.8	3.4	5.9	8.3	8.9	4.7
SB 3	n.d.	n.d.	n.d.	n.d.	3.2	n.d.	n.d.	3.3	5.4	6.7	4.6	8.4	6.5	6.4
SB 4	0.8	n.d.	2.0	3.9	9.7	0.6	5.6	3.0	8.2	6.9	7.4	9.1	7.1	2.2
FB 1	1.8	n.d.	n.d.	3.8	7.3	1.1	3.6	2.7	9.2	5.8	12	7.8	6.0	8.9

Table S8: Combined and expanded measurement uncertainties for average concentrations in high and low contamination sites according to ISO 20988.

	High contamination sites				Low contamination sites			
	combined		expanded		combined		expanded	
	pg m^{-3}	%	pg m^{-3}	%	pg m^{-3}	%	pg m^{-3}	%
6:2 FTA	762	45	1 660	99	45	8.6	97	19
4:2 FTOH	63	151	137	328	160	31	350	67
6:2 FTOH	13 634	60	29 722	130	1 534	74	3 345	162
8:2 FTA	1 659	51	69 017	112	680	41	1 481	89
8:2 FTOH	70 996	54	154 770	117	476	8.7	1 038	19
10:2 FTA	4 406	51	9 604	112	69	12	151	25
10:2 FTOH	19 998	56	43 596	123	173	11	378	23
12:2 FTOH	7 378	47	16 084	102	284	34	619	75
EtFOSA	113	10	246	22	124	10	270	23
MeFBSA	399	29	869	64	127	32	277	69
MeFOSA	134	12	292	26	129	15	281	32
MeFOSE	95	6.5	208	14	104	5.5	227	12
MeFBSE	9 014	28	19 652	61	194	7.6	424	17
EtFOSE	2 459	84	5 361	183	172	10	375	23

Table S9: Pearson correlation coefficients for all analytes of the sites of clusters 3 and 4 (FS2, CAS, OS1, OS2a, OS2b). [a] $p < 0.05$, [b] $p < 0.01$.

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTA	8:2 FTA	10:2 FTA	EtFOSA	MeFBSA	MeFOSA
6:2 FTOH	-0.12										
8:2 FTOH	0.51	0.77									
10:2 FTOH	0.35	0.82[a]	0.98[b]								
12:2 FTOH	0.21	0.62	0.52	0.42							
6:2 FTA	0.62	0.67	0.99[b]	0.94[b]	0.52						
8:2 FTA	0.76	0.55	0.95[b]	0.86[a]	0.53	0.98[b]					
10:2 FTA	0.79	0.47	0.93[a]	0.85[a]	0.40	0.97[b]	0.99[b]				
EtFOSA	-0.12	0.95[b]	0.78	0.88[a]	0.36	0.69	0.54	0.51			
MeFBSA	-0.37	-0.26	-0.61	-0.69	0.35	-0.61	-0.55	-0.65	-0.52		
MeFOSA	-0.37	0.97[b]	0.59	0.69	0.49	0.47	0.32	0.24	0.93[a]	-0.18	
MeFOSE	-0.37	-0.80	-0.97[b]	-0.99[b]	-0.36	-0.93[a]	-0.86[a]	-0.86[a]	-0.87[a]	0.73	-0.66

Table S10: Pearson correlation coefficients for all analytes of the sites of cluster 3 (FS2, OS1, OS2a, OS2b). [a] $p < 0.05$, [b] $p < 0.01$.

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTA	8:2 FTA	10:2 FTA	EtFOSA	MeFBSA	MeFOSA
6:2 FTOH	-0.34										
8:2 FTOH	0.53	0.61									
10:2 FTOH	0.28	0.78	0.96[a]								
12:2 FTOH	0.23	0.82	0.95[a]	1.00[b]							
6:2 FTA	0.68	0.43	0.98[a]	0.89	0.87						
8:2 FTA	0.81	0.27	0.93[a]	0.79	0.76	0.98[a]					
10:2 FTA	0.90	0.09	0.85	0.68	0.63	0.93[a]	0.98[b]				
EtFOSA	-0.54	0.97[a]	0.42	0.65	0.69	0.24	0.05	-0.12			
MeFBSA	-0.40	1.00[b]	0.56	0.75	0.79	0.38	0.21	0.03	0.99[b]		
MeFOSA	-0.60	0.96[a]	0.34	0.57	0.62	0.15	-0.03	-0.21	0.99[b]	0.97[a]	
MeFOSE	-0.35	-0.76	-0.97[a]	-0.97[a]	-0.98[a]	-0.90	-0.83	-0.71	-0.59	-0.72	-0.53

Table S11: Pearson correlation coefficients for all analytes of the sites of clusters 1 and 2 (H1, H2, OF1, OF2, COS, ABS, EP, FS1). [a] $p < 0.05$, [b] $p < 0.01$.

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTA	8:2 FTA	10:2 FTA	EtFOSA	MeFBSA	MeFOSA
6:2 FTOH	0.35										
8:2 FTOH	0.54	0.30									
10:2 FTOH	0.40	0.35	0.97[b]								
12:2 FTOH	0.42	0.20	0.69[a]	0.77[a]							
6:2 FTA	-0.37	0.30	0.02	0.22	0.50						
8:2 FTA	-0.20	0.57	0.13	0.32	0.52	0.95[b]					
10:2 FTA	0.06	0.48	0.52	0.66[a]	0.77[a]	0.84[b]	0.88[b]				
EtFOSA	0.49	0.41	0.73[a]	0.79[b]	0.92[b]	0.47	0.55	0.79[b]			
MeFBSA	-0.43	-0.61	-0.67[a]	-0.61	-0.19	0.01	-0.18	-0.42	-0.31		
MeFOSA	0.68[a]	-0.07	0.40	0.29	0.42	-0.31	-0.29	-0.03	0.55	0.10	
MeFOSE	0.67[a]	0.50	0.87[b]	0.82[b]	0.60	0.06	0.21	0.57	0.78[a]	-0.75[a]	0.51

Table S12: Pearson correlation coefficients for all analytes of the sites of cluster 1 (H1, H2, OF1, OF2). [a] p < 0.05, [b] p < 0.01.

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTA	8:2 FTA	10:2 FTA	EtFOSA	MeFBSA	MeFOSA
6:2 FTOH	0.17										
8:2 FTOH	0.50	-0.40									
10:2 FTOH	0.26	-0.34	0.95[a]								
12:2 FTOH	-0.26	-0.31	0.66	0.86							
6:2 FTA	-0.94[a]	0.04	-0.36	-0.07	0.45						
8:2 FTA	-0.83	0.31	-0.41	-0.11	0.39	0.96[a]					
10:2 FTA	-0.83	-0.15	-0.01	0.28	0.74	0.93[a]	0.86				
EtFOSA	-0.19	-0.19	0.68	0.87	0.99[b]	0.41	0.39	0.69			
MeFBSA	-0.95[a]	0.01	-0.37	-0.08	0.44	1.00[b]	0.95[a]	0.93[a]	0.40		
MeFOSA	0.82	-0.34	0.86	0.66	0.18	-0.79	-0.82	-0.52	0.21	-0.79	
MeFOSE	0.74	-0.45	0.89	0.71	0.27	-0.72	-0.77	-0.42	0.28	-0.72	0.99[b]

Table S13: Pearson correlation coefficients for all analytes of the sites of cluster 2 (COS, ABS, EP, FS1). [a] p < 0.05, [b] p < 0.01.

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTA	8:2 FTA	10:2 FTA	EtFOSA	MeFBSA	MeFOSA
6:2 FTOH	-0.85										
8:2 FTOH	-0.81	0.98[a]									
10:2 FTOH	-0.85	1.00[b]	0.97[a]								
12:2 FTOH	0.96[a]	-0.70	-0.69	-0.69							
6:2 FTA	-0.54	0.28	0.42	0.27	-0.72						
8:2 FTA	-0.89	0.99[b]	0.93[a]	0.99[b]	-0.73	0.22					
10:2 FTA	0.38	0.00	0.17	0.00	0.39	0.11	-0.17				
EtFOSA	0.72	-0.34	-0.20	-0.33	0.74	-0.22	-0.47	0.91			
MeFBSA	0.80	-0.40	-0.31	-0.39	0.86	-0.46	-0.50	0.80	0.97[a]		
MeFOSA	0.71	-0.34	-0.20	-0.34	0.72	-0.17	-0.48	0.92[a]	1.00[b]	0.95[a]	
MeFOSE	0.18	0.21	0.37	0.21	0.23	0.19	0.04	0.98[a]	0.81	0.68	0.82

ACKNOWLEDGEMENT

First of all I would like to kindly thank Prof. Dr. Ralf Ebinghaus and Dr. Wolf Palm for supervising my Diploma thesis and for general support and help throughout great parts of my studies. I would also like to thank the GKSS Forschungszentrum for enabling me to write my Diploma thesis at the Institute for Coastal Research and for the opportunity to participate in several valuable conferences. Thank you to all the generous people who kindly allowed me to collect air samples in their shops, homes and buildings. My work would not have been possible without these compliances. I thank Dr. Annekatrin Dreyer for helping and supporting me throughout my work at GKSS. Thank you also to the rest of the HD office for keeping up a cheerful, positive work climate. I would like to thank Armando Caba for always having a helping hand in the labatory. Thanks to everyone from KSC for interesting and inspiring lunch breaks, Christmas parties and DVD evenings. I thank Mahiba Shoeib for email tips. Thanks to Lotta for positive distraction. Last but not least I would like to thank my family, friends and Daniel for supporting me in any possible way.