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Method development and determination of anthropogenic poly- and perfluorinated compounds in air, water, soil, house dust, and several consumer products

Stefan Andreas Fiedler

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Table of Contents

List of Publications

I. Method development for the determination of fluorotelomer alcohols in semipermeable membrane devices.
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II. Partitioning of fluorotelomer alcohols (FTOH) to semipermeable membrane devices (SPMD).
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III. Poly- and Perfluorinated Compounds in Household Consumer Products.
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IV. Field Intercomparison on the Determination of Volatile and Semi-volatile Polyfluorinated Compounds in Air.
Dreyer, A., Shoeib, M., **Fiedler, S.**, Barber, J., Harner, T., Schramm, K.-W., Jones K.C., Ebinghaus, R.; (submitted) Environmental Chemistry

List of Abbreviations

4:2 FTOH	4:2 fluorotelomer alcohol
6:2 FTOH	6:2 fluorotelomer alcohol
8:2 FTOH	8:2 fluorotelomer alcohol
10:2 FTOH	10:2 fluorotelomer alcohol
ACN	acetonitril
asl	above sea level
BCF	bioconcentration factor
BHFSA	Bavarian Health and Food Safety Authority
CA	cleaning agent
CAS	Chemical Abstracts Service registration number
CO	Conditioner
DE	dialysis extraction
EC	effective concentration
ECF	electro chemical fluorination
ENCA	Environment Canada
ESI	electrospray ionisation
EtAc	ethyl acetate
F	female
FA	fluorinated alcohol
FF	fire fighting foam
FTCA	saturated fluorotelomer carboxylic acids
FTUCA	unsaturated fluorotelomer carboxylic acids
FTOH	fluorotelomer alcohol
GC	gas chromatography
GCE	glass chamber experiment
GPC	gel permeation chromatography
HEX	n-hexane
HPLC	high performance liquid chromatography
HMGU	Helmholtz Zentrum München
IA	impregnation agent
IS	internal standard
K_{OW}	octanol-water partition coefficient

K_{TA}	triolein-air partition coefficient
LC	lethal concentration
LD	lethal dose
LDPE	low density polyethylene
LLE	liquid liquid extraction
LOD	limit of detection
LU	lubricant
M	male
MEM	membrane
MeOH	methanol
MS	mass spectrometry
MTBE	methyl-tert.-butyl ether
MW	molecular weight
Muc	Munich
m/z	mass to charge ratio
nd	not detected
NMR	nuclear magnetic resonance
NOEC	no observed effect concentration
nq	not quantified
PBDE	polybrominated dipheny ethers
PCB	polychlorinated biphenyls
PE	pesticide
PFC	polyfluorinated compounds
PFCA	perfluoroalkyl carboxylates
PFNA	perfluorononanoate
PFOA	perfluorooctanoate
PFOS	perflurooctane sulfonate
PFSA	perfluoroalkyl sulfonates
POP	persistent organic pollutant
PRC	performance reference compounds
PUF	polyurethane foam
R	recovery rate
R_s	sampling rate
RF	response factors

S	water solubility
SAX	strong anion exchange
SD	standard deviation
SPE	solid phase extraction
SPMD	semipermeable membrane device
TOF	time of flight
TRIO	trioleine
ULA	University of Lancaster
UPLC	ultra pressure liquid chromatography
WAX	weak anion exchange
XAD	polystyrene-based adsorption resin

List of Figures

List of Tables

Summary

Polyfluorinated organic compounds (PFC) are a widely used class of chemicals combining both hydrophobic and oleophobic properties. They are applied as stain repellents of paper, carpets and textiles, in aqueous film forming foams, for polymer production, and as emulsifiers in pesticides. However, some PFC, particularly perfluorinated carboxylates (PFCA) like perfluorooctanoate (PFOA) or perfluorinated sulfonates (PFSA) such as perfluorooctane sulfonate (PFOS), are extremely persistent and bioaccumulative. Others, such as fluorotelomer alcohols (FTOH) are volatile and prone to long range atmospheric transport. Furthermore, these volatile substances were identified as PFCA and PFSA precursors. Thus, PFC are considered as an emerging class of environmental pollutants.

In this PhD thesis, several analytical methods were developed for the determination of PFC in different matrices applying gas chromatography-mass spectrometry (GC-MS) for detection of FTOH and ultra performance liquid chromatography- time of flight mass spectrometry (UPLC-TOF MS) for the detection of FTOH, PFOA and PFOS. For the determination of FTOH concentrations in air, the suitability of semipermeable membrane devices (SPMD) as passive air samplers was evaluated. For this purpose, extractions using acetonitrile, n-hexane, methanol, or ethylacetate combined with purification by several solid phase extraction adsorbents (C-18, C18-E, Carboxen) were assessed. Field and laboratory experiments were conducted, to investigate the partitioning of FTOH between SPMD and air. It was observed that FTOH are generally able to pass the SPMD membrane. However, FTOH partitioning to SPMD was hampered at environmentally relevant concentrations. Additionally, SPMD were compared to sorbent impregnated polyurethane foam (SIP) disks acting as passive samplers and to high volume active sampling (high vol) within an interlaboratory comparison study. During this study, FTOH were only detected occasionally in SPMD, whereas they were present in all SIP and high vol samples confirming the limited applicability of SPMD. 8:2 fluorotelomer alcohol (8:2 FTOH) air concentrations determined during three sampling periods were between 38 and 59 pg m^{-3} and 10:2 fluorotelomer alcohol (10:2 FTOH) air concentrations were between 5 and 13 pg m^{-3}. The conducted sampler comparison study was used to calculate the first SPMD sampling rates for FTOH. For 8:2 FTOH, an average sampling rate of 0.81 m^{3} d^{-1} was observed whereas for 10:2 FTOH an average sampling rate of 0.77 m^{3} d^{-1} was calculated.

An analytical method was developed for the determination of FTOH adsorbed to spruce needles in order to evaluate the needles suitability acting as natural passive samplers for

FTOH. Needles were extracted using acetonitrile. After concentration, extracts were further purified by SPE using Envi-Carb cartriges. However, FTOH were not detected in spruce needle samples taken in Munich, Germany, Thus, it was assumed that spruce needles do not sufficiently accumulate FTOH to be suitable natural passive air samplers.

Bulk deposition of non-volatile PFOA and PFOS was determined using Amberlite-XAD-2^{TM} (XAD) deposition samplers at three sites in the Alps. XAD was cold extracted using methanol. The extract was further purified by SPE using Envi-Carb cartriges. PFOA and PFOS were regularly detected in these deposition samples. Deposition of PFOA and PFOS was calculated to be up to 12 ng m^{-2} d^{-1} and up to 10 ng m^{-2} d^{-1}, respectively.

Furthermore, FTOH were determined in dust samples from seven households. Dust samples were extracted with acetone/methyl-tert.-butyl ether using ultra sonication, purified by Envi-Carb SPE cartridges, and detected by GC-MS. In these samples a total FTOH concentration of up to 434 ng g^{-1} was observed. This suggests that FTOH are pollutants, which are already commonly present at human domiciles resulting in an everyday exposure of those persons living therein.

PFOA, PFOS, and FTOH were analysed in household consumer products, such as impregnation agents, lubricants, and cleaners. Consumer products were diluted in methanol and determined without further clean-up by UPLC-TOF MS. In 14 of 26 products, at least one PFC was detected, indicating a potential source for PFC present in house dust. PFC were predominately found in impregnating agents and lubricants. In most cases FTOH concentrations exceeded those of PFOA and PFOS. With 396 µg mL^{-1}, the highest total PFC amount was observed in one of the lubricants. Determined PFC concentrations were used to estimate human exposure to PFC originating from the application of these agents. By means of three different scenarios, consumer exposure to PFC was calculated to be between 43 and 464 ng kg^{-1} d^{-1} revealing the importance of consumer products as PFC sources next to PFC originating from food and drinking water.

Finally, PFOA and PFOS were analysed in soil and water samples taken in the national park Serra dos Órgãos in the federal state of Rio de Janeiro, Brazil. 1 L water samples were extracted using weak anion exchange cartridges for SPE, which thereafter were eluted with methanol. Soil samples were extracted with methanol. Extracts were purified by SPE using Envi-Carb cartridges. However, PFOA and PFOS were neither detected in soil samples nor in water samples. This confirms the expectations that PFC concentrations in that remote area are far below those detected in source regions or industrialized countries like Germany.

Zusammenfassung

Polyfluorierte organische Verbindungen (PFC) stellen eine weit verbreitete Chemikaliengruppe dar, die sowohl hydrophobe als auch lipophobe Eigenschaften in sich vereinigt. Unter anderem werden sie als schmutzabweisende Stoffe für Papier, Teppiche und Textilien eingesetzt. Desweiteren werden sie in Löschschäumen, für die Produktion von Polymeren und als Lösungsvermittler in Pestizidzubereitungen verwendet. Einige PFC, besonders die perfluorierten Alkylcarboxylate (PFCA) wie das Perflurooctanoat (PFOA), oder die perfluorierten Alkylsulfonate (PFSA) wie das Perfluoroctansulfonat (PFOS), sind hoch persistent und bioakkumulativ. Andere PFC, wie die Fluortelomeralkohole (FTOH) oder die perfluorierten Sulfonamide sind flüchtig und können über weite Strecken in der Atmosphäre transportiert werden. Außerdem wurden diese flüchtigen PFC als Vorläufersubstanzen identifiziert, die zu den persistenten PFCA und PFSA abgebaut werden.

In der vorliegenden Dissertation wurden verschiedene analytische Methoden zur Bestimmung von PFC in unterschiedlichen Matrices entwickelt. Dabei wurde Gaschromatographie-Massenspektrometrie (GC-MS) zum Nachweis von FTOH und Ultraleistungsflüssigkeits-chromatographie-Flugzeitmassenspektrometrie (UPLC-TOF MS) zum Nachweis von FTOH, PFOS und PFOA eingesetzt. Semipermeable Membransammler (SPMD) wurden für die Bestimmung von FTOH in der Luft getestet. Zu diesem Zweck wurden Extraktionen mit Acetonitril, n-Hexan, Methanol, and Ethylacetate und verschiedene Festphasenextraktionen (C-18, C-18E, Carboxen) zur Aufreinigung erprobt. Labor- und Feldexperiment wurden durchgeführt, um die FTOH Verteilung zwischen SPMD und Luft zu untersuchen. Es wurde beobachtet, dass FTOH generell die SPMD-Membran passieren konnten. Jedoch war bei typischen FTOH-Umweltkonzentrationen die FTOH-Aufnahme in den SPMD-Sammler behindert. Desweiteren wurden SPMD mit adsorbensbeschichteten Polyurethanschaum (SIP) - Passivsammlern und Aktivluftsammlern, die von anderen Forschungsinstituten eingesetzt wurden, verglichen. Während dieser Studie konnten FTOH nur gelegentlich mit SPMD nachgewiesen werden, wogegen sie mit SIP und Aktivsammlern in allen Proben detektiert wurden. Dies bestätigte die eingeschränkte Einsetzbarkeit von SPMD als FTOH Passivsammler. Die 8:2 FTOH Luftkonzentrationen während drei Sammelperioden lagen zwischen 38 und 59 pg m^{-3} und 10:2 FTOH Luftkonzentrationen zwischen 5 und 13 pg m^{-3}. Diese Vergleichstudie ermöglichte die erste Berechnung der FTOH Aufnahmeraten von SPMD. Für 8:2 FTOH und 10:2 FTOH wurde eine mittlere Aufnahmerate von 0,81 m^3 d^{-1} bzw. von 0,77 m^3 d^{-1} ermittelt.

PFOA und PFOS wurden mit XAD Depositionssammlern an drei Standorten in den Alpen bestimmt. Das XAD wurde mit Methanol extrahiert und die Extrakte mittels Festphasenextraktion mit EnviCarb-Kartuschen weiter aufgereinigt. PFOS und PFOA wurden regelmäßig in diesen Proben nachgewiesen. Für PFOA und PFOS wurden Depositionsraten von bis zu 12 beziehungsweise 10 ng m^{-2} d^{-1} ermittelt.

Weiterhin wurde eine analytische Methode zur Bestimmung von an Fichtennadeln adsorbiertes FTOH entwickelt um deren Eignung als natürlicher Passivsammler zu testen. Die Nadeln wurden mit Acetonitril extrahiert und die Extrakte mit EnviCarb Festphasenextraktionskartuschen weiter aufgereinigt. Jedoch konnten in Nadelproben aus München, Deutschland, keine FTOH nachgewiesen werden. Daraus wurde gefolgert, dass Fichtennadeln nicht genügend FTOH anreichern, um als natürlicher Passivsammler verwendet werden zu können.

Weiterhin wurden FTOH Konzentrationen in sieben Staubproben aus Haushalten bestimmt. Der Staub wurde im Ultraschallbad mit Aceton/Methyl-tert.-butylether extrahiert und die Extrakte über EnviCarb Festphasenextraktionskartuschen weiter aufgereinigt. In diesen Proben wurde mit GC-MS eine FTOH Gesamtkonzentration bis zu 434 ng g^{-1} detektiert. Dies lässt vermuten, dass FTOH bereits eine weite Verbreitung in Wohnräumen gefunden haben und somit zu einer täglichen Exposition der dort lebenden Menschen mit PFOA führen können.

Außerdem wurden PFOA, PFOS und FTOH in Haushaltsprodukten wie Imprägniermitteln, Schmiermitteln, und Reinigern untersucht. Die Haushaltsprodukte wurden in Methanol gelöst und ohne weitere Aufreinigung mit UPLC-TOF MS gemessen. In 14 von 26 analysierten Produkten wurde wenigstens ein PFC detektiert. Das lässt vermuten, dass Haushaltsprodukte eine Quelle für PFC im Hausstaub darstellen. PFC wurden hauptsächlich in Imprägniermitteln und Schmiermitteln gefunden. Meistens übertrafen die FTOH Konzentrationen die von PFOA und PFOS. Die höchste PFC Konzentration wurde mit 396 µg mL^{-1} in einem Schmiermittel bestimmt. Die ermittelten PFC Konzentrationen wurden dazu verwendet, die PFC Exposition für Menschen abzuschätzen, die diese Mittel anwenden. Mit Hilfe von drei Szenarien wurde eine PFC Exposition zwischen 43 und 464 ng kg^{-1} d^{-1} errechnet. Dies verdeutlichte den hohen Stellenwert von Haushaltsprodukten als PFC-Quelle für den Menschen neben der Nahrung und dem Trinkwasser.

PFOS- und PFOA-Gehalte wurden in vier Wasser- und Bodenproben aus dem Nationalpark Serra dos Órgãos, Bundesstaat Rio de Janeiro, Brasilien, untersucht. Für die Wasserproben (1 L) wurden schwache Anionenaustauscher Kartuschen für die Festphasenextraktion verwendet, die mit Methanol eluiert wurden. Die Bodenproben wurden mit Methanol extrahiert und die Extrakte mit EnviCarb Festphasenextraktionskartuschen weiter aufgereinigt. PFOA und PFOS konnten weder im Wasser noch im Boden nachgewiesen werden. Das bestätigt die Erwartung, dass die PFC Konzentrationen in dieser abgelegenen Region weit unterhalb derer von Quellengebieten oder industrialisierten Ländern wie Deutschland liegen.

1 Introduction

1.1 Poly- and perfluorinated compounds

1.1.1 Investigated poly- and perfluorinated compounds

Per- and polyfluorianted compounds (PFC) consist of a variety of substance classes. The most important groups are perfluorinated carboxylates (PFCA) and perfluorinated sulfonates (PFSA) with their major representatives perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) (Figure 1). PFCA and PFSA of different chain length (C_4-C_{15}) were usually manufactured by the electrochemical fluorination process (ECF). Besides ECF, PFCA and PFSA were produced by telomerization, as well. However, this process was only of minor importance compared to ECF (Hekster *et al.*, 2003; Prevedouros *et al.*, 2006; Paul *et al.*, 2009). During the ECF manufacturing process, an electric current is passed through hydrogen fluoride and therein dissolved or dispersed organic compounds. All hydrogen atoms of those organic compounds are replaced by fluorine. This procedure results in about. 85% linear and 15% branched isomers. Additionally, some impurities are produced.

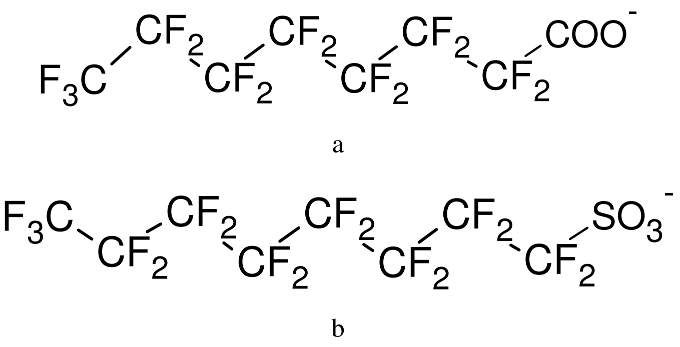


Figure 1: Molecular structures of PFOA (a) and PFOS (b).

Another important group are the fluorotelomer alcohols (FTOH) (Figure 2). These polyfluorinated chemicals are named after their ratio of the number of fluorinated to non-fluorinated carbon atoms (e.g. 8:2 FTOH). They are produced via telomerization. During this process, perfluoroalkylethyliodides are synthesized. In a second step iodide is replaced by a functional group, in case of FTOH with a hydroxyl group. By this way FTOH are generated, which can further be oxidized to PFCA. In contrast to ECF, telomerization generates only linear molecules with an even number of carbon atoms (Hekster *et al.*, 2003).

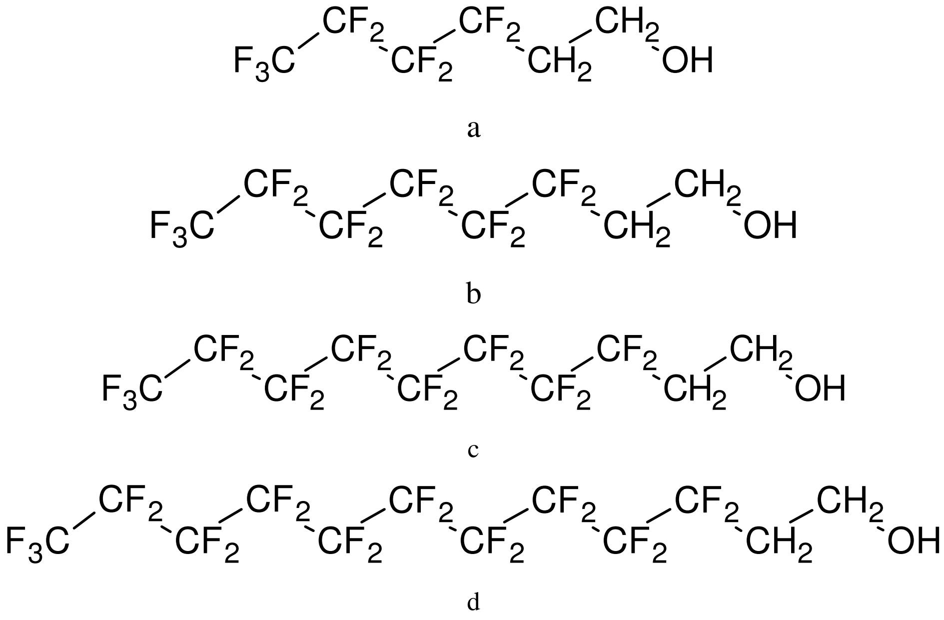


Figure 2: Molecular structures of 4:2 FTOH (a), 6:2 FTOH (b), 8:2 FTOH (c), and 10:2 FTOH (d).

Besides PFCA, PFSA, and FTOH, there are also other classes of PFC such as perfluroalkyl phosphonates, perfluroalkyl sulfonamids, polyfluorinated N-alkyl sulfonamids, saturated and unsaturated fluorotelomer acids, and fluorotelomer acrylates. As far as it is known today, PFC are of anthropogenic origin only. Although fluorinated molecules do exist in nature, e.g toxins of higher plants and microorganisms, completely fluorinated molecules are not observed, with the exception of trifluoroacetic acid (Key *et al.*, 1997; Giesy and Kannan, 2002).

The substances that were chosen for investigations in this thesis were PFOA and PFOS, as major representative compounds of PFCA and PFAS, and four fluorotelomer alcohols of different chain lengths, 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, building the most important group of volatile PFC (Prevedouros *et al.*, 2006). These compounds are presented in the following sections.

1.1.2 Properties of PFC

PFC have unique physico chemical properties. One reason for this is the strength of the carbon fluorine bond (≥ 450 kJ mol^{-1}). Moreover, perfluorinated molecules are shielded by three pairs of nonbonding electrons belonging to each fluorine atom. Therefore, PFC resist degradation by acids, oxidizing agents, alkalis, hydrolysis, photolysis, heat, and metabolism of organisms far better than their hydrocarbon or even chlorinated analogues (Kissa, 1994).

Due to charged moieties such as a carboxyl moiety or sulfonyl moiety, PFCA and PFSA are strong surfactants. They are non-volatile and persistent (Prevedouros *et al.*, 2006). They reduce water surface tension more than hydrocarbon based surfactants (Kissa, 1994; Schultz *et al.*, 2003). PFC are both water and oil repellent. This results in three immiscible phases, when they are mixed with water and hydrocarbons (Kissa, 1994).

In contrast to the ionic PFCA and PFSA, neutral PFC, such as FTOH, are volatile and degradable (Ellis *et al.*, 2004). FTOH are more volatile than their non fluorinated analogues. Partial fluorination increases the vapour pressures by about one to two orders of magnitude (Lei *et al.*, 2004; Stock *et al.*, 2004a).

Table 1: Physico chemical properties of PFC. Molecular weight, octanol air partition coefficients, and octanol water partition coefficients of investigated PFC.

Compound	CAS	MW ($g\ mol^{-1}$)	log K_{OA} (20°C,) [a]	log K_{OW} (25°C,) [b]	S ($mg\ L^{-1}$)	pK_a
4:2 FTOH	2043-47-2	264	4.65	3.30	974 (22°C) [c]	-
6:2 FTOH	647-42-7	364	4.91	4.54	18.8 (22°C) [c]	-
8:2 FTOH	678-39-7	464	5.65	5.58	0.19 (22°C) [c]	-
10:2 FTOH	865-86-1	564	5.83	6.63	0.006-0.885 (22°C) [c]	-
PFOA	335-67-1	414	-	4.3	4100 (22°C) [d]	-0.5 [f]
PFOS	1763-23-1	500	-	-	519 (20°C) [e]	-3.27 [g]

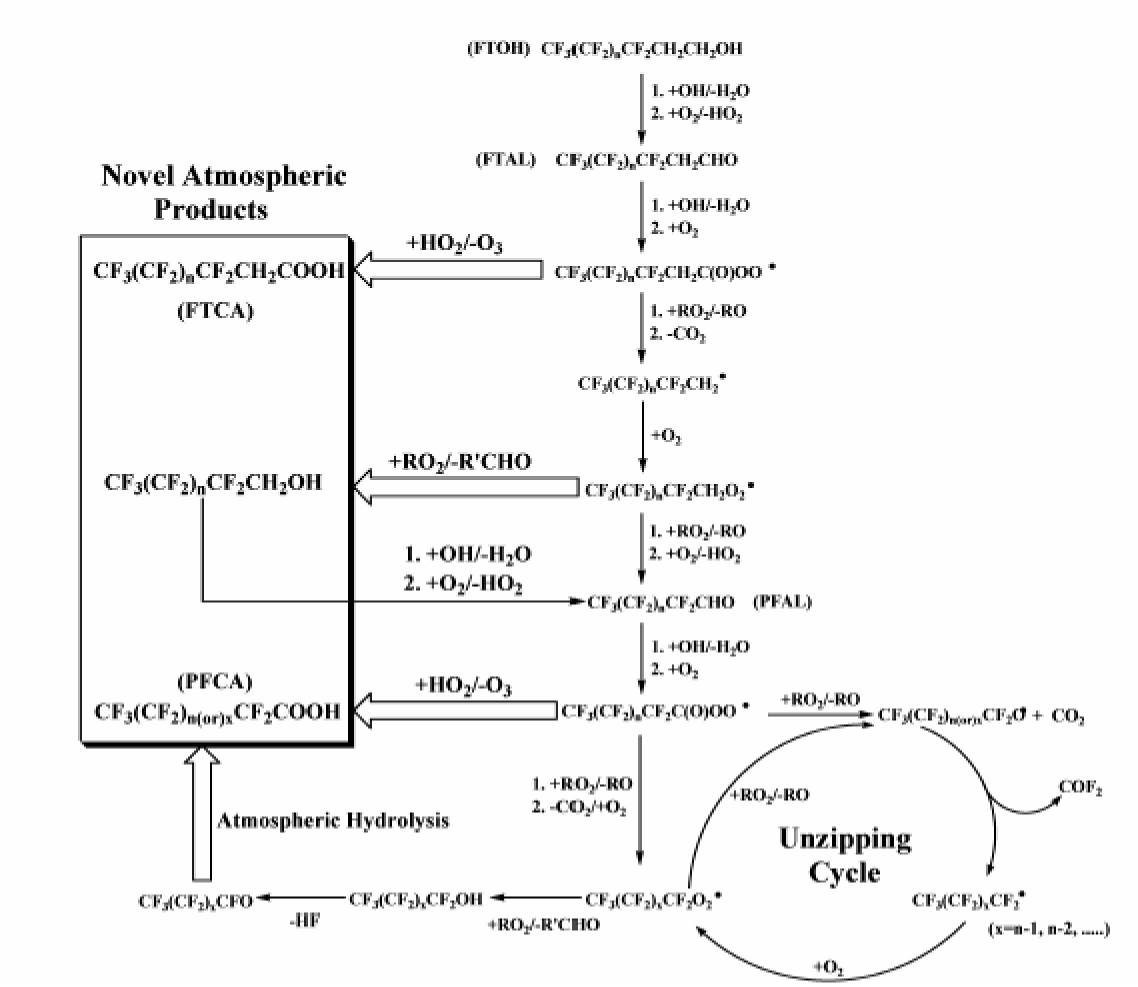
CAS: Chemical Abstracts Service registration number
MW: Molecular weight
K_{OA}: Octanol air partition coefficient
K_{OW}: Octanol water partition coefficient
S: Water solubility
[a]: (Thuens *et al.*, 2008)
[b]: (Carmosini and Lee, 2008)
[c]: (Liu and Lee, 2007)
[d]: (Prokop *et al.*, 1989)
[e]: (Brooke *et al.*, 2004)
[f]: (Goss, 2008)
[g]: (Kissa, 1994)

1.1.3 Sources and fate of PFC in the environment

Because of their unique properties, PFC have a wide range of applications. They are used as protecting and impregnation agents for carpets, leather, and other textiles. They are applied in food packaging, fires retardants, pharmaceuticals, lubricants, adhesives, cosmetics, insecticides, as paper coatings, water and stain repellents, industrial surfactants, and for the production of fluoropolymers, such as Teflon® (Kissa, 1994; Dinglasan-Panlilio and Mabury, 2006; Villagrasa *et al.*, 2006; Sinclair *et al.*, 2007; Jensen *et al.*, 2008). Manufacturing of PFC started in the late 1940ies using the ECF process. The historical total global production of PFOA is estimated to be between 3600-5700 Mg (Prevedouros *et al.*, 2006). PFCA were emitted by direct (manufacture, consumer, and industrial products) and indirect sources (residual impurities, degradation of precursors, such as FTOH). Overall 3200-7300 Mg were released to the environment (Prevedouros *et al.*, 2006). Total historical worldwide production of PFOS and its precursors was estimated to be 122,500 Mg reaching its maximum of 4500 Mg per year during 1990 to 2000 (Paul *et al.*, 2009). Annual manufacturing volumes of fluorotelomer-based products increased to 11-14 * 10^3 Mg in 2004 (Dinglasan-Panlilio and Mabury, 2006). Due to their persistence, toxicity, and bioaccumulation, main producers like 3M and Dupont phased out production of long-chain PFSA (Prevedouros *et al.*, 2006; Paul *et al.*, 2009) in 2001 and replaced those by analogue butyl based substances (3M, 2000). Today, PFOS is classified persistent organic pollutant (POP) under the Stockholm Convention and the European Community and US-EPA restricted manufacturing and use of PFOS (EPA, 2002; EU, 2006; Paul *et al.*, 2009). Eight major companies voluntarily agreed to reduce facility emissions and product content of PFOA and related chemicals by 95% no later than 2010 (EPA 2009). FTOH, which degrade to PFCA longer than C8, are part of this agreement. However, the production and application of short-chain FTOH, PFCA, and PFSA is not restricted so far.

Due to their non volatility and high water solubility, PFCA and PFSA are not presumed to undergo noteworthy atmospheric long range transport, (Shoeib *et al.*, 2006; Barber *et al.*, 2007). Thus, only rivers and ocean currents are considered as important direct route of transport for PFCA and PFSA (Armitage *et al.*, 2006; Prevedouros *et al.*, 2006; Wania, 2007).

Volatile PFC like FTOH and polyfluorinated sulfonamids have atmospheric half life times of 20 to 50 days (Ellis *et al.*, 2003; Ellis *et al.*, 2004). Thus, they can undergo atmospheric long range transport and are able to reach remote areas like polar regions (Shoeib *et al.*, 2006; Schenker *et al.*, 2008; Dreyer *et al.*, 2009b). Because these compounds are not completely fluorinated, they can be degraded both in the atmosphere and in organisms to persistent PFCA and PFSA to a certain extent (Dinglasan *et al.*, 2004; Ellis *et al.*, 2004; Martin *et al.*, 2005; Wallington *et al.*, 2006). In the atmosphere FTOH are degraded by OH radicals to fluorotelomer aldehydes and perfluorinated aldehyds, which can enter an “unzipping cycle” resulting in a sequential loss of COF_2 moieties (Ellis *et al.*, 2004; Schenker *et al.*, 2008) (Figure 3). Molecules leaving this “unzipping cycle” are transformed to PFCA with shortened chain lengths. In organisms, FTOH are oxidized to their acidic analogues by cytochrome P450 monooxygenase (Martin *et al.*, 2005) (Figure 4). Then the alkyl chain is shortened by α or β oxidation. Thus, 8:2 FTOH for instance can be degraded to perfluorononanoate (PFNA) or PFOA. Around 5% of FTOH are converted to PFCA in the atmosphere, and less than 5% in isolated rat hepatocytes after 2 hours (Ellis *et al.*, 2004; Martin *et al.*, 2005). However, despite of those low percentages, FTOH and polyfluorinated sulfonamids identified as precursor substances that are of great importance for the global distribution of PFCA and PFSA in humans and the environment (Ellis *et al.*, 2004; Simcik, 2005; Shoeib *et al.*, 2006; Barber *et al.*, 2007). Source apportionment of PFCA and PFSA in the environment is difficult to conduct. Roughly, it can be distinguished between PFC produced by ECF and telomerisation looking at the ratio between branched and linear molecules. As mainly linear molecules are found in remote regions, it was concluded that PFC originated to a high extent from telomer-based compounds (De Silva and Mabury, 2004; De Silva and Mabury, 2006).



FTAL: fluorotelomer aldehyde

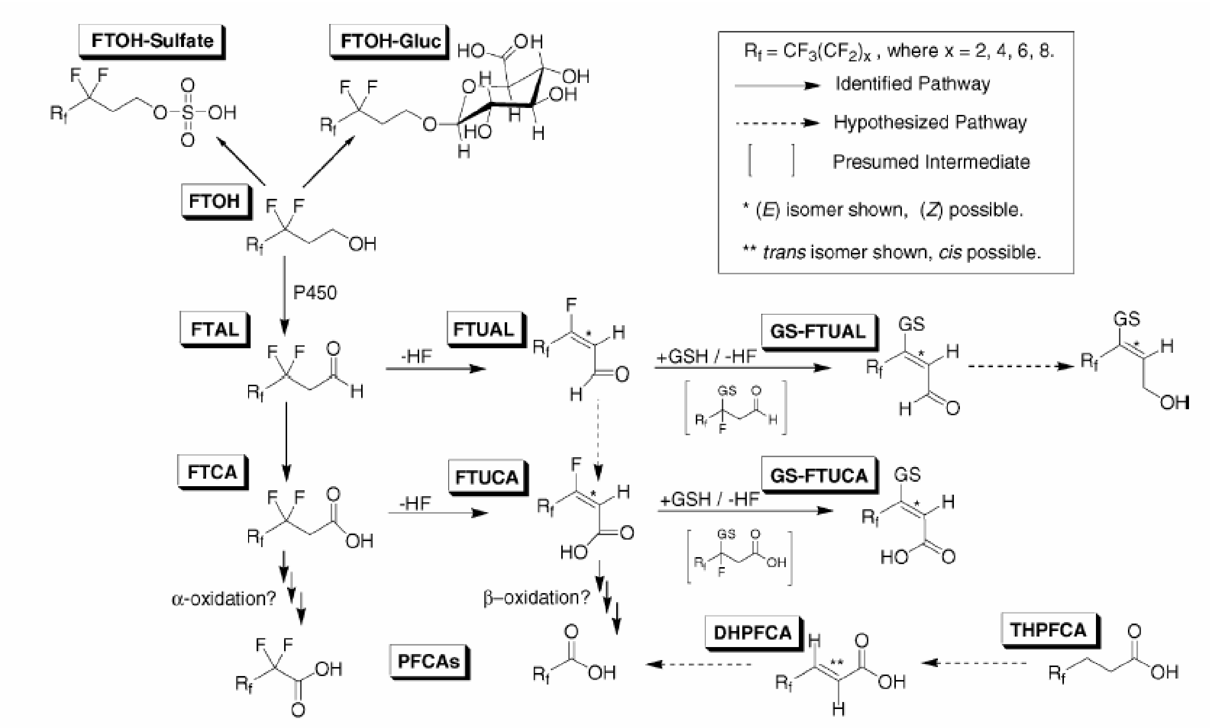
FTCA: fluorotelomer carboxylates

FTOH: fluorotelomeralcohol

PFAL: perfluorinated aldehyd

PFCA: perffluorinated carboxylates

Figure 3: OH-initiated oxidation pathways for fluortelomer alcohols in the atmosphere leading to formation of perfluorinated carboxylates (Ellis *et al.*, 2004).



DHPFCA:	dihydroperfluoroalkyl carboxylate
FTAL:	fluorotelomer aldehyde
FTCA:	fluorotelomer carboxylate
FTOH:	fluorotelomer alcohol
FTOH-Gluc:	fluorotelomer glucuronide
FTUAL:	unsaturated fluorotelomer aldehyd
FTUCA:	unsaturated fluorotelomer acid
GS-FTUAL:	unsaturated fluorotelomer aldehyd glutathione conjugate
GS-FTUCA:	unsaturated fluorotelomer fluorotelomer acid glutathione conjugate
PFCA:	perfluorinated carboxylates
THPFCA:	tetrahydroperfluoroalkyl carboxylate

Figure 4: Generalized FTOH metabolic products and pathways in isolated rat hepatocytes (Martin *et al.*, 2005).

Sewage treatment plants are important sources of PFC, as well (Schröder, 2003; Higgins *et al.*, 2005; Sinclair and Kannan, 2006). Along treatment steps, degradation of precursor substances to PFCA and PFAS is enforced (Sinclair and Kannan, 2006). PFCA and PFSA originating from the influent are not further degraded during wastewater treatment. Therefore concentrations of PFCA and PFSA can increase from the influent to the effluent of a sewage treatment plant. Short chain PFC (C_3 – C_9) remain diluted in the water phase because of their higher water solubilitycompared to longer chained PFC (C_{10} – C_{15}), which partition to the sewage sludge (Schultz *et al.*, 2006; Sinclair and Kannan, 2006). For effective elimination of persistent PFC in wastewater, complex techniques like adsorption to activated carbon, separation by membranes, or advanced oxidation are necessary (Schröder, 2008). However, these procedures are not routinely applied in common sewage treatment plants. Therefore PFC are usually not eliminated, but emitted to rivers, from which they finally may reach human drinking water supplies and the aquatic food web.

1.1.4 Concentrations and effects of PFC in humans and the environment

In the 1960s, organofluorine chemicals were measured in human blood for the first time (Taves, 1968). Applied nuclear magnetic resonance (NMR) analysis revealed the PFOA anion or a structurally related compound and three other components as a likely source of the organic fluorine (Guy *et al.*, 1976). At the beginning of this millennium, development and application of high performance liquid chromatography (HPLC) coupled with mass spectrometry (MS) enabled routine analysis of specific organofluorine compounds (Giesy and Kannan, 2001; Hansen *et al.*, 2001). Since that time PFC where detected in humans (Olsen *et al.*, 2003b; Kannan *et al.*, 2004; Olsen *et al.*, 2004; Yeung *et al.*, 2006), biota (Giesy and Kannan, 2001; Kannan *et al.*, 2002a; Kannan *et al.*, 2002b; Kannan *et al.*, 2002c; Houde *et al.*, 2005; Butt *et al.*, 2007), food (Begley *et al.*, 2005; Fromme *et al.*, 2007b; Tittlemier *et al.*, 2007), water (Hansen *et al.*, 2002; Boulanger *et al.*, 2004; Rostkowski *et al.*, 2006; Lange *et al.*, 2007), air (Martin *et al.*, 2002; Shoeib *et al.*, 2004; Stock *et al.*, 2004b; Barber *et al.*, 2007; Oono *et al.*, 2008; Dreyer *et al.*, 2009a), soil (Powley *et al.*, 2005; Washington *et al.*, 2008), and house dust (Kubwabo *et al.*, 2005; Shoeib *et al.*, 2005b; Strynar and Lindstrom, 2008), even in remote regions of the world. Tables 2 to 6 present exemplarily some PFC concentrations in several matrices.

Table 2: Overview of PFC concentrations in air.

Location	Compound	Level (pg m^{-3})	Reference
Toronto, Canada (n=4)	4:2 FTOH	<LOD	Martin *et al.* (2002)
	6:2 FTOH	30-196	
	8:2 FTOH	9-123	
	10:2 FTOH	7-46	
Long Point, Canada (n=2)	4:2 FTOH	<LOD	Martin *et al.* (2002)
	6:2 FTOH	16-41	
	8:2 FTOH	25-40	
	10:2 FTOH	15-20	
Griffin, USA (n=5)	Σ FTOH *	49-224	Stock *et al.* (2004b)
Cleves, USA (n=3)	Σ FTOH *	103-181	
Long Point, Canada (n=3)	Σ FTOH *	<LOD-52	
Toronto, Canada (n=3)	Σ FTOH *	113-213	
Reno, USA (n=3)	Σ FTOH *	51-93	
Winnipeg, Canada (n=3)	Σ FTOH *	<LOD-18	

´Table 2: Overview of PFC concentrations in air, continued.

Location	Compound	Level (pg m^{-3})	Reference
Arctic (n=20)	6:2 FTOH	<LOD-6	Shoeib *et al.* (2006)
	8:2 FTOH	5.8-26	
	10:2 FTOH	1.9-17	
Hamburg, Germany (n=7)	4:2 FTOH	22-117	Jahnke *et al.* (2007b)
	6:2 FTOH	33-149	
	8:2 FTOH	62-275	
	10:2 FTOH	16-93	
Waldhof, Germany (n=4)	4:2 FTOH	3.3-45	Jahnke *et al.* (2007b)
	6:2 FTOH	17-125	
	8:2 FTOH	33-112	
	10:2 FTOH	10-32	
Sakyo, Japan (n=10)	6:2 FTOH	<LOD-28	Oono *et al.* (2008)
	8:2 FTOH	48-1743	
	10:2 FTOH	<LOD-197	
Higashiyodogawa, Japan (n=10)	6:2 FTOH	27-44	Oono *et al.* (2008)
	8:2 FTOH	199-999	
	10:2 FTOH	45-143	
Morinomyia, Japan (n=4)	6:2 FTOH	<LOD-170	Oono *et al.* (2008)
	8:2 FTOH	310-4585	
	10:2 FTOH	35-518	
German Bight, North Sea (n=7)	4:2 FTOH	<LOD-1.8	Dreyer and Ebinghaus (2009)
	6:2 FTOH	3.3-15	
	8:2 FTOH	8.2-130	
	10:2 FTOH	2.1-29	
Barsbüttel, Germany (n=117)	4:2 FTOH	0.3 [b]	Dreyer *et al.* (2009a)
	6:2 FTOH	22 [b]	
	8:2 FTOH	62 [b]	
	10:2 FTOH	21 [b]	
	PFOS	1.3 [a, b]	
	PFOA	0.3 [a, b]	
Geesthacht, Germany (n=114)	4:2 FTOH	0.1 [b]	Dreyer *et al.* (2009a)
	6:2 FTOH	23 [b]	
	8:2 FTOH	50 [b]	
	10:2 FTOH	21 [b]	
	PFOS	0.6 [a, b]	
	PFOA	0.2 [a, b]	

[a] particle phase

[b] average concentration

LOD: Limit of detection

* total FTOH concentrations reported only

Table 3: Overview of PFC concentrations in solid samples.

Matrix (Country)	Compound	Level (ng g^{-1})	Reference
Sediment (USA)	PFOS PFOA	<LOD-3.76 <LOD-0.25	Higgins *et al.*, (2005)
Sediment (Germany)	PFOS PFOA	<LOD-175 <LOD-506	Becker *et al.* (2008b)
Sewage sludge (USA)	PFOS PFOA	14.4-2610 <LOD-506	Higgins *et al.* (2005)
Sewage sludge (Germany)	PFOS PFOA	<LOD-120 <LOD-23	Becker *et al.* (2008a)
Soil (USA)	PFOA	0.08-0.69	Washington *et al.* (2008)
Dust (Canada)	PFOS PFOA	<LOD-5065 <LOD-1234	Kubwabo *et al.* (2005)
House dust (Canada)	6:2 FTOH 8:2 FTOH 10:2 FTOH	2-2500 3-16315 2-8176	Shoeib *et al.* (2005a)
House dust (USA)	6:2 FTOH 8:2 FTOH 10:2 FTOH PFOS PFOA	74.9 [a] 167 [a] 95.8 [a] 761 [a] 296 [a]	Strynar and Lindstrom (2008)
Popcorn bags (USA)	PFOA	6-290	Begley *et al.* (2005)
Total diet (Germany)	PFOS PFOA	0.03-1.0 0.03-118	Fromme *et al.* (2007b)
Food (Canada)			
Fish, marine	PFOS	2.6	Tittlemier *et al.* (2007)
	PFOA	<LOD	
Ground beef	PFOS	2.1	
	PFOA	<LOD	
Microwave popcorn	PFOS	1.0	
	PFOA	3.6	

[a] average concentration
LOD: Limit of detection

Table 4: Overview of PFC concentrations in aqueous samples.

Matrix (Country)	Compound	Level (ng L^{-1})	Reference
Rain water (North America)	PFOS PFOA	0.59 [a] 0.6-89	Loewen *et al.* (2005) Scott *et al.* (2006)
Snow (USA)	PFOS PFOA	<LOD-1.9 <LOD-19.6	Kim and Kannan (2007)
Ground water (USA)	PFOA	<LOD-6570000	Moody and Field (1999)
Ground water (USA)	PFOS PFOA	19-87 <LOD-18	Plumlee *et al.* (2008)
River water (USA)	PFOS PFOA	16.8-140 <LOD-598	Hansen *et al.* (2002)
River water (Germany)	PFOS PFOA	<LOD-193 <LOD-3640	Skutlarek *et al.* (2006)
River water (Europe)	PFOA	<LOD-200	MacLachlan *et al.* (2007)
Lake water (Canadian Artic)	PFOS PFOA	0.9-57 0.5-16	Stock *et al.* (2007)
Tap water (Japan)	PFOS	0.1-50.9	Harada *et al.* (2003)
Drinking water (Germany)	PFOS PFOA	<LOD-22 <LOD-519	Skutlarek *et al.* (2006)
Sewage treatment plant effluent (USA)	PFOS PFOA	3-68 58-1050	Sinclair and Kannan (2006)

[a] average mean

LOD: Limit of detection

Table 5: Overview of PFC concentrations in human blood (ng mL^{-1}), liver (ng g^{-1}), and milk (ng mL^{-1}).

Matrix (Country)	Compound	Level	Reference
Human blood (USA)	PFOS	34.9 ng mL$^{-1\ \mathrm{a}}$	Olsen *et al.* (2003a)
	PFOA	4.6 ng mL$^{-1\ \mathrm{a}}$	
Human blood, plasma (Belgium)	PFOS	4.5-27 ng mL^{-1}	Kannan *et al.* (2004)
	PFOA	<LOD-13 ng mL^{-1}	
Whole blood (Brazil)	PFOS	4.3-35 ng mL^{-1}	
	PFOA	<LOD	
Whole blood (Columbia)	PFOS	4.6-14 ng mL^{-1}	
	PFOA	3.7-12 ng mL^{-1}	
Serum (India)	PFOS	<LOD-3.1 ng mL^{-1}	
	PFOA	<LOD-3.5 ng mL^{-1}	
Serum (Italy)	PFOS	<LOD-10 ng mL^{-1}	
	PFOA	<LOD	
Serum (Japan)	PFOS	4.1-40 ng mL^{-1}	
	PFOA	<LOD-12 ng mL^{-1}	
Whole blood (Korea)	PFOS	3.0-92 ng mL^{-1}	
	PFOA	<LOD-256 ng mL^{-1}	
Whole blood (Malaysia)	PFOS	6.2-19 ng mL^{-1}	
	PFOA	<LOD	
Whole blood (Poland)	PFOS	16-116 ng mL^{-1}	
	PFOA	9.7-40 ng mL^{-1}	
blood (USA)	PFOS	<LOD-164 ng mL^{-1}	
	PFOA	<LOD-88 ng mL^{-1}	
Whole blood (Sweden)	PFOS	1.7-37 ng mL^{-1}	Karrman *et al.* (2006)
	PFOA	0.5-12 ng mL^{-1}	
Human plasma, (Germany)	PFOS	6.2-131 ng mL^{-1}	Fromme *et al.* (2007a)
	PFOA	1.7-39 ng mL^{-1}	
Breast milk (China)	PFOS	0.045-0.36 ng mL^{-1}	So *et al.* (2006)
	PFOA	0.047-0.21 ng mL^{-1}	
Breast milk (Germany)	PFOS	0.10-0.64 ng mL^{-1}	Völkel *et al.* (2008)
	PFOA	<LOD-0.46 ng mL^{-1}	
Human liver (USA)	PFOS	18.4/19.2 ng g$^{-1\ \mathrm{a}}$ (M/F)	Olsen *et al.* (2003b)
	PFOA	<LOD	

[a] Geometric mean

M: Male

F: Female

LOD: Limit of detection

Table 6: Overview of PFC concentrations in wildlife tissue.

Species	Compound	Level (ng g^{-1})	Reference
Bald eagle, plasma, USA	PFOS	1-2570	Giesy and Kannan (2001)
Mink, liver, USA	PFOS PFOA	20-4150 4.5-27	Kannan *et al.* (2002c)
River otter, liver, USA	PFOS PFOA	25-994 <LOD-19	
Cormorant, liver, Sardinian Sea	PFOS PFOA	32-150 29-450	Kannan *et al.* (2002b)
Bottlenose dolphin, liver, Mediterranean Sea	PFOS PFOA	<LOD-108 <LOD	
Sea gull, Japan	PFOS PFOA	<LOD-89 <LOD	Kannan *et al.* (2002a)
Polar bear, liver, Canada	PFOS PFOA	1700->4000 2.9-13	Martin *et al.* (2004a)

LOD: Limit of detection

Once taken up, PFC can enrich in organisms. In contrast to chlorinated organic compounds, which accumulate in fatty tissues of vertebrates, PFC partition to serum proteins and liver (Jones *et al.*, 2003; Kannan *et al.*, 2005; Houde *et al.*, 2006). Karrman et al. (2006) observed, that median total PFC concentrations in human blood samples from Sweden exceeded concentrations of total polychlorinated biphenyls (PCB) and p,p´-dichlorodiphenylethen by factor 20-50, and concentrations of hexachlorobenzene (HCB), chlordanes, and polybrominated diphenylethers (PBDE) by factor 300-450. (Skutlarek *et al.*, 2006; Lange *et al.*, 2007). Ingestion of contaminated drinking water and food, and the use of PFC containing consumer products were supposed to be the major exposure pathways for humans (Fromme *et al.*, 2007b; Trudel *et al.*, 2008).

PFAS are more bioaccumulative than PFCA of equal chain length, because PFAS have one more fluorinated carbon than corresponding PFCA. Bioaccumulation of PFC is increasing with the length of the fluorinated alkyl chain due to a decreasing water solubility (Martin *et al.*, 2004b; Houde *et al.*, 2006; Higgins *et al.*, 2007). Bioaccumulation potential of PFCA with seven fluorinated carbons or less is considered as very low (Conder *et al.*, 2008). Moreover, bioaccumulation rates are species dependent. Elimination half life times of PFOA and PFOS in rats were up to 9 days and 90 days respectively, whereas in humans they were 1-3.5 years and 8.7 years, respectively (Kudo *et al.*, 2001; Hekster *et al.*, 2003; Lau *et al.*, 2004). Moody et al. (2002) reported bioaccumulation factors for PFOS in the common shiner (fish) between 6300 and 125000. In rainbow trout bioconcentration factors (BCF) for PFOS were 690 (carcass) and 3100 (blood) after 12 days. Accordant BCF for PFOA were 3.2 and 25, respectively (Martin *et al.*, 2003a; Martin *et al.*, 2003b). In wild turtles, BCF for PFOS and PFOA was 10964 and 3.2 respectively (Morikawa *et al.*, 2006).

PFC induced several toxicological effects in organisms (Table 7). Most of the conducted studies focussed on PFOA and PFOS. PFCA and PFAS can cause peroxisome proliferation and thereby affect the organisms lipid metabolism (Luebker *et al.*, 2002; Kudo *et al.*, 2005). Perfluorinated compounds with carbon chain lengths of 7 to 10 are also capable of downregulating the gap junctional intercellular communication and thus affect the cells growth regulation (Upham *et al.*, 1998). Peroxisome proliferation and a disturbed cell communication also result in the promotion of tumors. Chronic PFOS intake led to hepatocarcinogenic effects in rats. Intake of PFOA induced tumors in liver, pancreas, and Leydig cells (Upham *et al.*, 1998; Biegel *et al.*, 2001). Furthermore, PFCA and PFAS affected thyroid hormone circulation (Giesy and Kannan, 2002; Seacat *et al.*, 2002), reduced body weight and affected the development of rats, mice, and rabbits (Thibodeaux *et al.*, 2003; Lau *et al.*, 2004). Recently, PFCA, PFAS, and FTOH were also supposed to be endocrine disruptors, as they showed estrogenic effects in cell cultures and reduced testosterone levels in adult rats (Maras *et al.*, 2006; Jensen and Leffers, 2008).

PFCA and PFAS exhibit only moderate acute toxicity. Generally, toxic effects increase with length of the fluorinated alkyl chain. Saturated and unsaturated fluorotelomer carboxylic acids (FTCA and FTUCA), which have been identified as intermediates in the degradation of FTOH to PFCA, were found to be up to 10000 times more toxic than analogous PFCA (Phillips *et al.*, 2007).

Table 7: Acute and chronic toxicities (EC_{50}, LC_{50}, LD_{50} and NOEC) of some PFC for several organisms.

Compound	Species	Toxicity	Reference
PFHxA	*Vibrio fischeri*	30min EC_{50} 4266 µM	Mulkiewicz *et al.* (2007)
PFHpA	*Vibrio fischeri*	30min EC_{50} 3020 µM	Mulkiewicz *et al.* (2007)
PFOA	*Vibrio fischeri* *Rattus rattus*	30min EC_{50} 1380 µM LD_{50} 500 mg kg^{-1} bw	Mulkiewicz *et al.* (2007) Pabel *et al.* (2008)
PFNA	*Vibrio fischeri*	30min EC_{50} 1148 µM	Mulkiewicz *et al.* (2007)
PFOS	*Daphnia magna* *Lemna gibba* *Oncorhynchus mykiss* *Rattus rattus*	48 hr EC_{50} 67.2 mg L^{-1} 7d EC_{50} 59.1 mg L^{-1} 96 hr EC_{50} 7.8 mg L^{-1} LD_{50} 251 mg kg^{-1} bw	Boudreau *et al.* (2003) Hekster *et al.* (2003) Giesy and Kannan (2002)
8:2 FTOH	*Daphnia magna* *Danio rerio*	48 hr NOEC 0.16 mg L^{-1} 96 hr NOEC 0.18 mg L^{-1}	Hekster *et al.* (2003)
8:2 FTCA	*Daphnia magna* *Chirinomus tetans* *Lemna gibba*	48 hr EC_{50} 3.0 mg L^{-1} 10d EC_{50} 12.4 mg L^{-1} 7d EC_{50} 0.9 mg L^{-1}	Phillips *et al.* (2007)
8:2 FTUCA	*Daphnia magna* *Chirinomus tetans* *Lemna gibba*	48 hr EC_{50} 4.0 mg L^{-1} 10d EC_{50} 21.2 mg L^{-1} 7d EC_{50} 1.9 mg L^{-1}	Phillips *et al.* (2007)

1.1.5 Instrumental analysis of PFC

Organofluorine compounds were analysed since the second half of the last century. However, in the beginning only non-selective analytical methods were available. Organofluorine molecules were combusted yielding hydrogen fluoride, which was determined by an fluoride-ion selective electrode (Taves, 1968; Kissa, 1986). Application of ^{19}F NMR spectroscopy elucidated the molecular structure of organofluorine molecules, as it determines the presence of CF_2 and CF_3 moieties (Guy *et al.*, 1976; Ellis *et al.*, 2000; Moody *et al.*, 2001). However, this analytical method is non-selective, as well. The first selective method for routine determination of PFCA and PFAS was developed by Hansen et al. (2001) applying high performance liquid chromatography (HPLC) tandem mass spectrometry (MS) with negative electrospray ionisation (ESI) for biota. In order to facilitate ionisation of the analytes, ammonium acetate was used to buffer methanol and water used for gradient elution. This method was adapted by many research groups and modified for the determination of PFCA and PFSA in other matrices like water, food, or soil, etc. (Higgins *et al.*, 2005; Skutlarek *et al.*, 2006; Fromme *et al.*, 2007b; Washington *et al.*, 2007; Washington *et al.*, 2008). It is also possible to derivatise PFCA to their difluoroanilide (De Silva and Mabury, 2004) or methylester analogues (Schultz *et al.*, 2003) to enable determinations by GC-MS. In contrast to PFCA, PFSA do not form stable, volatile derivatives and therefore cannot be analysed by GC-MS (Schultz *et al.*, 2003).

Neutral, volatile PFC are routinely determined by GC-MS applying positive chemical ionisation (Martin *et al.*, 2002). For FTOH, ionisation by electron impact is used, as well (Szostek and Prickett, 2004). However, only small molecular fragments (mainly m/z 31 and m/z 69) can be used, which may not be specific enough for a reliable identification of the analyte. Chemical ionisation enables identification of FTOH by their protonated molecular ions (m/z 265, m/z 365, m/z 465, m/z 565). This method is more selective and less sensible to signal disturbance by other compounds or matrix effects than ionisation by electron impact. FTOH can also be determined by HPLC-MS (Berger *et al.*, 2004; Martin *et al.*, 2005; Taniyasu *et al.*, 2005). For electrospray ionisation of FTOH, gradient solvents buffered by ammonium acetate are often necessary. The ammonium salt forms an acetate adduct with the FTOH molecules ($[M+59]^-$) that can be detected by negative ESI MS (Martin *et al.*, 2005).

In the following paragraphs some analytical methods for the determination of PFC in several matrices are shortly described which are related to the objectives of this thesis.

For the determination of FTOH and other volatile PFC in the atmosphere, XAD-impregnated polyurethane foam (PUF) disks (SIP) are used as passive air samplers (Shoeib *et al.*, 2008). Those PUF disks were exposed to air for several weeks and afterwards soxhlet extracted using petroleum ether / acetone. Extracts were centrifuged and then analysed by GC-MS.

FTOH in air samples are also routinely analysed by high volume active sampling (Barber *et al.*, 2007; Dreyer *et al.*, 2009a). XAD-PUF cartridges are used for the enrichment of airborne PFC. Then cartridges are extracted using methyl-tert-butyl-ether (MTBE) / acetone. Extracts are concentrated and FTOH are determined by GC-MS.

FTOH were determined in housedust by Strynar and Lindstrom (2008). Dust samples were extracted in hexane applying ultrasonication. Then, extracts were purified by Supelclean LC Silica solid phase extraction (SPE) cartridges and FTOH were analysed by GC-MS. Shoeib et al. (2005b) determined perfluorinated sulfonamides in housedust. Samples were soxhlet-extracted using dichloromethane without further purification prior to GC-MS determination.

PFCA and PFSA are routinely analysed in water samples applying C_{18} sorbent, strong anion exchange (SAX) sorbent, weak anion exchange (WAX) sorbent, and hydrophilic lipophilic balanced (HLB) sorbent for SPE prior to HPLC-MS/MS determination (Moody and Field, 1999; Moody *et al.*, 2001; Taniyasu *et al.*, 2005).

PFCA and PFSA in the atmosphere were determined by high volume sampling applying glass fibre filters and PUF XAD cartridges (Kaiser *et al.*, 2005; Barber *et al.*, 2007; Dreyer *et al.*, 2009a). Methanol extracted PFC were concentrated and directly measured by HPLC-MS/MS.

An analytical method for determination of PFCA in soils was developed by Washington et al. (2007; 2008). Samples were alkalinised, extracted with ACN/water followed by an ion-pair extraction and HPLC-MS/MS measurement.

1.2 Objectives

Scientific and public concern regarding PFC increased during the past years. Due to their extensive application and high persistence, these compounds are now ubiquitously distributed. Whereas the role of direct PFC sources, mainly to the aquatic environment, was already assessed in various studies (Moody and Field, 1999; Moody *et al.*, 2002; Schultz *et al.*, 2004; Sinclair and Kannan, 2006; Skutlarek *et al.*, 2006; Lange *et al.*, 2007), the importance of indirect, diffuse sources is not well understood. Furthermore, a comprehensive understanding of PFC transport processes, such as riverine, oceanic, and atmospheric transport, is still lacking. Application of SPMD as passive samplers may provide a valuable tool to elucidate transport and distribution processes of neutral PFC, because SPMD can be easily deployed for al long time without need of energy and maintenance. However, volatile polyfluorinated precursor substances like FTOH were mainly analysed in air applying high volume active sampling or passive sampling by XAD impregnated PUF disks. There are no studies regarding use of SPMD for air sampling of FTOH and other volatile PFC. Until now, scientific studies mainly investigated perfluorinated compounds in biota and water samples. Studies investigating other environmental matrices and consumer products are scarce and only a few research groups determine FTOH and PFCA simultaneously.

The objective of this thesis was to develop several analytical methods to investigate volatile FTOH and non-volatile PFOA and PFOS in different natural and anthropogenic matrices. To enable the simultaneous determination of FTOH, PFOA, and PFOS by nanoflow UPLC-TOF-MS, an instrumental method had to be developed. This analytical system had never been used for PFC determination before. In addition, GC-MS was applied, when solely FTOH were analysed. By means of these methods, PFC concentrations were determined in different matrices.

1. Air and SPMD

Because air is considered as an important transport medium for volatile PFC, suitable tools are needed for the determination of PFC air concentrations. Therefore, SPMD were applied as passive air samplers for FTOH. Specific questions were: Are SPMD suited as passive samplers for the determination of PFC in air? How is the partitioning behaviour of FTOH to SPMD under laboratory and field conditions? How do SPMD perform in comparison to conventional FTOH air sampling using High volume active sampling and passive sampling by SIP discs? For this purpose, an analytical method for the extraction and purification of SPMD had to be developed and compared to routinely used analytical methods

2. Air and needles

Pine needles provide a natural passive sampling medium for airborne organic contaminants. Therefore a method for determination of FTOH adsorbed to needles was developed. Pine needles of two urban sites were investigated to verify whether FTOH adsorb to needles and whether needles are suitable passive samplers for FTOH.

3. Airborne particles

Airborne PFC, particularly ionic PFCA and PFSA can be deposited to the surface adsorbed to particles. Therefore a method was optimised to determine PFC on particles collected by deposition samplers. For this purpose, backup samples of the European project MONARPOP were used, in which the distribution of persistent organic pollutants in the Alpes was investigated. Specific questions were: Are significant amounts of PFOA and PFOS deposited? Do depositions of PFOA and PFOS differ between three sites in the Alpes?

4. Domestic particles

As natural airborne particles in outdoor air, house dust may represent a sink for PFC. Thus, a method was optimised to determine PFC in housedust. Here, only FTOH were investigated. The specific question was: Does housedust contribute to human exposure to PFC and to which extent?

5. Consumer products

Do consumer products contribute to exposure of humans to PFC? To answer this question, PFC concentrations in several consumer products such as impregnating agents, lubricants, cleaning agents were determined. Those concentrations were used to estimate human exposure to PFC when applying these agents.

6. Water and soil

During a cooperation project with the University of Rio de Janeiro, water and soil samples were collected in the National Park Serra dos Órgãos, Federal district of Rio de Janeiro, Brazil. Analytical methods were optimised for the determination of PFOA and PFOS in those samples. The specific question was: Are PFC present in this remote region in Brazil?

2 Material and Methods

2.1 Chemicals and reagents

Native and mass-labelled analytical standards used during method development and PFC analysis are presented in Table 8.

Table 8: Analytical standards, purity (%), and CAS of substances used.

Compound	Purity (%)	Company
4:2 FTOH	97	Fluorochem, Old Glossop, UK
6:2 FTOH	97	Fluorochem, Old Glossop, UK
8:2 FTOH	97	Fluorochem, Old Glossop, UK
10:2 FTOH	97	Fluorochem, Old Glossop, UK
PFOA	99	Fluorochem, Old Glossop, UK
PFOS	98	Sigma Aldrich, Taufkirchen, Germany.
$^{13}C_2{}^2H_2$ 4:2 FTOH	98	Wellington, Laboratories Guelph, Ontario, Canada
$^{13}C_2{}^2H_2$ 6:2 FTOH	98	Wellington, Laboratories Guelph, Ontario, Canada
$^{13}C_2{}^2H_2$ 8:2 FTOH	98	Wellington, Laboratories Guelph, Ontario, Canada
$^{13}C_2{}^2H_2$ 10:2 FTOH	98	Wellington, Laboratories Guelph, Ontario, Canada
$^{13}C_4$ PFOA	98	Wellington, Laboratories Guelph, Ontario, Canada
$^{13}C_4$ PFOS	98	Wellington, Laboratories Guelph, Ontario, Canada
9:2 FA	98	Fluorochem, Old Glossop, UK
7:1 FA	97	Donation of GKSS Research Center, Geesthacht, Germany
8:1 FA	98	Donation of GKSS Research Center, Geesthacht, Germany
9:1 FA	98	Donation of GKSS Research Center, Geesthacht, Germany

Acetone, acetonitrile (ACN), n-hexane (HEX), methyl-tert.butyl ether (MTBE) (all picograde quality), and methanol (MeOH; HPLC and LC-MS grade) were purchased from LGC-Standards, Wesel, Germany. Ethylacetate (EtAc; Pestanal) was obtained from Riedel-de-Haen, Seelze, Germany.

Envi-Carb (250 mg) cartridges, triolein (99% purity), and Carboxen 1016 cartridges were obtained from Sigma-Aldrich, Seelze, Germany. Strata C18-E cartridges and strata SDB-L syrene divenyl benzene cartridges were purchased from Phenomenex, Augsburg, Germany. Bulk C18 was obtained from Separtis, Grenzach-Whylen, Germany. Ammonium acetate (LC-MS grade) was purchased from Fluka, Buchs, Switzerland. Weak anion exchange cartridges (Oasis WAX) were obtained from Waters, Milford, USA.

2.2 Quality assurance / Quality control

All determinations of PFC concentrations in samples were conducted using mass-labelled internal standards in order to check recoveries of PFC during extraction and clean-up. Additionally, 9:2 FA was used as internal standard added to samples and calibration standards to control performance of GC-MS and UPLC-MS. At least one blank sample was analysed and measured with every set of samples (n=2-5).

Glassware used for PFC analysis was rinsed with methanol and acetone (technical quality), washed in a laboratory dish washer at 80 °C, rinsed with deionised water and baked for 8 hrs at 450 °C. Laboratory equipment not allowed to be baked was rinsed with methanol (HPLC grade) and acetone (picograde) after cleaning in the dishwasher. For cleaning of small plastic materials also ultra sonication was used.

2.3 Optimisation of PFC determination by nanoflow UPLC – TOF MS

PFCA and PFSA like PFOA and PFOS are routinely detected by HPLC-MS (Giesy and Kannan, 2001; Hansen *et al.*, 2001; Martin *et al.*, 2003b). FTOH are usually detected by GC-MS (Martin *et al.*, 2002; Stock *et al.*, 2004b; Jahnke *et al.*, 2007a), but there are some authors using HPLC-MS for the detection of FTOH, as well (Berger *et al.*, 2004; Martin *et al.*, 2005; Szostek *et al.*, 2006). However, until now nanoflow UPLC coupled to a TOF MS had never been applied for PFC analysis. Compared to HPLC, this analytical system enables gradient elution at a higher system pressure (up to 690 bar), which allows the use of nanobore columns with small particles at high linear flow rates resulting in a higher analyte sensivity and resolution.

The optimisation process for PFC determination applying UPLC-TOF MS included the evaluation of flow rates, peak shape, and peak separation by two different column materials (C18 BEH and C18 Atlantis, both Waters, Milford, USA) for the gradient elution.

Morevover, concentration of the ammonium acetate buffer (0, 2, and 10 mM) and MS tune parameters such as cone voltage (42, 35 and 17 V), collision energy (40 and 11 eV) and capillary voltage (1800 and 2000 kV) were evaluated to optimise electrospray ionisation for the simultaneous determination of PFOA, PFOS, and FTOH.

2.4 Method development for the determination of FTOH in SPMD

2.4.1 Theory of passive sampling

Passive samplers are defined as "human-made devices, where sample collection and residue extraction occur simultaneously in a complete passive manner" (Huckins *et al.*, 2006). Passive samplers do not need electricity or intensive maintenance and therefore can easily be operated and deployed for a long time even in remote areas lacking suitable infrastructure needed for active samplers.

A chemical is concentrated in the passive sample medium when the fugacity of the chemical in the passive sampler is lower than in the surrounding medium. To calculate the concentration of an analyte in ambient air from its concentration in the passive sampler, the following requirements have to be fulfilled: 1) the ananlyte concentration in the passive sampling medium and in the environment must be proportional; 2) the sampling rate and partition coefficients associated to chemical exchange have to be independent of the analyte concentration in ambient air; 3) the analyte concentration in the ambient air should not be reduced significantly by the sampling process itself (Huckins *et al.*, 2006).

The exchange of compounds between the passive sampling medium and the surrounding air can be separated in three phases (Figure 5) (Bartkow *et al.*, 2005): 1) a linear uptake stage. Here, the compound uptake is proportional to its concentration in ambient air. In this stage, the sampler is called "kinetic sampler"; 2) a curvilinear stage. The importance of the compound elimination from the sampling medium increases: 3) a steady state stage. Uptake and elimination of the compound have the same absolute value. The equilibrium is achieved.

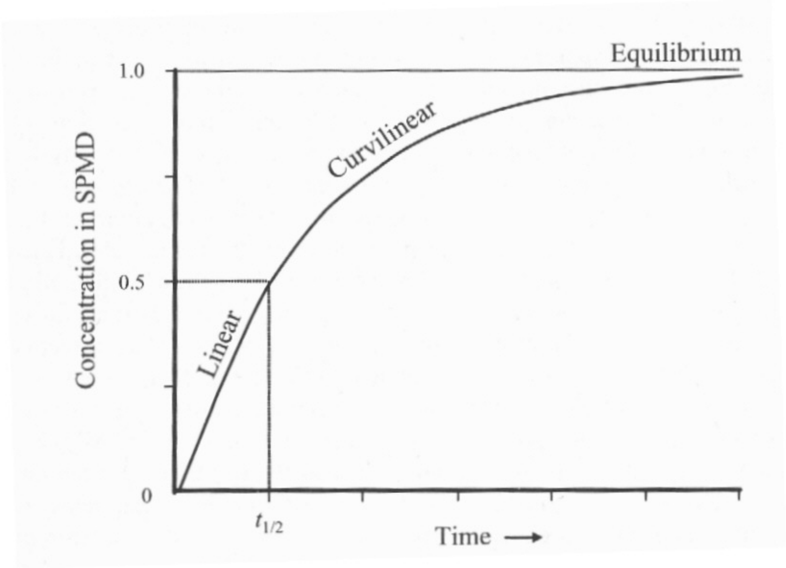


Figure 5: Plot of three phases of passive sampler uptake (Huckins *et al.*, 2006).

Hence, passive samplers accumulate a chemical in an integrative way until the equilibrium stage is reached. For the calculation of the analyte concentration in the air, performance reference compounds (PRC) are used, which ideally should have the same physico chemical properties as the analyte. PRC are spiked to the samplers prior to their deployment. Analyte sampling rates and thus the sampled volume of air can be derived from the PRC elimination. For a good passive sampler performance, it is important to optimize film thickness, area, volume, and the area to volume ratio of the sampler.

2.4.2 Semipermeable membrane devices

Dialysis tubings henceforth referred to as semipermeable membrane devices (SPMD) consist of a low density polyethylene membrane (LDPE) containing a lipid or other suitable substances for enrichment of target compounds. Transient polymeric cavities of approximately 10 A° in diameter are embedded in the LDPE membrane (Figure 6). Because of the size exclusion and the lipophilic properties of the membrane, SPMD accumulate only noncharged molecules with a molecular mass less than approximately 600 mu and a octanol water partition coefficient log $K_{OW} \geq 3$ (Petty *et al.*, 2000; Huckins *et al.*, 2006). Typically, the natural neutral triglyceride triolein (2,3-bis[[(E)-octadec-9-enoyl]oxy]propyl (E)-octadec-9-enoate; MW 885.4; melting point: +5 °C) is used as lipid. It is non-reactive and thus suitable for the accumulation of hydrophobic organic chemicals.

Compounds approaching SPMD by convection and eddy diffusion are confronted with three barriers before they reach the sampling medium: At first, the substances have to diffuse through the laminar boundary air layer. When the surface of the sampler is reached, the SPMD membrane with its transient cavity structure acts as barrier regarding to size and polarity of the compound. Entering and diffusion into the triolein represents the last barrier. The uptake of a compound into SPMD is controlled by the barrier offering the highest resistance (Petty *et al.*, 2000; Huckins *et al.*, 2006). In comparison to the other two barriers, the resistance of the triolein phase is negligible (Petty *et al.*, 2000; Huckins *et al.*, 2006).

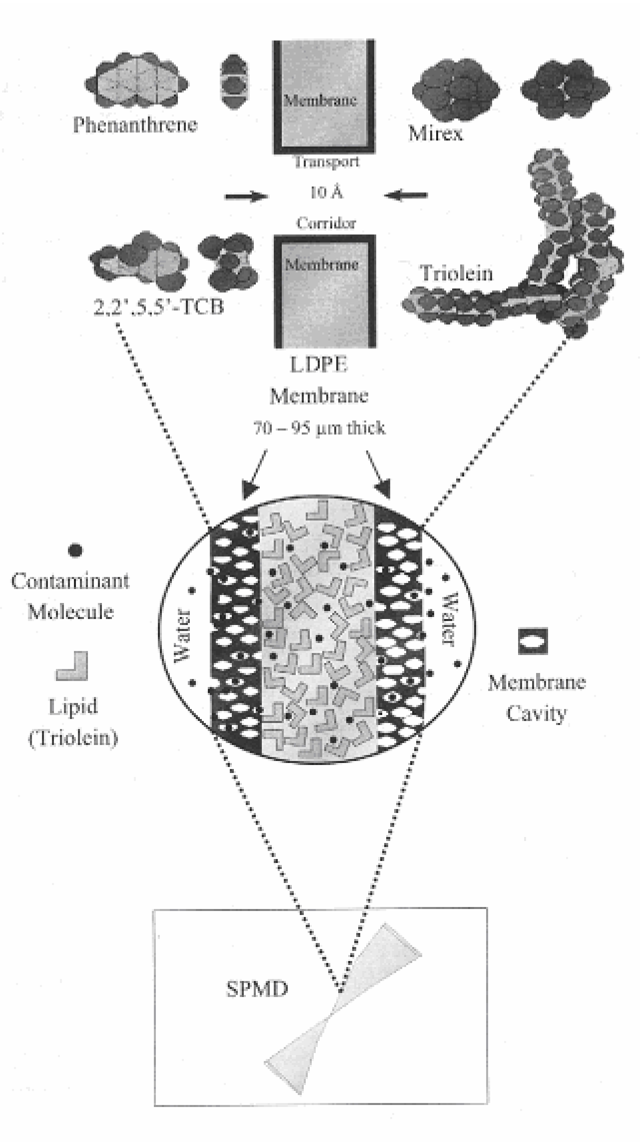


Figure 6: Movement of contaminants through transient pores and size exclusion phenomenon in SPMD (Huckins *et al.*, 2006).

SPMD have routinely been applied as passive samplers for accumulation and determination of various hydrophobic organic compounds such as polycyclic aromatic hydrocarbons, PCB, polychlorinated dibenzo dioxines and furans, and organochlorine pesticids from water (Huckins *et al.*, 1993; Booij and Van drooge, 2001; Luebker *et al.*, 2002; Setkova *et al.*, 2005) and air (Van drooge *et al.*, 2005; Levy *et al.*, 2007; Zhu *et al.*, 2007; Shoeib *et al.*, 2008).

So far, SPMD were not applied for FTOH air sampling and their suitability was not evaluated. Only PUF disks, impregnated with XAD-4, and tubes filled with XAD-2 were used as passive air samplers for FTOH determination (Loewen *et al.*, 2008; Shoeib *et al.*, 2008). In contrast to SPMD, chemicals can directly adsorb to the XAD without passing a membrane. On the other hand, those samplers can only be used in air and the material accumulating the pollutants is not as well protected against environmental disturbances as in SPMD.

2.4.3 Purification of SPMD extracts by GPC

Removal of co-extracted triolein is the essential step in SPMD analysis. Gel permeation chromatography (GPC) (Ockenden *et al.*, 2001; Yusa *et al.*, 2005) and liquid liquid extraction (LLE) (Esteve-Turrillas *et al.*, 2006) is often used for this purpose. To find out which method is suited best for purification, these methods as well as SPE were compared.

For all SPMD spike and recovery experiments, a 20 ppm FTOH solution in EtAc was used. 50 µL of this solution were spiked to SPMD prior to extraction and prior to SPE, respectively.

5 µg FTOH and 10 mL of EtAc were added to 0.7 mL of triolein. This solution was injected into a gel permeation chromatograph (Gilson, Limburg-Offheim, Germany) and eluted with cyclohexane : EtAc (1:1) at a flow rate of 5 mL min^{-1}. Size exclusion was conducted using Biobeads S-X3 (200-400, LC-Tech, Darfen, Germany). After the elution of triolein, four fractions (50 mL each) were collected. In a second experiment, 5 µg FTOH diluted in 10 mL EtAc were injected into the GPC without triolein and three fractions (0-16 min, 16-24 min, and 24-34 min) were collected.

Collected GPC fractions were evaporated to 2 mL using rotary evaporation. As injection standard 9:2 FA was added. FTOH were determined by GC-MS as described in section 2.12.

2.4.4 Optimisation of solid phase extraction of SPMD extracts

For the clean-up of SPMD extracts, different adsorbent materials and elution solvents were evaluated. For this purpose, SPMD were cut into slices and extracted using methanol (MeOH). The volume was rotary-evaporated to about 1 mL. Then, extracts were spiked with an FTOH standard solution and SPE was conducted to remove remaining triolein. As SPE materials, C18-E (500 mg and 1g), C18 (1g), SDB-L (200 mg), and C18-E (500 mg) + Carboxen 1016 (100 mg) were evaluated. Cartridges were conditioned with EtAc and MeOH, 3 mL each. Solvents tested for elution were EtAc, MeOH, MeOH/EtAc (1/1), and MeOH/EtAc (2/1). SPE cartridges were eluted with 5 mL of the solvent to be tested. The volume was reduced to about 0.5 mL under a gentle stream of nitrogen and transferred into a GC vial. 9:2 FA was added as internal standard and FTOH were determined by GC-MS.

2.4.5 Optimisation of SPMD extraction

FTOH were spiked into SPMD using a 50 µl syringe. After homogenisation, SPMD were cut in slices and extracted by shaking in 100 mL of different solvents (MeOH, ACN, acetone, and EtAc) for 24 hrs. MeOH and ACN extracts were liquid liquid extracted with 100 mL Hex. After phase separation, the MeOH and the ACN fractions were collected and rotary evaporated to about 1 mL. SPE was conducted with C18-E (500 mg) + Carboxen 1016 (100 mg). Cartridges were eluted with 8 mL MeOH. The volume was reduced to about 0.5 mL under a gentle stream of nitrogen and transferred into a GC vial. 9:2 FA was added as internal standard and FTOH were determined by GC-MS. SPMD extracts in acetone and EtAc were directly purified by SPE as described above.

2.4.6 Final method for FTOH determination in SPMD

SPMD were cut into slices and transferred into a glass vessel. Prior to the extraction mass labelled 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were added. 100 mL of ACN/HEX (1/1 v/v) were added and SPMD were extracted by shaking for 24 hours. Extracts were transferred into a separatory funnel and 100 mL ACN/HEX (1/1 v/v) were added and the funnels were shaken for about 2 min. After phase separation, ACN was collected and concentrated to about 1 mL by rotary evaporation, and finally to 200 µL by a gentle stream of nitrogen. 9:2 FA was added as internal standard and FTOH were determined by GC-MS. The HEX phase containing triolein was discarded.

2.5 Accumulation and elimination of FTOH in SPMD

2.5.1 FTOH migration out of SPMD

2.5.1.1 FTOH migration out of SPMD into air

In a first experiment, release rates of FTOH in SPMD were investigated. For this purpose triolein filled SPMD were spiked with 25 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, each, in 0.1 mL acetone and sealed again. FTOH were dissolved in acetone since the solvent volume was relatively high compared to the volume of triolein (0.7 mL). Acetone is very volatile and thus can easily penetrate through the SPMD membrane, resulting in a rapid decline of solvent content after deployment. By this measure, adverse effects of the solvent on the partitioning of FTOH between triolein and air were minimized. SPMD were fixed in a Stevenson screen box made of untreated wood and placed 2.5 m above ground level at a site located at the Helmholtz Zentrum München (HMGU) in the north of Munich, Germany. In this deployment device, SPMD were protected from direct sunlight and wet deposition, and air flow turbulences were minimized (Levy *et al.*, 2007). Conducting this experiment under field condition, prevents any saturation effects of FTOH in the ambient air resulting in an equilibrium between FTOH concentrations in air and SPMD. After 0, 8, 16, 32, and 64 days of deployment (September to November 2007; temperatures between 5 and 22°C), SPMD triplicates were collected and the FTOH concentrations were determined as described in sections 2.4.4 and 2.12. If SPMD were not analysed immediately after sampling, they were stored at –30°C. 7:1 FA, 8:1 FA, and 9:1 FA were used as internal standards for calculation of FTOH recoveries. For each triplicate sample, one blank SPMD that was shortly exposed to ambient air, was analysed simultaneously.

2.5.1.2 FTOH migration out of SPMD into solvent

In order to evaluate FTOH migration out of SPMD in presence of an organic solvent, SPMD were extracted by dialysis, which is a common extraction method in routine SPMD analysis (Booij and Van drooge, 2001; Lohmann *et al.*, 2001; Bartkow *et al.*, 2004; Huckins *et al.*, 2006). For this purpose triolein-filled SPMD were spiked with 0.1 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, each, in 50 µL EtAc and sealed again. EtAc was chosen, because evaporation of the carrier solvent was not necessary in this experiment. SPMD were extracted twice for 24 hrs using 200 mL acetone/MTBE (1/1 v/v) (Dreyer *et al.*, 2008). After that, the remaining FTOH in SPMD were extracted as described in section 2.4. It is important to note that for this third extraction step, the SPMD tubings were cut into slices and ACN/HEX (v/v 1/1) was used for extraction, because this solvent mixture is crucial for purification by liquid liquid extraction. Prior to each extraction, mass-labelled FTOH were added as interal standards for the determination of recovery rates. Extracts of the three extraction steps were analysed separately. Dialysis extracts were concentrated and purified by solid phase extraction using Envi-Carb cartridges, which were eluted with 5 mL acetone/MTBE (1/1). Afterwards, extracts were concentrated to 200 µL using rotary evaporation and a gentle stream of nitrogen. FTOH were determined by GC-MS as described in section 2.12.

2.5.2 FTOH migration from air into SPMD and pure triolein

To investigate the migration of gaseous FTOH through the polyethylene membrane of SPMD and their accumulation in triolein, several glass chamber experiments (GCE) were conducted. In general, a beaker with a known content of FTOH and some SPMD were placed into a glass chamber (volume 10 L, Figure 1). Beaker and SPMD were not in direct contact. Deployment time and spiked FTOH levels in the beaker varied. During exposure, the glass chamber was kept at room temperature and in the dark to avoid photochemical breakdown. After the deployment, the chamber was opened and FTOH concentration in exposed SPMD and in one blank SPMD was determined as described in sections 2.4 and 2.12.

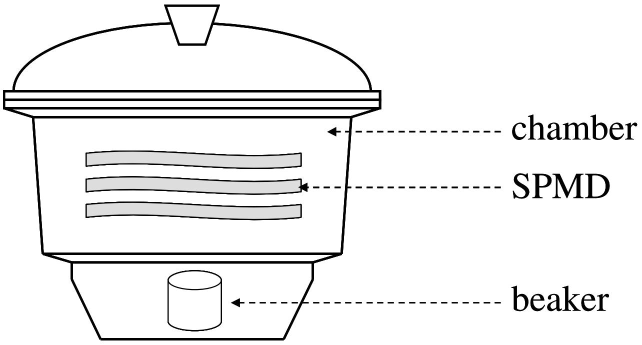


Figure 7: Experimental set up of glass chamber experiments.

2.5.2.1 High FTOH level experiments

In a first experiment 10,000 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, each, were directly weighed into a beaker and placed in the glass chamber. Three SPMD were then exposed to FTOH for 31 days (GCE I).

In a second experiment, four SPMD and a beaker with 1 mL of pure triolein without tubing were exposed to 10,000 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH and 10:2 FTOH, each, for 47 days. The volume of pure triolein was not supposed to decrease due to its very low volatility. For two of the SPMD, the outer side of the membrane was rinsed with EtAc. Triolein and the PE tubings of those SPMD were analysed separately for their FTOH content. The other two SPMD were analysed without further treatment prior to extraction. Pure triolein was dissolved in 50 mL HEX and then analysed the same way as SPMD (section 2.4.4), starting with liquid liquid extraction.

2.5.2.2 Low FTOH level experiments

GCE were used to investigate partitioning of FTOH to SPMD and triolein. In GCE III, three beakers filled with 0.7 mL of triolein (without tubings), each, were exposed to 0.2 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, each, dissolved in EtAc for 15 days. FTOH in triolein were analysed as described in section 2.5.2.1. Remaining FTOH in the beaker were determined by rinsing the beaker with EtAc followed by concentration to 200 µL by rotary evaporation and a gentle stream of nitrogen.

In GCE IV, three SPMD (triolein and tubings) were exposed to 0.1 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, each, dissolved in EtAc for 15 days. In addition, remaining FTOH in the beaker and adsorbed to the chamber were determined by rinsing the inner glass wall of the chamber and the beaker with EtAc followed by concentration to 200 µL as described above.

2.6 Comparison of SPMD with XAD impregnated PUF disks and high volume active sampling for determination of FTOH in air

To evaluate the performance of SPMD as FTOH passive air samplers compared to routinely applied sampling methods, a field intercomparison study of different research groups was conducted at Barsbüttlel, a semi-rural site located 20 km east of Hamburg, Germany, from April 2007 until March 2008. Among the investigated samplers were high volume active samplers (Dreyer and Ebinghaus, 2009) deployed and analysed by the GKSS Research Center, Geesthacht, Germany, XAD-impregnated polyurethane foam (SIP) disks (Shoeib *et al.*, 2008) analysed by Environment Canada and the University of Lancaster, UK, and SPMD applied by the Institute of Ecological Chemistry (Helmholtz Zentrum München, HMGU). Additionally, SIP disks of two sampling periods and two standard solutions were analysed by all participating research groups.

Active sampling was conducted continuously for periods of three and four days at flow rates of about 500 m^3 d^{-1}. All passive samplers were deployed for periods of two month. Six SPMD were deployed during each sampling period. Two blank SPMD samples were analysed with each set of SPMD of one sampling period. For analyis the six SPMD were combined to one sample. Except for a few modifications, they were analysed as described in section 2.4.4. Two of the six SPMD were shaken in 100 mL acetonitril/HEX (1/1 v/v) for 24 hrs and then liquid liquid extracted. After the extraction of the three pairs of SPMD, the three ACN phases were combined in one glass vessel, evaporated to 200 µl, and transferred into a GC vial.

SIP disks, deployed during sampling periods II and IV, were extracted three times using 100 mL acetone/MTBE (1/1). Prior to the extraction mass-labelled FTOH were added. Extracts of each sample were carefully combined in a new glass vessel to prevent the transfer of fine XAD particles. Afterwards, they were evaporated to 5 mL and centrifuged by 3000 rpm. Extracts were purified by SPE using EnviCarb cartridges (250 mg), evaporated to 200 µL, and transferred into GC vials. 9:2 FA was added as internal standard and FTOH were determined by GC-MS.

FTOH standard solutions of unknown concentration were combined with a defined amount of masslabelled FTOH and injection standard 9:2 FA and directly determined by GC-MS.

Average air concentrations derived from SPMD analysis were calculated by equation 1 according to Huckins *et al.* (2006).

$$c_{air} = \frac{N_{SPMD}}{R_s \cdot t} \qquad (1)$$

with: c_{air}: concentration of FTOH in air (pg m^{-3})
N_{SPMD}: amount of FTOH in SPMD
R_s: sampling rate (m^3 d^{-1})
t: duration of sampling period (d)

Sampling rates were calculated by equation 2. Because FTOH partition coefficients between air and SPMD ($K_{SPMD\ A}$) were not available, octanol air partition coefficients determined for 10°C (8:2 FTOH: 1122019, 10:2 FTOH: 1862087) by Thuens et al. (2008) were used instead (Huckins *et al.*, 2006).

$$R_s = V_s \cdot K_{OA} \cdot k_e \qquad (2)$$

with: R_s: sampling rate (m^3 d^{-1})
V_s: SPMD volume (m^3)
K_{OA}: octanol air partition coefficient
k_e: PRC release rate constant (d^{-1})

PRC release rate constants were calculated by equation 3 (Huckins *et al.*, 2006) using data from experiments investigating FTOH migration from SPMD into air described in section 2.5.1.1.

$$k_e = -\frac{\ln(N/N_0)}{t} \qquad (3)$$

with: k_e: PRC release rate constant (d^{-1})
N: amount of FTOH present in SPMD at the end of deployment
N_0: amount of FTOH in SPMD at the beginning of deployment
t: duration of SPMD deployment (d)

FTOH air concentrations derived from PUF samples were calculated using equation 1 with an uniform sampling rate of 3.5 m^3 d^{-1} for all FTOH established by Shoeib et al. (2008).

The FTOH air concentrations derived by high volume samplers were used for the calibration of SPMD. Therefore, FTOH sampling rates were calculated by resolving equation 1 for R_s and introducing air concentrations derived by High volume sampling into this equation 4.

$$R_s = \frac{N_{SPMD}}{c_{air} \cdot t} \qquad (4)$$

with: R_s: sampling rate (m^3 d^{-1})
c_{air}: concentration of FTOH in air derived by active sampling (pg m^{-3})
N_{SPMD}: amount of FTOH in SPMD
t: duration of sampling period (d)

2.7 Determination of fluorotelomer alcohols on spruce needles

Half year old to two year old spruced needles were sampled in downtown Munich (Schwabing and Englischer Garten). They were frozen and removed from Spruce branches using liquid nitrogen (Niu *et al.*, 2003). For method development, 10 g needles were spiked with 100 ng of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, each.

Acetonitril and acetone/MTBE (1/1) were tested for their suitability as extraction solvents. 100 mL of solvent were added to the needles. Needles were shaken for 24 hrs. Extracts were decanted, evaporated to a volume of 2 mL and purified by solid phase extraction applying EnviCarb (250mg and 500 mg) or silica cartridges (5 g), which were conditioned with 5 mL of the solvent used for elution. Afterwards, FTOH were eluted from the cartridges with 5 mL acetonitril or acetone/MTBE (1/1), respectively. Eluates were concentrated to 0.2 mL. Then FTOH were determined by GC-MS after addition of the injection standard 9:2 FA.

2.8 Determination of PFOA and PFOS in deposition samples collected at three sites in the Alps

Spare samples of three bulk deposition samplers, collected for the monitoring of POPs in the Alps (Monarpop, 2008), were analysed for PFOA and PFOS. Samplers were located close to the summits of the mountains Sonnblick (3100 m above sea level (a.s.l.)), Austria, Weissfluhjoch (2663 m a.s.l.), Switzerland, and Zugspitze (2650 m a.s.l.), Germany (Figure 8).

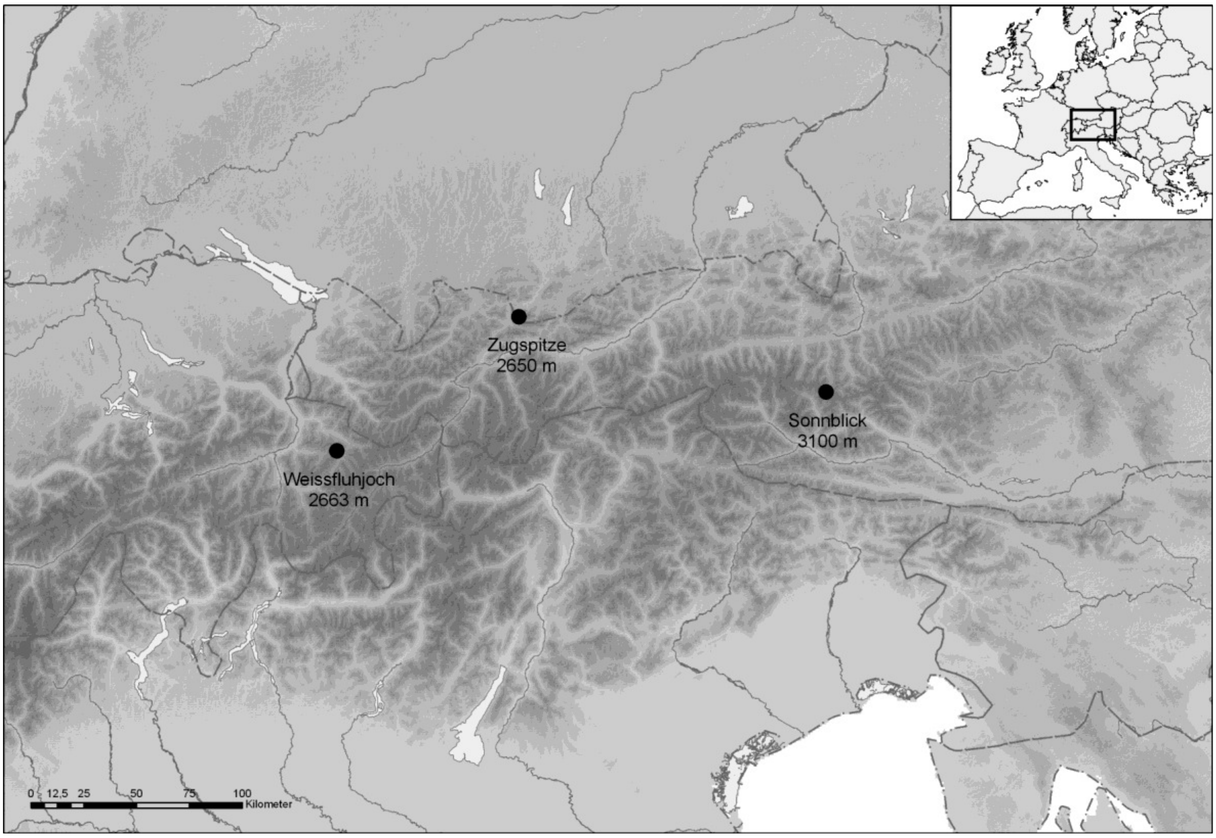


Figure 8: **Location of deposition samplers in the Alps (Monarpop, 2008).**

Samplers were equipped with heated glass funnels (diameter: 26 cm) and cartridge chambers to melt snow and to avoid frost shattering (Monarpop, 2008) (Figure 9). Bulk deposition samples were collected from June 2007 until July/August 2008 using cartridges filled with XAD-2 resin. The cartridges were exposed to ambient air for approximately three month (Table 9). For the sampling period Spring 2008, a sample from Weißfluhjoch (CH) was not available.

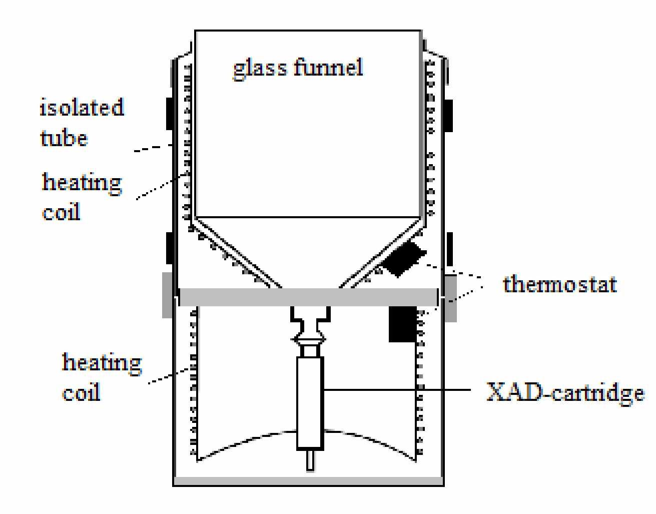


Figure 9: Deposition sampler (Monarpop, 2008).

Table 9: Sampling periods for the determination of PFOA and PFOS deposition at three sites in the Alps.

Location	Autumn 2007	Winter 2008	Spring 2008	Summer 2008
Zugspitze (D)	20.6.-4.10.07	4.10.07-14.1.08	14.1.-2.4.08	2.4.-29.7.08
Weißfluhjoch (CH)	25.6.-1.10.07	1.10.07-23.1.08	n.a.	25.4.-7.8.08
Sonnblick (AT)	19.6.-28.9.07	28.9.07-17.1.08	17.1.-20.3.08	20.3.25.7.08

n.a.: not analysed

Because FTOH in the atmosphere are predominatly present in the gaseous phase (Dreyer *et al.*, 2009b), deposition of FTOH was expected to be of minor importance. Furthermore, this sampling setup is not suited for the determination of FTOH deposition. FTOH adsorbed to XAD of the samplers cannot be inevitably attributed to deposition, because gaseous FTOH can also directly adsorb to the XAD. In this case, the sampler would act as a passive air sampler. In contrast, atmospheric PFOA and PFOS are predominatly present in the particle phase. Thus, the sampling set-up should be suitable for the determination of the deposition of PFOA and PFOS.

If the XAD-2 of the deposition samplers was wet, it was dried by a stream of nitrogen for four hours prior to analysis. Mass labelled PFOA and PFOS were added as internal standard prior to the extraction. PFC were extracted by three times using 80 mL of methanol. The methanol fractions were combined. The extracts were concentrated to 2 mL by rotary evaporation and cleaned up using ENVI-Carb SPE cartridges. PFC were eluted with 5 mL methanol, concentrated to 1 ml, and transferred into an LC vial. 9:2 FA was added as internal injection standard. PFC were determined by UPLC-TOF MS.

Depositon of PFOA and PFOS was calculated by normalizing the amount of PFOA and PFOS in the sampler by the sampler area and the sampling time.

2.9 FTOH in housedust

The following analytical method was tested for FTOH determination in indoor dust. For this purpose, dust samples from two flats of Munich, Schwabing were analysed. 0.5 g of the homogenised samples were weighed into an Erlenmeyer flask and mass-labelled FTOH standards and 100 mL acetone/MTBE (1/1) were added. The samples were extracted for 1 hr by ultrasonic extraction. Extracts and dust were transferred into an empty glass column with an incorporated frit for filtration and were eluted into a round flask. The column with the dust sample was filled again with 20 mL acetone/MTBE (1/1) for 1 h and afterwards eluted into the same round flask. This was repeated once. The combined extracts were evaporated to a volume of 1 mL. Extracts were transferred onto EnviCarb (250mg) cartridges, which were conditioned with 5 mL acetone/MTBE (1/1). The cartridges was eluted with 5 mL acetone/MTBE (1/1) and evaporated to 0.2 mL. Eluates were transferred into GC-vials and the internal standard 9:2 FA was added. FTOH were determined by GC-MS as described in section 2.12.

The method described above was applied for five housedust samples that were analysed for their content of FTOH. These samples were provided by the Department of Environmental Health, Bavarian Health and Food Safety Authority and were already homogenised.

2.10 PFC in household consumer products

2.10.1 Analysis of PFC in household consumer products

Ten impregnating agents obtained from nine different companies, six cleaning agents, four lubricants or corrosion inhibitors, three wood and leather conditioners, one fire fighting foam, and one pesticide formulation were analysed. All investigated agents were produced for private households and are applied as sprays. They were provided for a pure, non-diluted application. All the products, except for one impregnating agent which was purchased in Brazil, were obtained in Germany. Eight of the products were labelled as “PTFE”, “fluorocarbon resin”, or “fluoro additive” containing agents.

The liquids of the consumer products were diluted in methanol 1:100 by volume. 250 µL of the dilution, 250 µL of subboiled water, 20 µL of a solution containing mass-labelled 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, PFOA, and PFOS (1 ng μL^{-1}), and 20 µL of the injection standard 9:2 FA (1 ng μL^{-1}) were added into a LC glass vial. 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, PFOA, and PFOS were determined by UPLC-TOF-MS as described in section 2.7. Since 4:2 FTOH could not be determined by LC-MS, GC-MS was applied to detect this compound.

2.10.2 Calculation of consumer exposure

The daily uptake dose of PFC originating from analysed household agents (D_{spray_inhal}; (ng kg_{BW}^{-1} day^{-1})) was calculated using a model developed by Trudel et al. (2008) (equation 5). This research group estimated the uptake of PFOA by inhalation of spray droplets generated by application of consumer products for a conservative high exposure scenario. To assure comparability of results generated in this thesis and results of Trudel et al. (2008), all parameters except for the market fraction were adopted from Trudel et al. (2008).

$$D_{spray\_inhal} = \frac{c_{spray} \cdot MF_{spray} \cdot f_{\exp} \cdot t_{spray} \cdot r_{spray} \cdot F_{resp} \cdot V_{inh}}{m_{BW}} \cdot \left(\frac{t_{spray\_NF}}{V_{NF}} + \frac{t_{spray\_FF}}{V_{FF}} \right) \cdot F_{uptake} \qquad (5)$$

with
c_{spray}: concentration of PFC in impregnation sprays (ng g^{-1})
MF_{spray}: market fraction of consumer products containing PFC
f_{exp}: frequency exposed to consumer products (0.0120548 day^{-1})
t_{spray}: spraying time (30 min)
r_{spray}: rate of spray emission (42 g min^{-1})
F_{resp}: fraction of respirable aerosols generated (0.002589)
V_{inh}: inhalation rate (1.6 m^3 $hour^{-1}$)
$t_{\text{spray\_NF}}$: time exposed to aerosols in the near-field (1 hour)
V_{NF}: near-field volume around consumer (1 m^3)
$t_{\text{spray\_FF}}$: time exposed to aerosols in the far-field (4 hour)
V_{FF}: far-field volume around consumer (49 m^3)
m_{bw}: body weight (60.4 kg),
F_{uptake}: uptake fraction of PFC via the lungs (1)

Daily human PFC exposure was calculated for three different scenarios. In scenario I, the average PFC concentration of the consumer products was used for exposure calculations and the market fraction of consumer products was calculated by dividing the number of detections of one PFC in consumer products by the number of investigated consumer products. PFC exposure calculation in scenario II was similar to that of Trudel et al. (2008). Average PFC concentrations were used and the market fraction of PFC containing consumer products was set to 0.5. Scenario III represents a worst case situation, assuming that consumers are only using the product with the highest PFC concentration. Thus, the maximum value for PFC concentration was used for exposure calculation and the market fraction was set to 1. More information about uptake calculation and exposure scenarios are given in Trudel et al. (2008).

2.11 Analysis of PFC in water and soil samples collected in the national park Serra dos Órgãos, Brazil

The national park Serra dos Órgãos is located approximately 200 km north of Rio de Janeiro, Brazil. Water and soil samples were collected at four sites along an altitudinal transect between 900 m and 2200 m a.s.l.. One liter of surface water was sampled at four different brooks at altitudes of 900 m, 1500 m, 1800 m, and 2000 m a.s.l.. Mass-labelled PFOA, PFOS, 4:2 FTOH, 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were added to the samples. PFC were extracted by SPE using WAX cartridges. The cartridges were dried by nitrogen for 1 hour, frozen at -20°C, and transported to Helmholtz Zentrum München. There, cartridges were eluted with 5 mL of methanol. Eluates were concentrated to 0.5 mL and transferred into LC-vials. 9:2 FA was added as injection standard and PFC were determined by UPLC-TOF- MS.

Four topsoil samples were collected at sites close to the water sampling locations. They were filled in polypropylene bottles and kept frozen at -20°C until analyis at the HMGU. 10 g of soil were extracted with 100 mL of methanol applying ultrasonication for 1 hour. Prior to the extraction mass-labelled PFOA and PFOS were added to the sample. Extraction was repeated twice with 50 mL of methanol. Supernatant extracts were combined, concentrated to 5 mL and centrifuged. SPE-EnviCarb cartridges were used for purification. PFC were eluted with 5 mL of methanol. After concentration to 1mL and addition of 9:2 FA as injection standard, PFOA and PFOS concentrations were determined by UPLC-TOF-MS.

2.12 Chromatographic separation and detection of PFC

2.12.1 PFC determination by nanoflow Aquity UPLC-TOF-MS

6:2 FTOH, 8:2 FTOH, 10:2 FTOH, PFOA, and PFOS were determined by nanoflow Aquity UPLC (Waters, Milford, USA) coupled to a Q-TOF2 mass spectrometer (micromass, Manchester, UK) using negative electrospray ionisation (Table 10).

Table 10: PFC target ions and retention times for determination by UPLC-TOF-MS.

Analyte	UPLC-MS target ion (m/z)	UPLC-MS retention time (min)
6:2 FTOH	422.7	15.63
8:2 FTOH	522.6	16.27
10:2 FTOH	622.6	16.88
PFOA	412.8	14.21
PFOS	498.7	14.71
ML6:2 FTOH	426.8	15.63
ML8:2 FTOH	526.8	16.27
ML10:2 FTOH	626.7	16.88
MLPFOA	416.8	14.21
MLPFOS	502.8	14.71
9:2 FA	572.6	16.77

m/z: mass to charge ratio

The injection volume was 1 µL. Analytes were trapped on a Symmetrie C-18 column (5µm, 180µm x 20mm) for 4 min and separated on a BEH130 C-18 column or a Atlantis C-18 column, (both 17µm, 75µm x 150mm, all Waters, Milford, USA) with a 2 mM ammonium acetate mobile phase composed of water and methanol. The solvent gradient started with 15%

methanol and increased to 100% methanol after 8 min. After 25 min, it returned to initial conditions. The flow continued for another ten minutes. The flow rate was 0.4 µl min^{-1} at a column temperature of 30°C. Electrospray capillary voltage was 1800 kV, collision energy was 11 eV, and MS cone voltage was set to 17 V. FTOH were detected as acetate adducts $[M+59]^-$.

2.12.2 PFC determination by GC-MS

4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were determined by GC-MS applying positive chemical ionisation (Table 11). Measurements were performed in selected ion monitoring mode using an HP 5890 Series II gas chromatograph (Agilent Technologies, Waldbronn, Germany), coupled to a Finnegan Mat SSQ 7000 mass selective detector (Thermo Scientific, Dreieich, Germany). The GC was equipped with a 60 m VMS column (0.25 mm inner diameter, 1.4 µm film thickness; Restek, Bad Homburg, Germany). Helium (purity 5.0, Linde, Höllriegelskreuth, Germany) was used as carrier gas with a constant column head pressure of 175 kPa. Total helium flow was set to 80 sccm. Injections were performed in splitless mode at 220°C with an injection volume of 1 µL. The oven temperature program was as follows: Initial temperature was hold at 50°C for 2 min, then elevated to 80°C at 10°C min^{-1}, to 110°C at 5°C min^{-1} and held for 3 min, and finally elevated to 220°C at15 °C min^{-1} and held for 15 min. The transfer line was set to 300°C. Ionisations in the mass selective detector were performed at 70 eV, a manifold temperature of 80°C, and a source temperature of 150°C. Methane (purity 4.5, Linde, Höllriegelskreuth, Germany) was used as reagent gas with a pressure between 1600-2000 mTorr.

Table 11: PFC target ions and retention times for determination by GC-MS.

Analyte	GC-MS target ion (m/z)	GC-MS retention time (min)
4:2 FTOH	265	13.7
6:2 FTOH	365	17.2
8:2 FTOH	465	19.6
10:2 FTOH	565	21.3
ML4:2 FTOH	269	13.7
ML6:2 FTOH	369	17.2
ML8:2 FTOH	469	19.6
ML10:2 FTOH	569	21.3
9:2 FA	515	20.7
7:1 FA	401	18.1
8:1 FA	451	18.9
9:1 FA	501	20.4

m/z: mass to charge ratio

For PFC determination and recovery experiments, four point calibrations were carried out at the beginning and at the end of each sequence. Peak areas of target ions (TI) were integrated, if a signal to noise ratio of 3/1 was exceeded. Analytes were identified by their retention times and mass of TI, compared to those of the four point calibration and those of the isotope labelled standards.

2.13 Quantification of PFC

PFC were quantified, when the obtained peaks exceeded a signal to noise ratio of 5/1. Recoveries and concentrations of PFC in environmental samples were obtained by internal standard quantification method. PFC concentrations in samples were calculated using equation 6.

$$c(i) = \frac{c(IS1) * A(i)}{A(IS1)} \qquad (6)$$

c (i): concentration of compound i in the sample (ng mL^{-1})
c(IS1): spiked concentration of the internal standard 1 in the sample (ng mL^{-1})
A (i): peak area of compound i
A (IS1): peak area of IS1

In recovery experiments only native PFC were spiked to the samples. Thus, for calculation of PFC concentrations and recoveries obtained from these experiments, response factors (RF) were necessary. RF were also required for the calculation of recoveries of mass labelled PFC in environmental samples and to verify PFC concentrations obtained by equation 6. RF were calculated by linear regression of every compound i by plotting A(i)/A(IS2) versus m(i)/m(IS2) for calibration curve standards. The inclines of the calibration curves are equivalent to the RF (Oehme, 1996).

Analyte concentrations in environmental samples and in recovery experiments were calculated by equation 7, which is achieved by transforming of the regression equation obtained from the calibration curve plot.

$$c(i) = \frac{A(i)}{A(IS2)} * \frac{c(IS2)}{RF(i)} \qquad (7)$$

A (i): peak area of compound i
A (IS2): peak area of IS2
c (IS2): concentration of IS2 (ng mL^{-1})
c (i): detected concentration of compound i (ng mL^{-1})
RF (i): response factor of compound i

Recoveries of analytes and IS1 in samples and for recovery tests were calculated as shown in equation (8).

$$R(i) = \frac{c(i) * 100}{c(i_s)} \tag{8}$$

R(i): recovery of compound i (%)
c (i): concentration of compound i calculated by equation 7 (ng mL^{-1})
$c(i_s)$ spiked concentration of compound i in the sample (ng mL^{-1})

3 Results and Discussion

3.1 Optimisation of PFC determination by nanoflow UPLC – TOF MS

Differences in peak shapes and separation applying the Atlantis and the BEH analytical column were negligible. More important were the applied flow rates for gradient elution. A flow rate of 0.4 µL min^{-1} generated good peak shapes. However, due to elevated system pressure, flow rate often had to be reduced to 0.25 µL min^{-1}.

Ionisation, and thus peaks of PFOA, PFOS, and FTOH were not obtained applying methanol and water without an ammonium acetate buffer. The use of 2mM and 10mM buffered gradient elution resulted in the same PFC peak abundance. To prevent precipitation of the buffer in the UPLC-MS system, 2mM buffered methanol and water were used for gradient elution.

For electro spray ionisation similar peak abundances were obtained for 1800 and 2000 V capillary voltage. Ionisation of PFC was strongly influenced by cone voltage and collision energy. Application of 17 V cone voltage and 11 eV collision energy resulted in best peak abundances. Thus, the overall settings that were chosen for the determination of PFC were 1800 V capillary voltage, 17 V cone voltage, and 11 eV collision energy. This setting enabled simultaneous sensitive detection of PFOA, PFOS, and FTOH.

3.2 Method development for the determination of FTOH in SPMD

3.2.1 Purification of SPMD extracts by GPC

After separation of FTOH and triolein by GPC, FTOH were detected only in the first fraction (22-32 min). Recoveries were 3% (4:2 FTOH), 10% (6:2 FTOH), 12% (8:2 FTOH), and 13% (10:2 FTOH), and thus too low for an accurate separation from triolein and a reliable quantification of FTOH in SPMD.

When FTOH were injected into the GPC without triloein, FTOH were observed in all the three collected fractions (Table 12). However, recovery rates of FTOH were too high (up to 800%). There is not any explanation for this, since the same standard solution was used in both experiments. The majority of 10:2 FTOH was eluted in the fraction 0-16 min. Most of 4:2 FTOH, 6:2 FTOH, and 8:2 FTOH were detected in fraction 16-24 min. In this fraction triolein elutes as well. Thus, a separation of triolein and FTOH was not possible using GPC. Elution of FTOH extended for more than 30 min. This is also a great disadvantage, as it increases the solvent volume for elution and thus the time that is necessary for sufficient evaporation as well as the potential for analyte losses.

Table 12: FTOH recovery rates (%) in gel permeation chromatography eluates without triolein.

Substance	Recovery (%) fraction 0-16 min	Recovery (%) fraction 16-24 min	Recovery (%) Fraction 24-34 min
4:2 FTOH	0	36	0
6:2 FTOH	12	788	1.4
8:2 FTOH	256	480	1.4
10:2 FTOH	614	191	2.9

It was expected that triolein eluates earlier than FTOH, because theoretically substances of higher molecular weight elute earlier than those with lower molecular weight during size exclusion chromatography. However, FTOH eluted at the same time and even earlier than triolein although molecular weight of triolein is 1.6 to 3.4 times higher than the molecular weights of FTOH. These results may be explained by the formation of FTOH micelles, which will lead to an increasing FTOH particle size and mass (Kissa, 1994) and thus to an earlier elution. Additionally, all of the tubes of the GPC were made of Teflon® and can cause sorption of FTOH to the pipe walls and contamination of the following samples. Therefore GPC is not suitable for clean-up of SPMD extracts intended for the determination of FTOH.

3.2.2 Purification of SPMD extracts by solid phase extraction

There always was a breakthrough of triolein when SPE cartridges used for purification of SPMD extracts were eluted with EtAc or MeOH/EtAc (1:1). Thus, EtAc and MeOH/EtAc (1:1) as used by Martin et al. (2002) for the elution of high vol PUF/XAD/PUF cartridges were not suitable for cartridge elution. Due to their high content of triolein, samples were not measured to avoid contamination of the GC-MS system. Triolein content in eluates decreased with increasing polarity of the solvent that was used for elution (Table 13). For removal of triolein from SPMD extracts, elution with MeOH showed the best results.

Table 13: Mean FTOH recoveries (R, %, n=3) of different solvents used for elution of C18-E (500 mg) cartriges

	R (%) MeOH 5 mL	R (%) MeOH 8 mL	R (%) MeOH/EtAc (2/1) 5 mL	R (%) MeOH/EtAc (1/1) 5 mL	R (%) MeOH + EtAc 5 mL +3 mL
4:2 FTOH	51	43	50	35	37
6:2 FTOH	43	53	59	45	49
8:2 FTOH	24	49	53	40	43
10:2 FTOH	29	60	61	43	46
Triolein-removal	successful	successful	insufficient	insufficient	insufficient

In order to further increase the recovery rates of long chain FTOH, the elution volume of MeOH was increased from 5 to 8 mL. This resulted in an improvement of the recovery rates.

For further improvement of FTOH recoveries, different SPE adsorbents were tested which were eluted with 5 mL of MeOH/EtAc (2/1 v/v). Results are presented in Table 14. Retention of triolein was insufficient for SDB-L cartridges. These samples were not measured to avoid GC-MS contamination by matrix. Elution of C18-E (500 mg) + Carboxen (100 mg) with MeOH/EtAc 2/1 resulted in best triolein removal and highest FTOH recoveries. However, recoveries were still not satisfactory. Elution of this adsorbent combination was repeated with 5 mL of MeOH/EtAc 1/1. However, this resulted in a breakthrough of triolein (Table 14)

Table 14: Mean FTOH recoveries (R, %, n=3) applying different SPE adsorbents.

Adsorbent	**R (%)** **C18-E (1 g)**	**R (%)** **C18 (1 g)**	**R (%)** **C18-E (0.5 g) + Carboxen (0.1g)**	**R (%)** **C18-E (0.5 g) + Carboxen (0.1g)**
Elution	**MeOH/EtAc (2/1)**	**MeOH/EtAc (2/1)**	**MeOH/EtAc (2/1)**	**MeOH/EtAc (1/1)**
4:2 FTOH	41	40	45	49
6:2 FTOH	47	43	53	51
8:2 FTOH	33	32	45	39
10:2 FTOH	28	28	46	46
Triolein-removal	successful	successful	successful	insufficient

3.2.3 Optimisation of SPMD extraction

Extraction solvents for SPMD were compared as described in section 2.4.3. Extracts of SPMD slices in acetone and EtAc could not be rotary evaporated to 1 mL because of a high amount of dissolved triolein. Thus, the experiment was stopped and FTOH were not measured in acetone and EtAc extracts. Liquid-liquid extraction of those extracts with Hex or ACN were not performed, because solvents are miscible in each other. FTOH recoveries of other extraction solvents are presented in Table 15.

Best triolein removal was achieved by extraction of SPMD with ACN followed by liquid liquid extraction with HEX. After rotary evaporation, triolein was not visible in the flask anymore, which was in contrast in MeOH extracts. Extraction with MeOH as only solvent resulted in best recoveries. However, even after liquid-liquid extraction with HEX, triolein was visible in MeOH extracts after rotary evaporation. These results may be explained by a better solubility of triolein in MeOH. Moreover, HEX and MeOH are partly miscible and thus only suited to a limited extent for liquid liquid extraction.

Table 15: Mean FTOH recoveries (R, %, n=3) of extraction of SPMD with MeOH or ACN, optionally followed by liquid-liquid extraction with Hex.

	R (%) MeOH	**R (%) MeOH Hex**	**R (%) ACN Hex**
4:2 FTOH	47	37	42
6:2 FTOH	57	45	52
8:2 FTOH	63	57	64
10:2 FTOH	63	56	57
Triolein-removal	insufficient	insufficient	successful

3.2.4 Final analytical method for the determination of FTOH in SPMD

The method of choice with best triolein removal and acceptable FTOH recoveries was liquid liquid extraction with ACN/HEX 1/1 without further purification as described in section 2.4.6. FTOH recoveries of this procedure are below of the optimum range between 70 and 110% (Table 16). However, due to the high volatility of FTOH, particularly of 4:2 FTOH, it is very difficult to find a method with better recoveries. Volume concentration of extracts and eluats are critical steps concerning loss of FTOH during the clean-up step. In literature, recoveries higher than 70% for 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were mostly achieved, when only one concentration step was applied during the analytical procedure (Martin *et al.*, 2002; Shoeib *et al.*, 2005a; Jahnke *et al.*, 2007b). Moreover, the use of EtAc during analysis, which was applied in the above mentioned studies, as well, can result in a signal enhancement during GC-MS determination (Dreyer *et al.*, 2008). When other solvents were used, recovery rates between 25% and 60% were achieved for volatile PFC (Dreyer *et al.*, 2009a).

Table 16: Mean recovery rates (%, n=3) and absolute standard deviations for the determination of FTOH in SPMD

	Recovery rate (%)	**Standard deviation**
4:2 FTOH	38	8
6:2 FTOH	56	13
8:2 FTOH	64	10
10:2 FTOH	62	10

3.3 Accumulation and elimination of FTOH in SPMD

3.3.1 Analytical parameters and quality assurance

FTOH were detected in blank samples of GCE I, GCE II, and of experiments investigating FTOH migration out of SPMD into air. In all of these experiments high FTOH levels were involved (10,000 µg and 25 µg). In blank SPMD samples, FTOH were detected in a range between 0.005–0.02 µg, probably due to carry over during rotary evaporation. However, compared to the overall amount of FTOH, contamination was insignificant and results were not blank corrected.

3.3.2 FTOH migration out of SPMD

3.3.2.1 FTOH migration out of SPMD into air

Air temperatures during the time of SPMD deployment were between 5 and 22 °C and almost always above the melting point of triolein (5°C). Considering the volatility and molecular structure of the four investigated FTOH, it is expected that migration of those substances into air decreases with increasing chain length. However, a dependence of FTOH chain length was not observed (Figure 10). After 64 days of deployment, the content of FTOH in SPMD diminished by approximately 20%. Migration of FTOH out of SPMD was assumed to follow first order kinetics. An independent release of FTOH from SPMD at the beginning of the experiment followed by first order kinetics is another possibility. The highest decline of FTOH concentration over time was observed for 6:2 FTOH (Figure 10). The decrease of the 4:2 FTOH content in SPMD over time was lowest. However, since highest standard deviations were involved with the 4:2 FTOH decline, this result has to be considered with caution. Due to problems during GC-MS determination, only one value was achieved for 64 days of deployment and therefore means and standard deviations of the FTOH decline could not be calculated.

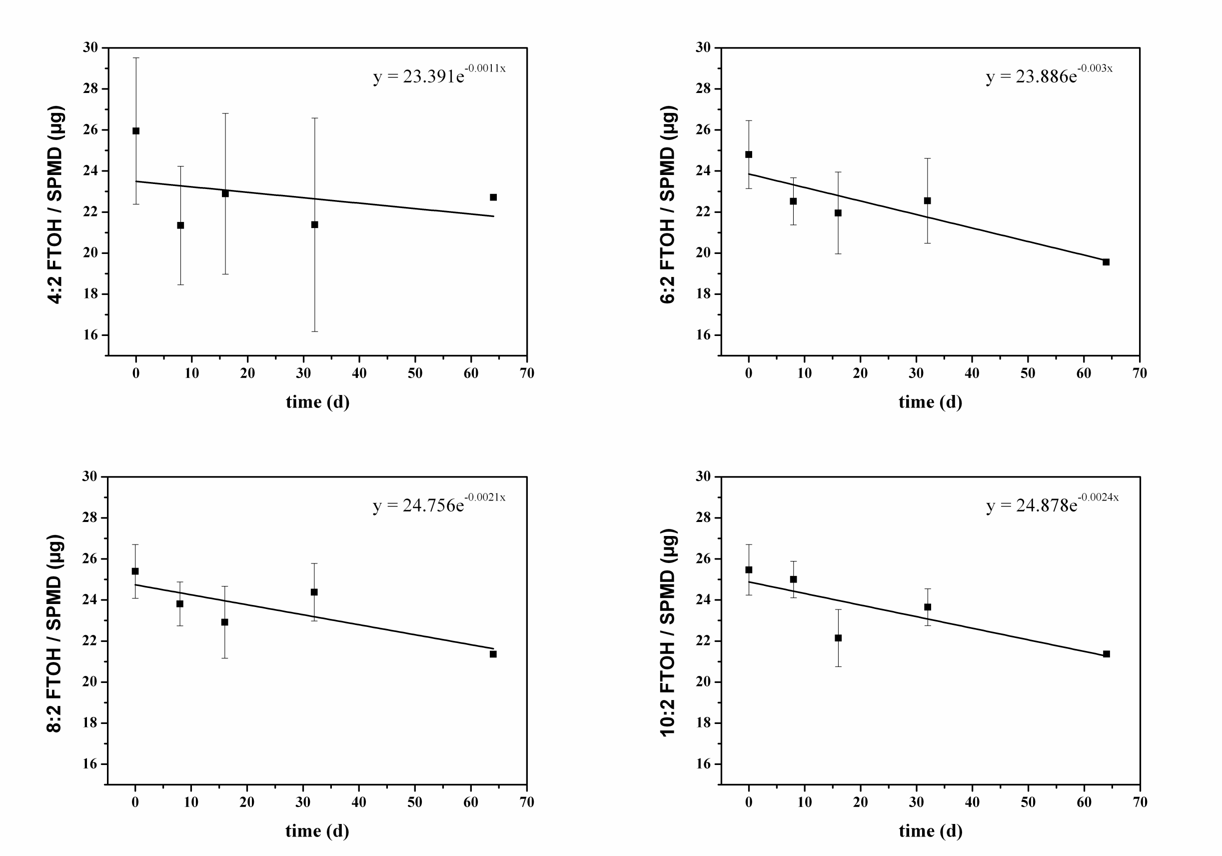


Figure 10: Decrease of FTOH content (µg) in SPMD over time during field deployment (n=3; Initial mass: 25 µg).

FTOH release rates calculated for the four sampling intervals were decreasing over deployment time (Table 17). Because of the high standard deviations of 4:2 FTOH, this compound was excluded from release rate calculations. Since the FTOH amounts in SPMD were elevated after 32 days compared to values after 16 days, the last two periods (interval 16-32 days and interval 32-64 days) were combined for determinations of release rates. For the first (days 0–8) and the third period (days 16-64) release rates were decreasing with FTOH chain length. In the second period (days 8–16), release was increasing with FTOH chain length.

Table 17: FTOH release rates of in SPMD during field deployment.

Compound	**Release rates days 0-8 (ng d^{-1})**	**Release rates days 8-16 (ng d^{-1})**	**Release rates days 16-46 (ng d^{-1})**
6:2 FTOH	12.0	3.2	2.4
8:2 FTOH	8.0	4.8	1.5
10:2 FTOH	2.3	15.6	0.7

3.3.2.2 FTOH migration out of SPMD into solvent

For dialysis extracts different results were obtained for individual FTOH (Table 18). After the first dialysis, 6.8% (10:2 FTOH) to 20% (4:2 FTOH) of the spiked amounts were observed. In extracts of the second dialysis, 4:2 FTOH was not detectable. Of the remaining FTOH, 1.5% (10:2 FTOH) to 3.0% (8:2 FTOH) were recovered. In the final liquid-liquid extraction of the SPMD slices, 9.9% (4:2 FTOH) to 63% (6:2 FTOH) were observed. FTOH yields of the different extraction steps were highly variable, resulting in strongly elevated standard deviations. Overall between 54% (4:2 FTOH) to 70% (10:2 FTOH) of the spiked FTOH amount was detected and quantified in total.

Table 18: Mean FTOH Recovery (R; %; n=3) and absolute standard deviations (SD) of three extraction steps (dialysis (DE) and liquid-liquid extraction (LLE)).

Compound	DE 1 R (%) ± SD	DE 2 R (%) ± SD	LLE 3 R (%) ± SD	Σ SPMD R (%)
4:2 FTOH	20 ± 12	n.d.	10 ± 136	30
6:2 FTOH	10 ± 60	2 ± 95	63 ± 50	75
8:2 FTOH	10 ± 74	3 ± 67	33 ± 52	46
10:2 FTOH	7 ± 106	2 ± 99	55 ± 59	64

3.3.3 FTOH migration from air into SPMD and pure triolein

3.3.3.1 High FTOH level experiments

In GCE I, (10,000 µg FTOH, 3 SPMD), around 40% and 29% of spiked 6:2 FTOH and 8:2 FTOH, respectively, were detected in SPMD (Table 19). 4:2 FTOH and 10:2 FTOH recoveries were one to two orders of magnitude lower, respectively. Low recovery rates may have resulted from adsorption of FTOH to the glass chamber, or, particularly for 10:2 FTOH, from an incomplete evaporation from the beaker.

Table 19: FTOH recovery rates (R; % of initial mass 10,000 µg) detected in three SPMD analysed completely (GCE I).

Compound	SPMD 1 R (%)	SPMD 2 R (%)	SPMD 3 R (%)	Σ SPMD R (%)
4:2 FTOH	3	2	2	7
6:2 FTOH	16	12	13	41
8:2 FTOH	11	9	9	29
10:2 FTOH	0.3	0.3	0.3	0.9

In GCE II (10,000 µg FTOH, 4 SPMD, 0.7 mL pure triolein, and rinse solvent), 1.2%, 3.3%, 14% and 30% of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively, were detected in triolein exposed to FTOH without PE tubing (Table 20). 2.1%, 9.7%, 29%, and, 16% of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively, were found in SPMD 1 and 2 that were completely analysed. Total FTOH amounts in those SPMD whose tubings and triolein were analysed separately, were in the same order of magnitude as the completely analysed SPMD. A high amount of all FTOH was detected in the membrane of the SPMD analysed separately. Since it was assured that at least 95-99% of the triolein was withdrawn during separation of triolein and tubing, it was assumed that a great portion of FTOH was adsorbed at or absorbed into the membrane. Long-chain FTOH, particularly 10:2 FTOH, were also detected in the solvent, which was used to rinse the outside of the membrane. This may point at condensation of the less volatile long-chain FTOH or their hindered diffusion through the PE membrane.

Table 20: FTOH recovery rates (R; % of initial mass 10000 µg) detected in completely analysed SPMD (SPMD 1 and 2), separately analysed membranes (Mem 3 and 4), triolein (Trio 3and 4), and rinse solvent (rinse 3 and 4) of SPMD 3 and 4 , and pure triolein (Trio) exposed without tubing in GCE II (n.d.: not detecable).

Compound	R Trio (%)	R SPMD 1 (%)	R SPMD 2 (%)	R Rinse 3 (%)	R Rinse 4 (%)	R Trio 3 (%)	R Trio 4 (%)	R Mem 3 (%)	R Mem 4 (%)	R Σ SPMD (%)
4:2 FTOH	1.2	1.1	1.0	n.d.	n.d.	0.3	0.4	0.6	0.3	3.5
6:2 FTOH	3.3	4.7	5.0	n.d.	n.d.	1.7	1.7	3.0	1.2	17
8:2 FTOH	14	14	15	0.01	0.01	4.6	4.6	8.0	3.3	48
10:2 FTOH	30	7.9	8	0.1	0.1	3.4	3.4	3.4	2.7	27

3.3.3.2 Low FTOH level experiments

In GCE III total amounts of 34%, 83%, 59%, and 4.5% of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively were determined in 3 beakers with 0.7 ml triolein, each (Table 21). 0.1%, 8.1%, 27%, and 4.1% of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively, were still present in the beaker.

Table 21: FTOH recovery rates (R, % of initial mass 0.2 µg) detected in Triolein exposed without tubing in GCE III.

Compound	R (%) Trio 1	R (%) Trio 2	R (%) Trio 3	R (%) Σ Trio	R (%) Beaker
4:2 FTOH	11	13	10	34	0.1
6:2 FTOH	27	32	23	83	4.1
8:2 FTOH	21	22	16	59	13
10:2 FTOH	1.9	1.7	1.0	4.6	2.1

In GCE IV (0.1 µg FTOH, 3 SPMD), total amounts of 28%, 6.5% 6.4% and 1.6% of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively were observed in SPMD (Table 22). 4.1% of 8:2 FTOH was still present in the beaker. 4.0%, 19%, and 5.4% of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively, were determined at the inner side of the glass chamber.

Table 22: FTOH recovery rates (R, % of initial mass 0.1 µg) detected in SPMD in GCE IV (n.d.: not detectable).

Compound	R (%) SPMD 1	R (%) SPMD 2	R (%) SPMD 3	R (%) Σ SPMD	R (%) Beaker	R (%) Chamber
4:2 FTOH	7.1	12	9.6	28	n.d.	n.d.
6:2 FTOH	1.6	3.0	2.0	6.6	n.d.	4.0
8:2 FTOH	1.7	2.7	2.1	6.5	4.1	19.2
10:2 FTOH	0.2	0.6	0.8	1.6	n.d.	5.4

3.3.4 Evaluation of SPMD as passive air samplers for FTOH

As described in section 3.3.3, FTOH accumulated differently in SPMD in dependence on the concentration level. For low FTOH levels (section 3.3.3.2), only 4:2 FTOH was observed at an increased amount (28%) in SPMD after 15 days of exposition. The longer the fluorinated alkyl chain the less FTOH were detected (1.6 – 6.6%). A strong increase of 6:2 FTOH and 8:2 FTOH uptake was observed in experiments where pure triolein was involved (GCE III). Detected 6:2 FTOH and 8:2 FTOH amounts in these experiments were even higher than those of 4:2 FTOH. This might have resulted from lower vapour pressures of long-chain FTOH compared to short-chain FTOH resulting in a lower revolatilisation from triolein. 10:2 FTOH accumulated in triolein only to a small amount, probably because it is the most oleophobic compound of the investigated FTOH. Enrichment of FTOH in pure triolein is dependent on the FTOH´s partition coefficient between air and triolein (K_{TA}). However, until to now, only octanol-air-partition coefficients (K_{OA}) (Lei *et al.*, 2004; Goss *et al.*, 2006; Thuens *et al.*, 2008) were determined for FTOH. K_{TA} are not available. For non-fluorinated organic compounds, K_{TA} values can easily be derived from K_{OA} values (Huckins *et al.*, 2006). However, the unique physicochemical properties of fluorinated compounds may hamper this estimate procedure.

In general, SPMD used as passive air samplers accumulate only noncharged gas-phase molecules with a molecular mass less than approximately 600 amu and an octanol-water-partition coefficient log $K_{OW} \geq 3$ (Petty *et al.*, 2000). The molecular weights of analysed FTOH are in the range between 264 and 564 amu and estimated log K_{OW} values are between 3.3 and 7.6 (Arp *et al.*, 2006; Carmosini and Lee, 2008). Considering the physico chemical constants mentioned above, SPMD are supposed to be suited for FTOH air sampling. However, FTOH partitioning to SPMD seemed to be hampered as observed during the conducted experiments. FTOH uptake may depend on different molecular structure as well as on oleophobicity of the fluorinated alkyl chain, which increases with chain length. Due to the differences between uptake in pure triolein and in SPMD (see section 3.3.3.2), we assume that enrichment, especially of long-chain FTOH, is limited by the PE membrane that acts as a control barrier and hampers the system reaching its equilibrium. Thus, in addition to air and triolein, the membrane has to be considered as a third component, for experiments determining the partitioning coefficients between SPMD/triolein or their calculation from other physical chemical properties.

At high FTOH levels (GCE I and GCE II), detected 4:2 FTOH concentrations in SPMD were lower than those of 6:2 FTOH, 8:2 FTOH, and for GCE II even lower than 10:2 FTOH. Thus, migration through the membrane and accumulation of long-chain FTOH was improved at higher concentrations. A reason for this observation may be the arrangement of FTOH as micelles (Kissa, 1994) or the adsorption of FTOH to the surface of membrane cavities that facilitate transport of other FTOH molecules. In GCE II, it was observed that four SPMD accumulated more FTOH than 0.7 mL of pure triolein, probably due to a higher surface-area to volume ratio of SPMD compared to pure triolein. Thus, at high FTOH concentrations, uptake seemed to be less membrane-controlled and partitioning between air and triolein becomes more important.

The results mentioned above were confirmed by experiments investigating FTOH migration out of SPMD, as well. During field deployment FTOH concentrations in SPMD decreased in the order of 4:2 FTOH, 8:2 FTOH, 10:2 FTOH, and 6:2 FTOH. However, due to its high standard deviations, the 4:2 FTOH release has to be considered with caution. For the periods between sampling, release rates were mostly decreasing with FTOH chain length. Due to applied high FTOH concentrations, FTOH release was less membrane controlled, but more dependent on the compounds volatility and partitioning between air and triolein.

In the presence of organic solvents, migration of FTOH out of SPMD spiked at low FTOH levels seemed to be membrane controlled, as well. Dialysis extraction of SPMD resulted in highest FTOH yields for short-chain FTOH, whereas 10:2 FTOH was only efficiently extracted when the membrane was cut and FTOH could directly move from triolein to the extraction solvent. It was not possible to explain the incomplete recovery of FTOH in this experiment. Thus, it was assumed that the different polarity of the used solvent mixtures was of minor importance. The application of less polar acetone/MTBE was supposed to facilitate the extraction of long-chain FTOH in contrast to ACN/HEX. The latter should have enhanced extraction of the short-chain FTOH. However, these effects were not observed. For the first dialysis extraction with acetone/MTBE, highest FTOH yields were obtained for the relatively polar short-chain FTOH. FTOH yields of the second dialysis were quite low and therefore less important. Also, the results for the final liquid liquid extraction with ACN/ HEX revealed no influence of solvent polarity. However, extraction efficiency was highly dependent on the presence of the PE membrane.

Results of conducted experiments reveal that passage through the membrane was influenced by the applied FTOH amount. If FTOH enrichment in SPMD actually depended on air concentration, this fact has to be considered for sampler calibration, i.e. for the determination of sampling rates. For field sampling, the application of suited performance reference compounds is absolutely essential.

When SPMD are deployed in the field, uptake of FTOH might additionally be influenced by particles adsorbed to the outside of the membrane. Reminding the low percentage of FTOH amounts that were detected after 15 days in SPMD (GCE IV), one should keep in mind that sampling durations of SPMD is usually in the range of one year, or partly longer. Thus, the sampling yield may be better after a longer sampling interval. However, this has to be evaluated in further studies.

Given the obtained results and methodology it is not recommend to use SPMD as FTOH passive samplers. There might be the potential to apply them at highly contaminated sites, but the incidence of such concentrations is rather unlikely. In remote areas, XAD impregnated PUF disks (Shoeib *et al.*, 2008) are the better choice, because analyte accumulation only depends on adsorption capacity and SIP-air-partitioning and is not additionally hampered by a membrane acting as a control barrier.

3.4 Comparison of SPMD with XAD impregnated PUF disks and high volume active sampling for determination of FTOH in air

3.4.1 Estimation of SPMD sampling rates and calibration of SPMD by High volume active sampling

During an one year deployment, FTOH were only identified occasionally in SPMD. 4:2 FTOH and 6:2 FTOH were not detected in any of the samples. In SPMD of the first three periods (April-September 2007), low amounts of 8:2 FTOH and 10:2 FTOH were observed, whereas in SPMD of the last three periods (October 2007-March 2008) FTOH were not detected at all (Table 23).

Table 23: FTOH content (pg) in SPMD during sampling periods I-VI (n.d.: not detected).

	FTOH (pg) Period I	FTOH (pg) Period II	FTOH (pg) Period III	FTOH (pg) Period IV	FTOH (pg) Period V	FTOH (pg) Period VI
4:2 FTOH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2 FTOH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8:2 FTOH	4851	3003	5005	n.d.	n.d.	n.d.
10:2 FTOH	1952	779	2059	n.d.	n.d.	n.d.

For the calculation of FTOH air concentrations, SPMD were calibrated using data obtained during the first three sampling periods. Sampling rates were calculated introducing the FTOH content of SPMD (Table 23) and average FTOH air concentrations derived by high volume sampling (Table 24) into equation 4 (see section 2.6).

Table 24: FTOH air concentrations (c_{air},) averaged for periods I, II, and III derived by high volume active sampling used for SPMD calibration (Dreyer *et al.*, 2009a).

	c_{air} (pg m^{-3}) Period I	c_{air} (pg m^{-3}) Period II	c_{air} (pg m^{-3}) Period III
8:2 FTOH	97.3	107.8	68.7
10:2 FTOH	33.9	32.1	32.8

The average sampling rate of 0.81 m^3 d^{-1} for 8:2 FTOH calibrated by High volume sampling was approximately half of the value of 1.4 m^3 d^{-1} derived by the theoretical estimation used for the calculation of 8:2 FTOH air concentrations (Table 25). Compared to 8:2 FTOH, deviations of calculated (0.77 m^3 d^{-1}) and estimated (2.6 m^3 d^{-1}) 10:2 FTOH sampling rates were much higher. This may have been caused by the hampered diffusion of long chain FTOH through the PE membrane as discussed in section 3.3.4. Equation (2) assumes increasing sampling rates with increasing K_{oa} values, which was used as substitution for the unknown $K_{sa.}$ The potential effects of the fluorinated chain hampering FTOH accumulation in SPMD are not considered in this equation. However, results presented in section 3.3 revealed that such effects are likely to occur. Consequently, theoretical sampling rates, especially for long-chain FTOH, are overestimated resulting in an underestimation of FTOH air concentrations.

Table 25: FTOH sampling rates (R_S; m³ d^{-1}) of SPMD obtained by calibration and theoretical estimation (SD: standard deviation).

	R_S (m³ d^{-1}) Period I	R_S (m³ d^{-1}) Period II	R_S (m³ d^{-1}) Period III	R_S (m³ d^{-1}) Mean ± SD	R_S (m³ d^{-1}) estimated
8:2 FTOH	0.79	0.49	1.14	0.81 ± 0.33	1.4
10:2 FTOH	0.91	0.42	0.98	0.77 ± 0.31	2.6

8:2 FTOH and 10:2 FTOH sampling rates calibrated by active sampling were characterized by period dependent variations for both analytes. Because only three sampling periods were used for the SPMD sampling rate calibration, the obtained sampling rates can only be considered as an approximation of the true value.

3.4.2 Calculation of SPMD derived FTOH air concentrations and comparison with SIP and high volume active sampling

Because SPMD used as passive air samplers for FTOH were not calibrated until this study was conducted, estimated sampling rates assessed by equation (2) had to be used for the calculation of FTOH air concentrations (Table 26).

Table 26: SPMD derived FTOH air concentrations (pg m^{-3}) during the first three sampling periods.

	Period I (pg m^{-3})	**Period II (pg m^{-3})**	**Period III (pg m^{-3})**
8:2 FTOH	55	38	59
10:2 FTOH	12	5	13

Air concentrations were between 38 and 59 pg m^{-3} for 8:2 FTOH and between 5 and 13 pg m^{-3} for 10:2 FTOH. Application of SPMD for FTOH sampling was compared to high volume active sampling and SIP passive samplers operated by GKSS Research Center and Environment Canada (Figure 11, 12). FTOH concentrations determined by high volume sampling were as high as concentrations of the passive samplers except for periods I and II. For 8:2 FTOH and 10:2 FTOH, deviations of air concentrations between SPMD and the other samplers were not systematically. Harner et al. (2004) compared PUF and SPMD passive sampler for PCB and organochlorine pesticides and observed that PUF derived air concentrations exceeded those from SPMD by approximately 25% due to sampler calibration.

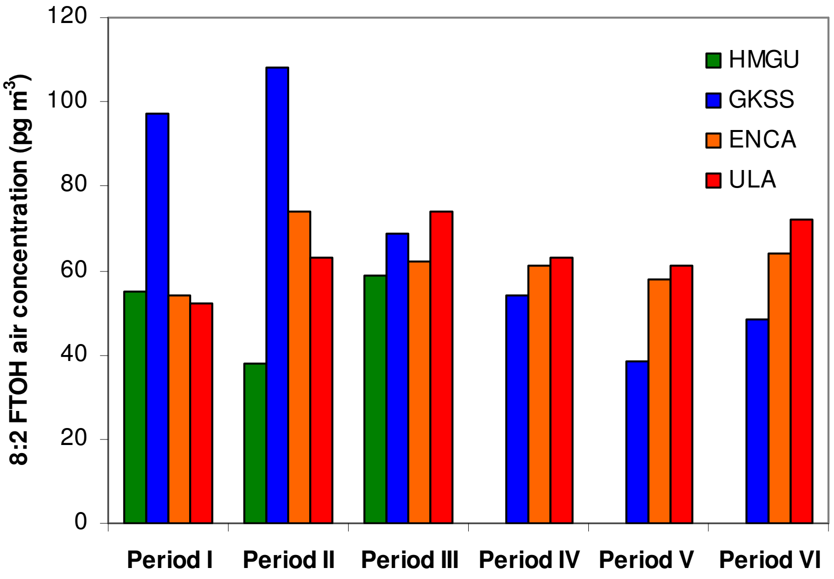


Figure 11: 8:2 FTOH air concentrations determined by SPMD, SIP, and high volume sampling.

During the last three sampling periods, 8:2 FTOH and 10:2 FTOH were not detected using SPMD, whereas these compounds still were detected in SIP and High volume samples. High volume sampler data revealed that FTOH air concentrations were approximately half of the value determined during the first three sampling periods. This may have resulted in FTOH contents in SPMD that were below the MDL, as maximum abundances of 8:2 FTOH and 10:2 FTOH during the first six month were only one order of magnitude above the MDL. The comparison of the different sampling techniques revealed that the assumptions made for the calculation of SPMD sampling rates for FTOH (substitution of $K_{SPMD\ A}$ with K_{OA}, and calculation of k_e from results in 3.3.2.1) resulted in reasonable FTOH air concentrations that were in good agreement with high volume sampling and SIP sampling. However, a certain threshold value of FTOH air concentration seemed to be necessary for the use of SPMD confirming the results presented in section 3.3.4.

In case of 10:2 FTOH, air concentrations derived by SPMD within the first three sampling periods were considerably lower than concentrations determined by High vol and SIP (Figure 9). This might be explained with the high deviation of the estimated and the calibrated sampling rate of SPMD for 10:2 FTOH. The estimated sampling rates used for the calculation of 10:2 FTOH air concentrations was more than twice as high as that of the calibrated sampling rate resulting in an underestimation of 10:2 FTOH air concentrations. On the other hand, during High volume sampling, 10:2 FTOH might be trapped by the filter and thereby the real gas concentration might be shifted to artificially lower values. High volume data revealed lower 10:2 FTOH air concentrations in periods IV – VI than those of periods I-III. This may explain why 10:2 FTOH was not detected in those SPMD.

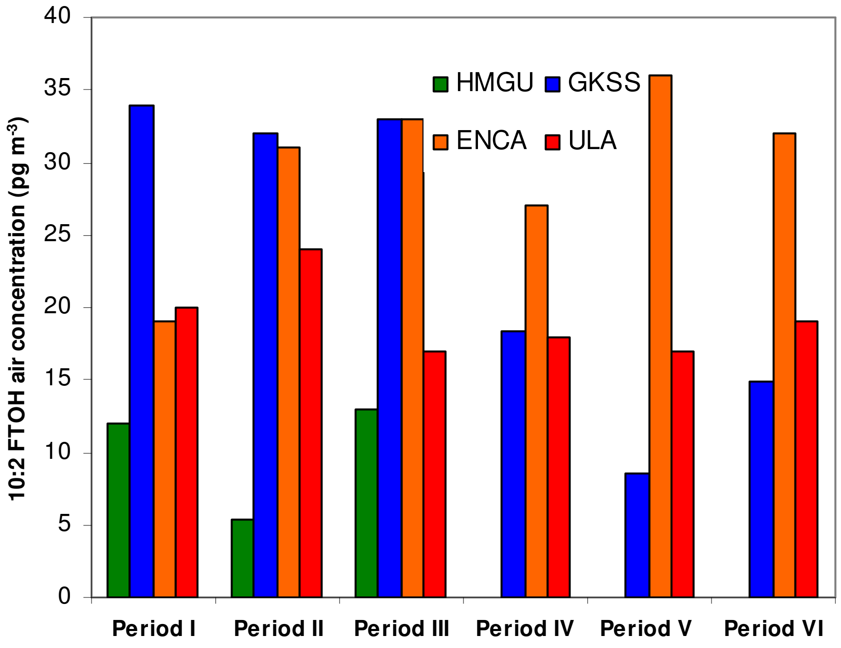


Figure 12: 10:2 FTOH air concentrations determined by SPMD, SIP, and high volume sampling.

In contrast to SPMD, FTOH were detected regularly using SIP disks due to different accumulation behaviour. FTOH sampling rates obtained for SPMD were smaller than sampling rates of SIP (Table 27). Thus, FTOH sampling applying SIP disks is more effective than using SPMD. However, in the above mentioned study the same sampling rate was applied for the calculation of air concentrations of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH. Due to the differences in volatility of those compounds, this sampling rate might not reflect the real sampling behaviour of FTOH.

Table 27: Comparison of SPMD and SIP derived sampling rates (R_S).

	R_S (m^3 d^{-1}) Period I	R_S (m^3 d^{-1}) Period II	R_S (m^3 d^{-1}) Period III
8:2 FTOH (SPMD)	0.8	0.5	1.2
8:2 FTOH (SIP)	1.4	1.3	2.1
10:2 FTOH (SPMD)	0.9	0.4	1.0
10:2 FTOH (SIP)	1.5	1.9	1.7

3.4.3 Determination of SIP derived FTOH air concentrations and comparison to the other research groups

Recoveries for the analysis of FTOH sampled with SIP disks were between 22% and 46% (Table 28). Since there were no redundant SIP disks, the applied analytical method could not be optimized further. Therefore, low recoveries were accepted.

Table 28: Mean recoveries (R) and absolute standard deviations (SD) for FTOH determination sampled by SIP disks.

	R (%)	SD (%)
4:2 FTOH	22.1	2.1
6:2 FTOH	30.2	3.2
8:2 FTOH	39.0	1.5
10:2 FTOH	46.2	4.6

As for the SPMD samples, 4:2 FTOH and 6:2 FTOH were not detected on SIP disks. This might be due to the low recoveries and LOD of the analytical method. 8:2 FTOH was observed in all SIP samples (Table 29), whereas 10:2 FTOH was detected only once.

Table 29: SIP derived FTOH air concentrations (pg m^{-3}).

	Period II		Period V	
	SIP I (pg m^{-3})	SIP II (pg m^{-3})	SIP I (pg m^{-3})	SIP II (pg m^{-3})
4:2 FTOH	nd	nd	nd	nd
6:2 FTOH	nd	nd	nd	nd
8:2 FTOH	38	51	30	88
10:2 FTOH	nd	nd	nd	27

nd: not detected

Calculated 8:2 FTOH air concentrations were between 30 and 88 pg m^3 for SIP. The SIP derived concentration of 10:2 FTOH during Period V was 27 pg m^{-3} and was close to the limit of detection. This explains why 10:2 FTOH was not detected in the remaining samples. Replicate 8:2 FTOH air concentrations of period II and V were in the same order of magnitude. However, there was a considerable difference between both SIP disks of period V. This inconsistency reveals that the method is not sufficiently optimised and needs further improvement.

SIP-based FTOH concentrations determined by the participating laboratories were quite similar (Figure 13 and Figure 14). The 8:2 FTOH air concentration for period II and IV determined during this thesis were close to the average mean values of the four laboratories.

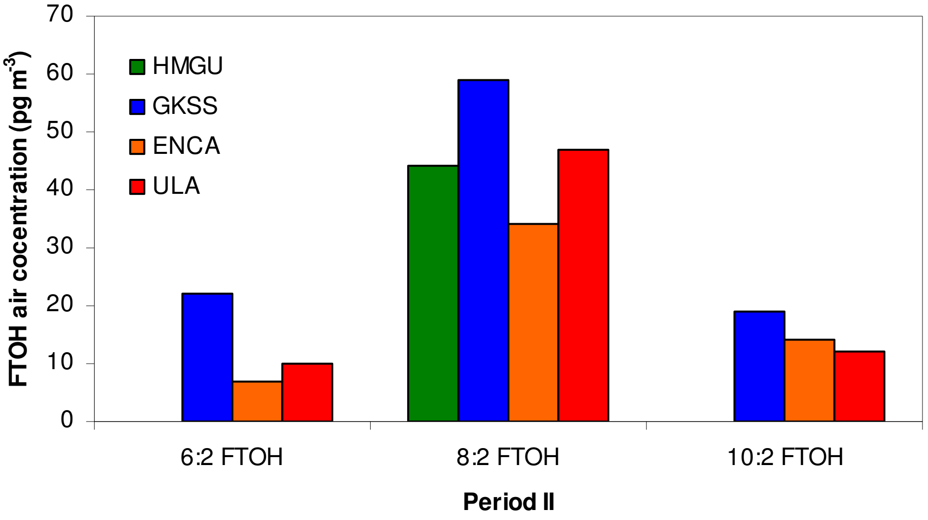


Figure 13: Comparison of mean FTOH air concentrations derived by SIP disks of sampling period II analysed by Helmholtz Zentrum München (HMGU), GKSS Research Center Geesthacht (GKSS) and Environment Canada (ENCA), and Lancaster University (ULA).

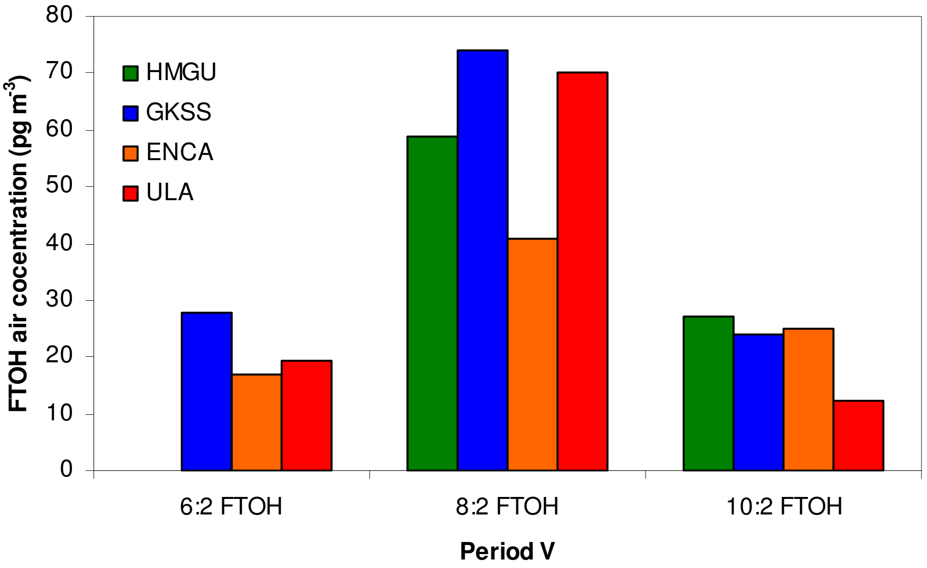


Figure 14: Comparison of mean FTOH air concentrations derived by SIP disks of sampling period V analysed by Helmholtz Zentrum München (HMGU), GKSS Research Center Geesthacht (GKSS), Environment Canada (ENCA), and Lancaster University (ULA).

The fact that 6:2 FTOH and 10:2 FTOH was detected regularly by the other laboratories can be explained by better analyte recoveries and lower LOD of the used GC-MS systems compared to analysis at HMGU. In samples analysed at HMGU, 6:2 FTOH was not detected at all, and 10:2 FTOH was detected only once in SIP disks. 4:2 FTOH was not detected in SIP disks by any of the participating laboratories.

3.4.4 Comparison of the determination of FTOH standard solutions analysed by the laboratories of HMGU, GKSS, Lancaster University, and Environment Canada

In addition to SIP and sampling device comparison, two FTOH standard solutions of unknown concentrations were analysed by the four participating laboratories to elaborate analytical consistency. FTOH concentrations of standard solution 1 determined in this thesis differed partly from the concentrations obtained by the other laboratories (Figure 15). The 4:2 FTOH concentration was underestimated compared to the mean value. Concentrations of 6:2 FTOH and 10:2 FTOH were overestimated compared to the mean value. However, the 8:2 FTOH concentration and the mean value were in good agreement.

The FTOH concentrations obtained at HMGU for standard solution 2 (Figure 16) were in good agreement with the other laboratories and, except for 10:2 FTOH, always very close to the mean value of all laboratories. However, at HMGU the highest standard deviations were obtained, revealing the lowest analytical precision of all participating laboratories. This has to be improved for further studies.

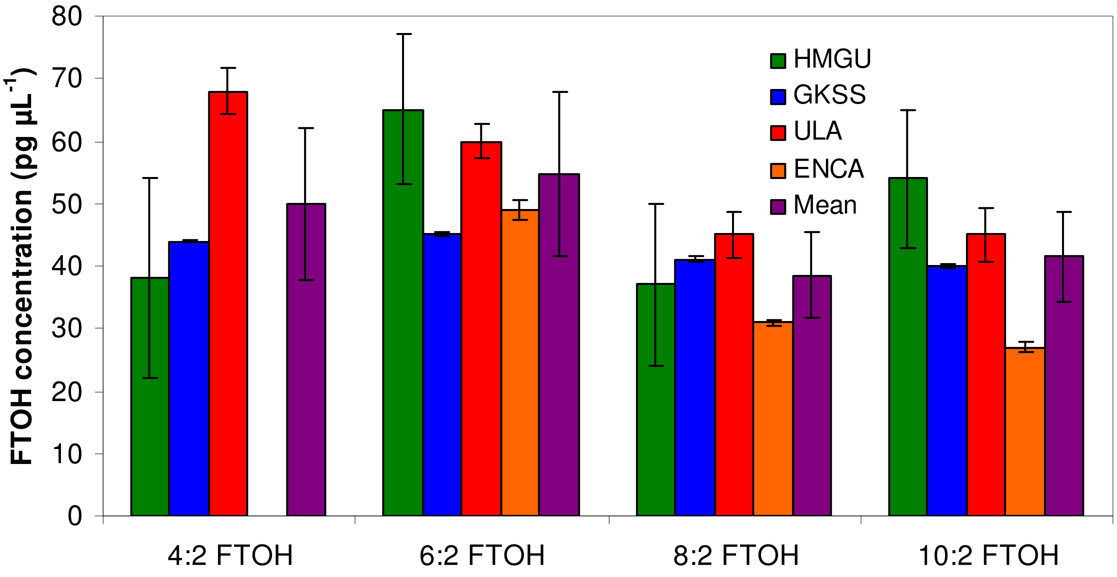


Figure 15: Comparison of FTOH concentrations and absolute standard deviations (SD) of standard solution 1 determined by Helmholtz Zentrum München (HMGU), GKSS Research Center Geesthacht (GKSS), University of Lancaster(ULA), and Envrionment Canada (ENCA).

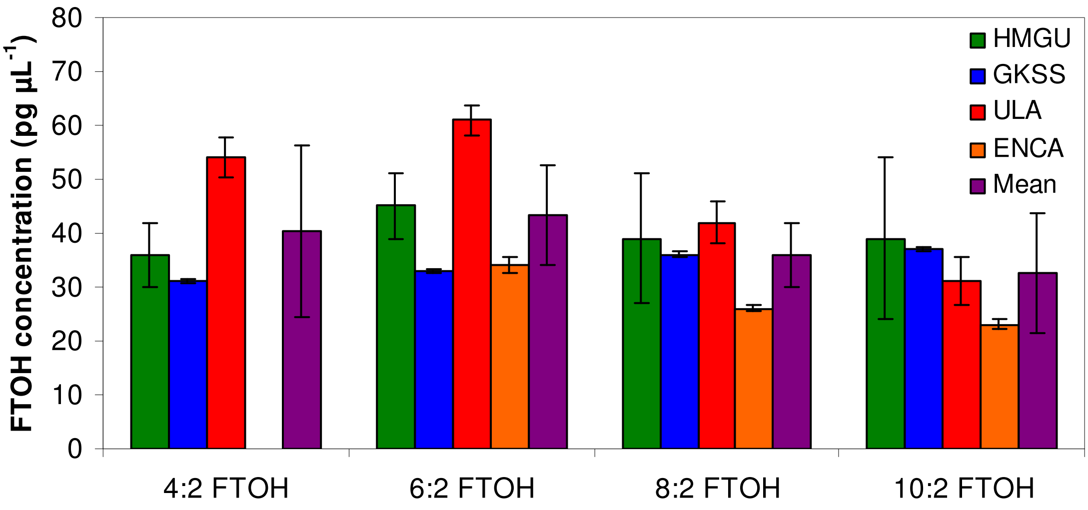


Figure 16: Comparison of FTOH concentrations and absolute standard deviations (SD) of standard solution 2 determined by Helmholtz Zentrum München (HMGU), GKSS Research Center Geesthacht (GKSS), University of Lancaster (ULA), and Environment Canada (ENCA).

3.5 Method development for determination of FTOH adsorbed to spruce needles

The extraction of spruce needles with acetone/MTBE (1/1) caused a high matrix content in the extracts. Purification of those extracts was not sufficient by EnviCarb SPE cartridges (250 mg and 500 mg) or silica SPE cartridges. Extracts were dark green and still contained diluted waxes. Thus, FTOH concentrations and recovery rates of those samples were not determined. Also clean-up of ACN extracts using silica and Envi Carb cartridges eluted with acetone/MTBE (1/1) were not clean enough for determination at the GC-MS.

The only method yielding satisfactory recovery rates and acceptable extract purity was the extraction of spruce needles by ACN followed by a clean-up with EnviCarb and ACN as elution solvent. For spruce needles older than one year, one Envi carb cartridge (250 mg) was enough. Extracts of needles younger than one year had to be to be purified by two EnviCarb cartridges (500 mg). Average recovery rates of this method were between 45% (4:2 FTOH) and 97% (8:2 FTOH) (Table 30).

Table 30: Average recovery rates (R) and relative standard deviations (SD, %) for FTOH determination in spruce needles

Analyte	R (%)	SD (%)
4:2 FTOH	45	12
6:2 FTOH	72	3.8
8:2 FTOH	97	13
10:2 FTOH	83	8.4

In spruce needle samples taken in Munich, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were not detected. However, small amounts (1.6 and 4.4 ng g^{-1}) of 4:2 FTOH were determined. This is surprising, since of all FTOH, 4:2 FTOH should have the lowest tendency to partition from air to needles surface, due to its high volatility. A potential contamination of needles during laboratory treatment may explain these findings. However, neither 4:2 FTOH nor the other FTOH were detected in blank samples. Therefore, it was assumed that in contrast to the other FTOH, 4:2 FTOH may be able to enter and accumulate via the stomata in the needles.

Despite of log K_{OA} values between 4.65 and 5.83 (Thuens *et al.*, 2008), FTOH seem to have a low tendency to partition to needle surfaces, since they were not detected in needle samples from Munich. Compared to PCB, PCDD/F, and PAH were even detected in needles of rural and remote areas (Kirchner *et al.*, 2006; Levy *et al.*, 2007; Zhu *et al.*, 2007; Shoeib *et al.*, 2008). Maybe this can be explained by the oleophobic properties of the fluorinated alkychain hampering the sorption of FTOH to the wax surface of needles. Thus, spruce needles seem to be no suitable passive sampler for airborne FTOH.

3.6 Determination of PFOA and PFOS deposition in the Alps

During the determination of PFOS and PFOA in deposition samples, highly enhanced recovery rates were observed. Recovery rates of mass-labelled PFOS were between 293% and 1121%, those of mass-labelled PFOA between 85% and 920%. The reason for this signal enhancement could not be identified. Because of these extraordinary high recoveries, an estimate about analyte “loss” during extraction and clean-up is certainly not possible. Nevertheless, PFOA and PFOS were quantified in those samples, because analyte and the corresponding surrogate standard do behave equally in a chemical point of view during extraction, clean-up, and determination. That means that native as well as mass-labelled analytes will be affected equally by signal enhancement. However, uncertainty of the resulting PFOA and PFOS concentrations does increase. As conclusion from the recovery rates it is obvious that the methodology for the analysis of PFOA and PFOS in XAD deposition samples has to be improved to obtain reliable results, e.g. by an optimised clean-up and a matrix matched calibration of the recoveries.

PFOA and PFOS were detected in deposition blank samples at mean concentrations of 4.2 and 3.7 ng per sampler, respectively. Deposition of PFOA a PFOS was only calculated when the sampler content of these substances exceeded the average PFOA and PFOS content in blank samples added to three fold the blank standard deviation (8.9 and 10.4 ng per sampler, respectively).

At the Zugspitze, PFOA and PFOS were detected in almost all of the deposition samples. Only in Spring 2008, PFOS was not detected. Bulk deposition rates of PFOA and PFOS were between 3.3 and 6.2 ng m^{-3} d^{-1} and between n.d. and 6.3 ng m^{-3} d^{-1}, respectively (Figure 17).

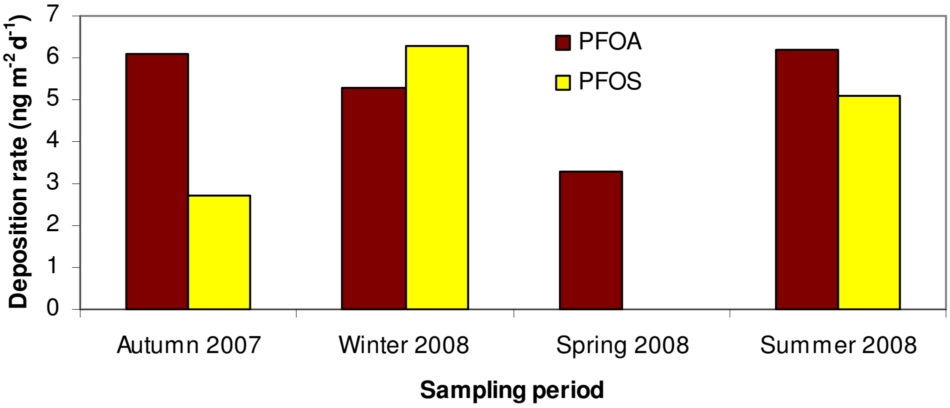


Figure 17: Deposition rates of PFOA and PFOS at Zugspitze; PFOS was not detected during Spring 2008.

At Weißfluhjoch, bulk deposition rates of PFOA and PFOS were between n.d. and 7.0 ng m^{-3} d^{-1} and between n.d. and 4.0 ng m^{-3} d^{-1}. PFOA and PFOS were detected only during two sampling periods (Figure 18).

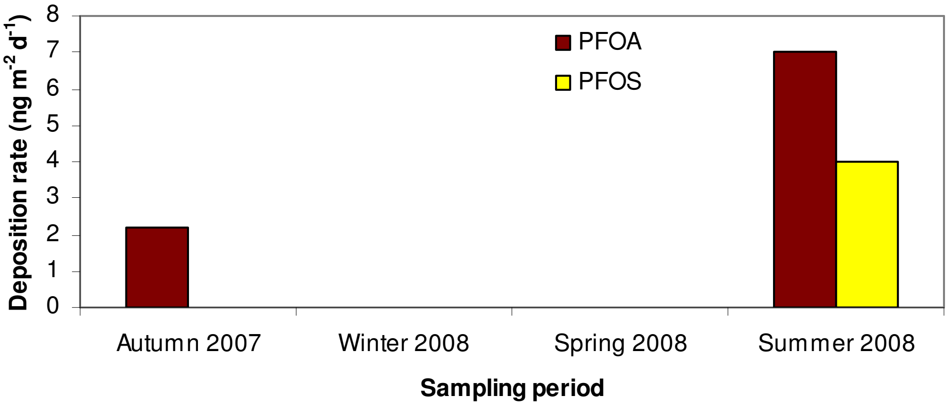


Figure 18: Deposition rates of PFOA and PFOS at Weißfluhjoch; PFOS was not detected during Autumn 2007, Winter 2008, and Spring 2008. PFOA was not detected during Winter 2008 and Spring 2008.

At Sonnblick, PFOA was detected in deposition samples during three consecutive sampling periods (Figure 19), whereas PFOS was only observed during Autumn 2007. Bulk deposition rates of PFOA and PFOS were between n.d. and 12 ng m^{-3} d^{-1} and between n.d. and 11 ng m^{-3} d^{-1}.

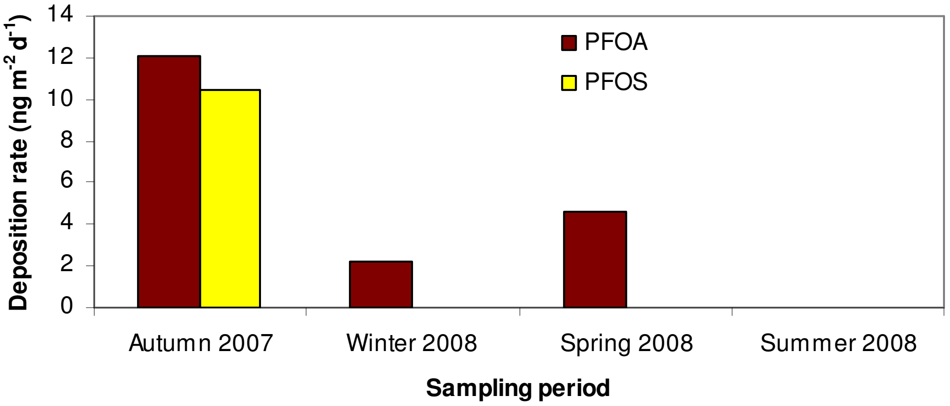


Figure 19: Deposition rates of PFOA and PFOS at Sonnblick; PFOS was not detected during Winter 2008, Spring 2008, and Summer 2008. PFOA was not detected during Summer 2008.

PFOA and PFOS were only detected sporadically in deposition samples of the three investigated sites. At the Zugspitze PFC deposition was observed for all sampling periods. Deposition rates of PFOA exceeded those of PFOS except for the Winter 08 sampling interval. A reason for this could be the higher water solubility of PFOA (4100 mg L^{-1} (Prokop *et al.*, 1989)) compared to PFOS (519 mg L^{-1} (Brooke *et al.*, 2004)). Highest deposition rates of both PFOA and PFOS was observed at Sonnblick during the autumn 07 sampling period. However, during the following sampling periods, PFOA deposition decreased considerably, and PFOS was no longer detected in deposition samples of this site. At Weißfluhjoch, PFOA and /or PFOS were detected only during two of the sampling periods.

Above calculated PFOA and PFOS deposition rates were similar to wet deposition rates of PFOA (up to 15 ng m^{-2} d^{-1}) and PFOS (up to 10 ng m^{-2} d^{-1}) at Barsbüttel, Germany (Dreyer *et al.*, 2010). Scott et al. (2006) determined PFOA deposition rates at areas far from significant emission sources and adjacent to point sources in North America between 0.14 and 30.1 ng m^{-2} d^{-1}. Modelled PFOA deposition rates at the same sites were between 0.0055 and 0.55 ng m^{-2} d^{-1} (Yarwood *et al.*, 2007).

PFOA and PFOS deposition rates determined in this study exceeded those of many chlorinated hydrocarbons such as DDT isomers, chlordane, heptachlor, or hexachlorobenzene, which were investigated at the same sites (Monarpop, 2008). Deposition rates of γ hexachlorcyclohexane were in the same order of magnitude as depositons rates of PFOA and PFOS. For endosulfan isomers, observed depositions were one to two orders of magnitude higher than those of PFOA and PFOS (Monarpop, 2008).

If the results in this study are representative, which cannot be assured due to the low number of samples and intervals, PFOA and PFOS must not be negelected, when imission of pollutants into this sensible area is investigated.

3.7 FTOH in domestic dust

FTOH recovery rates of in housedust samples were between 49% and 82% for dust samples from Munich and between 135% and 146% for dust samples from the Bavarian Health and Food Safety Authority (BHFSA) (Table 31). The difference between recovery rates of samples of different origin, may be explained by different sample pre-treatment and/or signal enhancement due to matrix effects in the samples. Since there is always loss of volatile FTOH during evaporation (see section 3.2.4), FTOH recoveries close to or even above 100% are unlikely. Therefore, it is important to use peak areas/heights of the mass-labelled standards in the sample or a matrix matched calibration for quantification. Because of the signal enhancement, limits of quantification were 0.5 ng g^{-1} for 4:2 FTOH and 0.3 ng g^{-1} for the other FTOH and thus relatively low.

Table 31: Average recovery rates (R, %) of dust samples from Munich (MUC; n=2) and from Bavarian Health and Food Safety Authority (BHFSA; n=6).

Analyte	R (Muc) (%)	R (BHFSA) (%)
4:2 FTOH	49	135 ± 28
6:2 FTOH	65	140 ± 12
8:2 FTOH	77	138 ± 10
10:2 FTOH	82	146 ± 11

Highest FTOH concentrations were observed in the dust sample of the BHFSA I (Table 32). There, 173 ng g^{-1} of 6:2 FTOH, 187 ng g^{-1} of 8:2 FTOH, and 75 ng g^{-1} of 10:2 FTOH were detected. FTOH concentrations in the samples BHFSA II and BHFSA IV were one order of magnitude and in the samples BHFSA III and BHFSA V even two orders of magnitude lower.

Table 32: FTOH concentrations (ng g^{-1}) in house dust samples from Munich (Muc) and from Bavarian Health and Food Safety Authority (BHFSA).

	Muc I (ng g^{-1})	Muc II (ng g^{-1})	BHFSA I (ng g^{-1})	BHFSA II (ng g^{-1})	BHFSA III (ng g^{-1})	BHFSA IV (ng g^{-1})	BHFSA V (ng g^{-1})
4:2 FTOH	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
6:2 FTOH	< LOD	< LOD	173	32	< LOD	< LOD	< LOD
8:2 FTOH	< LOD	< LOD	187	51	5.3	43	2.7
10:2 FTOH	< LOD	< LOD	75	23	1.4	9.5	1.0
Σ FTOH	< LOD	< LOD	434	105	6.7	53	3.7

8:2 FTOH always was the most abundant analyte. 6:2 FTOH was only detected in two samples (BHFSA I, BHFSA II). 4:2 FTOH was not detected in any sample. In both samples from Munich, concentrations of all FTOH were below limit of detection.

FTOH concentrations determined in this thesis are relatively low compared to those of other studies. Strynar and Lindstrom (2008) observed maximum FTOH concentrations of 804 (6:2 FTOH), 1660 (8:2 FTOH), and 883 ng g^{-1} (10:2 FTOH) in dust. Mean concentrations were 75, 167, and 96 ng g^{-1}, respectively. In house dust from Ottawa, Canada, maximum concentrations of 2500 (6:2 FTOH), 16315 (8:2 FTOH), and 8176 ng g^{-1} (10:2 FTOH) were determined (Shoeib *et al.*, 2005a). Mean concentrations were 156, 410, and 233 ng g^{-1}, respectively. As in consumer products analysed in this thesis and by other research groups (Dinglasan-Panlilio and Mabury, 2006; Sinclair *et al.*, 2007), as well as in outdoor air samples (Shoeib *et al.*, 2006; Barber *et al.*, 2007; Oono *et al.*, 2008; Dreyer *et al.*, 2009a; Dreyer *et al.*, 2009b) 8:2 FTOH was the most abundant FTOH, as well, probably due to an enhanced production.

3.8 PFC in household consumer products

In 14 of the 26 analysed products at least one PFC was detected. Most of these products belong to the groups of impregnating agents and lubricants. In impregnating agents, 8:2 FTOH and 10:2 FTOH were observed as the dominant PFC. They were present in all but two samples in concentrations up to 61 and 32 µg mL^{-1}, respectively (Table 33). 4:2 FTOH, 6:2 FTOH, and PFOA were detected at low concentrations in some impregnating agents. 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were detected in two of four lubricants, whereas 4:2 FTOH, PFOA and PFOS were not detected. The PFC burden of these products was higher than that of the remaining ones. Highest concentrations of 6:2 FTOH (148 µg mL^{-1}), 8:2 FTOH (149 µg mL^{-1}), and 10:2 FTOH (99 µg mL^{-1}) were determined in sample LU2, which overall, was also the sample containing most of PFC in this study. 4:2 FTOH and PFOA were not detected in any of the lubricants. PFOA was detected at 7.3 µg mL^{-1} in the fire fighting foam and at 14.5 µg mL^{-1} in the pesticide solution. These were the highest PFOA concentrations observed in this study. Cleaning agents and conditioners did not appear to contain any of the investigated PFC. PFOS was not detectable in any of the consumer products. This may be due to phase out of PFOS production in 2001 (3M, 2000; EPA, 2002).

Table 33: PFC content (µg mL^{-1}) of impregnating agents (IA), conditioners (CO), lubricants (LU), fire fighting foam (FF), pesticide solution (PE), and cleaning agents (CA). (nd: not detectable; nq: not quantifiable).

Product	4:2 FTOH (µg mL^{-1})	6:2 FTOH (µg mL^{-1})	8:2 FTOH (µg mL^{-1})	10:2 FTOH (µg mL^{-1})	PFOA (µg mL^{-1})	PFOS (µg mL^{-1})	Σ PFC (µg mL^{-1})
IA1	nq	1.2	61	32	0.4	nd	95
IA2	0.3	nd	2.9	1.7	0.1	nd	5.0
IA3	nq	2.1	52	32	0.2	nd	86
IA4	nq	1.3	43	23	0.2	nd	67
IA5	nd	0.6	30	17	0.4	nd	47
IA6	nd	nd	0.5	0.3	nd	nd	0.8
IA7	nd	nd	33	20	nd	nd	54
IA8	nd	nd	nd	nd	0.9	nd	0.9
IA9	nd	nd	nd	nd	3.6	nd	3.6
CO1	nd	nd	nd	nd	nd	nd	nd
CO2	nd	nd	nd	nd	nd	nd	nd
CO3	nd	nd	nd	nd	nd	nd	nd
CO4	nd	nd	nd	nd	nd	nd	nd
LU1	nd	72	76	61	nd	nd	209
LU2	nd	148	149	99	nd	nd	396
LU3	nd	nd	nd	nd	nd	nd	nd
LU4	nd	nd	nd	nd	nd	nd	nd
FF	nd	nd	nd	nd	7.3	nd	7.3
PE	nd	nd	nd	nd	14.5	nd	15
CA1	nd	nd	nd	nd	nd	nd	nd
CA2	nd	nd	nd	nd	nd	nd	nd
CA3	nd	nd	nd	nd	nd	nd	nd
CA4	nd	nd	nd	nd	nd	nd	nd
CA5	nd	nd	nd	nd	nd	nd	nd
CA6	nd	nd	nd	nd	nd	nd	nd

A Danish survey revealed that eleven of thirteen analysed impregnating agents contained FTOH in concentrations between 0.76 and 9420 µg mL^{-1} (Jensen *et al.*, 2008). In all analysed samples, FTOH concentrations exceeded those of PFCA. Washburn et al. (2005) observed

PFOA concentrations of up to 50 µg mL^{-1} in impregnating sprays. Unfortunately, FTOH were not analysed in this study. In this thesis, PFOA concentrations in impregnating agents reached 3.6 mg L^{-1} and were one order of magnitude below concentrations of Washburn et al. (2005). Highest PFOA contents in impregnating agents were found in sprays that did not contain any FTOH (IA8, IA9). In those sprays PFOA concentrations were higher than PFOA concentrations + standard deviation in FTOH containing impregnating agents (IA1-IA7).

In seven of eight products labelled as “PFC containing”, one or more of the investigated PFC were detectable. Probably other PFC, which were not analysed, are additionally contained in the consumer products. This might be the reason that in one product, labelled as “PFC containing”, none of the investigated PFC was detected.

Figure 20 demonstrates the proportions of PFC in the 14 PFC containing consumer products. Except for the fire fighting foam, the pesticide solution and two impregnating agents, FTOH were the dominant class of PFC. Only in these four products, concentrations of PFOA exceeded those of FTOH. Among the FTOH, 8:2 FTOH was always observed in highest proportions. Only in the two FTOH containing lubricants, the contribution of 6:2 FTOH was almost as high as that of 8:2 FTOH.

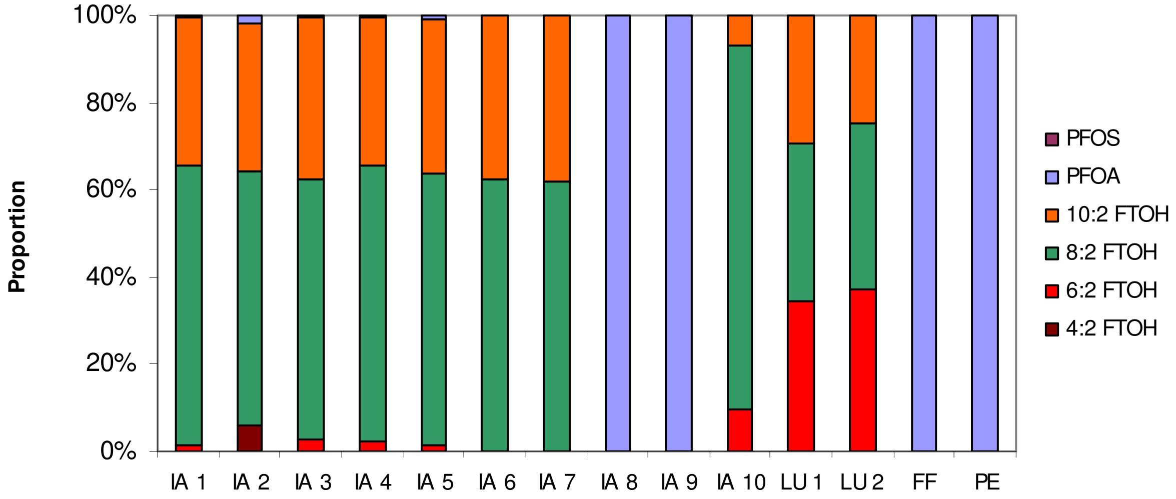


Figure 20: Contribution (%) of individual PFC analysed in impregnating agents (IA), conditioners (CO), lubricants (LU), fire fighting foams (FF), and pesticide solution (PE)

These results are consistent with studies analysing FTOH in outdoor air. In these studies, 8:2 FTOH was almost exclusively observed in highest proportions (Shoeib *et al.*, 2006; Barber *et al.*, 2007; Jahnke *et al.*, 2007b; Oono *et al.*, 2008; Dreyer *et al.*, 2009b) and in housedust (Strynar and Lindstrom, 2008). Only at very few places concentrations of 6:2 FTOH were equal or exceeded concentrations of 8:2 FTOH (Martin *et al.*, 2002; Stock *et al.*, 2004b; Dreyer *et al.*, 2009b).

In FTOH containing impregnating agents, the average ratio between the concentration of 10:2 FTOH and 8:2 FTOH was 0.58 ± 0.05 (n=7) (Table 34).

Table 34: Concentration ratios between 6:2 FTOH and 8:2 FTOH and 10:2 FTOH and 8:2 FTOH in consumer products and outdoor air.

Site	Medium	$\frac{c(6:2\,\text{FTOH})}{c(8:2\,\text{FTOH})}$	$\frac{c(10:2\,\text{FTOH})}{c(8:2\,\text{FTOH})}$	Reference
Germany	impregnating agents	0.02	0.58	this study
Germany	lubricants	0.98	0.74	this study
Canada, Toronto	air	1.58	0.53	Martin *et al.* (2002)
Canada, Long Point	air	0.91	0.53	Martin *et al.* (2002)
Canada, Toronto	air	0.44	0.52	Shoeib *et al.* (2006)
Artic	air	0.24	0.55	Shoeib *et al.* (2006)
Germany, Hamburg	air	0.55	0.29	Jahnke *et al.* (2007b)
Germany, Waldhof	air	0.85	0.31	Jahnke *et al.* (2007b)
Germany, Hamburg	air	0.3	0.27	Dreyer and Ebinghaus (2009)
Germany, Hamburg	air	0.25	0.25	Dreyer and Ebinghaus (2009)
Germany, Hamburg	air	0.57	0.47	Dreyer and Ebinghaus (2009)
Germany, Geesthacht	air	0.46	0.27	Dreyer and Ebinghaus (2009)
Germany, Geesthacht	air	0.34	0.29	Dreyer and Ebinghaus (2009)
Germany, Geesthacht	air	0.47	0.43	Dreyer and Ebinghaus (2009)
Germany, Geesthacht	air	0.41	0.35	Dreyer and Ebinghaus (2009)
Germany, Geesthacht	air	0.56	0.33	Dreyer and Ebinghaus (2009)
Japan, Higashiyodogawa	air	0.03	0.11	Oono *et al.* (2008)
Japan, Horinomiya	air	0.05	0.12	Oono *et al.* (2008)
Japan, Sakyo	air	0.03	0.12	Oono *et al.* (2008)

The average ratio between the 6:2 FTOH and the 8:2 FTOH amount in impregnating agents was 0.02 ± 0.01 (n=5). IA10, which was obtained in Brazil, had a different FTOH composition than impregnating agents purchased in Germany. Therefore IA10 was not considered for the calculation of the FTOH ratio average.

In FTOH containing lubricants (LU1, 2) a ratio between 10:2 FTOH and 8:2 FTOH of 0.81 and 0.66, respectively, and a ratio between 6:2 FTOH and 8:2 FTOH of 0.96 and 0.99, respectively, were observed. Because there were only two FTOH containing lubricants, differences in composition between impregnating agents and lubricants were not tested for significance. However, there is a considerable difference in FTOH composition in those two product groups, since concentrations of individual FTOH in lubricants were beyond the standard deviation ranges of FTOH concentrations in impregnating agents.

Also, FTOH ratios of IA10 were outside of these standard deviation ranges. Thus, above calculated FTOH proportions possibly could be used as a fingerprint for FTOH containing impregnating agents from Europe. However, FTOH ratios found in the atmosphere (Martin *et al.*, 2002; Stock *et al.*, 2004b; Shoeib *et al.*, 2006; Jahnke *et al.*, 2007b; Oono *et al.*, 2008; Dreyer and Ebinghaus, 2009) at diverse locations were obviously dissimilar to those of lubricants or impregnating agents (Table 34), indicating that FTOH composition of outdoor air is affected by many different sources and applications.

Human exposure to PFC calculated for the three scenarios differed (Table 35). Total daily PFC exposure was found to be between 43 ng kg^{-1} d^{-1} (scenario I) and 464 ng kg^{-1} d^{-1} (scenario III). Given these scenarios, exposure was dominated by 8:2 FTOH, which was calculated to be between 20 (scenario I) and 172 ng kg^{-1} d^{-1} (scenario III). Exposure to PFOA was between 1 (scenario I) and 8 ng kg^{-1} d^{-1} (scenario III). Exposure to 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH was one order of magnitude higher than exposure to PFOA for all scenarios.

Table 35: Human exposure (ng kg^{-1} d^{-1}) to PFC in consumer products calculated for three different scenarios.

Compound	Scenario I (ng kg^{-1} d^{-1})	Scenario II (ng kg^{-1} d^{-1})	Scenario III (ng kg^{-1} d^{-1})
4:2 FTOH	<0.1	0.2	0.3
6:2 FTOH	10.1	18.6	170
8:2 FTOH	20.1	26.4	172
10:2 FTOH	11.4	15.0	113
PFOA	1.2	1.8	8.4
Σ PFC	42.8	62.0	464

Uptake of PFOA, PFOS, and their precursors originating from contaminated food and drinking water was identified to be the most important exposure pathway for the general population (Trudel *et al.*, 2008; Vestergren *et al.*, 2008). Total daily doses of PFOA and its precursors between 0.3 and 150 ng kg^{-1} d^{-1} were varied (Vestergren *et al.*, 2008). Contribution of precursor substances in impregnating agents to the total daily dose of PFOA was calculated to be 9-11% in a high exposure scenario, in which the proportion of precursors biotransformed to PFOA was regarded by a factor of 0.017 (Vestergren *et al.*, 2008). Multiplying 8:2 FTOH exposures obtained in this thesis by this factor results in PFOA exposures between 0.34 and 2.9 ng kg^{-1} d^{-1}. Human exposure to PFOA from spray droplets was one order of magnitude lower than values calculated by Trudel et al. (2008) due to lower PFOA concentrations in consumer products. Thus, these results confirm the hypothesis that consumer products as PFOA exposure source are of minor importance compared to food and drinking water. Nevertheless, results obtained in this thesis and other studies (Begley *et al.*, 2005; Dinglasan-Panlilio and Mabury, 2006; Sinclair *et al.*, 2007; Jensen *et al.*, 2008) reveal that PFC are present in many products and tools, which are preferentially applied in households, and therefore are a direct source for human exposure. PFC in consumer products can be an explanation for PFC determined in domestic dust samples. However the applied model (Trudel *et al.*, 2008) only accounted the exposure to PFC in droplets, there is additionally an exposure to gaseous compounds that is no considered by these calculations. Since incorporated FTOH are metabolised to PFCA in the human body (Martin *et al.*, 2005) an ongoing accumulation of PFCA can be anticipated despite the phase out of the production of long-chain PFCA and PFSA.

3.9 Analysis of PFC in water and soil samples collected in the national park Serra dos Órgãos, Brazil

Recovery rates of mass-labelled PFOS and mass-labelled PFOA in soil samples were not calculated by internal quantification due to disturbed detection of the injection standard 9:2 FA. However, quantification by external standard calibration resulted in average recoveries of 65% and 71% for MLPFOA and MLPFOS, respectively in soil samples of an altitude of 1800 m and 2000 m asl. However, because of the disturbed internal quantification, uncertantiy of the obtained results is strongly enhanced. PFOA and PFOS were not detectable in any of the soil samples, probably due to the remoteness of the sampling location.

Neither PFOS nor PFOA were detected in water samples. Recoveries of mass-labelled PFOS and PFOA were 58% and 61%, respectively. Since PFOA and PFOS were determined in remote mountain areas (Loewen *et al.*, 2008; Jahnke and Berger, 2009) the non-detects in this study may have been caused by the low sampling volume, which was limited to 1 L, because the national park area could only be arrived by walking. Increasing the sampling volume to at least 4 L may result in detectable concentrations (Loewen *et al.*, 2005; Loewen *et al.*, 2008; Jahnke and Berger, 2009). However, high altitude water was analysed at the northern hemisphere only. Dreyer et al. (2009b) observed that concentrations of airborne PFC, which will be responsible for PFOA and PFOS contamination at high altitudes, were significantly lower in the southern hemisphere than in the northern hemisphere. Thus, the sampling volume may have to be increased to even more than 4 L in order to detect PFC in the national park Serra dos Órgãos. High volume water sampling (>100 L) and subsequent enrichment may provide an interesting alternative.

4 Conclusion

In this thesis, a simultaneous determination of four FTOH of different chain length and the perfluorinated acids PFOA and PFOS was developed. UPLC TOF-MS was applied to detect these substances, although they were routinely analysed by GC-PCI-MS and HPLC tandem MS, respectively. Because FTOH are precursors of PFCA such as PFOA, simultaneous determination facilitates research regarding fate, metabolism, degradation, and distribution of these compounds in humans and the environment. Further studies should investigate if perfluroalkyl sulfonamides and polyfluorinated N-alkyl sulfonamides are suitable for determination by LC-MS. This would enable the simultaneous determination of PFSA and their precursors.

UPLC-TOF MS was applied for samples analysed for PFOA, PFOS, and FTOH. For samples that were analysed for FTOH, only GC-PCI-MS was used as detection method. Thus, 4:2 FTOH was determined, as well, which can still not be detected by LC-MS.

Several analytical methods were developed or optimized during this thesis. FTOH were determined in spruce needles that were extracted by acetonitrile followed by a clean-up procedure using EnviCarb cartridges. Moreover, FTOH were analysed in SIP disks and house dust that were extracted by acetone/MTBE and SPE applying EnviCarb cartridges. PFOA and PFOS were analysed in water samples that were extracted using WAX SPE cartridges. Those analytes were also determined in soil samples and in XAD deposition samples, both extracted in methanol and purified by SPE using EnviCarb cartridges. However, some of the described analytical methods still encounter strong matrix effects, usually expressed as signal disturbance or enhancement during PFC detection by GC-MS and UPLC-TOF MS. Thus, these methods should be further optimized.

An analytical method based on liquid liquid extraction was developed for the determination of FTOH in SPMD. SPMD were intensively evaluated as FTOH passive samplers. It turned out that SPMD are generally not well suited for the analysis of PFC in air, although FTOH are able to migrate through PE membranes of SPMD. However, accumulation is influenced by FTOH air concentration, the length of the fluorinated alkyl chain, and seems to be strongly influenced by the SPMD membrane. A field intercomparison also revealed that active sampling or passive sampling using SIP disks are a better choice for the determination of airborne PFC. These experiment was also used to determine FTOH sampling rates of SPMD with respect to high volume sampling.

However, to obtain accurate sampling rates of SPMD for FTOH, the partitioning coefficient of FTOH between air and SPMD has to be determined precisely. In addition, membranes of different materials should be investigated for their suitability to accumulate FTOH in triolein. The interlaboratory comparison of the analysis of SIP disks and standard solution highlighted that the GC-MS system used during this thesis had the lowest sensitivity and precision of the four partizipating laboratories.

In this thesis, deposition of PFOA and PFOS in the Alps was investigated for the first time. PFOA and PFOS were detected frequently in samples from three different sites in the Alps. It was observed, that deposition of PFOA and PFOS exceeded deposition of many organochlorine pesticides at the investigated sites. PFOA and PFOS were not detected in water and soil samples from the national park Serra dos Órgãos, Brazil, due to low environmental concentrations. However, immission of PFC into the Alps should be further studied. Therefore PFC should be included into existing projects monitoring POP such as PCB, PCDD/F, PAH, and chlorinated organic compounds in this remote and sensitive ecosystem.

In more than half of the investigated consumer products at least one PFC was detectable. As in all environmental samples, 8:2 FTOH was the dominant PFC. Thus, it was demonstrated that PFC are present in high concentrations in consumer products. Human exposure to PFC originating from consumer products was calculated using an adopted model. Relating to the assumptions of this model, total human exposure to 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, and PFOA was calculated to be 62 ng kg^{-1} d^{-1}. Besides PFC intake by food and drinking water, these results may explain PFC observed in blood samples of the general population. To elucidate importance of consumer products as origin of PFC incorporated by humans further laboratories should be conducted, since until now only modelling studies are available.

In house dust samples, total FTOH concentrations of up to 434 ng g^{-1} were observed. 8:2 FTOH was always the dominant FTOH exhibiting concentrations up to 187 ng g^{-1}. This reveals that humans are exposed to FTOH in their direct ambiance. Application of consumer products analysed may explain some PFC determined in house dust. Further studies should be conducted to identify and quantify possible diffuse and point sources for PFC present in house dust.

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6 Appendix

List of publications:

Publication I……………………………………………………………………………………**83**

Method development for the determination of fluorotelomer alcohols in semipermeable membrane devices.

Fiedler, S., Pfister, G., Schramm, K.-W. (2007); Proceedings of the International Conference on Environmental Management, Engineering, Planning, and Economics, Skiathos, Greece; 2697-2702

Publication II…………………………………………………………………………………**86**

Partitioning of fluorotelomer alcohols (FTOH) to semipermeable membrane devices (SPMD).

Fiedler, S., Pfister, G., Schramm, K.-W. (2010); Environmental Science and Pollution Research **17**; 420-428

Publication III………………..……………………………………………………………….**95**

Poly- and Perfluorinated Compounds in Household Consumer Products.

Fiedler, S., Pfister, G., Schramm, K.-W; Toxicological & Environmental Chemistry (accepted).

Publication IV..…………………..…………………………………………………………..**..105**

Field Intercomparison on the Determination of Volatile and Semi-volatile Polyfluorinated Compounds in Air.

Dreyer, A., Shoeib, M., **Fiedler, S.**, Barber, J., Harner, T., Schramm, K.-W., Jones K.C., Ebinghaus, R.; (submitted) Analytical Chemistry

Method development for the determination of fluorotelomer alcohols in semipermeable membrane devices

S. Fiedler[1*], G. Pfister[1], and K.W. Schramm[1,2]
[1] GSF – National Research Centre for Environment and Health, Institute of Ecological Chemistry,
Ingolstaedter Landstrasse 1, 85764 Neuherberg, Germany
[2] TUM - Wissenschaftszentrum Weihenstephan für Ernährung und Landnutzung, Department für
Biowissenschaftliche Grundlagen, Weihenstephaner Steig 23, 85350 Freising, Germany

*Corresponding author: E-mail: stefan.fiedler@gsf.de; Tel: +49893187293 2 Fax: +4989318733 71

Abstract

Fluorotelomer alcohols (FTOH) are volatile and widely used compounds. Recently, they were identified as precursors of perfluorocarboxylates detected in humans and in the environment. For the determination of FTOH in the atmosphere appropriate sampling is needed.

In this study we present an analytical method for the determination of FTOH in semipermeable membrane devices (SPMD) used as passive air samplers. Different procedures for extraction and clean-up were compared. In the method we recommend, spiked SPMD were cut in slices and extracted in acetonitrile. Extracts were liquid-liquid extracted with hexane for removal of triolein. After that, solid phase extraction was conducted for further purification. Finally, FTOH were determined by gas chromatography mass spectrometry in positive chemical ionisation mode. FTOH recoveries of this method were between 40 and 64%.

Keywords: fluorotelomer alcohols, FTOH, SPMD, passive sampler, atmosphere

1. INTRODUCTION

Fluorotelomer alcohols (FTOH) are important raw materials that find use in many commercial and industrial applications including polymers, paints, and coatings [1,2]. FTOH are detectable in the atmosphere in urban and remote regions of the world [3,4,5,6]. Recently, FTOH were found to be probable precursor substances of persistent and potential carcinogenic perfluorocarboxylates (PFCA) like perfluorooctanoic acid (PFOA) [7]. Due to their volatility, FTOH may play an important role in the distribution of PFCA in environmental compartments [8,9].

For the determination of FTOH in isolated areas, appropriate passive samplers are needed, which do not require electricity and intensive maintenance. Semipermeable membrane devices (SPMD), consisting of a polyethylene membrane filled with triolein, are used as passive samplers for the determination of various hydrophobic organic compounds in water and air [10,11]. Purification of extracts is an important step for the analysis of SPMD. Gel permeation chromatography is often used for the removal of co extracted triolein [12,13]. For moderately polar compounds, liquid-liquid extraction with acetonitrile (ACN) is applied as well for exclusion of triolein [14]. Thus, the purpose of this study was to develop an analytical method suitable for determination of FTOH accumulated in SPMD.

2. MATERIAL AND METHODS

2.1 Chemicals

Native FTOH (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH) and perfluoromethyldecanol (9:2 FA) were purchased from Chempur, Karlsruhe, Germany. Mass labelled FTOH (6:2 FTOH, 8:2 FTOH, 10:2 FTOH; [M+4] in each case) were obtained from Campro Scientific, Berlin, Germany. Methanol (HPLC grade), n-hexane, and acetonitrile (both picograde) were distributed by Promochem, Wesel, Germany. Ethylacetate (pestanal) was purchased from Riedel-de-Haen, Seelze, Germany. Triolein (98% purity) and Carboxen 1016 cartridges were obtained from Sigma-Aldrich, Seelze. Strata C18-E cartridges and strata SDB-L syrene divenyl benzene cartridges were purchased from Phenomenex, Augsburg, Germany. Bulk C18 was obtained from Separtis, Grenzach-Whylen, Germany.

For spike and recovery experiments a 20 ppm FTOH solution in ethylacetate was used. 50 µL of this solution were spiked to SPMD prior to extraction and prior to solid phase extraction (SPE), respectively.

2.2 Optimisation of solid phase extraction

For clean-up of SPMD extracts, different adsorbent materials and solvents for elution were tested. For this purpose, SPMD were extracted in methanol (MeOH) and the volume was rotary evaporated to about 1 mL. After that extracts were spiked with FTOH standard solution and SPE was conducted to remove remaining triolein. Tested SPE materials were C18-E (500 mg and 1g), C18 (1g), SDB-L (200 mg), and C18-E (500 mg) + Carboxen 1016 (100 mg). Cartridges were conditioned with ethylacetate (EtAc) and MeOH, 3 mL each. Solvents tested for elution were EtAc, MeOH, MeOH/EtAc (1/1), and MeOH/EtAc (2/1). SPE cartridges were eluted with 5 mL of solvent. The volume was reduced to about 0.5 mL under a gentle stream of nitrogen and transferred into a GC vial. 9:2 FA was added as internal standard and FTOH were determined by GC-MS.

2.3 Optimisation of extraction

SPMD were spiked by injection of FTOH solution using a 50 µL syringe. After that SPMD were cut in slices and extracted by shaking in 100 mL of different solvents for 24 hrs. MeOH, ACN, acetone, and EtAc were tested for extraction efficiency. MeOH and ACN extracts were liquid-liquid extracted with 100 mL n-hexane (Hex). The MeOH fraction and the ACN fraction, respectively, was collected and rotary evaporated to about 1 mL. SPE was conducted with C18-E (500 mg) + Carboxen 1016 (100 mg). Cartridges were eluted with 8 mL MeOH. The volume was reduced to about 0.5 mL under a gentle stream of nitrogen and transferred into a GC vial. 9:2 FA was added as internal standard and FTOH were determined by GC-MS.

2.4 GC-MS determination

Measurements were performed in selected ion monitoring mode using an HP 5890 Series II gas chromatograph coupled to a Finnegan Mat SSQ 7000 mass selective detector. The gas chromatograph was equipped with a 60 m Restek VMS column (0.25 mm inner diameter, 1.4 µm film thickness). Helium was used as carrier gas with a constant column head pressure of 175 kPa. Injections were performed in splitless mode at 220 °C with an injection volume of 1 µL. The oven temperature was held at 50 °C for 2 min, then elevated to 80 °C at 10 °C min^{-1}, to 110 °C at 5 °C min^{-1} and held for 3 min, and finally elevated to 220 °C at 15 °C min^{-1} and held for 15 min. The transfer line was set to 300 °C.

Ionisations in the mass selective detector were performed by positive chemical ionisation at 40 eV and a source temperature of 150 °C. Methane was used as reagent gas.

2.5 FTOH penetration and accumulation in SPMD

For the use of SPMD as passive samplers, it is necessary to show that FTOH are able to penetrate through the polyethylene membrane and accumulate in triolein. For this purpose, a beaker with FTOH (50 µL for 4:2 FTOH and 6:2 FTOH each, and about 10 mg for 8:2 FTOH and 10:2 FTOH) and three SPMD were placed in a glass chamber, with no direct contact between beaker and SPMD.

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After one month, the chamber was opened and the SPMD were rinsed with ethylacetate to remove FTOH adsorbed to the SPMD surface. SPMD were spiked with mass labelled FTOH (6:2 FTOH, 8:2 FTOH, and 10:2 FTOH) and extracted for 24 hrs in 100 mL ACN, followed by liquid-liquid extraction with 100 mL Hex. Then, SPE was conducted with C18-E (500 mg) + Carboxen 1016 (100 mg). Cartridges were eluted with 8 mL MeOH. The volume was reduced to about 0.5 mL under a gentle stream of nitrogen and transferred into a GC vial. 9:2 FA was added as internal standard and FTOH were determined by GC-MS.

3. RESULTS AND DISCUSSION

3.1 Optimisation of solid phase extraction

Elution of SPE cartridges showed that using EtAc or MeOH/EtAc (1:1) always resulted in a breakthrough of triolein for all used SPE adsorbents. Due to the high content of triolein FTOH recoveries were not determined to avoid contamination of the GC-MS system. Thus, EtAc and MeOH/EtAc (1:1) were not suitable for cartridge elution. Triolein content in eluats decreased with increasing polarity of the solvent used for elution. However, a polar solvent may reduce recovery of the more nonpolar 8:2 FTOH and 10:2 FTOH. Hence, for removing of triolein from SPMD extracts, elution with MeOH showed the best results (Table 1).

Table 1. FTOH mean recoveries [%] of different solvents used for elution of C18-E (500 mg)cartridges (n=3).

	MeOH 5 mL	MeOH/EtAc 2/1 5 mL	MeOH + EtAc 5 mL +3 mL	MeOH/EtAc 1/1 5 mL	MeOH 8 mL
4:2 FTOH	51.4	49.8	37.1	35.2	42.5
6:2 FTOH	43.0	58.5	49.4	44.5	53.2
8:2 FTOH	24.0	52.9	42.5	40.2	49.4
10:2 FTOH	29.4	61.2	45.8	42.5	59.6
Trioleinremoval	successful	insufficient	insufficient	insufficient	successful

To get better recoveries of more nonpolar FTOH, it was decided to increase the amount of MeOH from 5 to 8 mL. Recoveries increased to 42.5 to 59.6%, but were still not satisfactory.

For further improvement of FTOH recoveries, different SPE adsorbents were tested. Results are shown in Table 2.

Table 2. FTOH mean recoveries [%] of different SPE adsorbents. Elution with 5 mL of solvent (n=3).

Adsorbent	C18-E 1g	C18 1g	C18-E + Carboxen	C18-E + Carboxen
Elution	MeOH/EtAc 2/1	MeOH/EtAc 2/1	MeOH/EtAc 2/1	MeOH/EtAc 1/1
4:2 FTOH	41.0	39.8	45.0	48.9
6:2 FTOH	46.7	43.0	52.7	51.2
8:2 FTOH	32.7	32.0	44.7	39.1
10:2 FTOH	28.4	27.9	45.5	45.5
Trioleinremoval	successful	successful	successful	insufficient

* 500 mg

Retention of triolein was not sufficient for SDB-L cartridges. FTOH recoveries were not determined to avoid GC-MS contamination. Elution of C18-E (500 mg) + Carboxen (100 mg) showed best triolein removal and highest FTOH recoveries. However, recoveries were still not satisfactory.

3.2 Optimisation of extraction

Extracts in acetone and EtAc could not be rotary evaporated to 1 mL because of a high amount of dissolved triolein. Thus, no further clean-up was conducted and no FTOH recoveries were determined for acetone and EtAc extracts. Liquid-liquid extraction with Hex or ACN was not performed, because solvents are mixable in each other. FTOH recoveries of different solvents used for extraction are shown in Table 3.

Table 3. FTOH mean recoveries [%] of extraction of SPMD with MeOH or ACN, optionally followed by liquid-liquid extraction with Hex (n=3).

	MeOH	MeOH Hex	ACN Hex
4:2 FTOH	46.8	36.5	41.8
6:2 FTOH	56.9	45.4	51.7
8:2 FTOH	62.9	56.5	63.6
10:2 FTOH	62.9	55.6	56.9

Without liquid-liquid extraction, extraction with MeOH showed best recoveries. However, best triolein removal was achieved by extraction with ACN followed by liquid-liquid extraction. After rotary evaporation to 1 mL, no triolein was visible in the flask, in contrast to extraction with MeOH. Even with liquid-liquid extraction, triolein was visible in MeOH extracts after rotary evaporation. This, on the one hand, may be explained by a better solubility of triolein in MeOH. On the other hand, when performing liquid-liquid extraction, Hex and therefore triolein as well is partly dissolved in the MeOH fraction.

Hence, the method of choice with best triolein removal and acceptable FTOH recoveries was extraction with ACN followed by liquid-liquid extraction with Hex. Extracts are further purified by SPE with C18-E (500 mg) and Carboxen 1016 (100 mg) cartridges and then measured by GC-MS.

FTOH recoveries of this procedure are below of the optimum range between 70 and 110%. However, due to the high volatility of FTOH, especially of 4:2 FTOH, it is very difficult to achieve better recoveries. Volume concentration of extracts and eluats are critical steps concerning loss of FTOH during clean-up. In literature, recoveries higher than 70% for 6:2 FTOH, 8:2 FTOH and 10:2 FTOH are mostly achieved, when only one concentration step is applied during the analytical procedure [3,4,15]. Thus, for further improvement of the method, it is necessary to find extraction and clean-up procedures with a minimum of concentration steps.

3.5 FTOH penetration and accumulation in SPMD

FTOH showed good penetration and accumulation in SPMD. Mass areas of FTOH in extracted SPMD were much higher than mass areas of standards used normally for quantification. Thus, only an order of magnitude can be given for the accumulation of SPMD: More than 1 mg was found for 4:2 FTOH and 6:2 FTOH in one SPMD containing about 0.5 mL triolein. 8:2 FTOH was a little bit less and 10:2 FTOH was about one order of magnitude less than 4:2 FTOH and 6:2 FTOH. We assume that 4:2 FTOH and 6:2 FTOH penetrate into the SPMD more easily, because these compounds are more volatile and have a shorter alkylchain. In general, SPMD sample only substances with a molecular mass less than about 600 [16]. Molecular masses of analysed FTOH are in the range between 264 and 564.

4. CONCLUSION

It was shown that SPMD can be used as passive air samplers for FTOH. FTOH are able to penetrate through the PE membrane and accumulate in triolein. FTOH recoveries of the extraction and purification procedure are acceptable having in my mind the high volatility of the compounds. In future studies we plan to test SPMD as passive air samplers in the field, where SPMD are exposed to impacts of weather conditions, varying temperature, and low FTOH concentrations in air.

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AREA 6 • ENVIRONMENTAL ANALYSES AND MONITORING • RESEARCH ARTICLE

Partitioning of fluorotelomer alcohols (FTOH) to semipermeable membrane devices (SPMD)

Stefan Fiedler · Gerd Pfister · Karl-Werner Schramm

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Abstract

Background, aim, and scope Fluorotelomer alcohols (FTOH) are widely used substances that were detected even in remote regions of the world. For the determination of FTOH in the atmosphere, appropriate sampling techniques are needed. In this study, triolein-filled low-density polyethylene tubes were used as semipermeable membrane devices (SPMD) and tested for their suitability as passive air samplers for FTOH.

Materials and methods Partitioning to and from SPMD were investigated for four FTOH of different chain length and concentration levels in laboratory and field experiments. FTOH were extracted by liquid–liquid extraction with acetonitrile:n-hexane 1:1 and determined by gas chromatography (GC)-positive ion chemical ionisation mass spectrometry (MS).

Results FTOH behaved differently depending on applied concentrations. At high FTOH levels, compound passage through the membrane and uptake appeared to be best for 6:2 FTOH, but passage of long-chain FTOH was in the same order of magnitude. At low FTOH concentration levels, mass transfer and uptake was best for short-chain FTOH. Partitioning of 4:2 FTOH to SPMD exceeded partitioning of 10:2 FTOH by nearly two orders of magnitude.

Discussion FTOH partitioning to SPMD seems to be dependent on the fluorinated chain length and controlled by the SPMD membrane acting as a barrier. Migration of long-chain FTOH through the membrane was hampered, probably due to the oleophobic properties of the fluorinated alkyl chain. Because of the constricted diffusion of FTOH through the SPMD membrane at low FTOH levels, an adequate accumulation in the passive sampler is prevented. Thus, sensitivity of the analytical method in combination with the enrichment of FTOH in SPMD was not sufficient to achieve adequate method detection limit at low FTOH levels.

Conclusions Application of SPMD as passive air samplers for FTOH did not seem to be a suitable method for environmentally relevant FTOH concentrations.

Recommendations and perspectives As a consequence, we can only recommend the use of SPMD for FTOH of presumably high contamination levels.

Keywords Atmosphere · Carcinogenicity · Fluorotelomer alcohol · GC-MS · Passive samplers · Perfluorocarboxylates (PFCA)

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S. Fiedler (✉) · G. Pfister · K.-W. Schramm
Helmholtz Zentrum München, National Research Centre
for Environmental Health, Institute of Ecological Chemistry,
Ingolstaedter Landstrasse 1,
85764 Neuherberg, Germany
e-mail: fiedler.stefan@gmx.net

K.-W. Schramm
Department für Biowissenschaftliche Grundlagen,
TUM, Wissenschaftszentrum Weihenstephan
für Ernährung und Landnutzung,
Weihenstephaner Steig 23,
85350 Freising, Germany

1 Background, aim, and scope

Fluorotelomer alcohols (FTOH) are important raw materials that are applied in many commercial and industrial products including polymers, paints, and coatings (Dinglasan-Panlilio and Mabury 2006; Szostek et al. 2006; Villagrasa et al. 2006; Sinclair et al. 2007). They were detected in the atmosphere in urban and remote regions of the world (Dreyer et al. 2009; Martin et al. 2002; Shoeib et al. 2006; Sinclair and Kannan 2006). FTOH were identified as precursor substances of persistent and potentially carcinogenic perfluorocarboxylates (PFCA), like perfluorooctanoic acid (Dinglasan et al. 2004; Ellis et al. 2004; Martin et al. 2005; Wallington et al. 2006). Due to their volatility, atmospheric transport of FTOH is, besides transport by ocean currents, one of the hypothesized pathways considered as explanation of the global PFCA distribution (Wallington et al. 2006; Ellis et al. 2003).

Often, high volume sampling is applied for FTOH analysis in air (Kim and Kannan 2007; Dreyer and Ebinghaus 2009). However, for the determination of FTOH in isolated areas, appropriate passive samplers are needed, which do not require electricity and intensive maintenance. Polyurethane foam disks (PUF), impregnated with XAD-4, and tubes filled with XAD-2 were recently used for FTOH determination (Loewen et al. 2008; Shoeib et al. 2008). Dialysis tubings henceforth referred to as semipermeable membrane devices (SPMD), consisting of a low-density polyethylene (LDPE) membrane filled with triolein, were used as passive samplers for the determination of various hydrophobic organic compounds such as polyaromatic hydrocarbons, polychlorinated biphenyls, and polychlorinated dibenzo-p-dioxins and dibenzofurans (Levy et al. 2007; Lu et al. 2002; Van drooge et al. 2005; Zhu et al. 2007). In contrast to PUF disks mentioned above, they can be used in water and air. Furthermore, the material accumulating the pollutants is better protected against environmental disturbances. Accumulation of pollutants by XAD-impregnated PUF disks is only dependent on partitioning between XAD and air, whereas for SPMD, enrichment can also be affected by diffusion of the pollutants through the LDPE membrane. Until now, SPMD were not applied or evaluated for their suitability in the sampling of FTOH in air. Due to the oleophobicity of the fluorinated alkyl chain, it is important to know, whether FTOH are able to pass through the membrane of SPMD and accumulate in triolein. In this study, the migration of FTOH in and out of triolein-filled SPMD was quantified for different initial FTOH amounts and discussed in terms of overall effectiveness and limitations.

2 Materials and methods

2.1 Materials

Perfluorobutyl ethanol (4:2 FTOH), perfluorohexyl ethanol (6:2 FTOH), perfluorooctyl ethanol (8:2 FTOH), perfluorodecyl ethanol (10:2 FTOH; 97% each), and perfluoromethylnonyl ethanol (9:2 FA, 98%) were purchased from Chempur, Karlsruhe, Germany. $^2H_2{}^{13}C_2$ labelled 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH ([M+4], 98% each) were obtained from Wellington Laboratories, Guelph, Ontario, Canada. Perfluoroheptyl methanol (7:1 FA, 97%), perfluorooctyl methanol (8:1 FA, 98%), and perfluorononyl methanol (9:1 FA, 98%) were kindly donated by GKSS Research Centre, Geesthacht, Germany. Envi-Carb (250 mg) cartridges were obtained from Sigma-Aldrich, Taufkirchen, Germany. Acetone, acetonitrile, methyl-tert. butylether (MTBE), and n-hexane (all picograde) were purchased by LGC-Promochem, Wesel, Germany. Ethylacetate (pestanal) was obtained from Riedel-de-Haen, Seelze, Germany. SPMD (LDPE lay-flat tubing, length 23 cm, width 2.5 cm, membrane thickness 65 ± 2 µm) were purchased from VWR, Darmstadt, Germany, and filled with 0.7 mL triolein (99%, Sigma-Aldrich, Taufkirchen, Germany).

2.2 FTOH migration out of SPMD

2.2.1 FTOH migration out of SPMD into air

In a first experiment, release rates of FTOH in SPMD were investigated. For this purpose, triolein-filled SPMD were spiked with 25 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH each and sealed again. Because of the high FTOH amount, 0.1 ml was chosen as carrier solvent volume. Since the solvent volume was relatively high compared to the volume of triolein (0.7 mL), acetone was applied as carrier solvent. Acetone is very volatile and thus can easily penetrate through the SPMD membrane, resulting in a rapid decline of solvent content after deployment. By this measure, effects on the partitioning of FTOH between triolein and air were minimized. SPMD were fixed in a Stevenson screen box made of untreated wood and placed 2.5 m above ground level at the area of the Helmholtz Zentrum München located in the north of Munich, Germany. There, they were protected from direct sunlight and wet deposition, and air flow turbulences were minimized (Levy et al. 2007). This experimental set-up prevents any saturation effects of FTOH in the air resulting in an equilibrium between FTOH concentrations in air and SPMD. After 0, 8, 16, 32, and 64 days of deployment (September to November 2007; temperatures between 5°C to 22°C), SPMD triplicates were collected, and the FTOH concentrations were determined as described in sections 2.4 and 2.5. If SPMD were not analysed immediately after sampling, they were stored at −30°C. In this experiment, 7:1 FA, 8:1 FA, and 9:1 FA were used as internal standards for calculation of FTOH recoveries. For each triplicate sample, one blank SPMD that was shortly exposed to ambient air was analysed simultaneously.

2.2.2 FTOH migration out of SPMD into solvent

In a second experiment, FTOH migration out of SPMD was tested by dialysis of SPMD, which is a common extraction method in routine SPMD analysis (Bartkow et al. 2004; Booij and Van drooge 2001; Huckins et al. 2006; Lohmann et al. 2001). For this purpose, triolein-filled SPMD were spiked with 0.1 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH each in 50 µL ethylacetate and sealed again. Ethylacetate was chosen, because evaporation of the carrier solvent was not necessary in this experiment. SPMD were extracted two times 24 h using 200 mL acetone/MTBE (*v/v* 1/1; Dreyer et al. 2008). After that, remaining FTOH in SPMD was extracted as described in section 2.4. It is important to note that for this third extraction step, the SPMD tubings were cut into slices, and acetonitrile/hexane (*v/v* 1/1) was used for extraction, because this solvent mixture is crucial for extract purification. Prior to each extraction, mass-labelled FTOH were added as recovery standards. Extracts were analysed separately. Dialysis extracts were concentrated and purified by solid phase extraction using Envi-Carb cartridges, which were eluted with 5 mL acetone/MTBE (1/1). Then, extracts were concentrated to 200 µL using rotary evaporation and a gentle stream of nitrogen. FTOH were determined by gas chromatography-mass spectrometry (GC-MS) as described below.

2.3 FTOH migration into SPMD and pure triolein from air

To investigate migration of FTOH through the polyethylene membrane and accumulation in triolein, several glass chamber experiments (GCE) were conducted. In general, a beaker with a known content of FTOH and some SPMD were placed in a glass chamber (volume 10 L, Fig. 1). Beaker and SPMD were not in direct contact. Deployment time and spiked FTOH levels in the beaker were varied. During exposure, the glass chamber was kept in the dark at room temperature. After deployment, the chamber was opened, and FTOH concentration in exposed SPMD and in one blank SPMD was determined as described in sections 2.4 and 2.5.

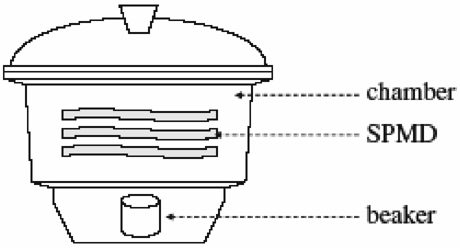

Fig. 1 Experimental set-up of glass chamber experiments

2.3.1 FTOH migration into SPMD and pure triolein for high FTOH levels

Firstly, three SPMD were exposed to a mixture of 10,000 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH each, which were directly weighed into the beaker, for 31 days (GCE I).

Secondly, four SPMD and a beaker with 1 mL of pure triolein were exposed to 10,000 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH each for 47 days. Pure triolein was not supposed to decrease in volume due to its very low volatility. For two of the SPMD, the outer side of the membrane was rinsed. Triolein and the PE tubings of those SPMD were analysed separately for their FTOH content. Pure triolein was dissolved in 50 mL n-hexane and then analysed like SPMD as described below, starting with liquid–liquid extraction.

2.3.2 FTOH migration into SPMD and pure triolein for low FTOH levels

Again, GCE were used to investigate partitioning of FTOH to SPMD and triolein. In GCE III, three beakers, each filled with 0.7 mL of triolein (without tubings), were exposed to 0.2 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH each for 15 days. FTOH in triolein were analysed as described above. Remaining FTOH in the beaker were determined by rinsing the inner glass wall of the chamber and the beaker with ethylacetate followed by concentration to 200 µL by rotary evaporation and a gentle stream of nitrogen.

In GCE IV, three SPMD (triolein and tubings) were exposed to 0.1 µg of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH each for 15 days. In addition, remaining FTOH in the beaker and adsorbed to the chamber were determined by rinsing the inner glass wall of the chamber and the beaker with ethylacetate followed by concentration to 200 µL as described above. Ethylacetate was used as carrier solvent in GCE III and GCE IV.

2.4 SPMD extraction and clean-up

Removal of co-extracted triolein is the essential step in SPMD analysis. Gel permeation chromatography (GPC) is often used for this purpose (Ockenden et al. 2001; Yusa et al. 2005). However, for FTOH analysis, GPC is not suited due to possible contamination from Teflon parts and analyte loss. Instead, an improved analytical method based on Esteve-Turrillas et al. (2006) and Fiedler et al. (2007) was applied, using liquid–liquid extraction for triolein removal. SPMD were cut into slices, transferred into glass vessels, and mass-labelled 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were added. After addition of 100 mL acetonitrile/n-hexane (*v/v* 1/1), SPMD were extracted by shaking for 24 h. Extracts were transferred into separatory funnels, and 100 mL acetonitrile/n-hexane (*v/v* 1/1) were added. Funnels were shaken for about 2 min. After phase separation, acetonitrile phases were collected and concentrated to 200 µL by rotary evaporation and a gentle stream of nitrogen. 9:2 FA was added as internal injection standard, and FTOH were determined by GC-MS. Triolein containing n-hexane was discarded.

2.5 GC-MS determination

Fluorochemicals were determined using an HP 5890 Series II gas chromatograph (Agilent Technologies, Waldbronn, Germany), coupled to a Finnegan Mat SSQ 7000 mass selective detector (Thermo Scientific, Dreieich, Germany). The gas chromatograph was equipped with a 60-m VMS column (0.25 mm inner diameter, 1.4µm film thickness; Restek, Bad Homburg, Germany). Helium (5.0, Linde, Höllriegelskreuth, Germany) was used as carrier gas with a constant column head pressure of 175 kPa. Injections were performed in splitless mode at 220°C with an injection volume of 1 µL. The oven temperature was held at 50°C for 2 min, then elevated to 80°C at 10°C min^{-1}, to 110°C at 5°C min^{-1} and held for 3 min, and finally elevated to 220°C at 15°C min^{-1} and held for 15 min. The transfer line was set to 300°C.

Ionisations in the mass selective detector were performed by positive chemical ionisation at 70 eV and a source temperature of 150°C. Methane (4.5, Linde, Höllriegelskreuth, Germany) was used as reagent gas. Detections were performed in selected ion monitoring mode.

3 Results

3.1 Analytical parameters and quality assurance

Using the new analytical method for SPMD, recoveries between 42% (4:2 FTOH) and 73% (8:2 FTOH) were achieved with relative standard deviations from 14% (6:2 FTOH) to 22% (10:2 FTOH). In contrast to the method described in Fiedler et al. (2007), only liquid–liquid extraction and no solid phase extraction was used for purification. Thus, just one concentration step was needed resulting in higher recoveries for volatile FTOH. Hence, the final volume could be reduced from 1 mL to 200 µL, and therefore, the methodical detection limit was improved to 5 pg µL^{-1} based on a signal to noise ratio of 3/1.

FTOH were only detected in blank samples of GCE I, GCE II, and of experiments investigating FTOH migration out of SPMD into air, when high FTOH levels were involved (10,000 and 25 µg, respectively). In these blank SPMD samples, FTOH were detected in a range between 0.005 and 0.02 µg, probably due to cross-contamination during rotary evaporation. Compared to the overall amount of FTOH, contamination was insignificant, and results were not blank corrected.

3.2 FTOH migration out of SPMD into air

Air temperatures during the time of SPMD deployment were between 5°C and 22°C and always above the freezing point of triolein (−4°C). Considering the volatility and molecular structure of the four investigated FTOH, it is expected that migration of those substances into air decreases with increasing chain length. However, a dependence of FTOH chain length was not observed. After 64 days of deployment, the content of all FTOH in SPMD diminished by approximately 20%. We assume first order kinetics for migration of FTOH out of SPMD. It is also possible that at the beginning of the experiment, release was independent from the FTOH concentration and followed zero order kinetics, and then turned after some time to first order kinetics. Slopes in Fig. 2 reveal the highest decline of FTOH concentrations in SPMD for 6:2 FTOH. The decrease of 4:2 FTOH content in SPMD was lowest. However, since 4:2 FTOH decline involved the highest standard deviations, it has to be considered with caution. Due to problems during GC-MS determination, only one value could be achieved for 64 days of deployment, and therefore, average means and standard deviations could not be calculated.

Release rates calculated for sampling intervals were decreasing during deployment (Table 1). Because of the high standard deviations of 4:2 FTOH, this compound was excluded from release rate calculations. Since FTOH amounts in SPMD after 32 days were elevated, the last two periods (days16–32 and days32–64) were combined for determinations of release rates. For the first (days0–8) and the third period (days16–64), release rates were decreasing with FTOH chain length. In the second period (days8–16), release was increasing with FTOH chain length.

3.3 FTOH migration out of SPMD into solvent

For dialysis extracts, different results were obtained for individual FTOH (Table 2). After the first dialysis, 6.8% (10:2 FTOH) to 20% (4:2 FTOH) of the spiked amounts were observed. In extracts of the second dialysis, 4:2 FTOH was not detectable. Of the remaining FTOH, between 1.5% (10:2 FTOH) and 3.0% (8:2 FTOH) were recovered. In the final liquid–liquid extraction of the cut SPMD, between 9.9% (4:2 FTOH) and 63% (6:2 FTOH) were observed. FTOH yields of the different extraction steps were highly

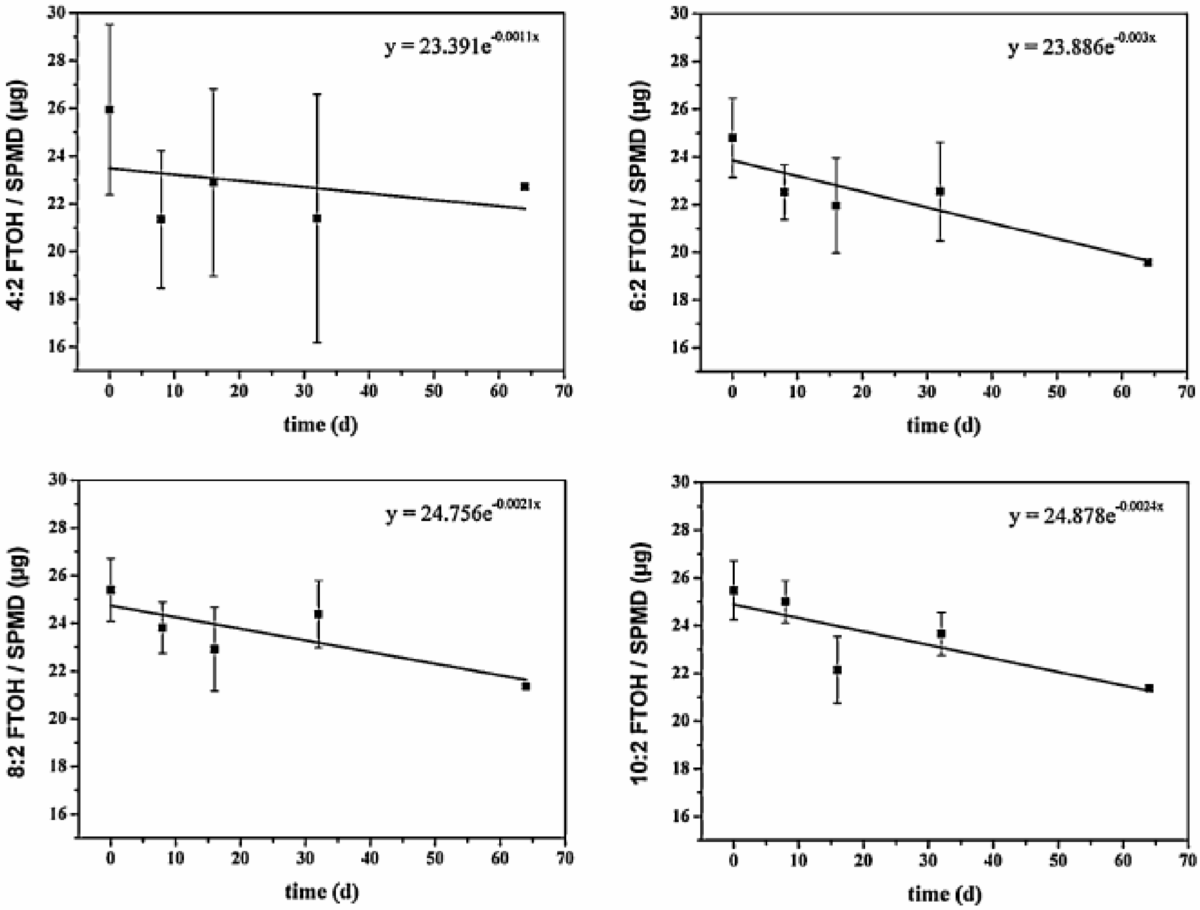

Fig. 2 Decrease of fluorotelomer alcohols content in semipermeable membrane devices during field deployment ($n = 3$; Initial mass: 25µg)

variable, resulting in particularly high standard deviations. Overall, between 54% (4:2 FTOH) and 70% (10:2 FTOH) of the spiked FTOH amount was detected and quantified in total.

3.4 FTOH migration into SPMD from air for high FTOH levels

In GCE I, (10,000µg FTOH, 3 SPMD), around 40% and 29% of spiked 6:2 FTOH and 8:2 FTOH, respectively, were detected in SPMD (Table 3). Results for 4:2 FTOH and 10:2 FTOH were one to two orders of magnitude lower, respectively. Remaining FTOH was assumed to adsorb to the glass chamber, or, particularly for 10:2 FTOH, to have not completely evaporated from the beaker.

In GCE II (10,000µg FTOH, 4 SPMD, 0.7 mL pure triolein, and rinse solvent), 1.2%, 3.3%, 14%, and 30% of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively, were detected in triolein exposed to FTOH without PE tubing (Table 4). Of 4:2 FTOH, 6:2 FTOH, 8:2

Table 1 Release rates (ng d^{-1}) of fluorotelomer alcohols in semipermeable membrane devices during field deployment

Compound	Days0–8	Days 8–16	Days16–46
6:2 FTOH	12.0	3.2	2.4
8:2 FTOH	8.0	4.8	1.5
10:2 FTOH	2.3	15.6	0.7

Table 2 Amount of fluorotelomer alcohols in semipermeable membrane devices (percent of initial mass 0.1µg) and relative standard deviations (percent) after dialysis (DE) and subsequent liquid–liquid extraction (LLE; $n = 3$)

Compound	DE 1	DE 2	LLE 3
4:2 FTOH	20 (12)	ND	10 (136)
6:2 FTOH	10 (60)	2 (95)	63 (50)
8:2 FTOH	10 (74)	3 (67)	33 (52)
10:2 FTOH	7 (106)	2 (99)	55 (59)

ND not detectable

Table 3 Amount of fluorotelomer alcohols (of initial mass 10,000µg) detected in semipermeable membrane devices analysed completely in glass chamber experiment I

Compound	SPMD 1	SPMD 2	SPMD 3	Σ SPMD
4:2 FTOH	3	2	2	7
6:2 FTOH	16	12	13	41
8:2 FTOH	11	9	9	29
10:2 FTOH	0.3	0.3	0.3	0.9

Table 5 Amount of fluorotelomer alcohols (percent of initial mass 0.2 µg) detected in Triolein exposed without tubing in glass chamber experiment III

Compound	Trio 1	Trio 2	Trio 3	Σ Trio	Beaker
4:2 FTOH	11	13	10	24	0.1
6:2 FTOH	27	32	23	83	4.1
8:2 FTOH	21	22	16	59	13
10:2 FTOH	1.9	1.7	1.0	4.6	2.1

FTOH, and 10:2 FTOH, respectively, 2.1%, 9.7%, 29%, and 16% were found in the two SPMD completely analysed. Total FTOH amounts in SPMD, of which tubings and triolein were analysed separately, were in the same order of magnitude. A high amount of all individual FTOH, mostly about 50%, was observed in the membrane fraction. Since it was assured that at least 95–99% of the triolein was withdrawn during separation of triolein and tubing, we assume that a great portion of FTOH was adsorbed at or absorbed into the membrane. Long-chain FTOH, particularly 10:2 FTOH, was also detected in the solvent, which was used to rinse the outer side of the membrane. This may point at condensation of the less volatile long-chain FTOH or their hindered diffusion through the PE membrane.

3.5 FTOH migration into SPMD from air for low FTOH levels

In GCE III (0.2µg FTOH, three beakers with 0.7 ml triolein), total amounts of 34%, 83%, 59%, and 4.5% of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively, were determined (Table 5). Of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively, 0.1%, 8.1, 27%, and 4.1% were still present in the beaker.

In GCE IV (0.1 µg FTOH, 3 SPMD), total amounts of 28%, 6.5%, 6.4%, and 1.6% of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively, were observed in SPMD (Table 6). Of 8:2 FTOH, 4.1% was still present in the beaker. Of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively, 4.0%, 19%, and 5.4% were determined at the inner side of the glass chamber.

4 Discussion

In GCE, FTOH expressed different accumulation patterns in SPMD. For low FTOH levels (GCE IV), only 4:2 FTOH was found at a higher amount (28%) in SPMD after 15 days of exposition. FTOH with longer fluorinated alkyl chains were only detected in minor quantity (1.6–6.6%). A strong increase of 6:2 FTOH and 8:2 FTOH uptake was observed in experiments where pure triolein was involved (GCE III). Detected amounts were even higher than for 4:2 FTOH, which might be due to lower vapour pressures of long-chain FTOH resulting in a lower revolatilisation from triolein. For 10:2 FTOH, low accumulation in triolein was always observed, maybe because it is the most oleophobic compound of the investigated FTOH. Enrichment of FTOH in pure triolein is dependent on their partition coefficient between air and triolein (K_{TA}). However, until today, only octanol air partition coefficients (K_{OA}; Lei et al. 2004; Goss et al. 2006; Thuens et al. 2008) were determined for FTOH. K_{TA} are not available. For non-fluorinated organic compounds, K_{TA} can be easily derived from K_{OA} (Huckins et al. 2006). However, the unique physical chemical properties of fluorinated compounds may hamper this estimate procedure.

In general, SPMD used as passive air samplers accumulate only non-charged gas-phase molecules with a molec-

Table 4 Amount of fluorotelomer alcohols (percent of initial mass 10,000 µg) detected in completely analysed semipermeable membrane devices (SPMD 1 and 2), separately analysed membranes, triolein, and wash solvent of semipermeable membrane devices (Trio 3 and 4, Mem 3 and 4, and Rinse 3 and 4), and pure triolein exposed without tubing (Trio) in glass chamber experiment II

Compound	Trio	SPMD 1	SPMD 2	Rinse 3	Rinse 4	Trio 3	Trio 4	Mem 3	Mem 4	Σ SPMD
4:2 FTOH	1.2	1.1	1.0	ND	ND	0.3	0.4	0.6	0.3	3.5
6:2 FTOH	3.3	4.7	5.0	ND	ND	1.7	1.7	3.0	1.2	17
8:2 FTOH	14	14	15	0.01	0.01	4.6	4.6	8.0	3.3	48
10:2 FTOH	30	7.9	8	0.1	0.1	3.4	3.4	3.4	2.7	27

ND not detectable

Table 6 Amount of fluorotelomer alcohols (percent of initial mass 0.1 µg) detected in semipermeable membrane devices in glass chamber experiment IV

Compound	SPMD 1	SPMD 2	SPMD 3	Σ SPMD	Beaker	Chamber
4:2 FTOH	7.1	12	9.6	28	ND	ND
6:2 FTOH	1.6	3.0	2.0	6.6	ND	4.0
8:2 FTOH	1.7	2.7	2.1	6.5	4.1	19.2
10:2 FTOH	0.2	0.6	0.8	1.6	ND	5.4

ND not detectable

ular mass less than approximately 600 and a octanol water partition coefficient log $K_{OW} \geq 3$ (Petty et al. 2000). Molecular masses of analysed FTOH are in the range between 264 and 564 amu, and estimated log K_{OW} are between 3.3 and 7.6 (Arp et al. 2006; Carmosini and Lee 2008). Considering the above-mentioned physicochemical constants, SPMD should be suitable for FTOH sampling in air. However, FTOH partitioning to SPMD seems to be hampered as observed during the conducted experiments. FTOH uptake might depend on different molecular structure as well as on oleophobicity of the fluorinated alkyl chain, which increases with chain length. Due to the differences between uptake in pure triolein and in SPMD, we suppose that enrichment, especially of long-chain FTOH, is limited by the PE membrane acting as a control barrier, which hampers the system reaching its equilibrium. Thus, in addition to air and triolein, the membrane has to be considered as a third component, when partitioning coefficients between SPMD/triolein and air are determined experimentally or are derived from other physical chemical properties.

At high FTOH levels (GCE I and GCE II), detected 4:2 FTOH concentrations in SPMD were lower than those of 6:2 FTOH and 8:2 FTOH, and for GCE II, even lower than 10:2 FTOH. Thus, migration through the membrane and accumulation of long-chain FTOH was improved at higher concentrations. A reason for this observation might be that FTOH are arranged as micelles, or FTOH adsorbed to the surface of membrane cavities facilitate transport of other FTOH molecules. In GCE II, it was observed that four SPMD accumulated more FTOH than 0.7 mL of pure triolein, probably due to a higher surface-area to volume ratio of SPMD compared to pure triolein. Thus, at high FTOH concentrations, uptake seems to be less membrane-controlled, and partitioning between air and triolein becomes more important.

Above-mentioned results were confirmed by experiments investigating FTOH migration out of SPMD, as well. During the entire field deployment, 4:2 FTOH concentrations in SPMD decreased the least, and 10:2 FTOH concentrations decreased the second most. However, due to its high standard deviations, 4:2 FTOH release has to be considered with caution. For the periods between sampling, release rates were mostly decreasing with FTOH chain length. Due to applied high FTOH concentrations, FTOH release was less membrane-controlled but more dependent on the compounds volatility and partitioning between air and triolein.

In the presence of organic solvents, migration of FTOH out of SPMD spiked at low FTOH levels seemed to be membrane-controlled, as well. Dialysis extraction of SPMD resulted in highest FTOH yields for short-chain FTOH, whereas 10:2 FTOH was only efficiently extracted when the membrane was cut and FTOH could directly move from triolein to the extraction solvent. We were not able to explain the incomplete recovery of FTOH in this experiment. We assume that difference in polarity of the used solvent mixtures in this experiment was of minor importance. The application of less polar acetone/MTBE should have facilitated the extraction of long-chain FTOH in contrast to acetonitrile/hexane. The latter should have enhanced extraction of the short-chain FTOH. However, these effects were not observed. For the first dialysis extraction with acetone/MTBE, highest FTOH yields were obtained for the relatively polar short-chain FTOH. FTOH yields of the second dialysis were quite low and therefore less important. Also, the results for the final liquid–liquid extraction with acetonitrile/hexane revealed no influence of solvent polarity. However, extraction efficiency was highly dependent on the presence of the PE membrane.

Results of conducted experiments reveal that passage through the membrane was influenced by the applied FTOH amount. If FTOH enrichment in SPMD really depended on air concentration, this fact has to be considered for sampler calibration, i.e., the determination of sampling rates, as well. For field sampling, use of suited performance reference compounds is absolutely essential.

When SPMD are deployed in the field, uptake of FTOH might additionally be influenced by particles adsorbed to the outer side of the membrane. Remembering low amounts of FTOH percentage were detected after 15 days in SPMD (GCE IV), one should keep in mind that usually, sampling duration of these kind of passive samplers is up to 1 year or partly longer.

Given the obtained results and methodology, we do not recommend the use of SPMD as FTOH passive samplers. They might probably be applied at highly contaminated sites, but the incidence of such concentrations is rather unlikely. In remote areas, we suggest that XAD-impregnated PUF disks (Shoeib et al. 2008) are the better choice, because here, analyte accumulation only depends on adsorption capacity, and partitioning and is not additionally hampered by a membrane acting as a control barrier.

5 Conclusions

Generally, FTOH are able to migrate through PE membranes of SPMD. Accumulation is influenced by FTOH air concentration and the length of the fluorinated alkyl chain. At low FTOH concentrations, enrichment seems to be sufficient for 4:2 FTOH only. Uptake seems to be strongly influenced by the SPMD membrane. At high FTOH concentrations, enrichment of long-chain FTOH is improved, particularly for 6:2 FTOH and 8:2 FTOH. Further investigations on the SPMD suitability for FTOH air sampling should be performed with accompanying determination of the actual air concentrations in order to calculate sampling rates and partitioning coefficients. For this purpose, a different experimental set-up will be necessary. In addition, membranes of different materials should be investigated for their suitability to accumulate FTOH in triolein. At the moment, we recommend the use of SPMD only at highly contaminated sites as passive air samplers for FTOH, but not at environmentally relevant concentrations.

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Poly- and Perfluorinated Compounds in Household Consumer Products

Stefan Fiedler[1*], Gerd Pfister[1], and Karl-Werner Schramm[1,2]

[1] *Helmholtz Zentrum München – National Research Centre for Environmental Health, Institute of Ecological Chemistry, Ingolstaedter Landstrasse 1, 85764 Neuherberg, Germany*
[2] *TUM - Wissenschaftszentrum Weihenstephan für Ernährung und Landnutzung, Department für Biowissenschaftliche Grundlagen, Weihenstephaner Steig 23, 85350 Freising, Germany*

**Corresponding author: E-mail: fiedler.stefan@gmx.net; Tel: +498931872932 Fax: +498931873371*
Gerd Pfister: e-mail: pfister@helmholtz-muenchen.de; Tel: +498931872207 Fax: +498931873371
Karl-Werner Schramm: e-mail: schramm@helmholtz-muenchen.de; Tel: +498931873147 Fax: +498931873371

Abstract

Several household consumer products were analysed for their content of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS), and fluorotelomer alcohols (FTOH) by liquid chromatography mass spectrometry and gas chromatography mass spectrometry. Among the investigated products, which are applied as sprays, were impregnating agents, cleaning agents, lubricants, and conditioners. Of 26 products analysed, at least one polyfluorinated compound (PFC) was detected in 14 samples. 8:2 FTOH was the dominating compound with concentrations up to 149 µg mL^{-1}. The maximum concentration of PFOA was 14.5 µg mL^{-1}, whereas PFOS was not detected in any sample. Investigated PFC were mostly found in impregnating agents and lubricants, but were not detected in cleaning agents and conditioners. FTOH containing impregnating agents revealed similar ratios between 6:2 FTOH, 8:2 FTOH, and 10:2. FTOH ratios of PFC containing lubricants were similar as well. Human exposure to PFC originating from consumer product aerosols was calculated for three scenarios. Total PFC exposure was found to be between 42.8 and 463.7 ng kg^{-1} d^{-1}.

Keywords: perfluorooctanoate, perfluorooctane sulfonate, fluorotelomer alcohols, exposure

1. Introduction

Poly- and perfluorinated compounds (PFC), such as fluorotelomer alcohols (FTOH), perfluorinated carboxylates (PFCA) and perfluorinated sulfonates (PFSA), have unique physicochemical properties and are therefore used for many commercial and industrial applications like water and stain repellents, coatings, emulsifier or as polymerisation aid (Hekster et al. 2003; Kissa 2001; Schultz et al. 2003). Due to this manifold application, their bioaccumulation and their persistence, some PFC have been found frequently in blood samples of the general population (Calafat et al 2006; Jones et al. 2003; Kannan et al. 2004). Perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), which were the most important PFC in the past, are supposed to induce adverse health effect, especially carcinogenicity and disruption of intercellular communication, and metabolism of fatty acids (Biegel et al. 2001; Kudo et al. 2005; Upham et al. 1998). In consequence, major producers phased out production of long-chained PFCA and PFSA (Prevedouros et al. 2006) and the European Community and US-EPA restricted use of PFSA (European Union 2006; EPA 2002).

FTOH were found to degrade to PFCA by atmospheric and metabolic oxidation processes and are thus being seen as precursor substances of PFCA (Dinglasan 2004; Ellis et. al 2004; Martin et al. 2005). However, FTOH are still in production. Due to their volatility and atmospheric half life times (Ellis et al. 2003; Goss et al. 2006; Thuens et al. 2008), FTOH were detected worldwide in the atmosphere of urban and remote regions (Jahnke et al. 2007; Martin et al. 2002; Shoeib et al. 2006; Stock et al. 2004). Thus, FTOH contribute to the environmental distribution of PFCA and human exposure to these compounds. Studies investigating PFC concentrations in urban areas focussed on their presence in food (Begley et al. 2005; Fromme et al. 2007), drinking water (Lange et al. 2007; Skutlarek et al. 2006),
ambient air (Shoeib et al. 2004; Barber et. al. 2007), and house dust (Shoeib et al. 2005; Strynar et al. 2008). There is one study investigating consumer articles (Washburn et al. 2005), but only PFOA was

considered. Trudel et al. (2008) developed a model to calculate human exposure to PFOA and PFOS for oral and inhalative incorporation pathways. Precursor derived doses of PFOA were estimated to be 9-11% originating from impregnation sprays (Vestergren et al. 2008). However, due to the phase out of the production of PFOA and PFOS, the importance of possible surrogates and PFCA precursors like FTOH may increase in the future.

To extend the knowledge about the human exposure to PFC originating from consumer products, we investigated the content of PFOA, PFOS, and FTOH in impregnating agents for shoes and textiles, lubricants, cleaning agents, wood and leather conditioners, and some other products used in households. These items are usually stored and applied in the direct surroundings of adults and children. In particular the use of sprays, which generate easily breathable aerosols, can be an important exposure pathway for humans. Treated articles like carpets, shoes, furniture, and clothes may act as PFC source in households for a long time.

2. Material and methods

2.1 Chemicals

Perfluorobutyl ethanol (4:2 FTOH), perfluorohexyl ethanol (6:2 FTOH), perfluorooctyl ethanol (8:2 FTOH), perfluorodecyl ethanol (10:2 FTOH) (97 % purity in each case), PFOA (99 %), and perfluoromethylnonyl ethanol (9:2 FA, 98 %) were purchased from Fluorochem Limited, Old Glossop, UK. PFOS (tetraethyl ammonium salt, 98 %) was obtained from Sigma Aldrich, Taufkirchen, Germany. $^{13}C_2{}^2H_2$ labelled 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, and $^{13}C_4$ labelled PFOA and PFOS ([M+4], 98 % in each case) were purchased from Wellington Laboratories Guelph, Ontario, Canada. Methanol (LC-MS grade) was obtained from LGC Standards, Wesel, Gemany. Ethylacetate (pestanal) was purchased from Riedel-de-Haen, Seelze, Germany.

2.2 Investigated products

Ten impregnating agents, obtained from nine different companies, six cleaning agents, four lubricants/corrosion prevention agents, three conditioners for wood and leather, one fire fighting foam, and one pesticide formulation were analysed. All investigated agents are produced for private households and are applied as sprays. With exception of the pesticide formulation all products are used in a pure, non-diluted form. All products, except for one impregnating agent which was purchased in Brazil, were obtained in Germany. Eight of the products were labelled as “PTFE”, “fluorocarbon resin”, or “fluoro additive” containing agent.

2.3 Analysis

Consumer products to be analysed were diluted in methanol 1:100 by volume. Then, 250 µL of the dilution, 250 µL of subboiled water, 20 µL of a solution containing masslabelled 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, PFOA, and PFOS (1 ng μL^{-1}), and 20 µL of the injection standard 9:2 FA (1 ng μL^{-1}) were added into a LC glass vial. 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, PFOA, and PFOS were determined by nanoflow Aquity UPLC (Waters, Milford, USA) coupled to a Q-TOF2 mass spectrometer (micromass, Manchester, UK) using negative electrospray ionisation. The injection volume was 1 µL. Analytes were trapped on a Symmetrie C18 column (5µm, 180µm * 20mm) and separated on a BEH130 C-18 column (17µm, 75µm * 150mm, both Waters, Milford, USA) with a 2 mM ammonium acetate (LC-MS grade, Fluka, Buchs, Switzerland) mobile phase composed of water and methanol. The solvent gradient started with 15 % methanol and increased to 100 % methanol after 8 min. After 25 min, it returned to initial conditions. The flow continued for another ten minutes. The flow rate was 0.3 $\mu l\ min^{-1}$ at a column temperature of 30 °C. Electrospray capillary voltage was 1800 kV and MS cone voltage was set to 17 V. Mass to charge ratios of PFC determined by TOF MS are presented in Table 1. FTOH were detected as acetate adducts $[M+59]^-$.

Table 1: Mass to charge ratio of PFC target ions determined by UPLC-TOF MS

Since 4:2 FTOH could not be determined by LC-MS, GC-MS operating with positive chemical ionisation was applied to detect this compound. Measurements were performed in selected ion monitoring mode using an HP 5890 Series II gas chromatograph (Agilent Technologies, Waldbronn, Germany), coupled to a Finnegan Mat SSQ 7000 mass selective detector (Thermo Scientific, Dreieich, Germany). The GC was equipped with a 60 m VMS column (0.25 mm inner diameter, 1.4 µm film thickness; Restek, Bad Homburg, Germany). Helium (5.0, Linde, Höllriegelskreuth, Germany) was used as carrier gas with a constant column head pressure of 175 kPa. Injections were performed in splitless mode at 220 °C with an injection volume of 1 µL. The oven temperature was held at 50 °C for 2 min, then elevated to 80 °C at 10 °C min^{-1}, to 110 °C at 5 °C min^{-1} and held for 3 min, and finally elevated to 220 °C at 15 °C min^{-1} and held for 15 min. The transfer line was set to 300 °C.

Ionisations in the mass selective detector were performed at 70 eV and a source temperature of 150 °C. Methane (4.5, Linde, Höllriegelskreuth, Germany) was used as reagent gas.

2.4 Calculation of consumer exposure

Daily uptake dose of PFC ($D_{\text{spray \_inhal}}$; (ng kg_{BW}^{-1} day^{-1})) was calculated using a model (equation 1) developed by Trudel. et al. (2008). In this study, among others uptake of PFOA by inhalation of spray droplets generated by application of consumer products was estimated for a conservative high exposure scenario. To assure comparability, all parameters except of market fraction were adopted from Trudel et al. (2008)

$$D_{spray\_inhal} = \frac{c_{spray} \cdot MF_{spray} \cdot f_{\exp} \cdot t_{spray} \cdot r_{spray} \cdot F_{resp} \cdot V_{inh}}{m_{BW}} \cdot \left(\frac{t_{spray\_NF}}{V_{NF}} + \frac{t_{spray\_FF}}{V_{FF}} \right) \cdot F_{uptake} \qquad (1)$$

with
c_{spray}: concentration of PFC in impregnation sprays (ng g^{-1})
MF_{spray}: market fraction of consumer products containing PFC (1)
f_{exp}: frequency exposed to consumer products (0.0120548 day^{-1})
t_{spray}: time spent spraying (30 min)
r_{spray}: rate of spray emission (42 g min^{-1})
F_{resp}: fraction of respirable aerosols generated (0.002589)
V_{inh}: inhalation rate (1.6 m^3 $hour^{-1}$)
$t_{\text{spray\_NF}}$: time exposed to aerosols in the near field (1 hour)
V_{NF}: near-field volume around consumer (1 m^3)
$t_{\text{spray\_FF}}$: time exposed to aerosols in the far field (4 hour)
V_{FF}: far-field volume around consumer (49 m^3)
m_{bw}: body weight (60.4 kg),
F_{uptake}: uptake fraction of PFC via the lungs (1)

Daily human PFC exposure was calculated for three different scenarios. In scenario I, the average PFC concentration of the consumer products was used for exposure calculations and the market fraction of consumer products was calculated by dividing the number of detections of one PFC in consumer products by the number of investigated consumer products. PFC exposure calculation in scenario II was similar to Trudel et al. (2008). Average PFC concentrations were used and the market fraction of PFC containing consumer products was set to 0.5. Scenario III represents a worst case situation, assuming that consumers are only using the product with the highest PFC concentration. Thus, the maximum value for PFC concentration was used for exposure calculation and the market fraction was set to 1. More information about uptake calculation and exposure scenarios are given in Trudel et al. (2008).

2.5 Quality assurance

To prevent cross contamination during analysis, blank samples were measured after each consumer product. FTOH were not detected in blank samples. PFOA and PFOS were detected frequently in blank samples at levels near to the MDL. They were subtracted from PFOA and PFOS concentrations in consumer products. MilliQ water used for dilution of consumer products and for LC gradient elution was further purified by a quartz subboiling system (Maassen, Reutlingen, Germany). Deactivated glass vials were used for LC determinations to prevent analyte sorption to glass surface. Stable isotope labelled standards spiked to consumer products were used for identification and quantification of analytes and to correct inaccuracies and matrix effects during measurement. Four PFC containing consumer products were injected three times each. Obtained PFC concentrations were in a range of 5%. Thus, all the rest of consumer products were injected only once. However, every LC-MS detection of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH was confirmed by a GC-MS determination, which deviated in a range of 15%. Methodical limits of detection of the LC-MS system were 0.04 µg mL^{-1} for PFOA and PFOS and 0.08 µg mL^{-1} for FTOH, respectively, based on a signal to noise ratio of 3/1. Instrumental limits of detection of the LC-MS system were 0.2 pg µL^{-1} for PFOA and PFOS and 0.4 pg µL^{-1} for FTOH. Methodical limit of quantification was 0.1 µg mL^{-1} for PFOA and PFOS and 0.3 µg mL^{-1} for FTOH, respectively, based on a signal to noise ratio of 10/1. For 4:2 FTOH, the methodical limit of quantification was 0.3 µg mL^{-1} and methodical limit of detection was 0.1 µg mL^{-1}. The instrumental limit of detection of the GC-MS was 2 pg µL^{-1}.

3. Results and discussion

In 14 of 26 products analysed at least one PFC was detected. Most of these products belong to the groups of impregnating agents and lubricants.

In impregnating agents 8:2 FTOH and 10:2 FTOH were found to be the dominant PFC. They were present in all but two samples showing concentrations up to 61 and 32 µg mL^{-1}, respectively (table 2). 4:2 FTOH, 6:2 FTOH, and PFOA were only detected in small amounts in some impregnating agents.

Table 2: PFC content (µg mL^{-1}) of impregnating agents (IA) and conditioners (CO). (nd: not detectable; nq: not quantifiable)

PFC were detected in two of four lubricants, as well. The PFC burden of these samples was higher than those of the remaining products. Similar to impregnating agents, the PFC content of lubricants was dominated by FTOH. Highest concentrations of 6:2 FTOH (148 µg mL^{-1}), 8:2 FTOH (149 µg mL^{-1}), and 10:2 FTOH (99 µg mL^{-1}) were determined in sample LU2, which was also the sample containing most of PFC in this study (table 3). 4:2 FTOH and PFOA were not detected in any of the lubricants.

PFOA was detected at 7.3 µg mL^{-1} in the fire fighting foam and at 14.5 µg mL^{-1} in the pesticide solution, which were the highest concentrations found for PFOA. Cleaning agents and conditioners did not appear to contain any of the investigated PFC. PFOS was not detectable in any of the consumer products. This could be due to phase out of PFOS production in 2001.

Table 3: PFC content (µg mL^{-1}) of lubricants (LU), fire fighting foam (FF), pesticide solution (PE), and cleaning agents (CA). (nd: not detectable).

Figure 1 demonstrates the proportions of PFC in the 14 PFC containing consumer products. In most cases FTOH were the dominant class of PFC. Only in four products, concentration of PFOA exceeded those of FTOH. Among the FTOH, 8:2 FTOH showed always highest concentrations. Only in the two lubricants containing FTOH, concentrations of 6:2 FTOH were almost as high as those of 8:2 FTOH. These results are consistent with the fact, that worldwide, 8:2 FTOH mostly is the dominant FTOH found in the atmosphere (Jahnke et al 2007; Shoeib et al. 2006; Barber et al 2007; Dreyer et al. 2009; Oono et al. 2008) and in housedust (Strynar et al. 2008). Only at a few places concentrations of 6:2 FTOH exceeded or were equal to concentrations of 8:2 FTOH (Martin et al. 2002; Stock et al 2004).

Figure 1: Proportions (%) of PFC in impregnating agents (IA), conditioners (CO), lubricants (LU), fire fighting foams (FF), and pesticide solution (PE).

In FTOH containing impregnating agents, an average ratio between 8:2 FTOH amount and 10:2 FTOH amount of 1.7 ± 0.13 (n=7) was found. IA10, which was obtained in Brazil, obviously had a different FTOH composition than impregnating agents purchased in Germany. Therefore IA10 was not considered for the calculation of FTOH ratios. The average ratio between 8:2 FTOH amount and 6:2 FTOH amount in impregnating agents was 80.9 ± 93.1 (n=5).

FTOH containing lubricants (LU1, 2) showed a ratio between 8:2 FTOH and 10:2 FTOH of 1.24 and 1.52, respectively, and a ratio between 6:2 FTOH and 8:2 FTOH of 1.05 and 1.01, respectively.

Because there were only two FTOH containing lubricants, differences in composition between impregnating agents and lubricants were not tested for significance. However, there is a considerable difference in FTOH composition in those two product groups, since relative amounts of FTOH in lubricants were beyond the standard deviations ranges of FTOH amounts in impregnating agents. Also FTOH ratios of IA10 were outside of these standard deviation ranges. Thus, above calculated FTOH proportions possibly could be used as a fingerprint for FTOH containing impregnating agents from Europe. However, FTOH ratios found in the atmosphere (Jahnke et al. 2007; Martin et al. 2002; Shoeib et al. 2006; Stock et al. 2004; Dreyer et al. 2009; Oono et al. 2008) at diverse locations were obviously dissimilar to those of lubricants or impregnating agents (table 4) A reason for this might be that FTOH composition of the atmosphere is affected by many different sources and applications of FTOH. Only Piekarz et al. (2007) found a ratio between 8:2 FTOH and 10:2 FTOH of 2 in Orgeon, USA, being close to the value of 1.7 determined for impregnating agents.

Table 4: Ratios between atmospheric concentrations of 6:2 FTOH and 8:2 FTOH and 10:2 FTOH and 8:2 FTOH, respectively.

Washburn et al. (2005) found PFOA concentration ranges up to 50 ppm in impregnating sprays. Unfortunately FTOH were not analysed in this study. In our study, PFOA concentrations in impregnating agents with a maximum of 3.6 mg L^{-1} were one order of magnitude below. Highest PFOA contents in impregnating agents were found in sprays that did not contain any FTOH (IA8, IA9). In those sprays PFOA amounts were beyond the standard deviation range of PFOA concentrations in the FTOH containing impregnating agents (IA1-IA7).

In seven of eight products labelled as “PFC containing”, one or more of the investigated PFC were detectable. Probably other PFC, which were not analysed, are used in consumer products as well. This might be the reason that in one product labelled as “PFC containing”, none of the investigated PFC was detected.

Calculated human exposure to PFC differed for the three scenarios (Table 5). Total daily PFC exposure was found to be between 42.8 ng kg^{-1} d^{-1} for scenario I and 463.7 ng kg^{-1} d^{-1} for scenario III.

Table 5: Calculated human exposure (ng kg^{-1} d^{-1}) to PFC in consumer products.

Given these scenarios, exposure is dominated by 8:2 FTOH with proportions between 37% (scenario III) and 47% (scenario I). Proportions of PFOA were between 2% (scenario III) and 3% (scenario I). Human exposure to PFOA from spray droplets was one order of magnitude lower than values calculated by Trudel et al. (2008) due to lower PFOA concentrations in consumer products. Calculated exposure to 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH was one order of magnitude higher than PFOA exposure in scenarios I, II, and III. However, in addition to the exposure by spray droplets as accounted for in the three scenarios, there is an exposure to gaseous FTOH as well, which was not considered in this exposure model. Since incorporated FTOH are metabolised to PFCA in the human body (Martin et al. 2005) an ongoing accumulation of PFCA can be anticipated despite phase out of production of long-chain PFCA and PFSA.

Although most of the consumer products were purchased in Germany, some companies are also selling these items in other European countries. Therefore, calculated daily intakes are also important to people in many other countries.

In conclusion, we hypothesize that sprays containing polyfluorinated precursor substances can be source of persistent perfluorinated compounds for people using those sprays affecting also the environmental distribution of those chemicals.

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Table 1: Mass to charge ratio of PFC target ions determined by UPLC-TOF MS

Analyte	**UPLC-MS target ion (m/z)**	**UPLC-MS retention time (min)**
6:2 FTOH	422.7	15.63
8:2 FTOH	522.6	16.27
10:2 FTOH	622.6	16.88
PFOA	412.8	14.21
PFOS	498.7	14.71
ML6:2 FTOH	426.8	15,63
ML8:2 FTOH	526.8	16,27
ML10:2 FTOH	626.7	16,88
MLPFOA	416.8	14.21
MLPFOS	502.8	14.71
9:2 FA	572.6	16.77

Table 2: PFC content (µg mL^{-1}) of impregnating agents (IA), conditioners (CO), lubricants (LU), fire fighting foam (FF), pesticide solution (PE), and cleaning agents (CA). (nd: not detectable; nq: not quantifiable)

Product	**4:2 FTOH (µg mL^{-1})**	**6:2 FTOH (µg mL^{-1})**	**8:2 FTOH (µg mL^{-1})**	**10:2 FTOH (µg mL^{-1})**	**PFOA (µg mL^{-1})**	**PFOS (µg mL^{-1})**	**Σ PFC (µg mL^{-1})**
IA1	nq	1.2	60.9	32.0	0.4	nd	94.5
IA2	0.3	nd	2.9	1.7	0.1	nd	5.0
IA3	nq	2.1	51.8	32.1	0.2	nd	86.2
IA4	nq	1.3	42.9	23.0	0.2	nd	67.4
IA5	nd	0.6	29.6	16.6	0.4	nd	47.2
IA6	nd	nd	0.5	0.3	nd	nd	0.8
IA7	nd	nd	33.1	20.4	nd	nd	53.5
IA8	nd	nd	nd	nd	0.9	nd	0.9
IA9	nd	nd	nd	nd	3.6	nd	3.6
CO1	nd	nd	nd	nd	nd	nd	nd
CO2	nd	nd	nd	nd	nd	nd	nd
CO3	nd	nd	nd	nd	nd	nd	nd
CO4	nd	nd	nd	nd	nd	nd	nd
LU1	nd	72.4	75.8	61.1	nd	nd	209.3
LU2	nd	148.0	149.4	98.5	nd	nd	395.8
LU3	nd	nd	nd	nd	nd	nd	nd
LU4	nd	nd	nd	nd	nd	nd	nd
FF	nd	nd	nd	nd	7.3	nd	7.3
PE	nd	nd	nd	nd	14.5	nd	14.5
CA1	nd	nd	nd	nd	nd	nd	nd
CA2	nd	nd	nd	nd	nd	nd	nd
CA3	nd	nd	nd	nd	nd	nd	nd
CA4	nd	nd	nd	nd	nd	nd	nd
CA5	nd	nd	nd	nd	nd	nd	nd
CA6	nd	nd	nd	nd	nd	nd	nd

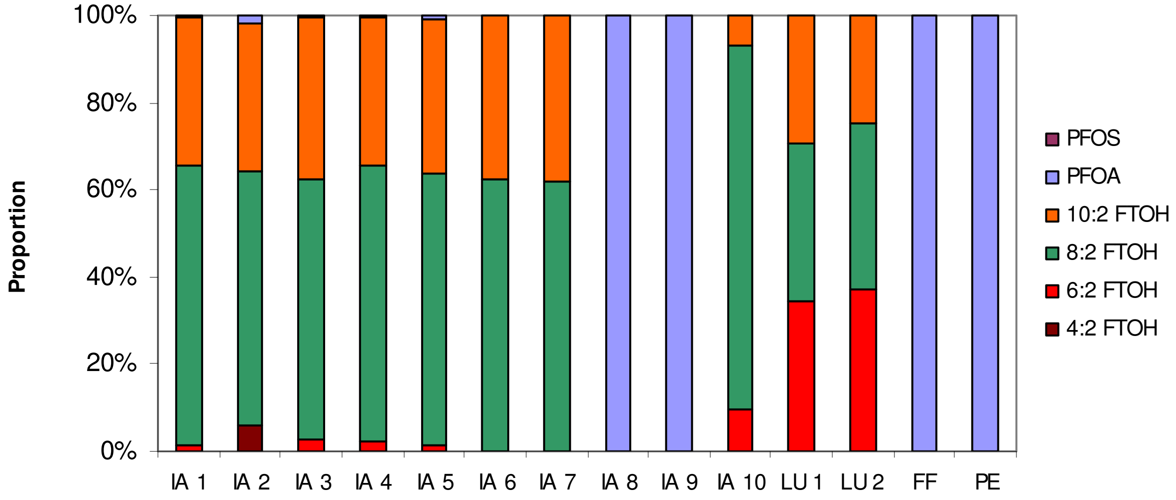
Table 3: Concentration ratios between 6:2 FTOH and 8:2 FTOH and 10:2 FTOH and 8:2 FTOH in consumer products and air.

Site	Medium	$\frac{c(6:2\,\text{FTOH})}{c(8:2\,\text{FTOH})}$	$\frac{c(10:2\,\text{FTOH})}{c(8:2\,\text{FTOH})}$	Reference
Germany	impregnating agents	0.02	0.58	this study
Germany	lubricants	0.98	0.74	this study
Canada,Toronto	air	1.58	0.53	(Martin et al., 2002)
Canada, Long Point	air	0.91	0.53	(Martin et al., 2002)
Canada, Toronto	air	0.44	0.52	(Shoeib et al., 2006)
Artic	air	0.24	0.55	(Shoeib et al., 2006)
Germany, Hamburg	air	0.55	0.29	(Jahnke et al., 2007b)
Germany, Waldhof	air	0.85	0.31	(Jahnke et al., 2007b)
Germany, Hamburg	air	0.3	0.27	(Dreyer and Ebinghaus, 2009)
Germany, Hamburg	air	0.25	0.25	(Dreyer and Ebinghaus, 2009)
Germany, Hamburg	air	0.57	0.47	(Dreyer and Ebinghaus, 2009)
Germany, Geesthacht	air	0.46	0.27	(Dreyer and Ebinghaus, 2009)
Germany, Geesthacht	air	0.34	0.29	(Dreyer and Ebinghaus, 2009)
Germany, Geesthacht	air	0.47	0.43	(Dreyer and Ebinghaus, 2009)
Germany, Geesthacht	air	0.41	0.35	(Dreyer and Ebinghaus, 2009)
Germany, Geesthacht	air	0.56	0.33	(Dreyer and Ebinghaus, 2009)
Japan, Higashiyodogawa	air	0.03	0.11	(Oono et al., 2008)
Japan, Horinomiya	air	0.05	0.12	(Oono et al., 2008)
Japan,Sakyo	air	0.03	0.12	(Oono et al., 2008)

Table 4: Human exposure (ng kg^{-1} d^{-1}) to PFC in consumer products calculated for three different scenarios

Compound	Scenario I	Scenario II	Scenario III
4:2 FTOH	<0.1	0.2	0.3
6:2 FTOH	10.1	18.6	170
8:2 FTOH	20.1	26.4	172
10:2 FTOH	11.4	15.0	113
PFOA	1.2	1.8	8.4
Σ PFC	42.8	62.0	464

Figure 1: Contribution (%) of individual PFC analysed in impregnating agents (IA), conditioners (CO), lubricants (LU), fire fighting foams (FF), and pesticide solution (PE)



Field Intercomparison on the Determination of Volatile and Semi-volatile Polyfluorinated Compounds in Air

Annekatrin Dreyer[1], Mahiba Shoeib[2], Stefan Fiedler[3], Jon Barber[4,5], Tom Harner[2], Karl-Werner Schramm[3], Kevin C. Jones[4], Ralf Ebinghaus[1]*

[1] GKSS Research Centre Geesthacht, Max Planck Str. 1, 21502 Geesthacht, Germany;
[2] Environment Canada, 4905 Dufferin St, Toronto, Ontario, M3H 5T4, Canada
[3] Helmholz Zentrum München, Ingolstädter Landstr. 1, 85764 Neuherberg, Germany;
[4] Lancaster University, Lancaster, LA1 4YQ, United Kingdom,
[5] Cefas, Pakefield Road, Lowestoft, NR330HT, United Kingdom

* corresponding author: annekatrin.dreyer@gkss.de, phone: +49-4152-872352, fax: +49-4152-872332

ABSTRACT

Fluorotelomer alcohols (FTOH) and -acrylates, as well as perfluorinated sulfonamids and sulfonamido ethanols are volatile precursors of persistent perfluorinated acids. So far, the published air sampling strategies and analytical methods for these compounds differ considerably. In this study, a laboratory (analytical) and field intercomparison comprising four international research groups was established to assess performance. Analytical consistency between laboratories was assessed through independent analyses of standard solutions. Variability in different sampling strategies was assessed for active (high volume sampler) versus passive samplers consisting of either semi permeable membrane devices (SPMD) or sorbent impregnated polyurethane (SIP) disks. Analytical consistency between the four laboratories varied depending on the compound class. Standard deviations for determined PFC were within 16 to 62 % of consensus (average) values. Results from passive samplers were typically within an order of magnitude of air concentrations from continuous high volume samples, averaged for the 2-month deployment intervals of the passive samplers. Smallest deviations (passive vs active) were observed for the SIP disk samplers with best agreement for the FTOH, where average agreement was within a factor of about 3. The study reveals that further work is required to calibrate and test passive samplers and to improve analytical methods and comparability among laboratories.

KEYWORDS

PFC, fluorotelomer alcohols, perfluoroalkyl sulfonamids, perfluoroalkylsulfonamido ethanols, fluorotelomer acrylates, intercomparison, air sampling

INTRODUCTION

Persistent, toxic, and partly bioaccumulative polyfluorinated compounds (PFC) such as perfluoroalkyl sulfonate (PFSA) and perfluoroalkyl carboxylates (PFCA) *(1,2)* have been detected globally in humans *(3,4)*, biota *(5,6)*, rivers and oceans *(7,8)*, polar ice caps *(9)*, precipitation *(10,11)*, and airborne particles *(12-14)*. Atmospheric transport and degradation of volatile and semi-volatile PFCA and PFSA precursors, e.g. fluorotelomer alcohols (FTOH) and acrylates (FTA) or perfluoroalkyl sulfonamids (FASA) and sulfonamido ethanols (FASE) is considered as an important transport and contamination mechanism to the environment. Precursors were determined in several indoor and outdoor air studies in North America, Europe, Asia, and the Atlantic Ocean *(13-21)*, however, sampling strategies and analytical methods differed considerably which brings to question the

consistency among these data sets. Worldwide interlaboratory studies have already been performed for several PFCA and PFSA in
water, fish tissue, and human blood samples and follow-up surveys revealed significant improvements in the analysis of perfluorinated compounds in these media *(22-25)*. To our knowledge, interlaboratory studies regarding the analysis of airborne PFC and different air sampling techniques have not been conducted so far. Therefore, the first field intercomparison on the determination of volatile and semi-volatile PFC in air applying active and different passive sampling techniques was organized and coordinated by the GKSS Research Centre, Geesthacht, Germany from April 2007 to March 2008. The objectives of this study were to elucidate the agreement between the different sampling approaches as well as the analytical consistency between the participating research groups for several volatile PFC.

EXPERIMENTAL SECTION

Experimental Design

From April 2007 to March 2008 air samples were taken at the German monitoring site Barsbüttel, situated approximately 20 km east of Hamburg (1 770 000 inhabitants) at 53.5706 N and 10.2153 E. Passive air sampling (PAS) was conducted using sorbent-impregnated polyurethane foam (SIP) disks (lab A, lab C) *(21)* and semi permeable membrane devices (SPMD, lab B) *(19)*. SPMD and SIP were deployed for periods of two months. For each period, duplicate samplers were deployed for SIP and six replicates for SPMD. Active air sampling was performed by lab D using a high volume air sampler *(14)*. Generally, samples were taken continuously for three (Monday to Thursday) and four (Thursday to Monday) days at flow rates of about 500 $m^3 d^{-1}$. Exceptions were periods when the sites were not accessible and sampling times had to be extended. The sampling schedule is outlined in chart S1. PAS mean air concentrations derived by the different sampling approaches were compared and evaluated over the same sampling intervals. Furthermore, two standard solutions containing a cocktail of volatile and semi-volatile target compounds of unknown concentrations were circulated to further elaborate on the analytical consistency between groups.

Sampling housing and sampling media were sent by the participants to GKSS. Installation, operation, and maintenance of the instruments as well as sampling were conducted by GKSS according to the participants' guidelines. Infrastructure of the sampling site including the observation of meteorological parameters was provided by the Environmental Agency (Staatliches Umweltamt Itzehoe). All samples were shipped refrigerated to the participants within four months after the sampling, either by air (international shipping) or by priority mail (national shipping). Standards solutions for the elaboration of the analytical consistency were prepared by GKSS. Standard solution and samples were stored at -20 °C at GKSS and were sent refrigerated in CERTAN® capillary vials (Promochem, Germany) to minimize evaporation. Chemical analyses of standard solutions and samples occurred in the participants laboratories according to their protocols.

Analytical Methods

Sorbent impregnated passive samples

Passive sampling with SIP disks was performed by lab A and C. Details on the preparation of SIPs are given by Shoeib et al. *(21)*. After sampling, samples were kept frozen (-20 °C) and in darkness. However, samples shipped to lab A were not frozen anymore upon arrival. Extraction procedures differed between the laboratories. Lab A applied a procedure described elsewhere *(21)*. Briefly, SIPs were soxhlet-extracted for 18 hours using petroleum ether:acetone (1:1). After extraction and rotary evaporation, samples were centrifuged to separate the extract from the fine XAD powder. A clean-up was performed using ENVI-Carb as sorbent and hexane:DCM (4:1, v:v) for elution. Analytes were separated by gas chromatography (GC) and detected by mass spectrometry (MS) using positive chemical ionization (PCI). Three mass-labelled polyfluorinated compounds (^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH) were spiked to the samples prior to the extraction to correct for analytes' losses. As injection standard, Me_2FOSA was used. At lab C, samples were spiked with seven mass-labelled polyfluorinated compounds (^{13}C 6:2 FTOH, ^{13}C8:2 FTOH, ^{13}C 10:2 FTOH, D_3 MeFOSA, D_5 EtFOSA, D_7 MeFOSE, D_9 EtFOSE) and four native 1H, 1H-perfluoro alcanols (5:1 FA, 7:1 FA, 9:1

FA, 11:1 FA). Samples were extracted by cold column extraction using ethyl acetate (3 x 30 min). The combined extracts were rotary-evaporated and cleaned up using ENVI-Carb and anhydrous sodium sulfate. As injection standards, Me_2FOSA, 13:1 FA, and PCB30 were used. Instrumental analysis occurred by GC-MS in the PCI mode [(13)]. All results of lab A and C were recovery-corrected.

SIP-based air concentrations of those PFC that were still in the linear uptake phase after two months of sampling (FASA, FASE) were calculated by:

$$c_{air} = \frac{N_{SIP}}{R_s \cdot t}$$

with: c_{air}: PFC air concentration, N_{SIP}: PFC amount in SIP, t: duration of sampling period, R_s: sampling rate. Sampling rates for several volatile PFC determined by Shoeib et al. [(21)] are presented in table 1. Sampling rates for the remaining substances were estimated based upon these numbers: 1.5 was used for MeFBSE and 2.6 for MeFBSA and MeFOSA. Air concentrations of PFC that were already in the equilibrium uptake phase (FTOH) were calculated by:

$$c_{air} = \frac{N_{SIP}}{V_{air}}$$

with N_{SIP}: PFC amount in SIP and V_{air}: the effective volume sampled by the SIP disk. V_{air} was determined by:

$$V_{air} = K'_{PSM-A} \cdot V_{PSM} \cdot (1 - e^{\frac{t \cdot k_A}{K'_{PSM-A} \cdot D}})$$

With K'_{PSM-A}: dimensionless passive sampler medium-air partition coefficient, V_{PSM}: volume of the passive sampling medium, t: deployment time, k_A: airside mass transfer coefficient, D: film thickness. Effective volumes used in this study are presented in table 2.

SPMD Samples

Sampling with SPMD was performed by the lab B only. Triolein-filled low density poly ethylene (LDPE) tubes were applied to accumulate volatile PFC. Six SPMD were deployed per two-month periods. After sampling, SPMDs were kept frozen (-20 °C) and in darkness until analysis that occurred within 2-14 months. Details on the analytical procedure are described elsewhere [(19)]. Briefly, SPMD replicates were combined, cut into small slices, and liquid-liquid extracted with hexane and acetonitrile. Rotary-evaporated extracts were analysed by GC-MS using the PCI mode. Compound-specific mass-labelled polyfluorinated compounds (^{13}C 4:2 FTOH, ^{13}C 6:2 FTOH, ^{13}C8:2 FTOH, ^{13}C 10:2 FTOH) were applied prior to the extraction to correct for analytes' losses and 9:1 FA was used as the injection standard. Results were recovery-corrected. Since all analysed PFC were still in the linear uptake phase after two months of sampling *(19)*, air concentrations were calculated using:

$$c_{air} = \frac{N_{SPMD}}{R_s \cdot t}$$

with: c_{air}: PFC air concentration, N_{SPMD}: PFC amount in SPMD, R_s: sampling rate, t: duration of the sampling period. PFC sampling rates were estimated by the method of Huckins et al. *(26)*:

$$R_s = V_s \cdot K_{SA} \cdot k_e \qquad \text{with} \qquad k_e = -\frac{\ln(N / N_0)}{t}$$

with: V_s: SPMD volume, K_{SA}: SPMD-air partition coefficient, k_e: release rate constant, N: PFC amount in SPMD at the end of deployment, N_0: PFC amount in SPMD at the beginning of deployment. As suggested by Huckins et al. *(26)*, octanol-air-partition coefficients *(27)* were used instead of SPMD-air-partition coefficients to derive the sampling rates. N and N_0 were derived from previous experiments [(19)]. Theoretical SPMD sampling rates are reported in table 1.

High Volume Samples

High volume samplers were operated by lab D only. Details on methodological aspects of the determination of volatile PFC in air samples are presented elsewhere *(14,28,29)*. Briefly, glass fibre filters and cartridges filled with PUF/XAD-2/PUF were applied to accumulate particle-bound and gas-phase PFC. Cartridges were spiked with eight mass-labelled polyfluorinated standards (^{13}C 4:2 FTOH, ^{13}C 6:2 FTOH, ^{13}C8:2 FTOH, ^{13}C 10:2 FTOH, D_3 MeFOSA, D_5 EtFOSA, D_7 MeFOSE, D_9 EtFOSE) prior to the sampling to account for analytes' losses during sampling and analyses. Samples were kept frozen (-20 °C) and in darkness until extraction. Extraction of the cartridges occurred by cold column extraction (2 x 60 min, 1 x 30 min) using acetone-MTBE (1:1). A clean-up step was not involved. Prior to the measurement, an injection standard (^{13}C HCB, ^{13}C TCB) was added to rotary-evaporated samples. Analytes were determined by GC-MS in the PCI mode. PFC concentrations were calculated using the internal standards method. All results were recovery-corrected. Air concentrations were calculated by:

$$c_{air} = \frac{N_{HighVol}}{V_{air}}$$

with: c_{air}: PFC air concentration, $N_{High\ Vol}$: PFC amount in the cartridge, V: ambient air volume measured using a flow meter.

Target Analytes

FTOH (C6-C12) were determined by all laboratories. MeFOSA, EtFOSA, MeFOSE, EtFOSE were determined by three laboratories (A, C, D). MeFBSA, MeFBSE, 12:2 FTOH, and FTA were determined by two laboratories (C, D) only.

RESULTS AND DISCUSSION

Standard solutions

Average or 'consensus' concentrations of volatile and semi-volatile PFC determined by each of the four groups in two circulated standards solutions of unknown PFC levels are presented in table 1. PFC concentrations were determined in triplicate by each group. Average standard deviation of triplicate PFC concentrations decreased in the order of lab B (27 %) > lab C (6 %) ≈ lab A (5.5 %) > lab D (2 %). PFC concentration deviations among the laboratories were analyte-dependent. Highest deviations were observed for MeFOSE with reported concentrations ranging from 16-86 % of the consensus value. This large difference may be associated with different calibration standard solutions used by each laboratory for quantification and variations in MeFOSE purity. Results for other analytes were better, with reported concentrations ranging from 5-36 (FTOH), 16-21 (FTA), 3-36 (FASA), and 4-47 (remaining FASE) % of consensus values (figure 1). Standard deviations for the consensus values (arithmetic mean for the results for the four laboratories) ranged from 16 % for 8:2 FTOH to 77 % for MeFOSE.

Field Intercomparison

Air concentrations of PFCs determined by different sampling approaches are presented in figure 2 and tables S2-S7. The results from the high volume samplers demonstrate the large variability from one week to the next with ranges in concentrations for some target compounds of almost two orders of magnitude. The implication for monitoring purposes, is that to assess 'average' concentrations for temporal trends analysis, it is necessary to perform high volume sampling continuously as intermittent sampling (e.g. 1 day in 10) will lead to considerable uncertainty. A less costly alternative is to deploy passive samplers over longer averaging periods – 2 months, in the case of this study.

A comparison of the active and passive sampling results, averaged over the 2-month passive deployment periods is also shown in Figure 2 for SIP disks analysed by lab A and C and SPMD analysed by lab B. Overall, better agreement with active air sample results was demonstrated for the SIP disks (vs. SPMD) with fair agreement also observed in the results reported by labs A and C. There was also greater detection of target analytes in the SIP disks compared to the SPMD. For instance, 6:2 FTOH was not detected in any SPMD sample and 8:2 FTOH and 10:2 FTOH were not detected in SPMD samples for periods IV, V, and VI. This may be due to FTOH uptake by the HDPE membrane

(19) or FTOH air concentrations being below the detection limit of lab B. Detection of FTA in ambient air was only possible with the active sampling approach.

The variation in derived air concentrations expressed as the ratio of active/passive (table S8 – S16) is described below for different compound classes, separately for the SIP disk and SPMD samplers. Note the different analyte spectra for the participating groups.

FTOH

The average ratios for active/SIP derived air concentrations for FTOH are as follows: Lab A: 0.9 (10:2 FTOH) to 1.3 (6:2 FTOH) and at maximum a factor of 2.4 (6:2 FTOH, period II). Lab C: 1.1 (8:2 FTOH) to 2.2 (12:2 FTOH) and at maximum a factor of 4.6 (12:2 FTOH, period VI). The average ratios for active/SPMD derived air concentrations for FTOH are 1.9 (8:2 FTOH) to 3.8 (10:2 FTOH) with a maximum of 6 (10:2 FTOH, period II). The observed deviations could not be explained by analytical differences between the laboratories as assessed during the standard comparison. With the exception of 12:2 FTOH, deviation factors were higher in period I, II, and III than in period IV, V, and VI, probably due to the occurrence of several events of strongly elevated FTOH concentrations that strongly influenced active sampling-derived concentration averages but were not reflected by the passive sampling.

FASE & FASE

FASA and FASE concentrations determined by high volume sampling were mostly lower than those of SIP-based samples, resulting in ratios for active/SIP-derived air concentration being usually below 1. The average ratios for active/SIP-derived air concentrations for FASA/E are as follows: Lab A: 0.2 (Me/EtFOSE) to 1.1 (EtFOSA). Observed FASA/E concentration deviation among active sampling and SIP samplers of Lab A was highest for EtFOSA in period IV with a factor of 2. Lab C: 0.2 (MeFOSE) to 0.9 (EtFOSA). Observed FASA/E concentration deviation among active sampling and SIP samplers of Lab C was highest for MeFOSE in periods IV-VI with a factor of 0.2. FASA and FASE were not determined by Lab C using SPMD. As for FTOH, observed deviations were not explained by analytical differences between the laboratories as assessed during the standard comparison. Note, since outdoor air concentrations of FASA and FASE were low and close to the detection limit, analytical uncertainty and imprecision of the data increased.

Calibration of passive samplers by high volume data

High volume and passive sampling data were used to calculate new sampling rates for FTOH (SPMD) and FASA and FASE (SIP):

$$R_{s(new)} = \frac{N_{PS}}{c_{air(HighVol)} \cdot t}$$

with $R_{s(new)}$: sampling rate calibrated by high volume data, N_{PS}: lab difference-corrected amount of PFC in the passive sampler (SPMD or SIP), $c_{air(High\ Vol)}$: High volume sampler derived PFC air concentrations, t: duration of the sampling period.

Sampling rates were calculated for each period and are summarised in tables S17-S22. Sampling rates for FTOH could not be calculated for the SIP disks since they approached equilibrium with ambient air during the two-month deployments.

Table 4 summarises the annual average sampling rates for the two SIP-disk-applying groups and the SPMD-applying laboratory. These correspond to an annual average temperature of 10 °C and an average wind speed of 2.7 m s^{-1}. Overall, SPMD sampling rates were lower than those of SIP (tables 1, 4) which may explain some of the non-detects of lab B. Although lab A and C used the same kind of sampling material, high volume-calibrated FASA and FASE sampling rates differed, probably due to differences in methodology and method uncertainties between the two laboratories. The field-calibrated sampling rates are higher than those reported by Shoeib et al.*(21)* for an indoor calibration. The higher sampling rates from this field study may be attributed to a wind-effect on sampling rates that tends to increase sampling rates in outdoor studies where the sampling chamber is exposed to wind *(30,31)*. The sampling rates listed in Table 4 are also comparable to the average value of ~4 m^3 d^{-1} derived for PUF-disk samplers (i.e. not impregnated with XAD) used under the GAPS network, for polychlorinated biphenyls and organochlorine pesticides *(32)*. This suggests that linear-phase sampling rates for the PUF vs SIP samplers are comparable, and driven mainly by the surface area of the sampling medium. This is consistent with theoretical predictions for compounds of similar size *(33)*.

CONCLUSION

During this field intercomparison, active and passive sampling strategies using different sampling materials (e.g. XAD/PUF, triolein/LDPE) were compared and evaluated for measuring PFC concentrations in air. A laboratory intercomparison exercise was also conducted to assess the analytical consistency between the participating groups. Analytical consistency between labs was between 38 and 84 % for the determination of PFC in standard solutions and between 7 and 90 % (relative to the concentrations maximum) for the determination of PFC outdoor air concentrations by different sampling strategies. Some discrepancies and inconsistencies between labs may be attributed to the different analytical methods or a different degree of experience in the analysis of airborne PFC, but also on the different temporal resolution or meteorological effects on PAS sampling rates. The results of the air sampling campaign showed that high volume air samples collected over durations of a few days were able to reveal the widely varying air concentrations of PFC from one sampling period to the next with concentrations changing by more than an order of magnitude. This has implications for monitoring programs which sample air intermittently (e.g. 10% of the time) as these results may not be representative of longer time periods. Because passive samplers are time-integrating, they are effective at capturing the 'average' air concentration but at the cost of temporal resolution, with results reported typically over deployments of a few months. This is not necessarily a disadvantage of the passive samplers given their much lower operating cost. However, more work is required to calibrate passive samplers for PFC and other compounds of interest.

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SUPPORTING INFORMATION

Supporting information covering several aspects of the intercomparison, group-specific air concentrations and sampling rates is available.

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Table 1: Linear SIP and SPMD sampling rates (Rs, m³ d^{-1}) reported in literature. Note that linear sampling rates were not applicable to calculate SIP-based FTOH concentrations in this study since SIPs already reached the equilibrium uptake phase. n.a.: not analyzed.

compound	**R_s(SIP)** *(21)*	**R_s(SPMD)** *(19)*
6:2 FTOH	4.6	n.a.
8:2 FTOH	4.6	1.4
10:2 FTOH	4.6	2.6
12:2 FTOH	n.a.	n.a.
MeFOSA	2.6	n.a.
EtFOSA	2.6	n.a.
MeFBSE	n.a.	n.a.
MeFOSE	1.5	n.a.
EtFOSE	1.4	n.a.

Table 2: Effective volumes (m³) used in this study to calculate FTOH air concentrations from SIP sampling.

	Period I	Period II	Period III	Period IV	Period V	Period VI
Deployment time (d)	63	56	61	64	64	56
Average air temperature (°C)	12.2	17.1	15.3	6.9	4.4	4.7
			Effective air volumes (m³)			
6:2 FTOH	160	121	137	198	210	190
8:2 FTOH	155	118	133	193	206	186
10:2 FTOH	158	121	136	194	207	188
12:2 FTOH	132	102	114	162	176	162

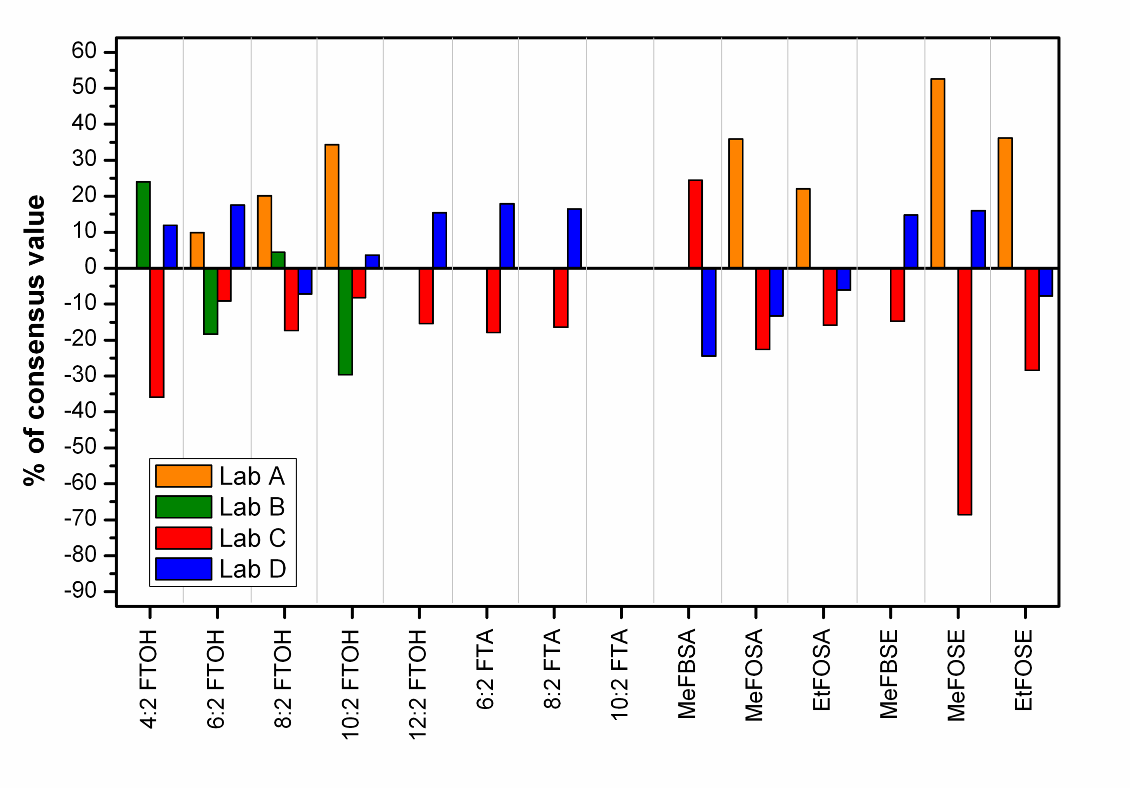
Table 3: Mean concentrations (pg µL^{-1}, n=3) of volatile PFC in two standards solutions of unknown concentrations that were circulated between the laboratories. c: concentration (pg µL^{-1}). SD: standard deviation (pg µL^{-1}). RSD: relative standard deviation (%). n.a.: not analyzed.

Standard Solution I (pg µL^{-1})																				
	Lab A				Lab B				Lab C				Lab D							
compound	c		SD	RSD	c		SD	RSD	c		SD	RSD	c		SD	RSD	Mean		SD	RSD
4:2 FTOH			n.a.		38	+/-	16	43	68	+/-	3.8	5.6	44	+/-	0.3	0.7	50	+/-	16	32
6:2 FTOH	49	+/-	1.5	3.0	65	+/-	12	18	60	+/-	2.8	4.6	45	+/-	0.3	0.8	55	+/-	9	17
8:2 FTOH	31	+/-	1.2	3.8	37	+/-	13	36	45	+/-	3.8	8.5	41	+/-	0.5	1.1	39	+/-	6	16
10:2 FTOH	27	+/-	0.5	1.9	54	+/-	11	20	45	+/-	4.4	9.9	40	+/-	0.4	0.9	41	+/-	11	27
12:2 FTOH			n.a.				n.a.		54	+/-	7.7	14	39	+/-	0.8	1.9	47	+/-	10	22
6:2 FTA			n.a.				n.a.		57	+/-	2.0	3.6	40	+/-	0.2	0.5	49	+/-	12	25
8:2 FTA			n.a.				n.a.		58	+/-	3.7	6.3	42	+/-	0.4	0.9	50	+/-	12	23
10:2 FTA			n.a.				n.a.				n.a.		39	+/-	0.5	1.2	39	+/-	-	-
MeFBSA			n.a.				n.a.		21	+/-	2.8	13	35	+/-	0.3	0.8	28	+/-	10	35
MeFOSA	22	+/-	0.9	4.2			n.a.		42	+/-	0.8	1.8	39	+/-	0.2	0.5	34	+/-	11	31
EtFOSA	27	+/-	0.4	1.4			n.a.		41	+/-	2.6	6.3	37	+/-	0.3	0.8	35	+/-	7	20
MeFBSE			n.a.				n.a.		45	+/-	3.1	6.8	34	+/-	0.4	1.0	39	+/-	8	21
MeFOSE	21	+/-	1.6	7.7			n.a.		73	+/-	2.2	3.1	37	+/-	2.4	6.5	43	+/-	27	62
EtFOSE	21	+/-	2.7	13			n.a.		43	+/-	4.6	11	36	+/-	1.7	4.8	33	+/-	11	33

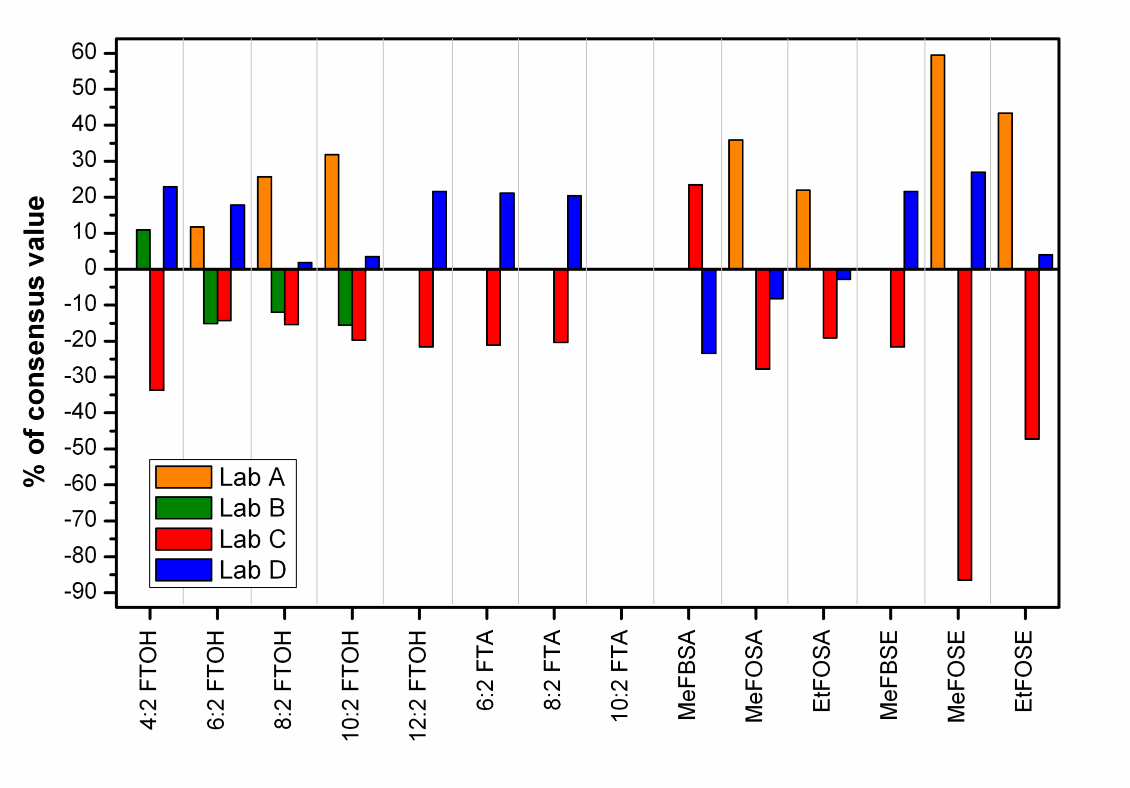
Standard Solution II (pg µL^{-1})																				
	Lab A				Lab B				Lab C				Lab D							
compound	c		SD	RSD	c		SD	RSD	c		SD	RSD	c		SD	RSD	Mean		SD	RSD
4:2 FTOH			n.a.		36	+/-	6	16	54	+/-	2.0	3.7	31	+/-	0.3	0.9	40	+/-	12	30
6:2 FTOH	34	+/-	1.5	4.3	45	+/-	6	13	44	+/-	1.0	2.3	32	+/-	0.3	1.1	39	+/-	7	17
8:2 FTOH	26	+/-	0.5	2.0	39	+/-	12	32	40	+/-	3.9	9.7	34	+/-	0.5	1.3	35	+/-	6	19
10:2 FTOH	23	+/-	0.9	4.0	39	+/-	15	40	40	+/-	1.5	3.7	32	+/-	0.4	1.2	33	+/-	8	24
12:2 FTOH			n.a.				n.a.		53	+/-	3.2	6.1	34	+/-	0.8	2.3	43	+/-	13	30
6:2 FTA			n.a.				n.a.		44	+/-	2.1	4.7	29	+/-	0.2	0.7	36	+/-	11	30
8:2 FTA			n.a.				n.a.		45	+/-	2.3	5.1	30	+/-	0.4	1.2	37	+/-	11	29
10:2 FTA			n.a.				n.a.				n.a.		31	+/-	0.5	1.5	31	+/-	-	-
MeFBSA			n.a.				n.a.		17	+/-	0.1	0.7	28	+/-	0.3	1.0	23	+/-	8	33
MeFOSA	18	+/-	1.9	10.1			n.a.		36	+/-	2.2	6.0	31	+/-	0.2	0.7	29	+/-	9	33
EtFOSA	22	+/-	1.1	5.3			n.a.		33	+/-	1.2	3.7	28	+/-	0.3	1.0	28	+/-	6	21
MeFBSE			n.a.				n.a.		39	+/-	3.1	8.1	25	+/-	0.4	1.4	32	+/-	10	31
MeFOSE	14	+/-	1.5	10.9			n.a.		64	+/-	3.1	4.8	25	+/-	2.4	9.4	35	+/-	26	77
EtFOSE	16	+/-	0.7	4.2			n.a.		41	+/-	1.6	3.9	26	+/-	1.7	6.5	28	+/-	13	45

Table 4: Average field SIP and SPMD sampling rates ($m^3 d^{-1}$) and standard deviation of airborne PFC calculated from on-site high volume data. R_s: sampling rate ($m^3 d^{-1}$). SD: standard deviation ($m^3 d^{-1}$). RSD: relative standard deviation (%). T: annual temperature average (°C). U: annual wind speed average ($m s^{-1}$). n.c.: not calculated. n.a.: not analyzed. n.d.: not detected.

	Average Sampling Rate (m^3d^{-1}) (T=10.1 °C, U=2.7 $m s^{-1}$)											
	SIP Lab A				**SPMD Lab B**				**SIP Lab C**			
compound	**Rs**		**SD**	**SD (%)**	**Rs**		**SD**	**SD (%)**	**Rs**		**SD**	**SD (%)**
6:2 FTOH			n.c.				n.d.				n.c.	
8:2 FTOH			n.c.		0.83	+/-	0.35	42			n.c.	
10:2 FTOH			n.c.		0.79	+/-	0.32	40			n.c.	
12:2 FTOH			n.a.				n.a.				n.c.	
MeFOSA	6.2	+/-	4.2	67			n.a.		4.8	+/-	2.2	45
EtFOSA	3.0	+/-	1.5	49			n.a.		4.8	+/-	3.2	66
MeFBSE			n.a.				n.a.		4.7	+/-	2.1	44
MeFOSE	11	+/-	7.1	66			n.a.		6.3	+/-	0.9	15
EtFOSE	6.7	+/-	2.0	30			n.a.				n.d.	



a



b

Figure 1: % deviation of the consensus concentrations of standard solution I (a) and II (b).

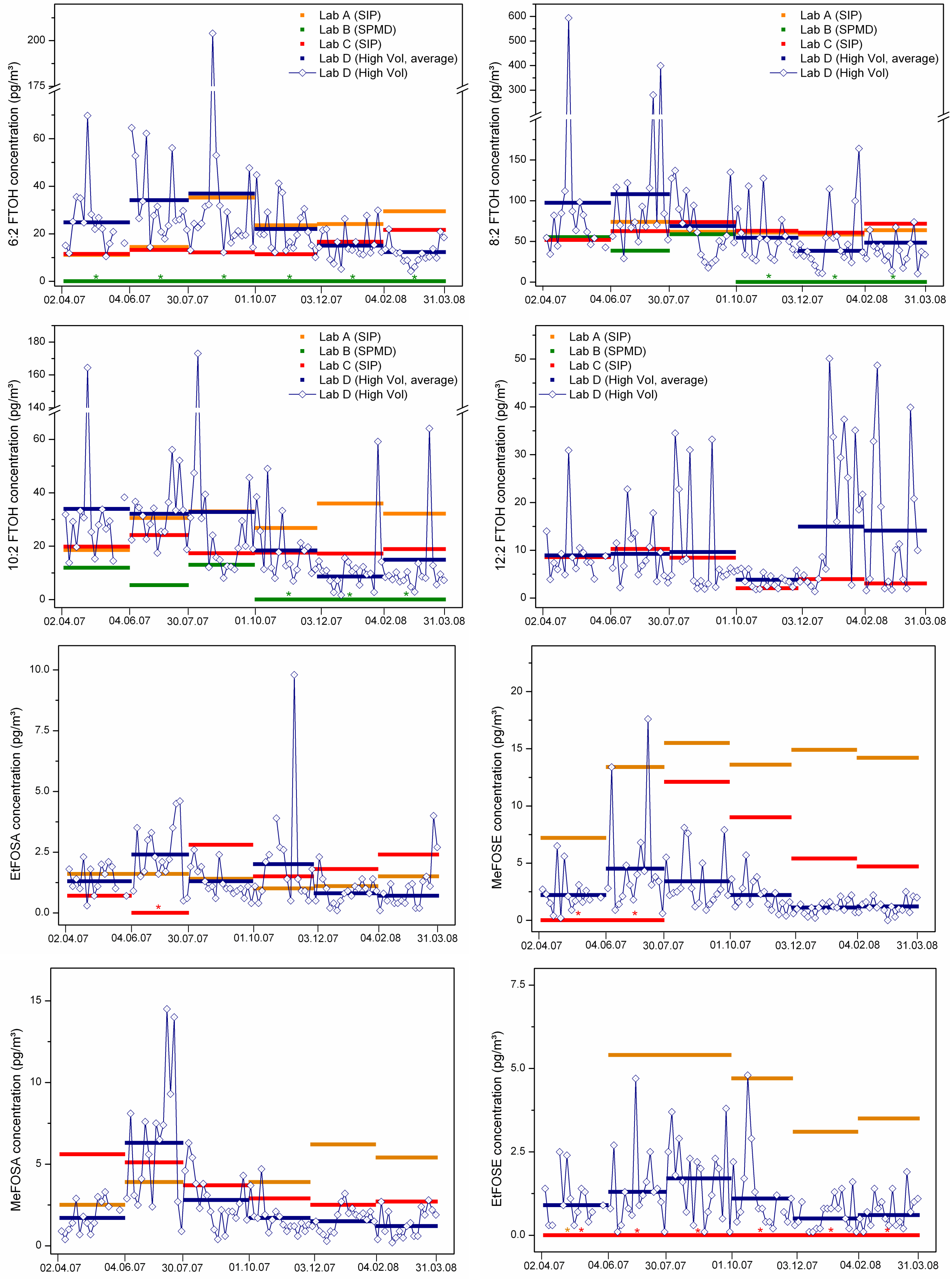


Figure 2: PFC concentrations determined by different sampling strategies during the field intercomparison. If an analyte was determined by a lab, but not detected, its concentrations was set to zero and an asterisk was placed above the corresponding bar. Lab A (SIP), Lab B (SPMD), Lab C (SIP), Lab D (High Vol average), N Lab D (High Vol)

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