Polyfluorinated Alkyl Substances (PFAS) in the Marine Atmosphere – Investigations on Their Occurrence and Distribution in Coastal Regions

(Von der Fakultät III – Umwelt und Technik der Universität Lüneburg als Dissertation angenommene Arbeit)

Autorin:
A. Jahnke

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Annika Jahnke

115 pages with 11 figures and 25 tables

Abstract

Polyfluorinated alkyl substances (PFAS) are a group of organic chemicals, many of which combine bioaccumulative potential, toxic effects and extreme persistence. Furthermore, certain PFAS are volatile and thus prone to long-range atmospheric transport (LRAT). Therefore, they are considered as 'candidates' for the Stockholm Convention list of persistent organic pollutants (POPs) and are regarded as a new and emerging class of environmental contaminants. Their widespread use for surface treatment in carpets and textiles, in polymer (e.g. polytetrafluoroethylene, PTFE) production, in fire-fighting foams and insecticides underlines the relevance of PFAS as a group of environmental pollutants.

The two most studied C_8-PFAS (perfluorooctane sulfonate, PFOS and perfluorooctanoate, PFOA) are distributed ubiquitously despite their non-volatility and only moderate water-solubility. The hypothesis that neutral, volatile precursor compounds of PFOS and PFOA could undergo LRAT and be degraded to the persistent, ionic PFAS in remote regions like the Canadian and European Arctic was the main motivation for this thesis. It was designed to improve our understanding of the occurrence, distribution pattern and transport mechanisms of neutral, volatile PFAS between source regions and remote, marine locations.

This PhD thesis can be subdivided into three basic sections. First of all, the development, optimisation and validation of a trace-analytical method for the sampling and determination of neutral, volatile PFAS in environmental air samples was indispensible *(see **publication I**)*. The analytical protocol included the following substances: four fluorotelomer alcohols (FTOHs), 4:2 FTOH, 6:2 FTOH, 8:2 FTOH and 10:2 FTOH, as well as two N-alkyl fluorooctane sulfonamides (NMeFOSA/NEtFOSA) and N-alkyl fluorooctane sulfonamidoethanols (NMeFOSE/NEtFOSE) each.

Secondly, the analytical method was tested at a location with presumed relatively high environmental air concentrations of the investigated compounds (metropolitan Hamburg). In comparison, it was also applied to air samples from a rural location in Northern Germany (Waldhof, background monitoring station of the German Federal Environmental Agency, UBA and European Monitoring and Evaluation Program, EMEP, see ***publication II***).

Thirdly, in order to investigate the concentration gradient of neutral, volatile PFAS between locations with relatively high production and emission and less industrialised areas, air samples were taken on board of the German research vessel Polarstern (see ***publication III***). Expedition ANTXXIII-1 between Bremerhaven, Germany, and Capetown, Republic of South Africa, was used to determine the latitudinal gradient of the investigated compounds in coastal regions of both hemispheres.

Further sampling was done in the European Arctic on Polarstern expeditions ARKXX-1/2. Additionally, in order to investigate European background levels of neutral, volatile PFAS for comparison with the ship-based data, a sampling campaign was performed at Mace Head, West coast of Ireland.

Finally, a new sampling method for airborne PFAS using commercially available solid-phase extraction (SPE) cartridges was developed and applied to indoor as well as outdoor air samples.

Prior to the PhD thesis at hand, no information on the occurrence and distribution of neutral, volatile PFAS outside North America was available. This work generated first concentration data of this group of compounds from Europe and the Southern Hemisphere. Finally, the data sets from Germany and the latitudinal transect help in the scientific discussion to estimate fluxes of airborne PFAS to remote, polar regions and to elucidate their worldwide occurrence.

Polyfluorierte Alkylverbindungen (PFAS) in der marinen Atmosphäre – Untersuchungen zum Vorkommen und zur Verteilung in Küstenregionen

Kurzzusammenfassung

Polyfluorierte Alkylverbindungen (PFAS) sind eine Gruppe organischer Chemikalien, die Bioakkumulationspotential, toxische Effekte und extreme Langlebigkeit vereinen. Zusätzlich sind einige PFAS flüchtig und können somit weiträumig über die Atmosphäre verteilt werden. Daher werden sie als „Kandidaten" für die Liste persistenter organischer Schadstoffe (POPs) der Stockholm Convention betrachtet und gelten als neu aufkommende, aktuelle Klasse von Umweltschadstoffen. Ihr vielfältiger Gebrauch zur Oberflächenbehandlung von Teppichen und Textilien, in der Polymerherstellung (bspw. von Polytetrafluorethylen, PTFE), in Feuerlöschschäumen und Insektiziden unterstreicht die Relevanz von PFAS als Gruppe von Umweltschadstoffen.
Die zwei meistuntersuchten C_8-PFAS (Perfluoroktansulfonat, PFOS und Perfluoroktanoat, PFOA) sind trotz mangelnder Flüchtigkeit und nur mäßiger Wasserlöslichkeit ubiquitär verbreitet. Die Hypothese, dass neutrale, flüchtige Vorläuferverbindungen von PFOS und PFOA weiträumig über die Atmosphäre transportiert und in entlegenen Gebieten zu den persistenten, ionischen PFAS abgebaut werden können, war die Hauptmotivation für die vorliegende Arbeit. Sie wurde darauf ausgerichtet, unser Verständnis des Vorkommens, der Verbreitungsmuster und Transportmechanismen von neutralen, flüchtigen PFAS zwischen Quellenregionen und abgelegenen, marinen Standorten zu verbessern.
Diese Dissertation kann in drei grundlegende Abschnitte untergliedert werden. Zunächst war die Entwicklung, Optimierung und Validierung einer spurenanalytischen Methode für die Probenahme und Bestimmung neutraler, flüchtiger PFAS in Außenluftproben unverzichtbar (s. ***publication I***). Das analytische Verfahren schloss die folgenden Substanzen ein: vier Fluortelomeralkohole, 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, sowie je zwei N-Alkyl Fluoroktansulfonamide (NMeFOSA/ NEtFOSA) und -sulfonamidethanole (NMeFOSE / NEtFOSE).
Zweitens wurde das analytische Verfahren an einem Standort mit relativ hohen Umweltkonzentrationen der untersuchten Verbindungen (Hamburg-Zentrum) getestet. Zum Vergleich wurde die Methode auf Luftproben eines ländlichen Standortes in Norddeutschland (Waldhof, Hintergrundmessstelle des Umweltbundesamtes, UBA und European Monitoring and Evaluation Program, EMEP) angewandt (s. ***publication II***).
Drittens wurde der Konzentrationsgradient neutraler, flüchtiger PFAS zwischen Standorten mit relativ hoher Produktion und Emission sowie weniger entwickelten Regionen untersucht. Dazu wurden Luftproben an Bord des deutschen Forschungseisbrechers Polarstern genommen (s. ***publication III***). Die wissenschaftliche Expedition ANTXXIII-1 zwischen Bremerhaven und Kapstadt, Republik Südafrika, wurde dazu genutzt, die Zielanalyte in Küstenregionen beider Hemisphären entlang eines Breitengradlängsschnitts zu untersuchen.
Zusätzlich wurden arktische Luftproben (Polarsternexpeditionen ARKXX-1/2) untersucht. Um europäische Hintergrundkonzentrationen neutraler, flüchtiger PFAS zum Vergleich mit den Schiffsdaten zu gewinnen, wurde eine Probenahmekampagne in Mace Head an der Westküste Irlands durchgeführt. Schließlich wurde im Rahmen eines deutsch-norwegischen Projekts eine neue Probenahmemethode für luftgetragene PFAS mit kommerziell erhältlichen Festphasen (SPE)-Kartuschen entwickelt und auf Innen- sowie Außenluftproben angewandt.
Vor Erstellung der vorliegenden Dissertation waren keine Informationen zu Vorkommen und Verteilung neutraler, flüchtiger PFAS außerhalb Nordamerikas verfügbar. Diese Arbeit erbrachte erste Konzentrationsdaten dieser Substanzgruppe aus Europa und von der Südhemisphäre. Schließlich bringen die gewonnenen Datensätze die wissenschaftliche Diskussion voran, um Flüsse luftgetragener PFAS in entlegene Gebiete und Polarregionen abzuschätzen und ihr weltweites Vorkommen näher zu beleuchten.

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Declaration

The cumulative PhD thesis "Polyfluorinated Alkyl Substances (PFAS) in the Marine Atmosphere – Investigations on Their Occurrence and Distribution in Coastal Regions" is based on the following scientific publications, which have been published in peer-reviewed journals.

Publication I.

Annika Jahnke, Lutz Ahrens, Ralf Ebinghaus, Urs Berger, Jonathan L. Barber, Christian Temme
An improved method for the analysis of volatile polyfluorinated alkyl substances in environmental air samples.

Reproduced with permission from *Anal. Bioanal. Chem.* ***2007***, 387, 965-975. © Springer-Verlag 2007. With kind permission of Springer Science and Business Media.

Publication II.

Annika Jahnke, Lutz Ahrens, Ralf Ebinghaus, Christian Temme
Urban versus remote air concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany.

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Publication III.

Annika Jahnke, Urs Berger, Ralf Ebinghaus, Christian Temme
Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53° N-33° S).

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List of abbreviations

6:2 FTS	6:2 fluorotelomer sulfonate
AFFF	aqueous film-forming fire fighting foam
BAF	bioaccumulation factor
BCF	bioconcentration factor (enrichment from surrounding media)
BMF	biomagnification factor (enrichment through dietary exposure)
BSH	Federal Maritime and Hydrographic Agency (Bundesamt für Seeschifffahrt und Hydrographie)
BTPA	3,5-bis(trifluoromethyl)phenyl acetic acid
bw	body weight
CI	chemical ionisation
CIC	combustion ion chromatography
DCM	dichloromethane
dw	dry weight
ECD	electron capture detection
EI	electron impact ionisation
EMEP	Environmental Monitoring and Evaluation Program
EtOAc	ethyl acetate
FA	fluorinated alcohol
FB	field blank
FBSAs	N-alkyl fluorobutane sulfonamides
FBSEs	N-alkyl fluorobutane sulfonamidoethanols
FOSAs	N-alkyl fluorooctane sulfonamides
FOSEs	N-alkyl fluorooctane sulfonamidoethanols
FTAL	fluorotelomer aldehydes, $C_xF_{2x+1}CH_2CHO$
FTCAs	saturated fluorotelomer carboxylic acids, $C_xF_{2x+1}CH_2COOH$
FTOHs	fluorotelomer alcohols
FTUCAs	unsaturated fluorotelomer carboxylic acids, $C_xF_{2x}CHCOOH$
GAW	Global Atmospheric Watch
GC/CI-MS	gas chromatography coupled to mass spectrometry with chemical ionisation
GFFs	glass-fibre filters
IS	internal standard (spiked before sampling / sample extraction)
ITC	inner tropical convergence
HPLC/(-)ESI-MS/MS	high-performance liquid chromatography tandem mass spectrometry with negative electrospray ionisation
HPLC/(-)ESI-TOF-MS	high-performance liquid chromatography coupled to time-of-flight mass spectrometry with negative electrospray ionisation
HR	hazard ratio
IDL	instrumental detection limit
IQL	instrumental quantification limit
K_{AW}	air-water partition coefficient
K_{OA}	octanol-air partition coefficient
K_{OW}	octanol-water partition coefficient
LD_{50}	lethal dose for 50% of the test organisms (acute toxicity)

LOAEL	lowest observed adverse effect level (chronic toxicity)
LOD	limit of detection
LOQ	limit of quantification
LRAT	long-range atmospheric transport
MDL	method detection limit
MeOH	methanol
MPI	Max Planck Institute
MQL	method quantification limit
MTBE	methyl *tert*-butyl ether
MW	molecular weight
m/z	ion mass to charge ratio
NCI	negative chemical ionisation
NEtFOSAA	N-ethyl perfluorooctane sulfonamido acetic acid
NILU	Norwegian Institute for Air Research
NMeFOSAA	N-methyl perfluorooctane sulfonamido acetic acid
NMeFOSEA	N-methyl perfluorooctane sulfonamidoethylacrylate
NMR	nuclear magnetic resonance
N,N-Et_2FOSA	N,N-diethyl fluorooctane sulfonamide
N,N-Me_2FOSA	N,N-dimethyl fluorooctane sulfonamide
NOAEL	no observed adverse effect level (chronic toxicity)
PCI	positive chemical ionisation
PP	polypropylene
PFAL	perfluoroalkyl aldehydes, $C_xF_{2x+1}CHO$
PFAS	polyfluorinated alkyl substances
PFCAs	perfluoroalkyl carboxylates, $C_xF_{2x+1}COO^-$
POPs	persistent organic pollutants
PTFE	polytetrafluoroethylene
PUF	polyurethane foam
RIS	recovery internal standard (spiked before analyses to determine recoveries of the IS)
SIM	selected ion monitoring
S/N	signal-to-noise ratio
SPE	solid-phase extraction
SPM	suspended particulate matter
STP	sewage treatment plant
TCN	1,2,3,4-tetrachloronaphthalene
UBA	German Federal Environmental Agency (Umweltbundesamt)
U.S. EPA	United States Environmental Protection Agency
ww	wet weight

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1. Introduction

This introduction gives a broad overview of the production and use (***1.1***), analytical methods used in the past and at present (***1.2***) as well as concentration levels of polyfluorinated alkyl substances (PFAS) in different environmental compartments (***1.3***). Special emphasis is placed on the analytical methodology and data available for neutral, volatile PFAS, which represent the focus of the PhD thesis at hand. Furthermore, human and ecotoxicological effects are described (***1.4***). Finally, the atmospheric chemistry of neutral, volatile PFAS is briefly elucidated (***1.5***).

1.1. Polyfluorinated alkyl substances (PFAS) – background, production, use and environmental behaviour

PFAS comprise a large group of chemicals, consisting of a hydrophobic alkyl chain (typically C_4-C_{16}, *De Voogt & Saez 2006*) and a hydrophilic functional group. PFAS are both oleophobic and hydrophobic and form strong surfactants. The alkyl chain is partly or fully fluorinated. PFAS comprise ionic compounds like perfluoroalkyl sulfonates (including perfluorooctane sulfonate, PFOS) and perfluoroalkyl carboxylates (PFCAs including perfluorooctanoate, PFOA, Table 1) as well as neutral, volatile PFAS like fluorotelomer alcohols (FTOHs) and N-alkylated fluorooctane sulfonamides and sulfonamidoethanols (FOSAs / FOSEs, Table 2).

Table 1. Ionic PFAS, acronyms and structures.

Analytes	*Acronyms*	*Example structures*
Perfluoroalkyl sulfonates		
C_4: Perfluorobutane sulfonate	PFBS	
C_6: Perfluorohexane sulfonate	PFHxS	
C_8: Perfluorooctane sulfonate	PFOS	
C_{10}: Perfluorodecane sulfonate	PFDS	PFOS
Perfluoroalkyl carboxylates		
C_5: Perfluoropentanoate	PFPeA	
C_6: Perfluorohexanoate	PFHxA	
C_7: Perfluoroheptanoate	PFHpA	
C_8: Perfluorooctanoate	PFOA	
C_9: Perfluorononanoate	PFNA	
C_{10}: Perfluorodecanoate	PFDA	
C_{11}: Perfluoroundecanoate	PFUnA	PFOA
C_{12}: Perfluorododecanoate	PFDoA	
C_{13}: Perfluorotridecanoate	PFTrA	
C_{14}: Perfluorotetradecanoate	PFTA	
C_{15}: Perfluoropentadecanoate	PFPDA	

Due to the high-energy C-F bond, ionic PFAS are extraordinarily persistent as they resist hydrolysis, photolysis, microbial degradation and metabolism. They show certain bioaccumulative and toxic properties as described in more detail in ***chapter 1.4***. Some precursors of PFOS and PFOA are volatile and thus prone to long-range atmospheric transport (LRAT). Therefore, PFAS can be classified as persistent organic pollutants (POPs). PFOS and other PFAS have already been declared 'candidate' POPs (*Kaiser & Enserink 2000*, *www.unep.org*).

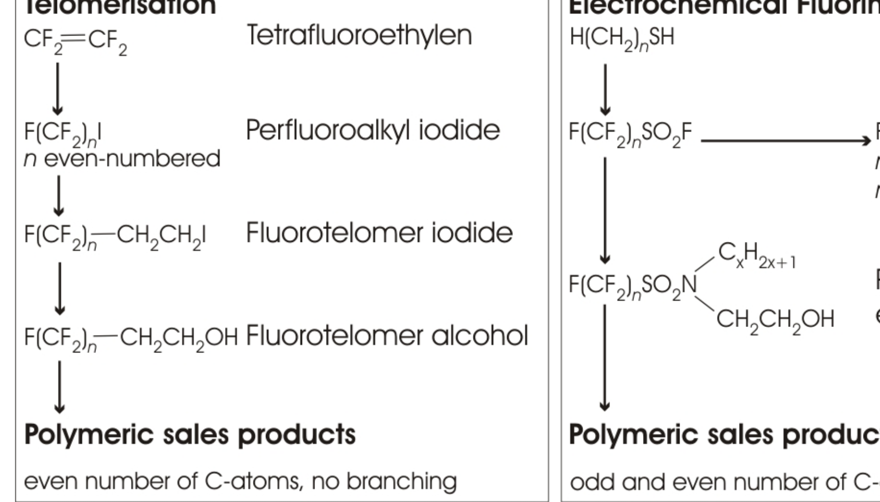
A recent publication by *Muir & Howard 2006* categorised chemicals fulfilling certain criteria of persistence, bioaccumulative properties (log octanol-water partition coefficient (log K_{OW}) ≥ 5) and LRAT characteristics. The register was assembled for the Canadian domestic substances list, scanning 11317 individual chemicals which are manufactured in Canada or imported at >100

kg/year. Sorted by the highest predicted bioconcentration factors (BCF) and then by degradation half-life extrapolated from two different models (for details see *Muir & Howard 2006*), N-methyl FOSE was ranked as no. 4 in the priority list. The authors point out the importance to characterise the major degradation products (here: PFOS) of chemicals in commerce for the identification of 'new and emerging' POPs that were previously unrecognised.

Table 2. Neutral PFAS, acronyms and structures.

Analytes	*Acronyms*	*Example structures*
Fluorotelomer alcohols		
C_6: 4:2 fluorotelomer alcohol	4:2 FTOH	
C_8: 6:2 fluorotelomer alcohol	6:2 FTOH	
C_{10}: 8:2 fluorotelomer alcohol	8:2 FTOH	
C_{12}: 10:2 fluorotelomer alcohol	10:2 FTOH	**8:2 FTOH**
Fluorooctane sulfonamides / sulfonamidoethanols		
Perfluorooctane sulfonamide	PFOSA	
N-methyl fluoroctane sulfonamide	NMeFOSA	
N-ethyl fluorooctane sulfonamide	NEtFOSA	
N-methyl fluorooctane sulfonamidoethanol	NMeFOSE	**NMeFOSE**
N-ethyl fluorooctane sulfonamidoethanol	NEtFOSE	

All PFAS with carbon chain lengths >2 are anthropogenic and are produced almost exclusively by one of two major manufacturing processes as visualised in Figure 1 and described in detail by *Schultz et al. 2003*. On the one hand, ***telomerisation*** is in use since the 1950s for the production of PFCAs and FTOHs, yielding exclusively linear compounds. FTOHs contain an even number of fully fluorinated and two non-fluorinated carbon atoms adjacent to the hydroxyl function. Their general structure is CF_3-$(CF_2)_n$-CH_2-CH_2OH, where n = 3, 5, 7, 9 and they are named based on the ratio of fluorinated to non-fluorinated carbon atoms, e.g. 8:2 FTOH for n = 7. On the other hand, ***electrochemical fluorination*** (ECF) used since the 1970s produced mixtures of linear and branched isomers of approx. 70% and 30%, respectively (*Giesy & Kannan 2002*).



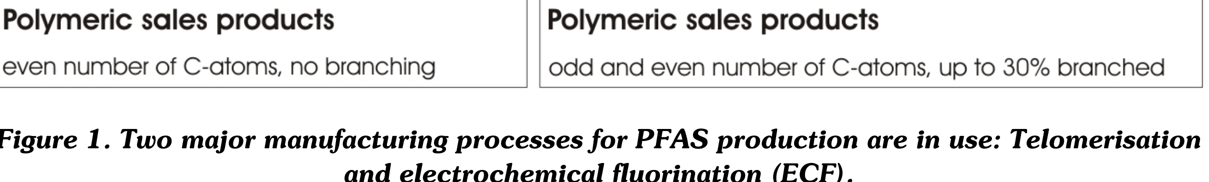


Figure 1. Two major manufacturing processes for PFAS production are in use: Telomerisation and electrochemical fluorination (ECF).

The application spectrum of PFAS is very broad. FOSAs / FOSEs were used in a variety of products for water- and dirt-proofing on carpets, leather, upholstery and textiles, as paper protectors and performance chemicals (e.g. in aqueous film forming fire-fighting foams (AFFFs), *De Voogt & Saez 2006*) or as an insecticide (N-ethyl fluorooctane sulfonamide (NEtFOSA): Sulfluramid®). FTOHs are used in similar applications as FOSAs / FOSEs, such as precursor compounds in the production of fluorinated polymers used in paper and carpet treatments, moreover in the production of paints, coatings, adhesives etc. (*Ellis et al. 2003a*, *Dinglasan et al. 2004*).

Production volumes of industrial chemicals are difficult to point out. *Prevedouros et al. 2006* published a global, historical, industry-wide estimate of direct and indirect PFCA emissions which were calculated to be 3200-7300 tons (1951-2004). The United States Environmental Protection Agency (U.S. EPA) reported a total anticipated production volume for sulfonyl-based PFAS produced by 3M, the major manufacturer of ECF-based chemicals, at 3×10^6 kg in 2000 (*U.S. EPA 2000*). The estimates for 2001 and 2002 were 0.5×10^6 kg and 0.2×10^6 kg, respectively. 3M completely phased out their C_8-production by the end of 2002. Recently, production has been substituted by C_4-analogs of similar structures (*Ridder 2003*), but much less bioconcentration potential and no known toxic effects. *Betts 2003* cited the Telomer Research Program with an estimate of annual FTOH production as intermediates in a wide variety of products at 5×10^6 kg.

Physical-chemical properties of PFAS are strongly affected by the unique properties of the C-F bond, which is the strongest observed in organic chemistry (~484 kJ/mol, increasing with increasing fluorination, *Stock et al. 2004a*). Even though the replacement of hydrogen by fluorine significantly increases the molecular weight of a compound, partial fluorination of the alkyl chain increases the vapor pressure. By comparison of polyfluorinated versus hydrogenated alcohols, the vapor pressure of 4:2 FTOH was 10 times greater than that of hexanol. Analogously, the vapor pressure of 10:2 FTOH was more than 100.000 times greater than that of dodecanol (*Stock et al. 2004a*). A possible reason for this observation is that intramolecular hydrogen bonding of the terminal ethanolic group to the perfluorocarbon portion of the molecule occurs, which is hypothesised to be stronger with increasing chain length.

Lei et al. 2004 published physical-chemical data on FTOHs as well as FOSAs / FOSEs. Furthermore, *Stock et al. 2004a* contributed vapor pressures for FTOHs, while *Shoeib et al. 2004* added data for FOSEs. However, physical-chemical data as given in Table 3 is still scarce which is partly attributable to the complicated experimental determination of these parameters due to the hydro- and lipophobicity of PFAS.

Table 3. Molecular weights (MW), vapor pressures (VP), log octanol-air (log K_{OA}) and log air-water (log K_{AW}) partition coefficients of selected PFAS from the literature.

	MW [g/mol]	***VP [Pa]***	***log K_{OA}***	***log K_{AW}***
4:2 FTOH	264	1670[a] / 992[b]	3.3[a]	1.8[a]
6:2 FTOH	364	876[a] / 713[b]	3.6[a]	1.7[a]
8:2 FTOH	464	227[a] / 254[b]	4.2[a]	1.3[a]
10:2 FTOH	564	53[a] / 144[b]	4.8[a]	n.a.
NEtFOSA	527	7	5.9[a]	n.a.
NMeFOSE	557	0.7[a] / 0.002[c]	6.8[a] / 7.7[c]	n.a.
NEtFOSE	571	0.35[a] / 0.009[c]	7.1[a] / 7.8[c]	n.a.

n.a. not available.

[a] *Lei et al. 2004, VPs at 25 °C,*

[b] *Stock et al. 2004a, VPs at 25 °C,*

[c] *Shoeib et al. 2004, VPs at 23 °C.*

The first detection of organofluorine compounds in human blood was described by *Taves 1968*. Until recently, more detailed investigations were impeded by the lack of adequate instruments to specificly identify and quantify single compounds at low concentrations. Appropriate instrumentation only became available in the 1990s. Even today, analytical challenges still remain as specified by *Martin et al. 2004a* and described in more detail in ***chapter 1.2***. Moreover, the first world-wide interlaboratory comparison study, including 13 PFAS in three environmental and two human matrices emphasised that further improvement of analytical methods and laboratory performance is needed to generate comparable results, especially concerning water and fish tissue analyses (*Van Leeuwen et al. 2006*).

In 1999, the U.S. EPA was alerted by data on PFOS showing that it was persistent, unexpectedly toxic, bioaccumulative, and found in the blood of the general population and in wildlife around the world (*www.epa.gov*). Since then, numerous studies have been performed to investigate levels in organisms at different trophic levels. Furthermore, PFAS concentrations in various environmental compartments like humans and biota, the aqueous phase (surface water, sewage treatment plant (STP) influents / effluents, precipitation), the solid phase (food, dust, sediment / soil, STP sludge), as well as indoor and outdoor air have been under intensive investigation as outlined in ***chapter 1.3***. The global distribution of PFAS has increased concern as underlined by rising amounts of publications in scientific as well as popular literature.

Moody & Field 1999 described the determination of derivatised PFCAs using gas chromatography coupled to mass spectrometry (GC-MS) with electron impact (EI) ionisation after solid-phase extraction (SPE) from groundwater impacted by fire-fighting activities. *Hansen et al. 2001* reported a new method for the compound-specific, quantitative determination of PFAS by liquid chromatography coupled to tandem mass spectrometry using negative electrospray ionisation (HPLC/(-)ESI-MS/MS) in biological matrices like blood sera or liver, which has been used in numerous studies. *Giesy & Kannan 2001* first described the global distribution of PFOS in wildlife, which has been shown for several PFAS in many other studies afterwards. To investigate the impact of this observation, a suite of toxicological studies has been conducted, a brief overview of which is given in ***chapter 1.4***.

PFOS, PFOA and a suite of additional PFAS were found in organisms from remote locations, such as polar bears from the Canadian and European Arctic (*Martin et al. 2004b*, *Smithwick et al. 2005a*, *Smithwick et al. 2005b*). As these compounds are non-volatile with relatively low vapour pressures and only moderately water-soluble, two transport hypotheses have been proposed:

a) Direct transport via oceanic currents and / or sea spray could occur as described by *Prevedouros et al. 2006* and *Armitage et al. 2006*.

b) Neutral, volatile precursors could undergo LRAT and be degraded (biotically / abiotically) to the persistent compounds in remote regions (*Ellis et al. 2004*). Airborne precursor compounds of PFOS and PFCAs include FTOHs as well as N-alkylated FOSAs / FOSEs. The atmospheric chemistry of neutral, volatile precursors of PFOS and PFCAs is briefly elucidated in ***chapter 1.5***.

Both suggested transportation pathways have recently received some supporting evidence. On the one hand, a number of ionic PFAS were detected in Arctic water samples as described by *Caliebe et al. 2005*. Furthermore, recent modelling results support the theory of long-range oceanic transport of PFOA to the Arctic (*Prevedouros et al. 2006*, *Armitage et al. 2006*).

On the other hand, the second hypothesis was supported by the ubiquitous detection of a suite of volatile, neutral precursors in North American (*Martin et al. 2002*, *Stock et al. 2004b*, *Shoeib et al. 2004*, *Shoeib et al. 2005*) and European environmental air (*Berger et al. 2005a*, ***publication II***). Furthermore, biodegradation (*Dinglasan et al. 2004*, *Tomy et al. 2004a*, *Wang et al. 2005a*, *Wang et al. 2005b*) as well as smog chamber degradation studies (*Ellis et al. 2003a*, *Martin et al. 2006*, *D´Eon et al. 2006*) indicated the plausibility of the LRAT theory. Finally, recent results from modelling studies seem to further substantiate the LRAT hypothesis (*Wallington et al. 2006*).

1.2. Analytical methods

Below, analytical methods for the determination of PFAS in different matrices are addressed. The chapter includes formerly used methods as well as up-to-date trace-analytical protocols for the extraction and determination of PFAS in humans, biota, aqueous and solid samples as well as environmental and indoor air.

1.2.1. Historical analytical methods for PFAS determination

Formerly used analytical protocols for the determination of PFAS are reviewed in more detail by *Kissa 2001*. One of the first methods for the determination of organic fluorine in human blood is known as the *Wickbold method* and uses combustion, therefore representing a destructive methodology (*Wickbold 1954*). It determines the sum of present organic fluorine after conversion into inorganic fluoride in the sample, and consequently is a non-specific method. However, for perfluorinated molecules, which are thermally stable, this vigorous combustion can still lead to incomplete decomposition, thus underestimating the total amount of organic fluorine (*De Voogt & Saez 2006*). Due to the lack of compound-specific analytical methodologies at that time, no identification of individual analytes was possible until recently.

Kissa 1986 published a method for the sum determination of organofluorine compounds in air. The analytes were collected on a solid adsorbent such as activated carbon (gaseous phase) and on filters (particulate phase), respectively, and determined by a combustion approach similar to the *Wickbold method*.

Gas chromatographic (GC) methods are only applicable to volatile PFAS. All the same, using analyte derivatisation, non-volatile compounds can be made available for GC analyses. *Belisle & Hagen 1980* described the determination of PFOA as its methyl ester after derivatisation with diazomethane using GC coupled to an electron capture detector (ECD). All the same, the ECD detector may not be sufficiently specific for complex matrices (*De Voogt & Saez 2006*). *Moody & Field 1999* used GC-MS with electron impact (EI) ionisation for the determination of C_6-C_8 and C_{12} PFCAs in groundwater impacted by fire-fighting activity. PFCAs were derivatised with methyl iodide to their methyl esters before analysis. A recent method used GC/negative chemical ionisation (NCI)-MS for the analysis of the PFCA isomer structure distribution in human blood after derivatisation with 2,4-difluoroaniline as described by *De Silva & Mabury 2006*.

Ellis et al. 2000 applied ^{19}F nuclear magnetic resonance (NMR) for the analysis of short-chain PFAS in rain water samples, in combination with GC-MS confirmation. NMR is non-specific, as it determines the presence of CF_2 and CF_3 moieties in a sample (*De Voogt & Saez 2006*). *Moody et al. 2001* used ^{19}F-NMR for the determination of total PFAS concentrations in surface water samples collected after an AFFF spill. For comparison of the ^{19}F-NMR results, they used HPLC/(-) ESI-MS/MS for target analyses of single compounds. As expected, LC-MS results were significantly lower as target analysis only quantified $\leq$30% of the total PFAS concentrations determined by ^{19}F-NMR.

Hansen et al. 2001 developed a compound-specific, quantitative method for PFAS in biological matrices using HPLC/(-)ESI-MS/MS. PFOS, PFHxS, PFOA and PFOSA were analysed in human serum samples. Confirmation of the target analytes by high-resolution time-of-flight (TOF)-MS was done.

Berger et al. 2004a compared three different types of mass spectrometers coupled to HPLC, namely ion-trap MS, triple-quadrupole MS/MS and high-resolution TOF-MS. In all cases, ESI was the ionisation method leading to best results. In their study, TOF-MS was found to be the most sensitive and selective methodology. However, due to low distribution of TOF-MS instruments in laboratories, triple-quadrupole MS/MS is the methodology used most frequently.

Recently, the total organic fluorine approach following *Wickbold 1954* has been improved in terms of sensitivity as described by *Miyake et al. 2007* by eliminating high background levels of instrument blanks. The authors determined total fluorine, inorganic fluorine and organic fluorine by combustion ion chromatography (CIC) in different matrices at environmental levels. Interestingly, in their pilot study with non-occupationally exposed human blood, the regularly analysed target compounds only represented a minor fraction ($\leq$15%) of total fluorine contents. The same holds for seawater samples taken far from known contamination sources.

Today, HPLC/(-)ESI-MS/MS is the instrumentation used most frequently for analysis of ionic and non-ionic PFAS in many kinds of sample matrices. Occasionally, HPLC/(-)ESI-MS or HPLC/(-)ESI-TOF-MS are applied. For analysis of neutral, volatile compounds, GC-MS with chemical ionisation (CI) has been used. Current analytical protocols for the determination of PFAS in different matrices are described in more detail in the following subchapters.

1.2.2. Analysis of PFAS in humans and biota

The original method for the determination of individual PFAS as described by *Hansen et al. 2001* is still the one used most frequently. It extracted the target analytes (PFOS, PFHxS, PFOA, PFOSA) from biological matrices like blood serum or homogenised liver samples using ion-pair extraction with methyl *tert*-butyl ether (MTBE). The extraction method was combined with selective determination by HPLC/(-)ESI-MS/MS. Limits of detection (LODs) were between 1-2 ng/mL sera and 2-8.5 ng/g liver, respectively.

Recently, a new extraction method for PFAS in human whole blood samples using solid-phase extraction (SPE) cartridges was described by *Kärrman et al. 2005*. Quantitative determination of PFBS, PFHxS, PFOS, PFDS, C_6, C_8-C_{12} and C_{14} PFCAs as well as PFOSA was done by HPLC/(-)ESI-MS with LODs of 0.1-2 ng/mL and limits of quantification (LOQs) of 0.3-3 ng/mL. A method for the determination of neutral PFAS in biota using gas chromatography coupled to mass spectrometry with positive chemical ionisation (GC/PCI-MS) was described by *Tittlemier et al. 2005*, with LODs of 0.1-0.25 ng/g. They also applied their analytical protocol to food samples (see ***chapter 1.2.4***).

Kuklenyik et al. 2004 developed a method for PFAS determination in human serum and milk. Samples were added to 0.1 M formic acid and sonicated before SPE on Oasis HLB columns. HPLC/(-)ESI-MS/MS was performed to determine PFHxS, PFOS, C_5-C_{12} PFCAs, PFOSA and two additional analytes at LODs of 0.1-1 μg/L milk. *So et al. 2006* used a slightly modified analytical protocol with Oasis WAX cartridges, thus allowing for a 100% MeOH wash step. The investigated analytes (PFBS, PFHxS, PFOS, C_6-C_{11} PFCAs, 8:2 saturated fluorotelomer carboxylate (FTCA), 8:2 unsaturated fluorotelomer carboxylate (FTUCA)) were then eluted using 0.1% NH_4OH and analysed with LOQs between 1.0 and 50 ng/L.

1.2.3. Analysis of PFAS in aqueous matrices

The first analytical method for the extraction of PFCAs from ***groundwater*** was reported by *Moody & Field 1999*. They performed SPE of the target analytes on strong anion exchange (SAX)-disks followed by derivatisation and GC/EI-MS analysis as already discussed above. Due to the non-volatility of PFOS and the instability of derivatives as also described by *De Voogt & Saez 2006*, this analytical protocol was not amenable to perfluoroalkane sulfonates. LOQs were very high, e.g. 36 μg/L for PFOA.

Moody et al. 2001 analysed PFCAs, PFBS, PFHxS and PFOS in ***surface water*** samples using HPLC/(-)ESI-MS/MS and ^{19}F-NMR, with LOQs of the LC-MS method for PFOA and PFOS of 9 and 17 ng/L, respectively. *Hansen et al. 2002* used a similar method applying SPE on C_{18} cartridges and achieved LOQs of PFOA and PFOS of 25-50 ng/L and 10-25 ng/L, respectively. Today, very sensitive analytical protocols for the analysis of PFAS in surface water such as the one described by *Yamashita et al. 2004* are used, achieving LOQs of PFBS, PFHxS, PFOS, PFOA, PFNA and PFOSA at the low pg/L level. However, blank problems resulting from instrument or method blank contamination often impede the trace-analytical determination of PFOA and similar compounds in water samples from remote locations.

Takino et al. 2003 used an automated on-line extraction system for the analysis of PFOS in river water. Atmospheric pressure photoionisation (APPI) was applied as HPLC-MS/MS interface with an LOQ of 17.9 ng/L. As an important advantage of the APPI interface, *Takino et al.* point out that it is significantly less susceptible to matrix effects than ESI.

Alzaga & Bayona 2004 described a method for the extraction of PFCAs from ***STP effluents and sea water*** using ion-pair solid-phase microextraction followed by in-port derivatisation-GC/NCI-MS. Due to high LODs (e.g. 0.75 μg/L for PFHpA), this method is only applicable to samples with high PFAS content. For the analysis of ***wastewater*** as described by *Sinclair & Kannan 2006*, samples were allowed to settle before careful decantation of an aliquot and subsequent SPE as described for surface water samples. According to *Schultz et al. 2006a*, large-volume injection into the HPLC/(-)ESI-MS/MS system was done directly after centrifugation of raw influent and final effluent STP samples without analyte preconcentration steps.

Regarding ***precipitation***, *Kallenborn et al.* used Oasis HLB SPE cartridges and analysed the samples by HPLC/(-)ESI-TOF-MS (*NMR 2004*). *Loewen et al. 2005* published a trace-analytical protocol for rainwater samples. Preconcentration of the analytes was done on C_{18} SPE cartridges, followed by HPLC/(-)ESI-MS/MS determination. The study focused on PFOS and C_8-C_{12} PFCAs with LODs of 0.39 ng/L (PFOS) up to 7.2 ng/L (PFOA), as well as on oxidative products of atmospherically transported FTOHs, including FTCAs and FTUCAs. LODs of FTCAs and FTUCAs were between 0.04 and 0.17 ng/L, respectively. *Scott et al. 2006a* developed a new analytical protocol for the determination of C_2-C_9 PFCAs from precipitation samples. They performed GC-MS analyses for the 2,4-difluoroanilides of PFCAs and achieved LODs of 0.5 ng/L for single compounds.

1.2.4. Analysis of PFAS in solid matrices

The analysis of neutral PFAS in ***food***, fish or Arctic marine mammal samples was described by *Tittlemier et al. 2005*. The analytes were solvent extracted with hexane/acetone (2:1, v/v) twice, centrifugated and the combined organic phases were concentrated. Co-extracted lipids were removed by washing with concentrated sulphuric acid, a silica gel clean-up was performed and isooctane was added. Quantitative determination of the analytes was done using GC/PCI-MS. PFOSA, NEtFOSA and N,N-diethyl fluorooctane sulfonamide (N,N-Et_2FOSA) showed LOQs of 0.83, 0.40 and 0.33 ng/g, respectively. *Gulkowska et al. 2006* used the modified *Hansen et al.*

2001 analytical protocol including ion-pair extraction and analysis by HPLC/(-)ESI-MS/MS for the determination of PFBS, PFHxS, PFOS as well as C_6-C_{11} PFCAs in seafood samples from China. LOQs for all analytes were 0.25 ng/g ww.

The analysis of PFOS and PFOA in vacuum cleaner ***dust*** was described by *Moriwaki et al. 2003*. Sample extraction was done with methanol (MeOH) by ultrasonic agitation. After centrifugation, an aliquot was filtered and analysed using HPLC/(-)ESI-MS/MS with LODs of 10 (PFOS) and 50 ng/g (PFOA). In the method developed by *Shoeib et al. 2005*, sieved household dust samples were Soxhlet-extracted with dichloromethane (DCM). Subsequently, analysis of neutral, volatile PFAS was done by GC-MS.

Powley et a. 2005 described a 'matrix effect-free' method for the determination of PFCAs in ***soil, sediment and sludge*** with LODs of 1 ng/g. MeOH was added to STP sludge samples before shaking for 30 min. The extract was allowed to settle before removing an aliquot. For soil and sediment, samples were suspended in 200 mM NaOH prior to shaking. Neutralisation was done with HCl. In the following, the sample aliquot was added to Envi-Carb graphitised carbon adsorbent with glacial acetic acid, and the vial was vortex-mixed. After centrifugation, the supernatant was pipetted into autosampler vials for HPLC/(-)ESI-MS/MS analysis.

Higgins et al. 2005 developed a method for the determination of PFAS in ***sediments and sludge***. The air-dried and acidified samples were washed with 1% acetic acid and liquid solvent extracted several times with MeOH / 1% acetic acid (90/10, v/v) in a heated sonication bath. Subsequently, a clean-up via SPE and HPLC/(-)ESI-MS/MS analysis were done. LODs of 0.7-2.2 ng/g and 0.011-0.246 ng/g dw were achieved for sludge and sediment, respectively.

The determination of PFAS in ***sediment*** was described by *Lucaciu et al. 2005*. Two extractions with MTBE were done, and the combined extracts were concentrated, filtered and evaporated to dryness. After reconstitution in MeOH, HPLC/(-)ESI-MS/MS analysis was done. The modified method described for biota samples by *Hansen et al. 2001* can also be applied for STP sludge. *Crozier et al. 2005* reconstituted dried ***STP sludge*** in water prior to ion-pair extraction with MTBE combined with HPLC/(-)ESI-MS/MS determination. *Nakata et al. 2006* described the analysis of PFAS in ***sediments***. Extraction was done twice with MeOH and ultrasonication for 30 min each. The method was characterised by LOQs of 0.3 (PFOS), 3.0 (PFOA), and 1.5 ng/g ww (PFHxS, PFNA, PFOSA).

1.2.5. Analysis of PFAS in air

In this subchapter, an overview of the current methodology for the quantitative trace analysis of airborne neutral PFAS is given, including GC/CI-MS and LC/(-)ESI-MS(/MS). The original method for the determination of neutral, volatile precursors of PFOS and PFCAs was developed by *Martin et al. 2002*. The analytical protocol was optimised for the determination of a suite of FTOHs (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH) and FOSAs / FOSEs (NEtFOSA, NMeFOSE, NEtFOSE) in ***high-volume air samples*** (850 m^3). The enrichment of the analytes was done on glass-fibre filters (GFFs, particulate phase) and a polyurethane foam (PUF)/XAD-2 resin/PUF cartridge (gaseous phase).

Extraction of both GFFs and PUF/XAD columns was done using ethyl acetate (EtOAc). The internal standard (IS), 7:1 fluorinated alcohol (7:1 FA), was added to the extracts before concentration to 150 μL and subsequent analysis by GC/CI-MS. For quantification of the analytes, PCI was used, yielding LODs between 0.15 (10:2 FTOH) and 6.2 pg/m^3 (NEtFOSE). However, as NEtFOSA only produced one *m/z*, NCI was additionally used for confirmation of this compound (*Martin et al. 2002*). A similar analytical protocol was used by *Stock et al. 2004b*.

Slight variations included the use of 9:1 FA as IS. Mean sample volumes were 880 ± 312 m^3 with LODs of 0.3 (NEtFOSA) up to 5.0 pg/m^3 (6:2 FTOH).

Sasaki et al. 2003 first described the determination of PFOS in airborne particulate matter. High-volume air samples of approx. 1400 m^3 were taken, and particles were collected on quartz-membrane filters. After accelerated solvent extraction (ASE) with 10% MeOH solution, the extracts were solid-phase extracted and eluted with MeOH. Samples were concentrated and analysed using HPLC/(-)ESI-MS. *Harada et al. 2005* extended the method to the analysis of PFOA.

Shoeib et al. 2004 published an analytical protocol for the determination of NMeFOSE, NEtFOSE and N-methyl perfluorooctane sulfonamidethylacrylate (NMeFOSEA) in high-volume air samples at LODs between <0.3-20 pg/m^3. The analytes were enriched on GFFs (particulate phase) and PUF plugs (gaseous phase). Both indoor and outdoor air were investigated, with sample volumes of 100-200 m^3 or 300-600 m^3, respectively. Sampling materials were Soxhlet extracted separately with DCM (GFFs) and 1:1 petroleum ether/acetone (PUFs). Extracts were concentrated, and the solvents were exchanged to EtOAc. The recovery internal standard (RIS, mirex) was added to final extracts just before GC/EI-MS determination.

In *Shoeib et al. 2005*, a different analytical protocol was used. ***Passive air samplers*** with PUF disks were used to enrich NEtFOSA, NMeFOSE, NEtFOSE and NMeFOSEA in indoor and outdoor environments. LODs of the target analytes were 0.01, 7.1, 5.4 and 0.05 pg/m^3, respectively. Passive samplers were calibrated against ***low-volume air samplers*** at selected indoor locations. Soxhlet extraction was done with petroleum ether, and the solvent was exchanged to isooctane. GC/EI-MS analyses were confirmed in some cases by GC/NCI-MS measurements. Recently, XAD-impregnated PUF disks were tested for passive sampling of FTOHs, which cannot be enriched on PUF only. However, results are not available yet.

Shoeib et al. 2006 presented a ***high-volume air sampling*** method for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, NMeFOSE, NEtFOSE and NMeFOSEA using GFFs for the particulate phase and PUF/XAD-2/PUF columns for the gaseous phase. Sampling volumes were approx. 300 m^3. LODs were the following (pg/m^3): 1.1 (6:2 FTOH), 3.5 (8:2 FTOH), 0.8 (10:2 FTOH), 1.9 (NMeFOSE), 1.0 (NEtFOSE) and 0.001 (NMeFOSEA). The IS (NMeFOSA [M+3]) was added before Soxhlet extraction with petroleum ether/acetone (50:50, PUF/XAD) or DCM (GFFs). EtOAc was added as a keeper. PUF/XAD extracts were additionally cleaned-up on alumina columns and eluted with DCM/EtOAc (32.5:67.5). The RIS (N,N-dimethyl fluorooctane sulfonamide, N,N-Me_2FOSA) was added to final extracts before GC/PCI-MS analysis. FOSEs were confirmed by GC/EI-MS (*Shoeib et al. 2006*).

Berger et al. 2005a presented an analytical protocol for the determination of neutral, volatile as well as ionic PFAS in high-volume air samples of 1000-1400 m^3. The method for 10:2 FT-olefin, 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, NMeFOSA, NEtFOSA, NMeFOSE and NEtFOSE was adapted from *Martin et al. 2002*, while ionic compounds (PFBS, PFHxS, PFOS, PFDS, C_6-C_{11} PFCAs) present in the particulate phase were extracted from halved GFFs with MeOH. The IS used were 7:1 FA (GC) or the branched PFDA isomer perfluoro 3,7-dimethyl octanoic acid (b-PFDA, LC). Before determination by GC/CI-MS or HPLC/(-)ESI-TOF-MS, the respective RIS were spiked: 1,2,3,4-tetrachloronaphthalene (TCN, GC) or 3,5-bis(trifluoro-methyl)phenyl acetic acid (BTPA, LC). LOQs were individually derived for each sample batch, but ranged from 0.2-50 or 0.45-56 pg/m^3 for neutral and ionic PFAS, respectively.

Regarding LC methods for neutral, volatile PFAS, MS/MS was used on one occasion for FTOHs with LODs of 1-20 pg (*Berger et al. 2004a*), and on another for NEtFOSA and two

fluorinated alcohols (LODs = 0.02-0.1 pg, *Taniyasu et al. 2005*). Furthermore, *Szostek et al. 2006* described a method for the LC-MS/MS determination of FTOHs in water samples at LODs of 0.09, 0.09 and 0.06 ng/mL for 6:2 FTOH, 8:2 FTOH and 10:2 FTOH, respectively.

LC-MS was applied for NEtFOSA and NEtFOSE with LODs of 0.02 pg (*Boulanger et al. 2004*). Despite lower or comparable LODs using LC methods compared with GC methodologies, possible co-analysis of non-ionic and ionic PFAS is impeded by ionisation suppression of FTOHs caused by buffered mobile phases, which are necessary to separate ionic PFAS (*Berger et al. 2004a*). The only application of an LC-MS method to air samples is described by *Boulanger et al. 2005a* without the specification of method detection or quantification limits (MDLs / MQLs), thus not permitting comparison of method sensitivities.

Boulanger et al. 2005a described ***high-volume air sampling*** (95-378 pg/m^3) of PFOS, NEtFOSA and NEtFOSE in the particulate as well as the gaseous phase on GFFs and XAD-2 resin, respectively. Both sampling materials were extracted separately with acetone/hexane. A clean-up using florisil columns was performed, followed by elution with EtOAc. The extracts were concentrated to 100 μL and analysed by LC/(-)ESI-MS.

Kaiser et al. 2005 published a method for the determination of PFOA in occupationally exposed ***low-volume air samples*** of 480 L. Occupational Safety and Health Administration (OSHA) Versatile Samplers (OVS) equipped with GFFs, XAD resin and PUFs were used in their study. Extraction was done with MeOH after spiking of the IS (PFDA). The RIS (^{13}C-labelled PFOA) was spiked to the extracts and HPLC/(-)ESI-MS(/MS) analysis was performed. However, due to the high validated concentration range (0.47-47 μg/m^3), this method is not applicable to environmental air. *Barton et al. 2006* used the same sampling setup, but additionally applied a ***high-volume cascade impactor***. This device was used to obtain different particle size fractions at >4.0, 1.7, 0.8, 0.5, 0.3 and <0.28 μm. The LOD was reported to be 70 ng/m^3.

1.3. Environmental concentration levels and time trends

In the following, PFAS levels in humans (***1.3.1***) with time trends, biota (***1.3.2***) with time trends, the aqueous phase including precipitation (***1.3.3***), solid samples including food, dust, sediment and STP sludge (***1.3.4***) as well as indoor and outdoor air (***1.3.5***) are outlined.

1.3.1. PFAS levels in humans

An overview of PFAS levels in humans is given in Table 4. The original method described by *Hansen et al. 2001* formed the first data set of PFOA, PFHxS, PFOS and PFOSA in non-occupationally exposed human blood from several biological supply companies in the ***U.S.***

Olsen et al. 2003a analysed ***occupationally exposed human blood serum*** taken at the 3M Decatur plant. PFAS levels in workers from the fluorochemical plant were approximately one order of magnitude higher than those of employees in a different branch of industry. In a further study, *Olsen et al. 2003b* analysed ***human serum and liver***. Among the 23 paired samples, the mean liver to serum ratio of PFOS was 1.3:1. For the additionally analysed PFOA, PFHxS and PFOSA, no liver to serum ratios were calculated because most of the liver samples and many serum analyses were <LOQ.

Kannan et al. 2004 compared the levels of PFOA, PFHxS, PFOS and PFOSA in human blood from different countries. A total of 473 human blood / serum / plasma samples were collected in the ***U.S.***, ***Colombia***, ***Brazil***, ***Italy***, ***Poland***, ***Belgium***, ***India***, ***Malaysia***, ***Korea*** and ***Japan***. *Kubwabo et al. 2004* analysed PFAS in human blood samples from ***Canada***. PFOS and PFOA were found at similar levels as in the U.S.

Table 4. Overview of PFAS concentration levels in human blood (ng/mL).

Origin	*n*	Date	PFHxS	PFOS	PFDS	PFOSA	PFHxA	PFOA	PFNA	PFDA	PFUnA	Remarks	Reference
U.S.	65		<1.5-21.4	6.7-81.5		<1.5 2.2		<5-35.2				from blood supply companies	*Hansen et al. 2001*
U.S.	126 60		5-1880 1-210	91-10600 15-946		0.5-612 <LOQ		21-6160 6-298				occup. exposed (occup. exposed)	*Olsen et al. 2003a*
U.S.			<1.2-5.9	<6.1-58.3		<1.3 22.1		<3.0-7.0				matched with liver samples	*Olsen et al. 2003b*
U.S.	175		0.2-32	<1.3-164		<1.3-26		<3-88					
Colombia	56		<0.4-0.9	4.6-14		<0.4-5.6		3.7-12.2					
Brazil	29		<0.6-15.3	4.3-35		<0.4-2.3		<20					
Italy	50		<1-2.1	<1-10.3		<1.3-2.3		<3					
Poland	25	2000-04	<0.4-2.6	16-116		<0.4-7.7		9.7-40					*Kannan et al. 2004*
Belgium	20		<1-1.4	4.5-27		<3		<1-13					
India	45		<1-2.9	<1-3.1		<3		<3-3.5					
Malaysia	23		1.2-6.8	6.2-18.8		1.3-11		<10					
Korea	50		0.9-20	3.0-92		<0.1-7.2		<15-256					
Japan	38		<2.6-7.6	4.1-40.3		<2.6-9.5		<6.8-12.3					
Canada	56	2002		3.7-65.1		<4.8		<1.2-7.2					*Kubwabo et al. 2004*
Sweden	66	1997-2000	0.4-28.4	1.7-37.0	<0.1-4.5	0.4-22.9	<0.1-1.6	0.5-12.4	<0.1-1.9	<0.1-0.6	<0.1-0.7		*Kärrman et al. 2006a*
Australia	20	2002-03	2.7-19	12.7-29.5		0.36-2.4		5.0-9.9	0.4-2.0			pooled samples	*Kärrman et al. 2006b*
Sweden	12	2004	1.8-11.8	8.2-48.0	<0.1-0.33	<0.10-0.49		2.4-5.3	0.43-2.5	0.27-1.8	0.20-1.5	matched with milk samples	*Kärrman et al. 2006c*
Germany	356	2005		2.1-55				0.5-19.1					*Fromme et al. 2006*
China	85	2004		mean 3.72-79.2									*Yeung et al. 2006*
U.S.	16	2004-05						0.9-8.6	0.17-1.2	0.05 0.25	n.d. 0.06	pooled samples	*De Silva & Mabury 2006*
Japan	15	2003		4.9-17.6 1.6-5.3		<1.0 <1.0		<0.5-2.3 <0.5				maternal blood cord blood	*Inoue et al. 2004*
Japan	39 23 225	1977 2003 2003		GM 1.1 GM 3.5 GM 3.5-28.1				GM 0.2 GM 2.8 GM 2.8-12.4				females only females only	*Harada et al. 2004*
Germany	10 16	1985 2004		14.9-103.7 8.3-33.1				5.6-32.8 3.0-36.0					*Schröter-Kermani 2005*
U.S.	178 178	1974 1989	<1.4-2.5 1.3-1.6	21.1-40.2 25.0-44.0				<1.0-3.0 4.4-6.7					*Olsen et al. 2005a*

GM geometric mean.

Kärrman et al. 2006a analysed PFOA, PFHxS, PFOS and PFOSA in all whole blood samples from ***Sweden***, while PFDS, PFNA, PFDA and PFUnA were additionally found in some samples.

In another study, *Kärrman et al. 2006b* investigated PFAS in 40 pooled serum samples from ***Australia***, revealing PFOA, PFNA, PFHxS, PFOS and PFOSA in all samples. Furthermore, PFDA, PFUnA, PFDoA and PFDS were detected in some samples. *Kärrman et al.* found higher concentrations for PFNA in females, while levels of PFOA, PFHxS and PFOS were higher in males. PFAS concentrations were positively correlated with age, although no regional trends (urban – rural) were observed.

Fromme et al. 2006 published a study on the occurrence of PFAS in blood plasma from Southern ***Germany***. PFOA and PFOS were found in all samples. The study showed that median PFOA and PFOS levels in males were significantly higher than in females. Furthermore, a significant correlation of PFOA and PFOS levels with age was found, although in females only.

Yeung et al. 2006 observed PFOS and related PFAS in human blood samples from nine different regions in ***China***. The authors found gender-dependent concentration differences (PFOS and PFHxS higher in males, PFUnA higher in females), but no age-dependence. Furthermore, regional patterns were observed.

De Silva & Mabury 2006 investigated the ***isomer distribution*** of PFCAs in human blood, thus showing potential correlations to the source. Exposure of the general human population to PFCAs is assumed to occur either via direct (industrially produced) or indirect (production from precursors) sources. PFOA was the predominant PFCA. Isomer profiles showed mainly (mean ~98%) the linear isomer for C_8-C_{11} PFCAs, suggesting exposure from telomerisation-derived PFAS.

Inoue et al. 2004 described the determination of PFAS in human ***maternal and cord blood*** samples. PFOS was found in both maternal and fetal samples at 4.9-17.6 and 1.6-5.3 ng/mL, respectively, while PFOA was found in maternal blood only and PFOSA was not detected in any kind of samples. For a discussion of possible adverse effects of the observed concentration levels, see ***chapter 1.4***.

Kuklenyik et al. 2004 screened two ***human milk*** samples from the ***U.S.*** for PFAS, but only found PFPeA in one sample (1.56 μg/L) and PFHxA in the other one (0.82 μg/L). So *et al. 2006* analysed PFAS in 19 human breast milk samples from ***China***. The method showed LOQs of ≤50 ng/L, thus allowing for quantification of several PFAS in many samples. PFOS and PFOA were the predominant compounds found in all samples with concentrations of 45-360 ng/L and 47-210 ng/L, respectively, followed by PFHxS (4.0-100 ng/L), PFNA (6.3-62 ng/L), PFUnA (7.6-56 ng/L) and PFDA (3.8-15 ng/L). Additional analytes were quantified in some samples.

Kärrman et al. 2006c reported PFAS levels in 12 matched samples of human breast milk and serum from ***Sweden***. In serum samples, PFOS showed highest concentrations, followed by PFHxS, PFOA, PFNA, PFDA, PFUnA and PFOSA. PFDS was only detected once. PFOS and PFHxS were found in all milk samples at mean concentrations of 201 ng/L and 85 ng/L, respectively. Furthermore, PFOSA was frequently detected (13 ng/L, n = 8), whereas PFOA and PFNA were only detected occasionally and PFUnA as well as PFDoA were <8 and <5 ng/L, respectively. The resulting serum-to-milk ratios were 113 (PFOS), 57 (PFHxS) and 22 (PFOSA), respectively. PFOS as well as PFHxS concentrations in serum and milk showed a significant positive linear relationship.

To conclude, PFAS levels from different studies in various countries can be set into context (see Table 4). Levels in the U.S. and in China turned out to be the highest, while Italy, India

and Colombia showed rather low values. Generally, PFOS levels are the highest observed among the target analytes, regardless of the origin of the investigated samples. An overview of concentration levels in humans is also given in a recent review article by *Houde et al. 2006a*. Concerning correlations between PFAS levels and age, gender or region (urban – rural), results are ambiguous and do not draw the same conclusions. Further research is needed in this respect. Finally, the observation of PFAS in maternal as well as fetal cord blood and human milk samples requires additional investigations on the daily intake and effects of PFAS levels in infants.

Time trends

Harada et al. 2004 described the influence of time, sex and geographic factors on levels of PFOS and PFOA in humans from Japan between ***1977 and 2003***. Significant differences between sexes were observed with higher levels in males, as well as regional patterns. However, no age-dependence was found. Over the last 25 years, levels of PFOS and PFOA increased by factors of 3 and 14, respectively. Geometric mean concentrations in females at one of the locations were 1.1 (PFOS, 1977) up to 3.5 ng/mL (PFOS, 2003) and 0.2 (PFOA, 1977) up to 2.8 ng/mL (PFOA, 2003). In another Japanese district, only PFOA levels in males increased significantly between 1991 (2.2 ng/mL) and 2003 (3.4 ng/mL), while PFOS concentrations in males as well as levels of both PFAS in females seem to have reached a plateau in the early 1990s.

One investigation from ***Germany*** was described by *Schröter-Kermani 2005*. Blood plasma samples from the German Specimen Bank from ***1985-2004*** were analysed for PFHxS, PFOS, PFOSA, PFHxA and PFOA. PFHxS was detected in 6 of 116 samples at >1 ng/mL, while PFHxA and PFOSA were <2 and <1 ng/mL, respectively. For PFOS and PFOA, detected in all samples, a significant decrease of concentrations was observed with a plateau of PFOS levels between 1990 and 2001. The mean PFOS concentration from 2004 (16.2 ng/mL) was higher than levels reported for Italy, but lower than U.S levels. However, the PFOA level (6.5 ng/mL, 2004) of the German population was in the same range as concentrations found in the U.S.

Another historical comparison of PFAS in human blood is given by *Olsen et al. 2005a*. Human blood samples were collected in the ***U.S.*** in 1974 (serum, n = 178), 1989 (plasma, n = 178) and 2001 (serum, n = 108). The median 1974 and 1989 PFAS concentrations were determined as: 2.3 against 5.6 ng/mL (PFOA), 1.6 against 2.4 ng/mL (PFHxS) and 29.5 against 34.7 ng/mL (PFOS), respectively. Statistical analysis showed that in 58 paired samples, PFOA, PFHxS and PFOS were significantly higher concentrated in 1989 compared to 1974. A comparison between levels determined in 1989 and 2001 showed no significant increase, thus representing again a plateau of PFAS levels in humans in the 1990s.

1.3.2. PFAS levels in biota

A summary of PFAS levels in biota is given in Table 5. The first overview of PFOS levels in biota was given by *Giesy & Kannan 2001*. They described its ***global distribution*** in wildlife samples from industrialised regions in North America and Europe as well as less urbanised locations such as the Arctic and the North Pacific Ocean. Samples included liver / muscle tissue and blood plasma of fish, birds and marine mammals. By means of this study, *Giesy & Kannan* demonstrated the ubiquitous occurrence of PFOS, with higher levels in animals from industrialised regions. Furthermore, predators showed higher levels than their diets, thus indicating biomagnification potential. Highest plasma concentrations were found for bald eagles at 1-2570 ng/mL. Liver tissue showed maximum values in mink (970-3680 ng/g ww).

Table 5. Overview of PFAS concentration levels in biota (ng/mL blood or ng/g tissue).

Species	Origin	PFBS	PFHxS	PFOS	PFOSA	8:2 FTUCA	10:2 FTUCA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrA	PFTA	PFPDA	Remarks	Reference
Ringed Seals	Arctic			<3-14												plasma	*Giesy & Kannan 2001*
Mink	U.S.			970-3680												liver	
Polar Skua	Antarctica			<1-1.4												plasma	
Bald eagles	U.S.			1-2570												plasma	
Mink	U.S.		<4.5-85	20-5140	<37-590			<4.5-27								liver	*Kannan et al. 2002a*
River otters			<4-76	25-994	<4-72			<7.5-19								carcass	
Birds	Japan		<7.5-34	<19-650	<75-215			<19-21								liver	*Kannan et al. 2002c*
Oysters	U.S.			<43-1230												whole body	*Kannan et al. 2002d*
Polar bears	Canadian Arctic			1700->4000	<0.5-44			2.9-13	108-230	35-76	56-78	4.7-8.2	7.5-14	<0.5-1.1	<0.5	liver	*Martin et al. 2004b*
Polar bears	Circumpolar Arctic		<3.2-4430	263-6340	<1.7-71.5			<2.3-57.1	12.2-540	9.3-209	6.4-179	<0.6-26.0	<0.6 - 46.9	<0.6-17.5	<0.6-16.3	liver	*Smithwick et al. 2005b*
Glaucous gulls	Norwegian Arctic		<0.27-1.23	51.7-196				<0.70	<2.33	<0.93-4.62	8.74-38.7	<0.78-7.25	4.0-42.4	<0.25	<0.25	egg	*Verreault et al. 2005*
			0.29-2.71	48.1-349				<0.70-0.74	<2.33-6.33	3.07-15.1	32.0-184	2.90-23.9	3.63-30.2	<0.25-2.77	<0.25-0.70	plasma	
Invertebrates	North Sea			9-877												whole body	*Van de Vijver et al. 2003*
Harbour Porpoises	Northern Europe			26-1149				<62	<14-47	~4-~55	~3-~55	~3-~25				liver	*Van de Vijver et al. 2004*
Harbour seals	North Sea	nd-3.28		8.9-2720				nd-11.6	nd-69.8	nd-59.1	nd-30.2	nd-3.42				diverse tissues	*Van de Vijver et al. 2005*
Harbour seals	Black Sea			33-1790					1.4-7.2	1.9-19	1.9-9.5	1.9-9.5				diverse tissues	*Van de Vijver et al. 2006*
Wood mice	Belgium			140-179000					<90-270	<50-190	<30-150	<40-220				liver	*Hoff et al. 2004*
Bottlenose dolphins	U.S.		2.2-332	46-3073	<0.5-102	0.5-1.3	1.1-1.4	0.6-163	3-547	4.3-542	1.7-343	<0.5-62	<0.5 -37	1-4	<0.5	plasma	*Houde et al. 2005*
Diverse	Japan		<1.5	<0.3-927	<1.5-10			<3.0-98	<1.5-44							different tissues	*Nakata et al. 2006*
Fish	Colombia		<0. 7-16	~700-~4500	<0.3			<50 1116								bile	*Olivero-Verbel et al. 2006*
Birds				0.7-132	<1.0-2.7											diverse tissues	
Birds and seals	Antarctica			<0.08-3.52												blood	*Tao et al. 2006*

nd not detected.

Kannan et al. published a series of studies about PFOS in ***marine and freshwater mammals*** from coastal waters (*Kannan et al. 2001a*) and fish-eating water birds including bald eagles and albatrosses from the ***U.S.*** and the central ***North Pacific Ocean*** (*Kannan et al. 2001b*). Further studies extended the analyte spectrum to PFOA, PFHxS, PFOS and PFOSA in mink and river otters from the U.S. (*Kannan et al. 2002a*), marine mammals from the ***Baltic and Mediterranean Seas*** (*Kannan et al. 2002b*), livers of birds from ***Japan and Korea*** (*Kannan et al. 2002c*) and Oysters from the ***Gulf of Mexico*** and the U.S. (*Kannan et al. 2002d*).

Martin et al. 2004b described the first determination of long-chain C_8-C_{15} PFCAs in biota (***polar bears, ringed seals, arctic fox, mink, birds and fish***) from the ***Canadian Arctic***. PFOS was also analysed and showed highest concentrations in most samples. An interesting observation was the pattern that odd-length PFCAs exceeded the concentrations of even-length PFCAs (e.g. PFNA > PFOA). This fact corroborated the LRAT theory of neutral, volatile precursors and subsequent degradation to the persistent PFOS and PFCAs in remote regions.

Smithwick et al. conducted further research on PFAS levels in liver tissue of ***polar bears*** from ***East Greenland*** (*Smithwick et al. 2005a*) and liver as well as blood of polar bears from several locations in the ***Canadian and European Arctic*** (*Smithwick et al. 2005b*). PFOS levels in populations from eastern locations (such as Svalbard) were found to be significantly higher than in western populations. PFCA concentrations with adjacent chain lengths (e.g. C_9:C_{10}, C_{11}:C_{12}) showed significant correlations, suggesting a common source within one location.

De Silva & Mabury 2004 isolated different PFCA isomers in ***polar bears*** from ***Greenland and the Canadian Arctic***. While a variety of branched PFOA isomers were found in addition to the prevailing linear isomer in the Greenland bears, Canadian bears only showed the linear isomer, indicating different sources. However, the fractions of branched isomers in Greenland bears were very small, so that an additional input from an exclusively linear isomer source was suggested. PFDA, PFUnA and PFDoA also had minor fractions of a single branched isomer each, while PFNA and PFTrA were exclusively linear.

Verreault et al. 2005 analysed PFAS in plasma, liver, brain and eggs of ***glaucous gulls*** from the ***Norwegian Arctic***. PFOS was the predominant compound in their study with highest levels in plasma, followed by liver ≈ egg > brain. Furthermore, C_{10}-C_{13} PFCAs were determined. Highest proportions were found for the odd-numbered PFUnA and PFTrA. Several PFAS were additionally analysed, but could not be quantified in any of the samples.

Van de Vijver et al. reported several studies on PFAS levels in marine biota from temperate regions. *Van de Vijver et al. 2003* conducted a study on PFOS in ***aquatic invertebrates*** (shrimp, crab, starfish) from the Western Scheldt estuary and the southern ***North Sea***. In general, higher concentrations were found near Antwerp, close to a major fluorochemical manufacturing facility. In liver samples from ***harbour porpoises*** by-caught along the ***coasts of the German Baltic Sea, Denmark, Iceland and Norway***, PFOS and C_8-C_{12} PFCAs were analysed as described by *Van de Vijver et al. 2004*. PFOS was the predominant compound. A decreasing geographical trend from south to north was observed. PFOA and PFNA were found only sporadically, while PFDA, PFUnA and PFDoA were frequently detected.

The compound-specific tissue distribution of PFAS in the liver, kidney, blubber, muscle and spleen tissue of ***harbor seals*** from the ***Dutch Wadden Sea*** was investigated by *Van de Vijver et al. 2005*. They analysed PFBS, PFOS as well as C_4 and C_8-C_{12} PFCAs. PFOS was found to be the predominant compound detected in all samples with the maximum concentration in muscle tissue. However, large differences between tissues were observed. Generally, PFNA was the

dominant PFCA found in all tissues, with decreasing levels along with increasing carbon chain length. PFBA was not detected above the LOD, while PFBS was detected in spleen tissue only at low levels. PFBS could be the atmospheric degradation product of C_4 chemicals which are produced as substitutes to the C_8 analogues phased out in 2002.

Van de Vijver et al. 2007 described PFAS concentrations in liver, kidney, muscle, brain and blubber of ***harbor porpoises*** from the ***Black Sea***. PFOS was the predominant compound, accounting for on average 90% of total PFAS. Levels were greatest in liver, followed by kidney, while blubber, muscle and brain showed lower concentrations. Only in liver tissue with highest PFOS levels, C_9-C_{12} PFCAs were found, while PFOA, PFBA and PFBS were not detected at >2.1, >3.2 and >1.6 ng/g ww, respectively. No significant sex or age-related differences could be observed in this study.

A study about PFAS levels in ***wood mice*** (*Apodemus sylvaticus*) captured close to a fluorochemical plant in Antwerp, ***Belgium***, was reported by *Hoff et al. 2004*. Concentrations of PFOS in liver tissues were extremely high (mean 26200 ng/g ww), whereas mice captured 3 km away from the respective site had much lower liver concentrations. No sex-dependence was observed, while higher PFOS levels were observed in older mice. In several samples from the contaminated site, C_9-C_{12} PFCAs were additionally detected.

Houde et al. 2005 published a study of PFAS in the plasma of ***bottlenose dolphins*** from the ***Gulf of Mexico and the Atlantic Ocean***. They determined eight compounds in all samples, with PFOS being the predominant analyte. For the first time, 8:2 FTUCA and 10:2 FTUCA, known degradation products of FTOHs and suspected precursors of PFCAs, were detected at low concentrations in the plasma of dolphins. A recent review of concentration levels in biota is given by *Houde et al. 2006a*.

Nakata et al. 2006 investigated concentrations of PFOA, PFNA, PFHxS, PFOS and PFOSA in ***aquatic organisms*** (fish, marine mammals, birds, mussels, crabs) from the Ariake Sea, ***Japan***. *Olivero-Verbel et al. 2006* investigated PFHxS, PFOS, PFOA and PFOSA in ***fish and birds*** from ***North Columbia***, thus representing the first data from Latin America. PFOS was found in all fish bile samples. PFHxS and PFOA were detected less frequently, while PFOSA was not detected at >0.3 ng/mL bile. PFOS concentrations in pelican organs decreased from spleen > liver > lung > kidney > brain > heart > muscle. PFOSA was detected in some pelican tissues, while PFHxS was only found in liver and lung, and PFOA was only detected in one spleen sample.

Further data from the Southern Hemisphere are given in a recent paper by *Tao et al. 2006*. They described PFAS concentrations in ***albatrosses, elephant seals, penguins and polar skuas*** collected in the ***Southern Ocean*** and ***Antarctica***. PFHxS, PFOS, PFDS, C_7-C_{12} PFCAs as well as PFOSA were analysed. PFOS was found to be the major contaminant in Southern Ocean albatross liver, present above the LOQ in 92% of the samples at <0.5-20.7 ng/g ww. PFOA was detected in 30% of the respective samples, at levels of <0.6-7.84 ng/g ww. Further PFAS were not detected. However, in additionally analysed albatross samples from Midway Atoll (***North Pacific Ocean***), long-chain PFCAs were found at concentrations similar to those of PFOS and PFOA. Furthermore, *Tao et al.* determined PFOS at low levels in blood of seals and polar skuas from Antarctica. However, in penguins from Antarctica, no PFOS was detected.

Time trends

The first investigation of time trends in biota was given by *Kannan et al. 2002b* with regards to PFOS in livers of white-tailed ***sea eagles from Germany and Poland***. Samples were taken

between ***1972 and 1999*** in inland and coastal regions. Even though PFOS levels were higher in the 1990s (40 ng/g ww) compared to the 1980s (25 ng/g ww), no clear increasing trends could be found. PFHxS, PFOA and PFOSA were not detected in liver samples at LOQs of 7, 38 and 40 ng/g ww, respectively.

Martin et al. 2004c described a significant increase of PFOS concentrations in ***lake trout from Lake Ontario*** between ***1980 and 2001***. Levels showed a 4.25-fold increase from 43 to 180 ng/g ww in whole body homogenates. However, this time trend was not steady, as levels rose from 1980 to 1989, declined slightly between 1989 and 1995 and rose between 1995 and 2001. The authors attributed the decreasing PFOS concentrations between 1989 and 1995 with a dramatic change in the Lake Ontario food web due to the appearance of zebra mussels.

Holmström et al. 2005 found an increasing time trend of PFOS in ***guillemot eggs*** from the ***Baltic Sea*** sampled in ***1968-2003***. Doubling times of 7-10 years were found. However, after a peak of concentrations (1324 ng/g ww in 1997), levels were declining (see Figure 2). PFOA was not detected in any of the samples at levels above the LOD of 3 ng/g ww.

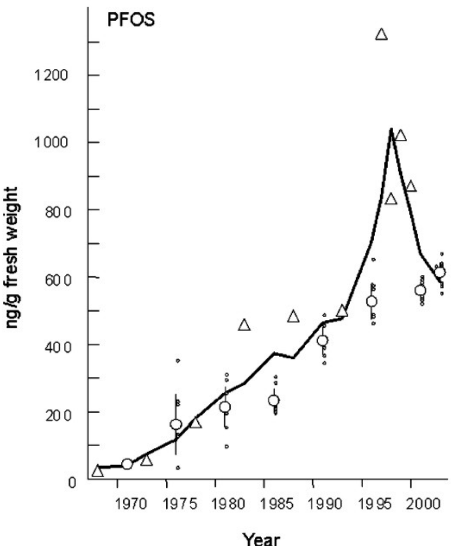


Figure 2. Temporal trend of PFOS concentrations in guillemot eggs from the Baltic Sea, 1968-2003. Reproduced from Holmström et al. 2005.

Bossi et al. 2005 investigated temporal trends of PFAS in ***ringed seals*** from the ***Greenland Sea***. Samples were collected between 1986 and 2003 in East Greenland, while sampling in West Greenland took place in ***1982-2003***. PFOS was found to be the compound contributing most to the PFAS burden, followed by PFUnA. PFNA and PFDA were detected in most samples, while PFHxS and PFOSA were found only sporadically. PFOA was not detectable in any of the samples at >1.2 ng/g ww. For PFOS, PFDA and PFUnA, a temporal trend with increasing concentrations was found.

Smithwick et al. 2006 described temporal trends of PFAS in ***polar bears*** from two locations in the ***Canadian Arctic*** between ***1972-2002***. Concentrations of PFOS, PFNA, PFDA and PFUnA showed exponentially increasing concentrations at both locations, with doubling times between 3.6 ± 0.9 years (PFNA, eastern group) and 13.1 ± 4.0 years (PFOS, western group). PFOSA concentrations decreased over time at both locations. *Butt et al. 2007* recently presented evidence of declining concentrations of PFOS and PFOSA in recent samples of ***ringed seals*** from the Canadian Arctic between ***2000 and 2005***. Levels increased from ***1972 to 2000***, and showed a decrease in 2004 and 2005. For C_9-C_{15} PFCAs, increasing levels were found between

the early 1990ies and 2005. The authors concluded that the relatively short PFCA doubling times (7.7-19.4 years) and PFOS disappearance half-lives (3.2-4.6 years) supported LRAT as the main transport mechanism of PFAS to the Arctic environment.

Kannan et al. 2006 published rather high concentrations of PFOS and PFOA in female ***sea otters from California*** (<1-884 (the upper value was classified as an outlier) ng/g ww and <5-147 ng/g ww, respectively). Mean PFOA levels (60 ng/g ww) were higher than mean PFOS concentrations at 55 ng/g wwt. Levels of PFNA were lower (<1-16 ng/g ww), while PFHxS was not detected in any sample at >1 ng/g ww. The authors described a significant increase of PFOA concentrations between ***1992 and 2002***, while PFOS levels first increased from 1992-1998 and then decreased after 2000. Furthermore, gender differences were observed, as in 6 male sea otters, no PFOA was observed at >5 ng/g wwt, whereas PFOS levels were significantly higher (11-413 ng/g ww) than in female animals. *Kannan et al.* suggested a connection of this observation to possible transfer to the offspring during parturition and/or lactation.

1.3.3. PFAS levels in aqueous samples

The levels of PFAS have been determined in a wide variety of aqueous samples, including groundwater, surface water (freshwater as well as saltwater), tap water, STP effluents and precipitation. An overview is given in Table 6. For consideration of the direct transport theory of ionic PFAS to remote regions, the investigation of ocean water concentration gradients from industrialised to remote locations is indispensable. However, sea water data far from production and use areas is still scarce.

Groundwater, surface water and tap water

The first report of PFCAs in aqueous samples was published for ***groundwater*** taken at two sites in the ***U.S.*** impacted by fire-fighting activity (*Moody & Field 1999*). Due to the extreme use of AFFFs applied to extinguish hydrocarbon-fuel fires at these locations, maximum concentrations of ∑PFHxA+PFHpA+PFOA were between 125 µg/L up to over 7 mg/L, even after 7-10 years of inactivity.

Moreover, *Moody et al. 2001* reported on C_5-C_8 PFCAs as well as PFBS, PFHxS and PFOS in ***surface water*** samples taken on the occasion of an accidential release of AFFF foam in Toronto, ***Canada***. Sum concentrations between 0.011 and 2270 µg/L were determined by HPLC/(-)ESI-MS/MS. PFOS was the predominant compound in AFFF spill samples (2210 µg/L in the highest contaminated sample). Interestingly, PFOA was also found in surface water samples taken upstream of the AFFF spill. In sample aliquots additionally analysed by ^{19}F-NMR, the surface water concentrations ranged from <10 up to 17000 µg/L, thus indicating that in addition to the target analytes determined by LC-MS, further PFAS were present in significant amounts.

In a follow-up investigation at the same site, *Moody et al. 2002* took water samples regularly for three weeks and once five months after the AFFF spill into Etobicoke Creek. Total PFAS levels 3.9 km upstream of the site were constant at 8-33 ng/L (n.d. after 5 months), while at 4.1 km downstream of the location, concentrations were 815000 ng/L after one day, 93500 ng/L on the second day and dropped further to 370-1920 ng/L afterwards. Five months after the incident, 280 ng/L of ∑PFHxS+PFOS+PFOA were detected.

Hansen et al. 2002 quantified PFOA and PFOS in the ***Tennessee River*** up- and downstream of a major fluorochemical manufacturing site. Downstream of the Decatur plant, levels of PFOA and PFOS were significantly elevated, thus indicating that industrial effluents are a likely source of PFAS to the river.

Table 6. Overview of PFAS concentration levels in aqueous samples (ng/L).

	PFHxS	PFOS	PFOSA	8:2 FTCA	8:2 FTUCA	PFBA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	Remarks	Reference
Groundwater															
U.S.							max. 372000	max. 149000	<36000-6570000					fire-fighting site	*Moody & Field 1999*
Precipitation															
Scandinavia	<LOQ-0.59	0.24-2.97	<LOQ-0.14				0.81-1.97		8.23-16.8	0.63-1.41					*Kallenborn et al. 2004*
Canada		0.59		1.0	0.12										*Loewen et al. 2005*
North America				<0.07-8.6	<0.07-0.9	<0.1-26	<0.1-42	<0.1-31	<0.1-89	<0.1-77	<0.07-1.1	<0.07-3.7	<0.07-5.2		*Scott et al. 2006b*
Surface water															
Canada		max. 2210000												AFFF spill	*Moody et al. 2001*
Tennessee River		32							<25					upstream of Decatur plant	*Hansen et al. 2002*
		114							394					downstream of Decatur plant	
Japan		GM 0.89-5.73							GM 0.97-21.2						*Saito et al. 2004*
Germany		2-43							<1-7						*Lange et al. 2004*
Germany		3.3							2.4					upstream STP	*Weremiuk et al. 2006*
		14.5-26							12-14					downstream STP	
Germany									max. 1149						*Skutlarek et al. 2006*
U.S.		23							8.7						*Boulanger et al. 2005b*
Seawater															
Hong Kong / South China Sea		0.02-12							0.24-16					Coastal waters	*So et al. 2004*
Korea		0.04-730							0.24-320					Contaminated areas	
Tokyo Bay	3.3-5.6	13-25							154-192						*Yamashita et al. 2004*
Pacific Ocean	0.0006-0.0028	0.0011-0.078	<0.001-0.0028						0.015-0.142						
Deep Seawater	<0.0002-0.0006	0.0032-0.024	<0.001-0.0027						0.045-0.117						
Tokyo Bay	0.017-5.6	0.338-57.7							1.8-192	0.163-71					*Yamashita et al. 2005*
Pacific Ocean	0.0001-0.0016	0.0011-0.020							0.015-0.062	0.001-0.016					
Greenland Sea	<0.006-0.015	<0.010-0.055					<0.010-0.030	<0.012-0.030	<0.030-0.055						*Caliebe et al. 2005*
Tap water															
Japan		GM <LOD-12							GM 0.12-40						*Saito et al. 2004*
Germany									max. 520						*Skutlarek et al. 2006*
STP effluent															
Spain									<100-4300		<20-8170				*Alzaga & Bayona 2004*
Canada		17-100							10-34						*Crozier et al. 2005*
U.S.		26							22						*Boulanger et al. 2005b*
U.S.	<2.5-39	3-68		<2.5-7	<2.5-29				58-1050	<10-376	<2.5-47	<2.5-10			*Sinclair et al. 2006*

GM geometric mean.

Saito et al. 2004 determined PFOS and PFOA in ***Japanese surface and drinking water*** with LOQs of 0.1 ng/L. *So et al. 2004* published a survey of PFAS in ***coastal waters*** from ***Hong Kong, South China and Korea***. LOQs were 5 pg/L for PFBS, PFHxS, PFOS and PFOSA, and 20 pg/L for PFOA, PFNA and 6:2 fluorotelomer sulfonate (6:2 FTS).

Yamashita et al. 2004 applied an extremely sensitive analytical protocol to the analysis of ***seawater*** samples. In the ***Tokyo Bay***, PFOA, PFHxS and PFOS were determined in the ng/L range. In offshore waters of the ***Pacific Ocean***, levels were approx. 3 orders of magnitude lower (pg/L). In open ocean water samples, PFAS concentrations were again by factor ~10 lower. Even in ***deep seawater*** samples collected at 1000-4400 m depth, trace levels could be detected. Applying their sensitive method, *Yamashita et al. 2005* conducted a ***global survey*** of PFAS in oceans. They described the analysis of sea water samples taken during several cruises in 2002-2004 in the central to eastern Pacific Ocean, South China Sea, north and mid Atlantic Ocean as well as from coastal regions of Japan, China and Korea. In accordance with other studies, PFOA was the predominant compound, followed by PFOS. PFNA was not included in sample analysis of the first cruises, but was always detected in subsequent studies. PFHxS was found to be approx. one order of magnitude lower concentrated than PFOS.

Seawater samples are taken regularly in the ***North Sea*** by the *Federal Maritime and Hydrographic Agency (BSH)*, mostly during their monitoring cruises. *Caliebe et al. 2004* described the determination of C_6-C_{10} PFCAs, PFHxS, PFOS and PFOSA in high-volume (~9 L) seawater samples from the estuary of the Elbe river and several stations in the German Bight. Highest concentrations were found for PFOS and PFOA. In May, 2003, their levels at the Elbe estuary were at ~20 ng/L, and were diluted along the Elbe plume to ~6 ng/L. In the open sea, levels of 0.5-1.2 ng/L were determined.

Moreover, samples were taken in the ***North Sea and Arctic North Atlantic*** on expedition ARKXX-1 of the German research vessel Polarstern (AWI Bremerhaven). *Caliebe et al. 2005* described concentrations of PFOA, PFOS, PFHxA, PFHpA, and PFHxS in the Greenland Sea. A small number of ***sea ice snow samples*** taken close to Greenland showed detectable levels of C_6-C_8 PFCAs, PFHxS, PFOS and PFOSA (*BSH*, unpublished results). Levels ranged from 12 pg/L (PFHxS) to 106 pg/L (PFOA). Additionally, samples were taken in the Baltic Sea, while further investigations were done in the South Atlantic (*BSH*, unpublished results).

Regarding aqueous samples from Germany, *Lange et al. 2004* reported on PFAS levels in ***surface waters*** from ***Southern Germany***, e.g. taken in the rivers Rhine, Neckar, Main, Mosel and Danube. PFOS was found to be the predominant analyte, followed by PFOA. Interestingly, mostly even-numbered PFCAs were determined. The authors suggest that this observation indirectly reflects the phase-out of PFAS produced by ECF. A recent study of PFOA and PFOS from Southern Germany was reported by *Weremiuk et al. 2006*. Surface water samples of the river Roter Main at Bayreuth were collected 1 km and 100 m up- and downstream of a STP. PFOA and PFOS were detected in all samples.

Skutlarek et al. 2006 presented a study on C_4-C_{12} PFCAs as well as PFBS, PFHxS and PFOS in ***German surface water*** (e.g. river Rhine) and ***drinking water***. Extremely high levels of PFOA were found in surface water samples. Maximum concentrations were 1149 ng/L in a sample from river Möhne, in which the sum of 11 other PFAS resulted in 552 ng/L. Moreover, very high PFOA concentrations of up to 520 ng/L were found in drinking water, whereas the other compounds only represented minor fractions of the PFAS burden ($\sum_{11\ PFAS}$ = 89 ng/L). A number of drinking water and surface water samples below the LOQ of 2 ng/L (PFOA) and 5 ng/L ($\sum_{11\ PFAS}$), respectively, seem to rule out that general blank contamination occurred.

STP influent and effluent

Alzaga & Bayona 2004 described the analysis of six PFCAs between C_4 and C_{12} in ***STP effluent*** samples from two urban-industrial STPs in Catalonia, ***Spain***. Due to high LODs, only PFOA and PFDA could be quantified. *Crozier et al. 2005* found PFOS and PFOA at considerable concentrations in STP effluent samples from ***Canada***. *Boulanger et al. 2005b* determined PFOS and PFOA in ***STP influent, effluent and river water*** just downstream of the effluent discharge in the ***U.S.*** Influent concentrations were only estimated at >400 and >4 ng/L, respectively, due to analytical uncertainties including low recoveries of field spikes.

Schultz et al. 2006a conducted a study on PFAS in ***raw influent and final effluent*** from ten STPs in the ***U.S.*** in 2004. Among other compounds, PFOS, C_6-C_{10} PFCAs and PFOSA were analysed. PFOS and PFOA were found in all samples. The highest concentration determined was PFOS at 400 ng/L in one raw STP influent sample. Perfluoroalkyl sulfonate concentrations generally decreased slightly from influent to effluent, which was attributed to sorption to STP sludge, as no biodegradation pathway is known. PFOA concentrations were often higher in effluents than in influents. However, the trend strongly depended on the specific STP investigated. Additionally, PFBS, PFHxS, PFHxA, PFHpA and 6:2 FTS were frequently found, whereas the longer-chain compounds and PFOSA were detected only sporadically.

Another investigation of PFAS ***mass flows*** in a municipal STP in the U.S. was described by *Schultz et al. 2006b*. They concentrated on a complete assessment of each wastewater treatment step. PFHxS, PFDA and PFHxA levels decreased during the treatment process, PFOA and 6:2 FTS were unaffected, while concentrations of PFOS, PFDS, PFNA and PFOSA increased. For example, PFOS concentrations in the aqueous phase remained at 6.9-34 ng/L, but levels in sludge increased as described in the respective subchapter.

A detailed study of ***mass loading and fate*** of PFAS in six STPs with different inflows and wastewater treatment processes from New York State is described by *Sinclair & Kannan 2006*. Both PFOA and PFOS were present in effluents of all six STPs. Additionally, PFHxS, C_9-C_{11} PFCAs, 8:2 FTCA as well as 8:2 FTUCA were analysed. As expected, effluent concentrations of PFCAs were found to decrease with increasing chain length. *Sinclair & Kannan 2006* observed no significant changes of PFAS levels following primary treatment. However, mass flows of most PFAS investigated in their study increased from influent to effluent by up to factor 2.4.

Precipitation

Kallenborn et al. determined PFAS concentrations in rainwater from ***Finland and Sweden*** as reported in *NMR 2004*. They included PFBS, PFHxS, PFOS, PFHxA, PFOA, PFNA and PFOSA. Regarding the samples analysed in this study, PFOA was the predominant compound. Generally, levels in rainwater were higher than concentrations determined in lake water in the Nordic environment (*Berger et al. 2004b*). *Loewen et al. 2005* reported levels of 8:2 and 10:2 FTCAs and FTUCAs in rainwater from Winnipeg, ***Canada***. These chemicals are proposed atmospheric oxidation products of FTOHs. Low levels were detected, suggesting that one possible way of removing FTOHs from the atmosphere is by means of oxidation and wet deposition. Furthermore, PFOS was detected, while C_8-C_{12} PFCAs were <LOD.

Scott et al. 2006a determined C_2-C_8 PFCAs in precipitation samples taken at different sites in ***Canada***. Concentrations were highest for trifluoroacetate (61-170 ng/L), followed by perfluoro propanoate (5.1-21 ng/L). Levels of C_4-C_8 PFCAs were between <0.5-3.2 ng/L. In a recent study, the same research group focused on the determination of PFOA in precipitation samples

from nine sites in ***North America*** (*Scott et al. 2006b*). In addition to PFCAs, FTCAs and FTUCAs were analysed. Again, trifluoroacetate showed highest levels. Both 8:2 and 10:2 FTCAs and FTUCAs were detected at all U.S. and urban Canadian sites.

1.3.4. PFAS levels in solid samples

The analysis of PFAS in solid samples includes food, household dust, sediment and soil as well as STP sludge, for which levels are described in the following. An overview of PFAS concentration levels in solid samples is given in Table 7.

Food

The analysis of neutral, volatile PFAS in fast food (pizza, hamburgers, french fries) and shark fillet was described by *Tittlemier et al. 2005*. Shark fillet were purchased in ***Canadian*** stores in 2001, while fast food samples were composites generated from a 1992-1994 Canadian total diet study. The authors found NEtFOSA in all types of food, while N,N-Et_2FOSA was only found in fast food and PFOSA was only detected in shark fillet, respectively.

In an additional study, *Tittlemier et al. 2006* investigated NEtFOSA, N,N-Et_2FOSA, NMeFOSA, N,N-Me_2FOSA and PFOSA in Canadian total diet study composite food samples collected between 1992 and 2004. NEtFOSA was found in all food groups tested (baked goods and candy, dairy, eggs, fast food, fish, meat, and foods to be prepared in packaging) in the pg/g to low ng/g range. PFOSA and N,N-Et_2FOSA were also detected frequently except for the dairy or dairy and egg matrices, respectively. In contrast to the N-ethyl FOSAs (used primarily on paper products), the analogous N-methyl compounds, used primarily for fabric coatings including carpeting, were observed at much lower concentrations. This observation was considered to be indicative of the different use patterns of N-methyl and N-ethyl FOSAs.

A study of nine ionic PFAS in seafood purchased from local markets in two ***Chinese*** cities in 2004 was described by *Gulkowska et al. 2006*. PFOS was the predominant analyte determined in all 27 muscle tissue samples including fish, molluscs, crabs, shrimp, oysters, mussels and clams. Additionally, PFBS, PFHxS and C_6-C_{11} PFCAs were investigated. Regarding PFCAs, PFUnA was most frequently found, followed by PFOA. Further analytes were mainly <0.25 ng/g ww except for occasional detections. *Schlummer et al. 2005* reported levels of PFHxS, PFOS, PFHxA, PFOA and PFOSA in mixed food samples purchased by volunteers in ***Germany*** in 2005.

Dust

Moriwaki et al. 2003 determined PFOS and PFOA in 16 vacuum cleaner dust samples from homes in ***Japan***. Both compounds were detected in all samples. *Sasaki et al. 2003* reported PFOS levels in dust samples from a rural and an urban site in Japan at <LOQ- 61 ng/g and 38-427 ng/g, respectively. Additionally, *Harada et al. 2005* determined PFOS and PFOA in dust from Japanese homes.

Shoeib et al. 2005 analysed neutral, volatile PFAS in indoor dust samples from 66 homes in Ottawa, ***Canada***. NMeFOSE and NEtFOSE were found in all samples at extremely high concentrations. *Kubwabo et al. 2005* described the occurrence of PFAS in dust from 73 Canadian homes. PFBS was not detected at >1.38 ng/g, while PFOSA was found in every tenth sample. Levels of PFOA, PFHxS and PFOS showed a significant positive correlation. Moreover, the PFAS concentrations were positively correlated with the percentage of carpeting.

Table 7. Overview of PFAS concentration levels in solid samples (ng/g dw / ng/g ww).

	PFBS	PFHxS	PFOS	PFOSA	NEtFOSA	N,N-Et_2FOSA	NMeFOSA	N,N-Me_2FOSA	NMeFOSE	NEtFOSE	PFHxA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTA	Remarks	Reference
Food																			
Canada				<0.25-0.78	<0.12-58	<0.1-3.7												ww, fast food, fish	*Tittlemier et al. 2005*
Canada				nd-3.07	nd-22.6	nd-9.86	nd-0.258	nd-0.082										ww, total diet	*Tittlemier et al. 2006*
China		nd-0.28	0.33-13.9									nd-1.67	nd-0.61	nd-0.30	nd-0.93			ww, fish	*Gulkowska et al. 2006*
Germany			4.7-10.5	<1.0-3.6								<1.0-9.5						ww, mixed food	*Schlummer et al. 2005*
Dust																			
Japan			11-2500									69-3700							*Moriwaki et al. 2003*
Japan			<LOQ-427																*Sasaki et al. 2003*
Japan			19.7-168									469-9049							*Harada et al. 2005*
Canada									3.3-8860	1.4-75449									*Shoeib et al. 2005*
Canada	nd	nd-4305	nd-5065									nd-1234							*Kubwabo et al. 2005*
Sediment																			
Scandinavia		nd-0.045	nd-0.892	nd								nd-0.312						ww	*Kallenborn et al. 2004*
U.S.		nd-0.072	nd-3.76									nd-0.625	nd-0.237	nd-1.11	nd-0.396	nd-0.584	nd-0.435	dw	*Higgins et al. 2005*
Netherlands			nd-47.6									nd-24.2						dw	*De Voogt & Van Roon 2005*
	63.7		17.9								11.2	7.0	5.6	nd	24.8	nd	nd	AFFF site, dw	
Japan		0.33-0.55	0.09-0.14									0.84-1.1						ww	*Nakata et al. 2006*
Soil																			
Netherlands	19.4		125.8	nd							6.9	8.3	6.7	nd	21.0	nd	nd	AFFF site, dw	*De Voogt & Van Roon 2005*
STP sludge																			
U.S.		nd-3.18	nd-2610									nd-29.4	nd-10.3	nd-72.6	nd-8.58	nd-32.7	nd-7.77	dw	*Higgins et al. 2005*
Canada		nd-4.0	72-600									nd-0.9	0.4-2.4	2.5-5.2				dw	*Crozier et al. 2005*
U.S.		nd	81-160									<3	9.2-10.3	5.4-6.4	5.9-8.4	3.6-4.2	<3	digested sludge, dw	*Schultz et al. 2006b*
U.S.		<10-18	<10-65									18-241	<25	<25-91	<25-115			dw	*Sinclair et al. 2006*

nd not detected.

Sediment and soil

In a study reporting PFAS concentrations in the ***European Nordic environment***, *Kallenborn et al.* found PFOS to be the predominant compound in most ***sediment*** samples (*NMR 2004*). Only in Norwegian sediments, PFOA levels (278-312 pg/g ww) were comparable to those of PFOS at 217-394 pg/g ww. PFOA was not detected in sediment samples from Finland, Sweden and the Faroe Islands. Additionally, PFHxA, PFHxS and PFNA were found in selected samples. Generally, sediment samples had lower PFAS content than STP sludge (*Berger et al. 2004b*).

A temporal trend study of PFAS in Niagara River sediments, ***Canada***, from 1980-2002 was presented by *Lucaciu et al. 2005*. Sum concentrations of perfluoroalkyl sulfonates (5-1100 pg/g dw) were higher than PFCA levels at 10-300 pg/g dw, with PFOS being the predominant analyte. The concentrations of PFOS increased from less than 400 pg/g dw to over 1000 pg/g dw during the study period. *Higgins et al. 2005* determined PFAS concentrations in ***San Francisco Bay*** sediments. Levels of total sulfonyl-based PFAS were higher than those of total PFCAs. Furthermore, several possible precursors of PFOS like N-methyl / ethyl perfluorooctane sulfonamido acetic acid (NMeFOSAA / NEtFOSAA) were determined in sediments at levels sometimes even exceeding those of PFOS. *Houde et al. 2006b* described the determination of mean sum concentrations of PFHxS, PFOS, PFOSA and C_8-C_{14} PFCAs in sediments from ***Sarasota Bay*** (0.6 ng/g ww) and ***Charleston*** (2.2 ng/g ww).

De Voogt & Van Roon 2005 reported PFAS levels in ***sediments, suspended particulate matter (SPM) and soils*** from freshwater and marine locations in the ***Netherlands***. In sediment and SPM from marine locations, PFOS was determined regularly, while PFOA was found in every second sample. In sediment and SPM from freshwater locations, PFOS concentrations seem to be higher, while for PFOA the opposite is observed (mostly <0.4 ng/g dw). Generally, PFAS levels were higher in SPM than in sediments. Furthermore, *De Voogt & Van Roon 2005* determined several compounds in ***soil*** from a terrestrial site contaminated with AFFF. Several PFAS including 6:2 FTS (11.5 ng/g dw) were found at rather high levels, whereas PFHpA, PFDA, PFDoA, PFTA and PFOSA were not detected.

Nakata et al. 2006 analysed five ***sediment*** samples from the Ariake Sea close to ***Japan***. In this study, PFOA was the predominant PFAS analysed, even though PFOS was prevailing in parallelly investigated biota samples from the same region. The finding of higher PFOA concentrations in sediments might indicate a local source of this compound.

STP sludge

In addition to the analysis of sediment samples, *Higgins et al. 2005* determined PFAS concentrations in domestic sludge from several municipal STPs in the ***U.S.*** Levels were more than two orders of magnitude higher than in sediments. As also observed in sediments, total perfluoroalkyl sulfonyl-based chemical concentrations (55-3370 ng/g dw) exceeded those of total PFCAs (5-152 ng/g dw). Several possible precursors of PFOS like NMeFOSAA and NEtFOSAA were determined in STP sludge at levels sometimes even higher than PFOS. *Crozier et al. 2005* described the analysis of STP sludge from ***Canada*** and found PFOS to be the predominant compound. Increasing PFCA concentrations were observed with increasing chain length from PFOA to PFDA.

Schultz et al. 2006b described the determination of PFAS in sludge samples from a ***U.S.*** STP taken at different treatment steps and in particulate matter from raw influent. During the wastewater treatment process, waterbourne concentrations of PFOS were unchanged, but levels

associated to particulates and sludge increased significantly from 2.5-8.7 ng/g in raw influent to 81-160 ng/g in digested sludge. Levels of C_8-C_{12} PFCAs were much lower, but also showed an increase from raw influent to sludge. In particulate matter from raw or primary influent, they were detectable only sporadically, while in sludge, C_9-C_{12} PFCAs were mostly detected. STP sludge samples were also analysed by *Sinclair & Kannan 2006* from the ***U.S.*** Even though PFOA was the predominant compound, preferential partitioning of longer-chain PFCAs to sludge was observed. PFOS was also found in most sludge samples, while PFHxS was <10 ng/g dw. The results of this study provide further evidence that PFAS are not removed from wastewater by conventional treatment methodologies.

1.3.5. PFAS levels in air

Prior to this PhD thesis, only one publication about levels of ***neutral, volatile PFAS*** in air was available, prepared by *Martin et al. 2002*. It reported on the levels of six neutral PFAS at two locations (Toronto, urban – Long Point, rural) in ***Canada***. In Toronto, NMeFOSE and NEtFOSE showed highest levels (86-123 and 51-393 pg/m^3). Within FTOHs, 6:2 FTOH had highest concentrations at 30-196 pg/m^3, followed by 8:2 FTOH (9-123 pg/m^3) and 10:2 FTOH (7-46 pg/m^3). NEtFOSA was found at 14 pg/m^3. At the remote location, levels ranged from 15 (10:2 FTOH) to 85 pg/m^3 (NEtFOSE).

In a follow-up study carried out by the same research group, *Stock et al. 2004b* investigated the occurrence of ***neutral, volatile PFAS*** at ground level of the ***North American*** troposphere. The sampling sites covered both urban (Toronto, Winnipeg) and rural (Long Point, Cleaves) locations as well as sampling sites in the proximity of carpet (Griffin) or paper production facilities (Reno). Airborne PFAS were shown to be widely distributed in North American air samples, ranging from 22-403 pg/m^3 ($\sum$FOSAs+FOSEs) or 11-165 pg/m^3 ($\sum$FTOHs), respectively. Depending on the specific sampling location, different patterns were recognised, thus indicating the importance of point sources for the distribution of these contaminants. Exceptionally high levels of NMeFOSE (359 pg/m^3, Griffin) and NEtFOSE (199 pg/m^3, Reno) were attributed to the presence of carpet and paper industries, respectively.

Sasaki et al. 2003 first described the determination of ***PFOS*** in airborne particulate matter. In samples from an urban location in ***Japan***, concentrations between <LOQ and 21.8 pg/m^3 were found. The same group determined PFOA and PFOS in the particulate phase of Japanese air samples at concentrations of 1.59-2.58 (rural) up to 72-919 pg/m^3 (urban) and between 0.46-1.19 (rural) and 2.51-9.80 pg/m^3 (urban), respectively (*Harada et al 2005*).

Shoeib et al. 2004 published concentration data of ***neutral, volatile PFAS*** in both indoor and outdoor air samples from Toronto, ***Canada***. NMeFOSE and NEtFOSE were found at 16.0-31.7 pg/m^3 or 8.47-9.79 pg/m^3, respectively, in environmental air samples, while levels determined indoors were 110 (mean NMeFOSE 2590 pg/m^3) and 85 (mean NEtFOSE 770 pg/m^3) times higher. Indoor air was thus identified as a significant source of neutral, volatile PFAS to outdoor air.

A more detailed study of neutral, volatile PFAS in Ottawa, Canada, was presented by *Shoeib et al. 2005*, including active and passive air sampling devices. NMeFOSE and NEtFOSE were again found at high levels in indoor air (366-8190 and 227-7740 pg/m^3, respectively), while outdoor air concentrations were by a factor of 10-20 lower (76-99 and 80-106 pg/m^3, respectively), underlining that indoor air is an important source of PFAS to the outside environment. In addition, NEtFOSA was determined at 5.9-646 pg/m^3 in indoor air, while it was <0.01 pg/m^3 in environmental air samples. Based on PFAS levels determined in indoor air and on dust (see ***chapter 1.3.4***), an estimation of human exposure was done, identifying the indoor

environment as an important human exposure route for PFAS as also discussed in ***chapter 1.4.3***.

Sum concentrations of neutral, volatile FTOHs and FOSAs / FOSEs at terrestrial locations (urban – remote) in North America and Europe from the literature and determined within this thesis are summarised in Table 8. Ship-based data presented by *Shoeib et al. 2006* and determined within this thesis are discussed in ***chapter 7***. Furthermore, an overview of the concentration levels of airborne, particle-bound PFOS and PFOA at terrestrial locations (urban – remote) in Japan, North America and Europe from the literature as well as ship-based levels determined within this thesis is given in Table 9.

Table 8. Concentrations of neutral, volatile PFAS at urban and remote locations.

	Location	***Inhabitants***	***ΣFTOHs (pg/m³)***	***ΣFOSAs+FOSEs (pg/m³)***
Martin et al. 2002	Toronto, ON (*n* = 4)	2.480.000	171[a]	320[a]
	Long Point, ON (*n* = 2)	500	78[a]	111[a]
Stock et al. 2004b	Griffin, GA (*n* = 5)	23.500	148 (49-224)	403 (57-1549)
	Cleaves, OH (*n* = 3)	2.200	132 (103-181)	69 (<MDL-134)
	Long Point, ON (*n* = 3)	500	26 (<MDL-52)	48 (29-65)
	Toronto, ON (*n* = 3)	2.480.000	165 (113-213)	95 (31-211)
	Reno, NV (*n* = 3)	180.500	76 (51-93)	291 (157-491)
	Winnipeg, MB (*n* = 3)	685.900	11 (<MDL-18)	22 (15-32)
Shoeib et al. 2004	Toronto, ON (*n* = 2)	2.480.000	n.a.	33 (24-41)[b]
Shoeib et al. 2005	Ottawa, ON (*n* = 7)	780.000	n.a.	171 (156-205)[a,c]
Boulanger et al. 2005a	Lake Erie (*n* = 5)	-	n.a.	2.0 (n.d.-3.2)[d]
	Lake Ontario (*n* = 3)	-	n.a.	1.3 (n.d.-1.9)[d]
Berger et al. 2005a	Manchester, UK (n=2)	2.240.000	39 (31, 47)	527 (789, 264)
	Hazelrigg, UK (n=2)	20	47 (36, 57)	283 (40, 525)
publication II	Hamburg (*n* = 7)	1.740.000	288 (150-546)	68 (29-151)
	Waldhof (*n* = 4)	20	181 (64-311)	34 (12-54)

n.d. not detected, n.a. not analysed, <MDL below the method detection limit.

[a] Sum of mean values.

[b] Analysis of FOSEs only.

[c] Analysis of FOSEs and NEtFOSA only, with NEtFOSA <MDL.

[d] Analysis of NEtFOSA and NEtFOSE only.

Table 9. Concentrations of particle-bound ionic PFAS.

	Location	***PFOS (pg/m³)***	***PFOA (pg/m³)***
Sasaki et al. 2003	Japan	<LOQ-21.8	n.a.
Harada et al. 2005	Japan	0.46-9.8	1.59-919
Boulanger et al. 2005a	North America	n.d.-8.1	n.a.
Berger et al. 2005a	UK	<LOQ-51	226-828
publication III	ANTXXIII-1	0.05-2.5	n.d.-2.0

n.d. not detected, n.a. not analysed.

Berger et al. 2005a presented the occurrence of a broad spectrum of both neutral and ionic PFAS in environmental air samples from the ***UK***. On the one hand, regarding ***neutral PFAS***, four FTOHs, four FOSAs / FOSEs and 10:2 fluorotelomer olefin (10:2 FT-ol) were determined in the gaseous and particulate phase. 8:2 FTOH was the compound present at highest concentrations (9-326 pg/m^3), followed by 6:2 FTOH (16-315 pg/m^3) and 10:2 FTOH (25-125 pg/m^3). FOSA / FOSE levels were considerably lower.

On the other hand, the analysis of ***ionic PFAS*** in the particulate phase, extracted from halved GFFs, included PFBS, PFHxS, PFOS, PFDS as well as C_6-C_{11} PFCAs. The predominant compound analysed in this study was PFOA, with levels of 226-455 pg/m^3 in Manchester (urban) and 276-828 pg/m^3 in Hazelrigg (semi-rural) (*Berger et al. 2005a*). This observation was surprising at first, but could be related to the proximity of the sampling site to a fluorochemical production facility. PFOS was also found at levels between <LOQ and 51 pg/m^3. Additionally, PFBS (<LOQ-2.5 pg/m^3), PFHxS (<LOQ-1.0 pg/m^3), PFDS (<LOQ-0.75 pg/m^3), 6:2 FTS (n.d.-9.7 pg/m^3), PFHpA (<LOQ-14.4 pg/m^3) and PFDA (n.d.-14.3 pg/m^3) were found in some of the samples.

Boulanger et al. 2005a found several ***neutral and ionic PFAS*** in air samples taken over ***Lake Erie and Lake Ontario***. In the gaseous phase, NEtFOSA and NEtFOSE levels ranged from n.d.-2.2 pg/m^3 and n.d.-1.0 pg/m^3, respectively. PFOS was determined in the particulate phase of several samples at n.d.-8.1 pg/m^3. In this study, PFAS were only detected in those samples which were taken close to Detroit and Toronto, underlining the importance of urban sites as sources. *Barton et al. 2006* used high-volume impactors for the determination of ***PFOA*** concentrations on different particle sizes (>4.0, 1.7, 0.8, 0.5, 0.3, <0.28 μm) along the fence line of a ***U.S.*** manufacturing facility at <75-900 ng/m^3. In this context, approx. 60% of PFOA were found on particles of less than 0.28 μm.

In summary, neutral, volatile PFAS in environmental air samples are detectable in urban as well as remote regions in the North American and European atmosphere. Furthermore, their concentrations are in similar ranges as those of several much discussed ‘classical’ POPs. 8:2 FTOH and 6:2 FTOH were found to be the highest concentrated POPs determined in air samples from Waldhof, as discussed in more detail in ***chapter 7***. Furthermore, ionic, non-volatile PFAS can be transported via the atmosphere associated to airborne particles. Considerable concentrations have been observed close to point sources.

1.4. Human and ecotoxicology

The human and ecotoxicology of PFAS have yet to be extensively investigated. In most of the studies so far, only PFOS and / or PFOA were investigated. Many existing reports have not been published in the peer-reviewed literature. Nevertheless, a great number of studies is available via the U.S. EPA public docket AR-226 (*http://www.epa.gov*). However, PFAS are recognised as very persistent and very bioaccumulative (*vpvb*) substances, so that toxicity does not have to be fully evaluated before taking regulatory actions. This chapter briefly summarises the human and ecotoxicology evaluation (***1.4.1***), bioaccumulation (***1.4.2***) and current human health risk assessment (***1.4.3***) of PFAS.

1.4.1. Human and ecotoxicology evaluation

The ***serum half-life in humans*** was investigated for selected PFAS by *Burris et al. 2002*. Serial blood samples of nine fluorochemical production plant retirees were monitored over 180 days. The results suggested that mean half-lives of 8.7 (2.3-21.3) and 4.4 (1.5-13.5) years applied for PFOS and PFOA, respectively. The authors emphasised the drawback of their study, which did not account for possible metabolism of precursor compounds, which would lead to artificially long half-life estimations. The mentioned study was carried on for up to 5.5 years analysing blood of 26 retirees (*Olsen et al. 2005b*) and confirmed the long half-lives of PFAS in human blood. Initial serum concentrations of PFOS, PFHxS and PFOA were 145-3490, 16-1300 and 72-5100 ng/mL, respectively. Mean half-lives of serum elimination were calculated to be 5.4 (2.4-21.7), 8.8 (2.8-27.0) and 3.8 (1.5-9.1) years, respectively.

However, PFAS half-lives reported for other species are markedly shorter than for humans. Regarding perfluoroalkyl sulfonates, elimination half-lives of PFOS are currently estimated to be in the range of 100-150 days for rats and monkeys, while for PFHxS, elimination times are much shorter as reported by *Olsen et al. 2005b*. As to PFCAs, significant sex and species differences in PFOA half-lives have been observed, ranging from 4-6 days in male and 2-4 hours in female rats. Sex hormones are supposed to influence urinary elimination of PFOA in rats. However, in cynomolgus monkeys with half-lives of 14-42 days, no sex-related differences in clearance were observed.

It was shown that PFAS ***bind to blood proteins instead of fatty tissues*** as is the case for 'classical' POPs. *Jones et al. 2003* reported that PFOS in serum is generally bound to albumin. It showed only weak ability to displace estrogen or testosterone from carp serum steroid binding proteins. However, perfluoroalkyl sulfonates were more potent than PFCAs. The authors concluded that based on current environmental PFOS concentrations, the displacement of hormones from serum proteins in wildlife is very unlikely. A study by *Han et al. 2003* confirmed that more than 90% of PFOA were bound to rat and human serum albumin, the most abundant protein in plasma.

Biliary ***enterohepatic recirculation*** of PFCAs was described by *Goecke-Flora & Reo 1996*, indicating that the human body recognises PFAS as endogenous bile acids. The process includes continuous recycling of compounds between the blood, liver, gall bladder, and intestines, where resorption occurs via the portal vein. The authors stress the importance of carbon chain length in induction of toxic effects. For PFCAs with carbon chain lengths ≤ 8, the aqueous solubility seems to induce acute toxic effects at facilitated urinary excretion, while for ≥ 9 carbon atoms, enterohepatic recirculation and prolonged toxic effects were observed. Furthermore, PFCAs of $\geq C_9$ showed an impact on hepatic ***phospholipid metabolism***.

Finally, an induction of ***peroxisome proliferation*** is described for PFCAs of ≥ 8 carbon atoms chain length (*Goecke-Flora & Reo 1996*). Peroxisomes are cell organelles present in most cells, whose proliferation is considered as a biomarker of effects caused by contaminants. Peroxisome proliferators are a structurally diverse group of chemicals which are capable of inducing enzymes associated with β-oxidation of fatty acids in peroxisomes, lowering serum cholesterol and causing an increase of liver weight (hepatomegaly).

Berthiaume & Wallace 2002 described the peroxisome proliferative effect of PFOS and PFOA, whereas NEtFOSE showed no activity. PFOS induced the same peroxisome proliferative response in rats with similar potency as PFOA, but without increasing liver weights. *Kudo et al. 2005* showed that the administration of 8:2 FTOH to mice caused liver enlargement. Moreover, peroxisome proliferation was observed. However, this effect was not attributable to 8:2 FTOH itself, but to *in vivo* biotransformation of 8:2 FTOH to PFOA, accumulation of PFOA in the liver and subsequent induction of peroxisome proliferation.

Hu et al. 2003 described ***alterations in cell membranes*** caused by perfluoroalkyl sulfonates. Increased permeability of cell membranes to two model compounds, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 17β-estradiol, was tested for PFBS, PFHxS and PFOS, but only PFOS showed an effect in fish leukocytes at concentrations of 5-15 mg/L. Furthermore, mitochondrial membrane potential was affected in a dose-dependent way. However, the authors stressed that it remained to be tested if these effects also occur during *in vivo* experiments.

Austin et al. 2003 showed that PFOS exhibits ***neuroendocrine effects*** in rats. The treatment affected estrous cyclicity and affected the levels of several hormones, thus inhibiting reproduction and activating stress factors. Additionally, the exposure to the higher administered PFOS doses

decreased food intake and body weight in a dose-dependent way. Finally, accumulation of PFOS in various tissues was observed.

Hoff et al. 2004 observed increased liver weight and an increased microsomal lipid peroxidation level (indicating oxidative stress) in wood mice living in proximity of a fluorochemical plant in Antwerp, Belgium. The study also suggested that hepatic PFOS bioaccumulation is age-dependent. Furthermore, as the youngest animal (20 days old) showed very high PFOS concentrations (52.7 μg/g ww), ***maternal transfer of PFOS to the young*** during pregnancy and / or lactation was suggested.

There are many reports on ***acute toxicity*** of PFOS and PFOA (LD_{50}, lethal dose for 50% of the test organism) available from the public docket AR-226 (*http//www.epa.gov*), whereas studies assessing the ***chronic toxicity*** (no observed adverse effect level – NOAEL, lowest observed adverse effect level – LOAEL) are relatively scarce.

Sanderson et al. 2002 investigated a freshwater zooplankton community exposed to different PFOS concentrations over 35 days. For 30 mg/L PFOS exposure, a 90-100% reduction of the zooplankton population was observed after one week, whereas for the 10 mg/L level, the same occurred after 2-3 weeks. Further experiments included the investigation of effects of both PFOS and PFOA on the zooplanktonic community as described in *Sanderson et al. 2004*. Zooplankton generally showed lower tolerance towards PFOS than towards PFOA. For higher PFAS concentrations, ***reduced biodiversity*** was observed. For *Daphnia pulicaria*, a 21-day ***NOAEL*** and ***LOAEL*** of 6 and 13 mg/L were determined, whereas for *Daphnia magna*, 25 and 50 mg/L were established.

Boudreau et al. 2003 determined a NOAEL of 0.2 mg/L PFOS for *Lemna gibba*. *Seacat et al. 2003* investigated the subchronic dietary toxicity of PFOS in rats. Serum concentrations were generally higher in females than in males. After 14 weeks, liver weights had increased. The NOAEL in serum was 44 μg/mL (males) and 64 μg/mL (females), while for liver, approx. 270 μg/mL were determined.

A review published by *Lau et al. 2004* summarised the ***developmental toxicity*** of PFAS. The authors indicated that due to the topicality of toxicological studies, publications in the peer-reviewed literature were scarce, as papers were still in preparation and substantial toxicity data were mainly available as reports submitted to the U.S. EPA. Subchronic exposure to PFOS was shown to lead to significant loss of body weight accompanied by hepatotoxicity and reductions of serum cholesterol and thyroid hormones.

Postnatal mortality in rats was 100% at 10 μg PFOS/g body weight (bw)/d administered to female rats during pregnancy and about 50% at 3 μg/g bw/d. Furthermore, gain of body weight and development (e.g. eye opening) was delayed as well at lower dosages. Moreover, *Lau et al. 2004* described the postnatal mortality in mice. The maternal dosages required for the same effects were higher. The ***LD_{50}*** was estimated at 10 μg/g bw/d, compared to approx. 3 μg/g bw/d in rats. The authors also mentioned a more pronounced increase of liver weight in PFOS-exposed neonatal mice. A similar developmental toxicity profile was described for NEtFOSE in rats. Regarding PFOA, at 30 μg/g bw/d dosage, an increase of pup mortality was observed. Reduced weight gain and delay in reaching sexual maturity were also described. However, as female rats are able to rapidly excrete PFOA (elimination half-life of 2-3 hours as opposed to days / weeks in male rats, dogs, monkeys, or years in humans), interpretation and extrapolation of these data to human health risk assessment is challenging.

Kennedy et al. 2004 published a ***review*** describing the ***toxicology of PFOA*** observed in numerous studies mainly with rats, but also including mice, hamsters, rabbits, monkeys and guinea pigs. An efficient absorption following oral, dermal, or inhalation exposure was observed. No metabolisation occurred, and the primary route of elimination seemed to be urine. Evidence of biliary excretion and enterohepatic recirculation was observed. PFOA was found to exhibit moderate acute oral and inhalation toxicity and slight acute dermal toxicity. Among the symptoms were decreases in body weight, increases in liver weight and liver effects. Therefore, the liver appeared to be the primary target organ.

Furthermore, PFOA was identified as a peroxisome proliferator, exerting morphological and biochemical effects, including increased β-oxidation of fatty acids and increases in several cytochrome P-450-mediated reactions. Furthermore, an effect on the lipid metabolism and transport was described, resulting in a reduction of cholesterol and triglycerides in serum and lipid accumulation in the liver. Three types of tumors were observed in rats: hepatocellular, testicular (Leydig cell) and pancreatic acinar-cell tumors. However, these effects were described as not likely to be relevant to humans (*Kennedy et al. 2004*).

Nevertheless, *Dahlgren et al. 2004* presented enhanced cancer rates of workers exposed to PFOA as well as residents close to a fluorochemical production facility as identified by means of 599 questionnaires. Additionally, the authors described the cancer distribution to be altered with a statistically relevant prevalence of prostate, kidney, bladder and colon cancer.

In a recent study, *Kannan et al. 2006* described a significant correlation of river otters who died of ***infectious deseases*** and relatively high concentrations of PFOS and PFOA. Further groups of animals which had died of nondesease and emaciation reasons did not show any correlation. No conclusive cause-effect linkage was found in their study.

Maras et al. 2006 described ***estrogen-like properties*** of 6:2 FTOH and 8:2 FTOH as determined by means of *in vitro* MCF-7 breast cancer cell proliferation. Both newly detected xenoestrogens showed similar behaviour as the reference compounds, the natural estrogen 17β-estradiol and the reference xenoestrogen 4-nonylphenol, while neither PFOS nor PFOA or PFNA showed corresponding effects. The authors stressed the need for further evaluation of this phenomenon in *in vivo* experiments.

1.4.2. Bioaccumulation of PFAS

Generally, contaminants can be enriched in biota through different pathways. On the one hand, *bioconcentration* merely comprises exposure of organisms to their particular surrounding environment, e.g. via inhalation. On the other hand, *biomagnification* includes only the pathway of dietary exposure, while *bioaccumulation* includes both the diet and non-diet based exposure pathways. An overview of the corresponding enrichment factors (bioconcentration factors – *BCFs*, biomagnification factors – *BMFs* and bioaccumulation factors – *BAFs*) published in the literature is given in Table 10.

Moody et al. 2002 estimated the ***BAF*** of PFOS in rainbow trout (*Oncorhynchus mykiss*) liver at a highly contaminated site after an AFFF spill to be 6300-125000. The authors hypothesised that the fish might accumulate precursors which are metabolised to form PFOS and therefore bias the BAF estimation. Furthermore, *Kannan et al. 2005* emphasised that taking into account that higher-trophic level organisms have a better potential of metabolisation of contaminants, levels of precursor compounds in their diet may contribute to higher PFOS levels. Similarly, *Houde et al. 2006a* pointed out that significant differences between laboratory- and field-based studies occur, as many uncontrollable factors like unmonitored trophic concentrations influence field studies.

Table 10. Literature overview of BCFs, BMFs and BAFs.

		PFHxS	PFOS	PFOSA	PFCAs						Remarks	Reference
					C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}		
BCF	***exposure through the surrounding environment***											
Rainbow trout	lab-based	9.6	1100		4.0		450	2700	18000	23000		*Martin et al. 2003b*
invertebrates	Great Lakes		1000									*Kannan et al. 2005*
turtles	field-based		11000		3.2							*Morikawa et al. 2006*
BMF	***dietary exposure***											
Mink	lab-based		11-23								fed with conta-minated carp	*Kannan et al. 2002a*
Rainbow trout	lab-based	0.14	0.32		0.038		0.23	0.28	0.43	1.0		*Martin et al. 2003a*
food web	Lake Ontario		2.9	1.4	0.41	2.3	2.7	3.4	1.6	>2.3	PFTrA 2.5	*Martin et al. 2004c*
food web	Arctic		0.4-9	0.7-889	0.04-2.7						NEtFOSA 0.04-238	*Tomy et al. 2004*
various predators	field-based		5-20									*Kannan et al. 2005*
bottlenose dolphins	field-based	3.3-14	0.8-4.6	1.3-30	1.8-13	1.4-24	2.4-8.8	0.9-3.9	0.1-1.8			*Houde et al. 2006b*
BAF	***combination of dietary and non-dietary exposure***											
Rainbow trout	AFFF spill site		6300-125000									*Moody et al. 2002*
fish livers	field-based		274-41600									*Taniyasu et al. 2003*

A study by *Martin et al. 2003a* indicated that no biomagnification of PFAS occurs (***BMFs*** ≤1). In a parallel study, *Martin et al. 2003b* described experiments to determine PFAS bioconcentration of rainbow trout in a flow-through system. PFCAs of carbon chains <7 and perfluoroalkyl sulfonates of <6 did not accumulate in any of the analysed tissues. Sulfonates showed higher ***BCFs*** than carboxylates of the same chain length. Concentrations were highest in the blood, followed by kidney, liver and gall bladder.

Martin et al. 2004c described the biomagnification of PFAS in a food web from Lake Ontario. The study included two invertebrates, three forage fish species and the top predator, lake trout (*Salvelinus namaycush*). The discovery of highest PFAS concentrations in the organism at the lowest trophic level investigated, the benthic macroinvertebrate *Diporeia*, was surprising. The authors hypothesised that sediments must be a major source of PFAS due to uptake by benthic invertebrates. A further investigation in the Lake Ontario food web was published by *Kannan et al. 2005*. *Tomy et al. 2004b* described a biomagnification study of PFOA, PFOS, PFOSA and NEtFOSA in an Eastern Arctic marine food web. By means of concentrations correlated to trophic levels, it was shown that PFOS biomagnifies.

Houde et al. 2006b reported ***BMFs*** of PFAS in bottlenose dolphins using whole prey homogenates and whole body burden of dolphins. This approach resulted in up to 30-fold lower values than reported in other studies. This observation was explained by the frequent usage of liver or blood plasma levels with highest PFAS concentrations for predators while the prey data often originates from whole body homogenates as also emphasised by *Tomy et al. 2004b*.

1.4.3. Human health risk assessment

Human exposure to PFAS occurs by means of different pathways. Chemicals can already be transferred *in utero* via cord blood or later be carried forward through breast milk. Furthermore inhalation, dust absorption, intake through drinking water / food consumption or uptake from PFAS-treated consumer articles can occur. However, few studies deal with this issue, and only a limited number of PFAS is taken into account. The potential toxicity of PFAS is not well characterised, and even less is known about their different metabolism, mechanisms of action and risks to humans as stressed by *Moriwaki et al. 2003*. However, some attempts to characterise the ***relative importance of exposure from different media*** are summarised in the following.

The levels of PFOS in 15 pairs of ***maternal and cord blood*** samples was investigated by *Inoue et al. 2004*. A high correlation was found between PFOS concentrations in maternal (4.9-17.6 ng/mL) and cord blood (1.6-5.3 ng/mL). PFOA was only detected in 4 of 15 maternal blood samples at <0.5-2.3 ng/mL, while PFOSA was not detected at >1.0 ng/mL. The study revealed that PFOS may be able to cross the placental barrier and enter fetal blood circulation. Due to the known developmental toxicity and postnatal effects of PFOS observed in rats and mice as described above by *Lau et al. 2004*, *in utero* exposure of the human fetus requires further investigation.

So et al. 2006 assessed health risks in infants associated with the exposure to PFAS in ***human breast milk*** using a hazard ratio (HR) approach. First of all, reference doses for noncancer health effects were estimated on the basis of a rat chronic carcinogenicity study and a rat multigenerational study to be 0.025 μg/kg/d (PFOS) and 0.333 μg/kg/d (PFOA). Taking into account the mean PFAS concentrations in breast milk, an average daily intake was calculated and devided by the reference dose to yield HRs. A HR >1 indicates that the average exposure level exceeds the benchmark concentration. PFOS and PFOA were found in all breast milk samples with concentrations of 45-360 ng/L and 47-210 ng/L, respectively (*So et al. 2006*). For PFOA, HRs were usually about two orders of magnitude lower than unity. However, for PFOS, the daily intake of the child via breast milk exceeded the predicted conservative reference dose in 1 of 19 samples, indicating that there may be a small potential risk of PFOS for Chinese infants via breast milk consumption. However, due to the application of uncertainty factors (e.g. animal to human – average human to sensitive human – subchronic to chronic – database insufficiency), actual risks may have been overestimated.

Moriwaki et al. 2003 determined PFOS and PFOA in ***dust*** at 11-2500 (mean 196) ng/g and 69-3700 (mean 384) ng/g, respectively, with a significant positive relationship, indicating similar sources. It was emphasised that dust can be an exposure pathway among others, but however, no attempt was made to quantify daily intake rates via dust.

Sasaki et al. 2003 reported PFOS levels in ***dust*** from two sites in Japan at <LOQ-60.6 (rural) and 38.0-427 ng/g (urban). Higher levels were found in summer at both locations. Under the assumptions that an adult inspires 15 m^3 of air daily, that all airborne dust particles are respirable (diameters of 1-10 μm) and that particle-bound PFOS was absorbed completely, the estimated daily intake was 10 pg/d and 100 pg/d at the rural and urban site, respectively. By means of a one-compartment pharmacokinetic model, the authors reported resulting plasma levels of 1.2 pg/mL and 12 pg/mL, respectively. As human blood levels were in the ng/mL range, *Sasaki et al.* concluded that the relative PFOS exposure from airborne particles was relatively low.

Harada et al. 2005 determined PFOS and PFOA in ***dust*** at 19.7-168 and 469-9049 ng/g, respectively. Under the same assumptions as mentioned above for *Sasaki et al. 2003*, the daily PFOA intake was estimated to be up to 3.9 ng/day. The authors stressed the lack of focusing on respirable particles, so that the calculated exposure dose was probably significantly overestimated. Taking into account the report by *Saito et al. 2004* who determined PFOS and PFOA in ***tap water*** from the same area at 4.9 ng/L and 5.4 ng/L, respectively, and assuming that 2 L of water are ingested per day, daily intakes of 9.8 and 10.8 ng, respectively, are calculated via drinking water. Therefore, PFOA uptake via airborne particles was in the same order of magnitude.

In a follow-up study, *Harada et al. 2006* investigated the burden of PFOS and PFOA on different particle sizes to estimate the respirable fraction bound to particles of 1.1-11.4 μm. The respirable proportions of PFOS and PFOA were 89.8% and 58.3%, respectively. Taking into

account the particle size distributions, the estimated daily human exposure to PFOA through inhalation was 3.4 ng.

Shoeib et al. 2005 analysed neutral, volatile PFAS in ***dust*** and found high mean levels for NMeFOSE (412 ng/g) and NEtFOSE (2200 ng/g). The authors stressed that detectable PFOS concentrations in human sera from around the world could either be directly uptaken and / or biotransformation of precursors might occur. An estimation of human exposure via inhalation and ingestion of dust was undertaken. Dust ingestion was assumed to be of particular concern for children. A worst-case scenario was adopted (100% absorption efficiency and concentrations measured in winter times at low ventilation). With median levels of NMeFOSE and NEtFOSE, the daily inhalation and dust ingestion were calculated to be 39-41 and 20 ng, respectively, for adults, while for children, 27 and 44 ng were estimated. *Shoeib et al.* concluded that indoor air and dust are important human exposure routes for FOSEs.

Gulkowska et al. 2006 calculated HRs of PFAS uptake by ***fish consumption*** (see description above, *So et al. 2006* / human breast milk). Taking into account the mean PFAS concentrations in seafood, the average daily intake was calculated and divided by the reference dose to yield HRs. In this study, HRs were always <1 due to relatively low PFAS levels, leading to the conclusion that the present PFAS concentrations in seafood were unlikely to cause immediate harm to the population.

Falandysz et al. 2006 described PFAS accumulation in humans caused by extensive ***fish consumption***. In their study, Baltic seafood was found to highly influence the human body burden of PFHxS, PFOS, PFOSA, PFHxA, PFHpA and C_9-C_{12} PFCAs. For PFOA, fish intake influenced concentration levels to a lesser extent. Additionally, PFBS, C_{14}, C_{16} and C_{18} PFCAs, NEtFOSA, 8:2 FTCA and 8:2 FTUCA were analysed, but not found in any of the samples.

In a study published by *Tittlemier et al. 2006*, a basic estimate of dietary exposure to FOSAs by means of a ***total diet*** study with composite food samples was described. All investigated food groups (baked goods and candy, dairy, eggs, fast food, fish, meat, and foods to be prepared in packaging) showed detectable levels. The daily exposure of Canadians (older than 12 years) to ∑NEtFOSA+N,N-Et_2FOSA+NMeFOSA+N,N-Me_2FOSA+PFOSA was estimated at 73 ng. NMeFOSA and N,N-Me_2FOSA were detected at much lower concentration levels than the NEtFOSA and N,N-Et_2FOSA. Arranged by sex and age groups, males are expected to be exposed to higher amounts (41-120 ng), while females have median uptakes of 29-81 ng. Generally, the younger population was expected to be exposed to higher daily doses. As these estimated daily exposures were of the same order of magnitude as via indoor dust and air (*Shoeib et al. 2005*), food is assumed to be an important route of exposure to PFAS.

An exposure assessment for PFOA in selected ***consumer articles*** including nonstick cookware, treated apparel, upholstery and home textiles, latex paint, floor waxes and carpet-care solutions was described by *Washburn et al. 2005*. The study was designed to understand the magnitude of PFOA exposure occurring through consumer use of certain articles. Unused articles were extracted with water and artificial saliva or perspiration, thus simulating human exposure (e.g. dermal contact). Health benchmarks of 3.9 (noncancer systemic toxicity), 22 (developmental effects) and 5.1 mg/kg/d (carcinogenic effects) were identified. The authors concluded that, using a simple compartment model, serum concentrations resulting from consumer product use were below the current LOQ (~0.5 ng/mL) for PFOA.

Another study published by *Begley et al. 2005* investigated the potential migration of PFAS from ***food packaging and cookware***. In microwave popcorn bags they found 6-290 ng/g of PFOA. However, the authors came to the conclusion that due to the lack of migration to the food

oil, fluoropolymer food-contact materials did not appear as a significant source of PFAS. Furthermore, the tested PTFE-coated cookware did not seem to be a significant source of PFOA. Even at an extreme, abusive heating test, the cookware did not increase the residual amount of PFOA.

1.5. Atmospheric chemistry of neutral, volatile PFAS

The LRAT hypothesis of precursors to remote regions followed by *in situ* degradation to the persistent PFOS and PFCAs received substantiation several years ago. *Ellis et al. 2003a* showed that the atmospheric lifetime of FTOHs is determined by reaction with OH radicals and is ~20 days, independent of their chain length. By contrast, reactions with NO_3 and O_3 radicals were regarded to be too slow to be of importance for saturated compounds, whereas Cl atoms were too low concentrated to compete with OH radical reactions. Furthermore, neither dry nor wet deposition were considered to be of importance. The atmospheric lifetime of ~20 days implied that compounds travelling at an average wind speed of 4 m/s could cover ~7000 km and thus reach remote regions. In a further study, the same research group determined atmospheric lifetimes of short-chain fluorinated alcohols (1:1 up to 4:1 FA) to be approx. 164 days (*Hurley et al. 2004a*). The degradation, determined by reactions with OH radicals, yielded small, but significant amounts of PFCAs.

Ellis et al. 2004 showed by means of smog chamber experiments that 4:2 FTOH, 6:2 FTOH and 8:2 FTOH can be atmospherically degraded to form persistent PFCAs (see Figure 3). This process only occurs in remote, pristine regions with low NO_X abundance, thus yielding enough OH radicals to initiate the oxidation of FTOHs. The analysis of FTOH photooxidation products indicated that each FTOH yielded a PFCA with intact perfluorinated chain, e.g. PFNA for 8:2 FTOH. Additionally, the entire suite of PFCAs ranging from trifluoroacetic acid to PFOA was observed.

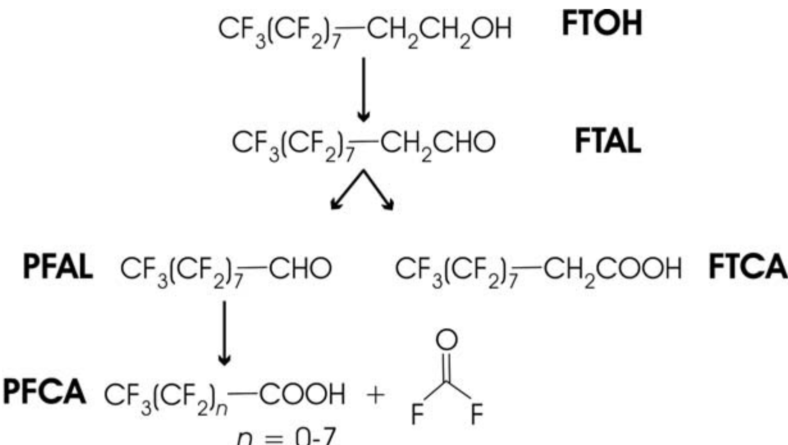


Figure 3. OH-initiated oxidation pathways for FTOHs, leading to PFCA formation. Reproduced from Young et al. 2005 (modified).

In their study, yields of individual PFCAs were between <0.1% (C_2-C_4) and 1.6% (C_9) of the original 8:2 FTOH (*Ellis et al. 2004*). For PFOA and PFNA, the same percentages were observed, which, together with higher bioaccumulation potential of longer-chain PFCAs, may explain the finding of higher levels of odd-length PFCAs in polar bears (see ***chapter 1.3.2***). Reactions of OH radicals with 8:2 FTOH occur via the fluorotelomer aldehyde (FTAL, $C_8F_{17}CH_2CHO$, 6% yield). Moreover, FTCAs ($C_8F_{17}CH_2COOH$, 26% yield), perfluoroaldehydes (PFALs, $C_8F_{17}CHO$, 21% yield), carbonylfluoride (COF_2, 22% yield), PFOA and PFNA are formed, see Figure 3. *Hurley et al. 2004b* described a detailed study on atmospheric oxidation products of 4:2 FTOH.

While wet deposition seems quite insignificant for FTOHs it is more probable for their atmospheric intermediates, FTCAs (yield 26%, see above) due to higher water solubility and lower vapour pressure as described by *Loewen et al. 2005*. A modeling study presented by *Wallington et al. 2006* brought further evidence regarding the plausibility of the LRAT theory of FTOHs and subsequent degradation to form PFCAs. It showed that molar yields of PFOA from 8:2 FTOH were 1-10%, depending on location and season, which was high enough to explain the observed PFCA levels in Arctic fauna through LRAT of FTOHs.

FOSAs / FOSEs are suspected to contribute to the PFCA and PFOS burden in remote locations by means of atmospheric transport and oxidation. However, the low volatility of FOSAs / FOSEs hampered smog chamber experiments for the C_8 analogues. Only recently, *Martin et al. 2006* investigated the degradability of N-alkylated fluorobutane sulfonamides (FBSAs) in a smog chamber. As for FTOHs, reaction with OH radicals was found to be the dominant mechanism. leading to an atmospheric lifetime of NEtFBSA of 20-50 days. The reaction mechanism showed a ketone ($C_4F_9SO_2N(H)C(O)CH_3$) and aldehyde 1 ($C_4F_9SO_2N(H)CH_2CHO$) as primary products, while aldehyde 2 ($C_4F_9SO_2N(H)CHO$) was presumed to be a secondary oxidation product (see Figure 4). PFBS was not observed in any sample, but C_2-C_4 PFCAs were detected in all samples with a proposed yield of 45%.

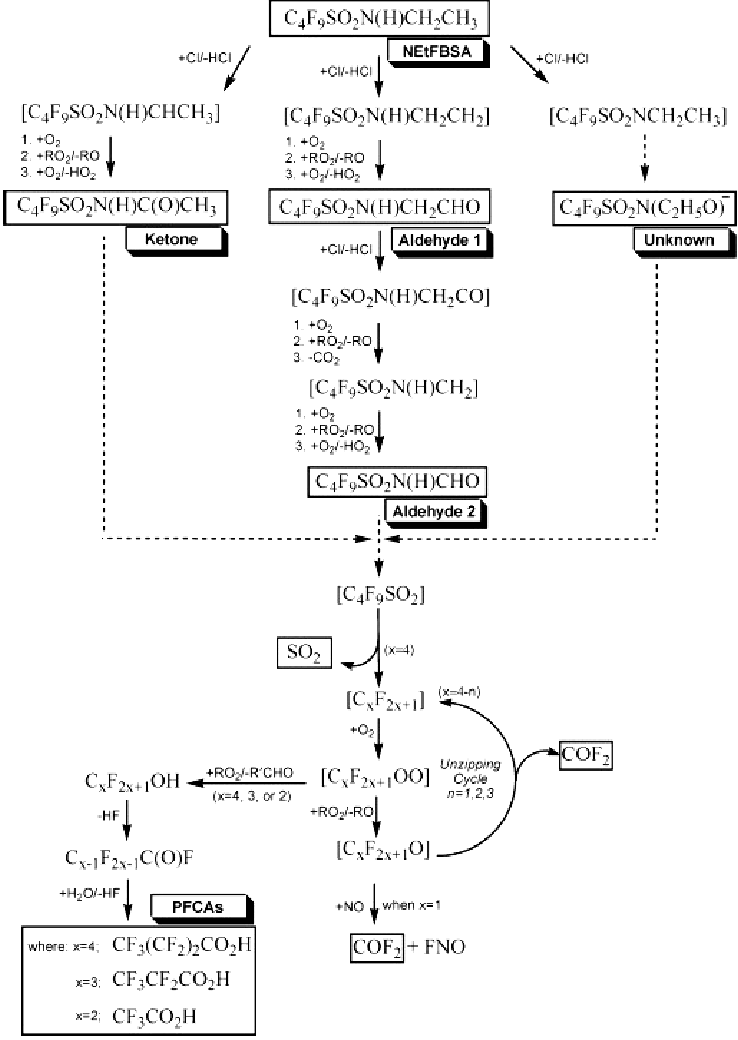


Figure 4. OH-initiated gas-phase oxidation of NEtFBSA, leading to PFCA formation. Reproduced from Martin et al. 2006.

D´Eon et al. 2006 described an atmospheric lifetime of ~2 days for N-methyl fluorobutane sulfonamidoethanol (NMeFBSE). Again, reaction with OH radicals was found to be the dominant process. Degradation products included the aldehyde $C_4F_9SO_2N(CH_3)CH_2CHO$, NMeFBSA, PFBA, perfluoropropanoic acid, trifluoroacetic acid, carbonyl fluoride (COF_2) and PFBS (see Figure 5). Yields of PFBS and C_2-C_4 PFCAs were determined at 1% and 10%, respectively. The atmospheric N-dealkylation product, NMeFBSA with an atmospheric lifetime of ~20 days as discussed above ensures that NMeFBSE may also contribute to the PFAS burden in remote locations despite its relatively short atmospheric lifetime.

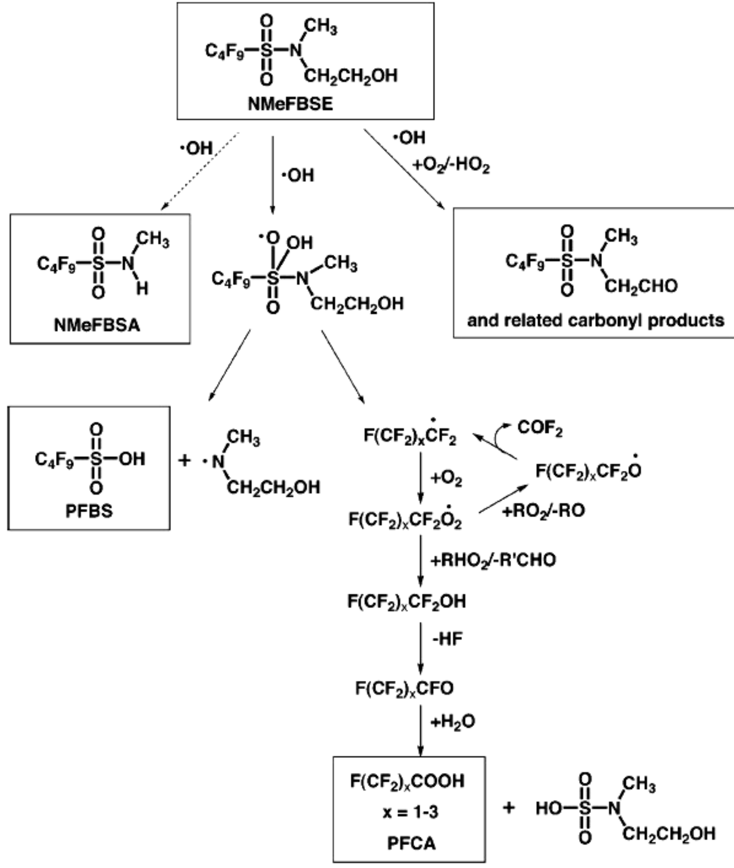


Figure 5. OH-initiated gas-phase oxidation of NMeFBSE, leading to the formation of both PFBS and PFCAs. Reproduced from D´Eon et al. 2006.

Young et al. 2005 estimated the PFOA flux to the Arctic due to LRAT to be 114-586 kg/year. Ice caps were sampled far away from water bodies to ensure inputs would be mainly atmospherically derived, and analysed for PFOS, PFOA, PFNA as well as PFDA. Individual PFAS were found in the sub-ng/L up to low ng/L range in melted snow samples.

2. Aim and outline of the work

Within this chapter, the focus and realisation of this work are described.

The main aim of this PhD thesis was to improve our understanding of the occurrence, distribution pattern, concentration gradients and transport mechanisms of neutral, volatile PFAS between source regions and remote, marine locations.

To achieve this aim the following objectives were defined:

a) Development, optimisation and validation of a trace-analytical method for the compound-specific determination of neutral, volatile PFAS in environmental air samples.

b) Application of the protocol to investigate levels of the target analytes in urban as well as remote areas, with a special focus on coastal regions.

Prior to the PhD thesis at hand, little information about the transport of PFAS in air was available. There was no published concentration data of neutral, volatile PFAS outside North America. The need for methods to monitor these compounds in the lower troposphere was also emphasised by *Giesy & Kannan 2002*. In Tables 11 and 12, the analytes of interest of this work are shown. They comprise FTOHs, an additional analyte, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octyl acrylate (6:2 PFOAc), the non-alkylated PFOSA as well as N-alkyl FOSAs / FOSEs. Additionally, the improvements of the original analytical protocol (*Martin et al. 2002*) targeted by this work are described. Finally, the different studies and sampling campaigns performed within this PhD thesis are briefly outlined.

Table 11. FTOHs and 6:2 PFOAc, their acronyms and structures.

Compound name	**Acronym**	**Structure**
1H,1H,2H,2H-perfluoro-1-hexanol	4:2 FTOH	
1H,1H,2H,2H-perfluoro-1-octanol	6:2 FTOH	
1H,1H,2H,2H-perfluoro-1-decanol	8:2 FTOH	
1H,1H,2H,2H-perfluoro-1-dodecanol	10:2 FTOH	
3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro octyl acrylate	6:2 PFOAc	

Table 12. FOSAs and FOSEs, their acronyms and structures.

Compound name	Acronym	Structure
Perfluorooctane sulfonamide	PFOSA	
N-methyl fluorooctane sulfonamide	NMeFOSA	
N-ethyl fluorooctane sulfonamide	NEtFOSA	
N-methyl fluorooctane sulfonamidoethanol	NMeFOSE	
N-ethyl fluorooctane sulfonamidoethanol	NEtFOSE	

Improvements of the original analytical method

The analytical protocol for the determination of neutral, volatile PFAS in high-volume air samples as described by *Martin et al. 2002* was optimised and fully validated in the first stage of this PhD thesis as described in detail in ***publication I***. Main modifications of the original method included the optimisation of the sample extraction. Originally, cold-column elution of PUF/XAD columns was done in five steps using a total volume of approx. 1000 mL EtOAc. Method improvement aimed at minimising this volume, thus making the extraction procedure much less time and solvent consuming and reducing losses of the most volatile compounds from the extracts during long concentration processes.

A substantial improvement of the original method was the application of a suite of mass-labelled IS spiked before sampling which allowed for correction of analyte losses during sampling, sample extraction, extract concentration and analysis. The IS used in the course of this PhD thesis are displayed in Table 13. Furthermore, the IS accounted for possible matrix enhancement / suppression effects, especially for the observed signal enhancement caused by the specific matrix resulting from extraction of PUF/XAD with EtOAc (for details see ***publication I***). By application of two odd-numbered FAs used as RIS (spiked just before sample analyses, Table 13), recoveries of the IS could be calculated. This allowed for an enhanced interpretation of the concentration data.

By means of parallel sampling with two pumps sampling at different velocities, an investigation of method precision was made possible. Furthermore, blank contamination is frequently observed concerning the analysis of ionic PFAS, especially PFCAs (compare ***chapter 1.2.3***). Therefore, a thorough investigation of field blanks was performed, so that false-positive results could be excluded: *Individual blanks* were taken during collection of each sample, whereas *overall blanks* were collected for the whole period during sampling at each location.

Table 13. Internal standards (IS), recovery internal standards (RIS), acronyms and structures.

Compound name	***Acronym***	***Structure***
2-perfluorohexyl-[1,1-$^{2}H_2$]-[1,2-$^{13}C_2$]-ethanol	6:2 FTOH [M+4] (IS)	
2-perfluorooctyl-[1,1-$^{2}H_2$]-[1,2-$^{13}C_2$]-ethanol	8:2 FTOH [M+4] (IS)	
2-perfluorodecyl-[1,1-$^{2}H_2$]-[1,2-$^{13}C_2$]-ethanol	10:2 FTOH [M+4] (IS)	
D_3-N-methyl fluorooctane sulfonamide	NMeFOSA [M+3] (IS)	
D_5-N-ethyl fluorooctane sulfonamide	NEtFOSA [M+5] (IS)	
1H,1H-perfluoro-1-octanol	7:1 FA (RIS)	
1H,1H-perfluoro-1-dodecanol	11:1 FA (RIS)	

Sampling campaigns

In the beginning of this work, sampling was done in the European Arctic on board of the German research vessel Polarstern during expeditions ARKXX-1/2 (***chapter 6.1***) During this campaign, the original analytical method described by *Martin et al. 2002* was applied. Furthermore, the optimised and validated analytical protocol was tested at a location with presumed high environmental air concentrations of the investigated compounds (metropolitan Hamburg). In comparison, it was also applied to air samples from a rural location in Northern Germany (Waldhof, background monitoring station of the German Federal Environmental Agency (UBA) and European Monitoring and Evaluation Program (EMEP), see ***publication II***).

In order to investigate the concentration gradient of neutral, volatile PFAS between locations with relatively high production and emission and less industrialised areas, air samples were taken on a second Polarstern cruise (***publication III***). Expedition ANTXXIII-1 between Bremerhaven, Germany and Capetown, Republic of South Africa was used to determine the latitudinal gradient of the investigated compounds in coastal regions of both hemispheres. Additionally, in order to investigate European background levels of neutral, volatile PFAS for comparison with the ship-based data, a sampling campaign was performed at Mace Head, EMEP and Global Atmospheric Watch (GAW) station on the West coast of Ireland (***chapter 6.2***). Finally, a new sampling method for airborne PFAS using commercially available solid-phase extraction (SPE) cartridges was developed and applied to indoor as well as outdoor air samples (***chapter 6.3***).

3. *Publication I*

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ORIGINAL PAPER

An improved method for the analysis of volatile polyfluorinated alkyl substances in environmental air samples

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Abstract This article describes the optimisation and validation of an analytical method for the determination of volatile polyfluorinated alkyl substances (PFAS) in environmental air samples. Airborne fluorinated telomer alcohols (FTOHs) as well as fluorinated sulfonamides and sulfonamidoethanols (FOSAs/FOSEs) were enriched on glass-fibre filters (GFFs), polyurethane foams (PUFs) and XAD-2 resin by means of high-volume air samplers. Sensitive and selective determination was performed using gas chromatography/chemical ionisation–mass spectrometry (GC/CI–MS). Five mass-labelled internal standard (IS) compounds were applied to ensure the accuracy of the analytical results. No major blank problems were encountered. Recovery experiments were performed, showing losses of the most volatile compounds during extraction and extract concentration as well as strong signal enhancement for FOSEs due to matrix effects. Breakthrough experiments revealed losses of the most volatile FTOHs during sampling, while FOSAs/FOSEs were quantitatively retained. Both analyte losses and matrix effects could be remediated by application of adequate mass-labelled IS. Method quantification limits (MQLs) of the optimised method ranged from 0.2 to 2.5 pg/m^3 for individual target compounds. As part of the method validation, an inter-laboratory comparison of instrumental quantification methods was conducted. The applicability of the method was demonstrated by means of environmental air samples from an urban and a rural location in Northern Germany.

Keywords Fluorotelomer alcohols · Fluorooctane sulfonamides/sulfonamidoethanols · High-volume air sampling · GC/PCI–MS · Isotope-labelled internal standards · Matrix effects

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Introduction

The recent determination of per- and polyfluorinated alkyl substances (PFAS) in biota from remote regions and even in human blood from all over the world [1–3] prompted much research into possible adverse effects [4, 5] and concentrations [6] in organisms. Among these ubiquitously found anthropogenic chemicals are perfluoroalkane sulfonates and perfluorocarboxylates (PFCAs) that are 4–15 carbon atoms

in chain length. The best investigated compounds of these groups are the C_8-chemicals perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). They have been produced in large amounts since the 1970s and 1950s, respectively. PFOS was applied in many industrial and consumer products, while PFOA is used in the production of fluoropolymers such as polytetrafluoroethylene.

The main manufacturer of PFOS-based chemicals in the US, 3M, phased out the production of this product line in 2002 [7]. 3M used the electrochemical fluorination (ECF) process, yielding an isomer mixture which is dominated by the linear isomer and additionally contains 15–30% branched isomers, and it was the only major company known to apply ECF [7]. *N*-alkylated fluorooctane sulfonamides and sulfonamidoethanols (FOSAs/FOSEs) were produced by ECF. Other manufacturers of PFAS make use of the telomerisation process, yielding exclusively linear compounds, which normally contain an even number of fluorinated and two nonfluorinated carbon atoms adjacent to the functional group. Telomerisation is also used to produce fluorotelomer alcohols (FTOHs) of the general structure CF_3-$(CF_2)_n$-CH_2-CH_2OH, where n=3, 5, 7, 9. They are named based on the ratio of fluorinated to nonfluorinated carbons (e.g. 8:2 FTOH for n=7). Both production processes are described in detail by Schultz et al. [8].

FOSAs/FOSEs were used in a variety of products for water- and dirt-proofing on carpets, leather, upholstery and textiles, as paper protectors and performance chemicals (e.g. in aqueous-film-forming fire-fighting foams [9]) or as an insecticide (*N*-ethyl fluorooctane sulfonamide (NEtFOSA): Sulfluramid). FTOHs are produced in large amounts and are used in similar applications as FOSAs/FOSEs, such as precursor compounds in the production of fluorinated polymers used in paper and carpet treatments, moreover in the production of paints, coatings, adhesives, etc. [10, 11].

The detection of ionic PFAS (PFOS and PFCAs) in organisms from remote locations [12–14] was surprising at first, as these chemicals are nonvolatile and only moderately water-soluble. Long-range atmospheric transport seemed quite unlikely for these compounds. To explain the mentioned observations, a theory arose that volatile PFAS precursors could be transported to remote regions via the atmosphere and be degraded in situ (e.g. in the polar regions) to form the persistent PFOS and PFCAs [15]. This hypothesis was strongly supported by the detection of the potential precursors (FTOHs and FOSAs/FOSEs) in air samples from North America [16, 17], and by a number of smog chamber degradation studies [10, 18, 19]. Furthermore, several studies showed the biodegradability of neutral, volatile precursors to form persistent, ionic PFAS [11, 20, 21].

Analytical methods for volatile PFAS include gas chromatography/chemical ionisation–mass spectrometry (GC/CI–MS) as well as liquid chromatography/negative electrospray ionisation–(tandem) mass spectrometry (LC/(−)ESI–MS(/MS)). GC methods have been published for both FTOHs and FOSAs/FOSEs in environmental [16, 17] and indoor [22] air with instrumental detection limits (IDLs) of 0.2–20 pg [16], 0.3–5.0 pg [17] and 3.6–3.7 pg (FOSEs only) [22]. Regarding LC methods, MS/MS was used on one occasion for FTOHs with IDLs of 1–20 pg [23], and on another for NEtFOSA and two fluorinated alcohols (IDLs=0.02−0.1 pg) [24]. LC–MS was applied for NEtFOSA and *N*-ethyl fluorooctane sulfonamidoethanol (NEtFOSE) with IDLs of 0.02 pg [25]. Despite the fact that lower or comparable IDLs can be obtained using LC methods, possible co-analysis of nonionic and ionic PFAS is impeded by ionisation suppression of FTOHs caused by the buffered mobile phases needed to separate ionic PFAS [23]. The only application of an LC–MS method to air samples is described by Boulanger et al. [26], where the method detection and quantification limits (MDLs/MQLs) are not specified, and so a comparison of method sensitivities is not possible.

The aim of this study was to optimise and validate a highly selective and sensitive analytical method for the simultaneous analysis of FTOHs and FOSAs/FOSEs in outdoor air samples. The analytical protocol developed by Martin et al. [16] using GC/CI–MS was adapted, further optimised and validated. Five mass-labelled internal standards (IS) were used to ensure the accuracy of analytical results. The instrumental method performance was evaluated by comparison to a similar method developed at the Norwegian Institute for Air Research (NILU) in Tromso. Finally, the applicability of the method was shown by means of environmental air samples from an urban and a rural site in Northern Germany.

Experimental

Chemicals and standards 4:2 FTOH (of 97% purity) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro octyl acrylate (6:2 PFOAc, 97%) were purchased from Aldrich (Steinheim, Germany). 6:2 FTOH (97%), 8:2 FTOH (97%), 10:2 FTOH (97%), 1H,1H-perfluoro-1-octanol (7:1 fluorinated alcohol (FA), 98%) and 1H,1H-perfluoro-1-dodecanol (11:1 FA, 90%) were from Lancaster Synthesis (Frankfurt a.M., Germany). NEtFOSA (95%) and perfluorooctane sulfonamide (PFOSA, 97%) were from ABCR (Karlsruhe, Germany). Mass-labelled compounds of >98% purity used as IS were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada): 6:2 FTOH [M+4], 8:2 FTOH [M+4], 10:2 FTOH [M+4], *N*-methyl fluorooctane sulfon-

amide (NMeFOSA [M+3]) and NEtFOSA [M+5]. Native NMe-FOSA and *N*-methyl fluorooctane sulfonamidoethanol (NMeFOSE) were donated by 3M, while NEtFOSE was obtained from the Mabury group at the University of Toronto, Canada. All native FOSAs/FOSEs were a mixture of linear and branched isomers at a ratio of approximately 70:30, as determined by GC/electron impact (EI)–MS analyses and also described in [27], while mass-labelled FOSAs only contained the linear isomer. Independent FTOH reference compounds (named "R-X") were purchased from Fluorochem (Old Glossop, UK): R-4:2 FTOH (97%), R-6:2 FTOH (97%), R-8:2 FTOH (97%), R-10:2 FTOH (97%). Mass-labelled IS were spiked before sampling (gaseous phase) or before sample extraction (particulate phase), respectively, to correct for analyte losses during sampling and/or extraction as well as for signal suppression/enhancement during determination. Recovery internal standards (RIS: 7:1 FA, 11:1 FA) were added to sample extracts just before analyses to determine recoveries of the IS. Structures of all compounds included in this study are depicted in Table 1.

Ethyl acetate (EtOAc) and methanol of SupraSolv quality as well as sodium sulfate for organic trace analysis were obtained from Merck (Darmstadt, Germany). All standards and solvents were used as received. Nitrogen of ≥99.9995% purity was purchased from Messer Griesheim/ Air Liquide (Wittenberg, Germany).

Preparation of sampling media For the enrichment of airborne PFAS, glass columns with a glass frit, a slice of polyurethane foam (PUF, 6.5 cm diameter/5 cm height, Klaus Ziemer GmbH, Langerwehe, Germany), 25 g of Amberlite XAD-2 resin (Supelco, Munich, Germany) and another slice of PUF were used. The PUF/XAD-2/PUF columns were prepared in a clean lab (class 10.000) at GKSS and extensively cleaned by Soxhlet extraction using 500 mL of methanol (2 d) and 500 mL of EtOAc (2 d). The sampling columns were dried using high-purity nitrogen at a pressure of ~1.5 bar and sealed in alumina-coated polypropylene (PP) bags. GF8 glass-fibre filters (GFF) of 15 cm in diameter were purchased from Schleicher & Schuell/ Whatman (Dassel, Germany), rinsed with EtOAc and heated overnight at 250 °C. GFFs were individually wrapped in aluminum foil and sealed in alumina-coated PP bags.

Sampling High-volume air samples were taken after spiking 40 ng of the IS 6:2 FTOH [M+4], 8:2 FTOH [M+4], 10:2 FTOH [M+4], NMeFOSA [M+3] and NEtFOSA [M+5] (10 μL of a 4 ng/μL solution in EtOAc) onto the upper PUF slice. Sampling was started immediately using SV 5.130/2-05 pumps purchased from ISAP (Asendorf, Germany) at a flow rate of approximately 12–15 m^3/h. The described method was used to analyse environmental air samples taken in spring 2005 at two locations in Northern Germany (Hamburg: urban; Waldhof: rural). Waldhof is a background monitoring site of the German Federal Environmental Agency (UBA) and European Monitoring and Evaluation Program (EMEP) station, located around 100 km south-east of Hamburg. A comprehensive sampling campaign at both locations is described in detail elsewhere [28].

Collection of environmental air samples was done for ~3.5 days, leading to average sample volumes of 1160 m^3. After sampling, GFFs were sealed into test tubes, stored in alumina-coated PP bags together with the respective PUF/ XAD columns, and stored at −18 °C until extraction within few days. To control possible background contamination, field blanks were taken by attaching open PUF/XAD columns close to the sampling sites during sampling. They were stored, extracted and analysed along with the samples.

Sample extraction PUF/XAD columns were extracted using cold column elution with 300 mL EtOAc (infusion time: 1 h) and another 200 mL-aliquot EtOAc (30 min), and the extracts were combined. GFFs were extracted in round-bottomed flasks after spiking 40 ng of the IS (i.e. 6:2 FTOH [M+4], 8:2 FTOH [M+4], 10:2 FTOH [M+4], NMeFOSA [M+3] and NEtFOSA [M+5], 10 μL of a 4 ng/μL solution in EtOAc) directly onto the filter using solvent soak with 50 mL EtOAc. The flask was placed on a mechanical shaker for 1 min. Subsequently, the extract was transferred to another flask and the procedure was repeated three more times (resulting in 200 mL EtOAc extract). Both PUF/XAD and GFF extracts were concentrated to approximately 1 mL using a Rotavapor R-200 (Büchi, Flawil, Switzerland), dried over sodium sulfate, filtered over precleaned cotton wool and transferred to graduated Wheaton vials. The extracts were finally concentrated to 200 μL under a gentle stream of high-purity nitrogen. Before GC/CI–MS determination, 40 ng of the RIS 7:1 FA and 11:1 FA (10 μL of a 4 ng/μL solution in EtOAc) were spiked to sample extracts as well as to calibration solutions.

Instrumental analysis Quantitative analytical determination was performed using positive chemical ionisation (PCI) GC–MS operating in the single ion monitoring (SIM) mode. For this study, an Agilent (Böblingen, Germany) 6890 N gas chromatograph coupled to an HP 5973 mass-selective detector (MSD) was used.

To separate the analytes, a polar Varian CP-Wax 57 CB capillary column for glycols and alcohols (25 m× 0.25 mm×0.2 μm) and an Agilent HP-INNOWax polyethylene glycol precolumn (~5 m×0.25 mm×0.2 μm) were used. Helium was employed as carrier gas at a constant flow of 1.1 mL/min. The GC oven was programmed as

Table 1 Analytes, acronyms, retention times (RT; for chromatographic conditions see the Experimental part), structures and ions detected in PCI and NCI mode

Analyte	Acronym, molecular weight (u)	RT (min)	Structure	Ions in PCI (*m/z*) (% rel. abundance)	Ions in NCI (*m/z*)
1H,1H,2H,2H-perfluoro-1-hexanol	4:2 FTOH, 264	6.52	$CF_3-CF_2-CF_2-CF_2-CH_2-CH_2OH$	265.0 (100), 227.0 (46), 293.1 (7)	-
3,3,4,4,5,5,6,6,7,7,8,8,8-trideca-fluoro octyl acrylate	6:2 PFOAc, 418	7.77	$CF_3-(CF_2)_5-CH_2-CH_2-O-C(=O)-CH=CH_2$	419.0 (100), 447.0 (15), 399.0 (10)	-
1H,1H,2H,2H-perfluoro-1-octanol	6:2 FTOH, 364	9.33	$CF_3-(CF_2)_5-CH_2-CH_2OH$	365.1 (100), 327.0 (56), 393.1 (13)	-
1H,1H,2H,2H-perfluoro-1-decanol	8:2 FTOH, 464	11.38	$CF_3-(CF_2)_7-CH_2-CH_2OH$	465.1 (100), 427.0 (46), 493.1 (14)	-
1H,1H,2H,2H-perfluoro-1-dodecanol	10:2 FTOH, 564	13.01	$CF_3-(CF_2)_9-CH_2-CH_2OH$	565.1 (100), 527.1 (36), 593.2 (13)	-
N-ethyl fluorooctane sulfonamide	NEtFOSA, 527	16.50[a]	$CF_3-(CF_2)_7-S(=O)_2-NH-CH_2-CH_3$	528.2[b]	483.0, 400.1, 526.1
N-methyl fluorooctane sulfonamide	NMeFOSA, 513	16.84[a]	$CF_3-(CF_2)_7-S(=O)_2-NH-CH_3$	514.1[b]	483.0, 512.0, 400.1
N-methyl fluorooctane sulfonamido-ethanol	NMeFOSE, 557	17.68[a]	$CF_3-(CF_2)_7-S(=O)_2-N(CH_3)-CH_2-CH_2OH$	540.1 (100), 558.1 (99)	400.1, 483.0, 494.0
N-ethyl fluorooctane sulfonamido-ethanol	NEtFOSE, 571	17.75[a]	$CF_3-(CF_2)_7-S(=O)_2-N(CH_2-CH_3)-CH_2-CH_2OH$	554.1 (100), 572.1 (98)	483.0, 400.1, 508.1
Perfluorooctane sulfonamide	PFOSA, 499	20.41[a]	$CF_3-(CF_2)_7-S(=O)_2-NH_2$	500.0[b]	483.0, 400.1
2-perfluorohexyl-[1,1-$^2H_2$]-[1,2-$^{13}C_2$]-ethanol	6:2 FTOH [M+4] (IS), 368	9.29	$CF_3-(CF_2)_5-{}^{13}CH_2-{}^{13}CD_2OH$	369.0 (100), 331.1 (33), 397.1 (11)	-
2-perfluorooctyl-[1,1-$^2H_2$]-[1,2-$^{13}C_2$]-ethanol	8:2 FTOH [M+4] (IS), 468	11.35	$CF_3-(CF_2)_7-{}^{13}CH_2-{}^{13}CD_2OH$	469.0 (100), 431.0 (33), 497.1 (13)	-
2-perfluorodecyl-[1,1-$^2H_2$]-[1,2-$^{13}C_2$]-ethanol	10:2 FTOH [M+4] (IS), 568	12.99	$CF_3-(CF_2)_9-{}^{13}CH_2-{}^{13}CD_2OH$	569.1 (100), 531.1 (32), 597.2 (14)	-
D_5-N-ethyl fluorooctane sulfonamide	NEtFOSA [M+5] (IS), 532	16.48	$CF_3-(CF_2)_7-S(=O)_2-NH-CD_2-CD_3$	533.1[b]	483.0, 531.1
D_3-N-methyl fluorooctane sulfonamide	NMeFOSA [M+3] (IS), 516	16.82	$CF_3-(CF_2)_7-S(=O)_2-NH-CD_3$	517.0[b]	483.0, 515.1
1H,1H-perfluoro-1-octanol	7:1 FA (RIS), 400	10.59	$CF_3-(CF_2)_6-CH_2OH$	401.0 (100), 381.0 (45), 345.0 (5)	-
1H,1H-perfluoro-1-dodecanol	11:1 FA (RIS), 600	13.75	$CF_3-(CF_2)_{10}-CH_2OH$	601.1 (100), 581.1 (42), 545.1 (5)	-

[a] The mentioned RT is that of the main peak of several isomers.
[b] Qualitative confirmation was performed in NCI mode.

follows: 50 °C (1 min)/50 °C > 70 °C (3 °C/min, 0 min)/ 70 °C > 130 °C (10 °C/min, 0 min)/130 °C > 225 °C (20 °C/min, 11.4 min)/225 °C > 50 °C (80 °C/min, 0 min), resulting in a run time of 32 min. Retention times (RT) of all compounds are given in Table 1. Injection volumes were 1 µL. The PTV inlet was programmed at 200 °C (2 min)/200 °C > 250 °C (500 °C/min, 3 min)/250 °C > 200 °C (100 °C/min, 10 min) with a pulsed splitless injection mode. The GC–MS interface was set to 250 °C.

EI was only used for the determination of standard purities, because of the low intensity of the molecular ions and the lack of specific fragments. PCI was chosen due to the simple yet definite mass spectra compared to negative chemical ionisation (NCI) [29]. The reagent gas (methane) was set to 20% in PCI mode and to 40% in NCI mode, respectively. For most analytes, at least two *m/z* were monitored, except for PFOSA, NEtFOSA, NMeFOSA and the respective mass-labelled analogues, where only one *m/z* could be detected (Table 1). For FOSAs, qualitative confirmation in NCI mode was performed (i.e. the determination of FOSAs was confirmed if the ions in NCI mode, as given in Table 1, were detected). Quantification was based on the most intensive ion (quantifier), while the other ions were used as qualifiers. Identification of the compounds was ensured (a) by monitoring several characteristic ions for each analyte, (b) by considering a specific time window of elution (mean RT of standards ±0.5 s), and (c) by specific ratios of quantifier and qualifier ions (±20% of the ratio determined in calibration solutions). For some analytes at very low concentrations, a reasonable confirmation by qualifier ratios was not possible, as peak areas were close to the noise in the chromatogram.

Internal standard compounds Quantification was done by normalisation of the analyte areas to those of the corresponding IS, followed by quantification using the external two-point calibration curve, as described in detail in the Results and discussion section. In the optimised method, several compounds were used as IS to be spiked before sampling in order to control the whole process from sampling and extraction to determination. RIS were spiked just before GC/PCI–MS analysis to determine recoveries of the IS. For analytes where mass-labelled IS were available (i.e. 6:2 FTOH [M+4], 8:2 FTOH [M+4], 10:2 FTOH [M+4], NMeFOSA [M+3], NEtFOSA [M+5]), those were applied. Due to the unavailability of further mass-labelled IS at the time of the study, 6:2 FTOH [M+4] was also used as IS for 4:2 FTOH and 6:2 PFOAc due to similar RTs, while NEtFOSA [M+5] was also assigned to the later-eluting NMeFOSE, NEtFOSE and PFOSA. Moreover, 7:1 FA and 11:1 FA were employed as RIS because of their chemical and structural similarities to the analytes of interest. The RIS had been shown to be not detected (n.d.) in environmental air samples. 11:1 FA was used to calculate recoveries of 10:2 FTOH [M+4] due to similar behaviour in the sample matrix, while 7:1 FA was used as RIS for all other IS.

Method validation

Blank experiments Solvent blanks (n=4) were determined using 500 mL EtOAc spiked with 40 ng of the IS mixture (10 µL of 4 ng/µL in EtOAc). *Column blanks* (n=4) were evaluated by spiking of the IS onto the upper PUF slice of sampling columns and subsequent drawing of 10 m^3 air through the material in order to preclude evaporative loss of the IS. Extraction, concentration and determination were done as described above.

Recovery experiments The first recovery experiment was to test how many elution steps were necessary for the quantitative recovery of the analytes. For this purpose, all analytes were spiked at high concentrations (400 ng) to the glass columns containing the sampling media. Immediately afterwards, the columns were soaked with 300 mL of EtOAc and allowed to infuse for 1 h. The solvent was eluted and replaced by 200 mL of EtOAc (30 min infusion, three additional repeats). All five fractions were concentrated separately to 200 µL and determined by GC/PCI–MS. The first two fractions together contained >96% of the analytes, so that in the following, elution was done with 300 mL EtOAc (1 h) and another 200 mL aliquot (30 min).

Several spiking experiments at two concentration levels were performed to determine the general recovery rates of the analytes in the gaseous and particulate phase. *Solvent recoveries* were evaluated by spiking of 40 ng of the IS mixture (10 µL of 4 ng/µL in EtOAc) as well as 20 or 80 ng absolute (n=3+3) of a standard mixture containing 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 6:2 PFOAc, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE and PFOSA at a concentration of 2 ng/µL in EtOAc (10 or 40 µL, respectively) into 500 mL EtOAc and subsequent concentration to 200 µL as described above. To determine *column recoveries*, 40 ng IS and 20 or 80 ng absolute (n=3+3) of the analytes were spiked onto the upper PUF slice of a sampling column. 10 m^3 of air were drawn through the material to ensure there was no evaporative loss, and the spiked columns were subsequently treated like real samples. Furthermore, *GFF recoveries* were investigated by spiking 40 ng of the IS and 20 or 80 ng absolute (n=4+4) of the analytes onto precleaned GFFs and subsequent extraction as described above.

Breakthrough experiments In order to check the quantitative collection of the analytes in the gaseous phase,

breakthrough experiments were conducted. Two sampling columns were operated in series (n=2). The upper column was spiked with 40 ng of IS as well as with 80 ng (40 µL of 2 ng/µL in EtOAc) of the analyte mixture, while the lower column was not spiked at all in order to investigate breakthrough of the analytes as well as the IS from the upper column. Subsequently, approximately 1000 m^3 of air were drawn through the tandem column. Quantification was done using the internal standard method for the upper column, while the lower column was quantified externally.

Interlaboratory comparison As part of the method validation, an interlaboratory comparison of instrumental quantification was conducted at GKSS Research Centre Geesthacht and the Norwegian Institute for Air Research (NILU) in Tromso. Two unknown standard mixtures were exchanged and analysed, containing 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE and PFOSA in a lower (20–250 pg/µL, prepared at GKSS) or an upper concentration range (100–900 pg/µL, prepared at NILU), respectively.

Results and discussion

Instrumental linear range The calibration procedure was adapted from the draft of ISO 22032 for the determination of polybrominated diphenyl ethers [30] and was applied to PFAS analysis for the first time. Calibration solutions for the quantification of the analytes were prepared to cover the range of 10–800 pg/µL. This range was subdivided into a lower and an upper calibration range: 10–200 and 200–800 pg/µL. Each range had been shown to be linear by analysis of individual calibration solutions at 10, 25, 50, 100, 200, 400 and 800 pg/µL. In the following, two-point calibrations for each subrange were carried out. Triplicate analyses at each level (10 and 200 or 200 and 800 pg/µL, respectively) were used for further calculations. In addition, two independent standard solutions containing the reference compounds (R-4:2 FTOH, R-6:2 FTOH, R-8:2 FTOH, R-10:2 FTOH) and 6:2 PFOAc, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE and PFOSA in the middle of the lower and upper calibration range (at 100 and 400 pg/µL, respectively) were also analysed in triplicate to check the accuracy and stability of the GC–MS system.

Blank experiments Solvent and *column blanks* are given in Table 2. Regarding *solvent blanks*, only NEtFOSA, NMeFOSE (<instrumental quantification limit, IQL as discussed below) and NEtFOSE could be detected, corresponding to absolute amounts in whole extracts of 0.02 ng (NEtFOSA) or 0.01 ng (NEtFOSE), respectively. In *column blanks*, only 8:2 FTOH (0.51–0.74 ng), 10:2 FTOH (0.23–0.41 ng), NEtFOSA (<IQL–0.09 ng) and NMeFOSE (n.d.–0.01 ng) could be quantified, while 6:2 FTOH and NEtFOSE were additionally detected below the IQL. Related to average sample volumes of 1160 m^3, these results imply a maximum blank contamination of 0.64 pg/m^3 (8:2 FTOH). In view of the high concentrations

Table 2 Solvent and column blanks, typical instrumental limits of detection and quantification (IDLs/IQLs) using the signal-to-noise (S/N) approach as well as the calibration method, and method quantification limits (MQLs) extrapolated from S/N ratios of real samples with lowest analyte concentrations

Analyte	Solvent blanks (pg/m^3)[a]	Column blanks (pg/m^3)[a]	IDL (pg injected)		IQL (pg injected)		MQL (pg/m^3)
			S/N=3	Calibration method	S/N=10	Calibration method	
4:2 FTOH	n.d.	n.d.	1.1	1.1	3.6	3.7	1.8
6:2 FTOH	n.d.	n.d.–<IQL	1.0	1.3	3.4	4.4	1.4
8:2 FTOH	n.d.	0.44–0.64	0.6	1.7	2.0	5.7	1.0[b]
10:2 FTOH	n.d.	0.20–0.35	0.4	2.2	1.4	7.2	0.7[b]
6:2 PFOAc	n.d.	n.d.	0.3	0.9	0.9	2.9	2.5[c,d]
NEtFOSA	n.d.–0.02	<IQL–0.08	0.2	1.4	0.7	4.7	0.3
NMeFOSA	n.d.	n.d.	0.2	1.3	0.7	4.5	0.2
NMeFOSE	n.d.–<IQL	n.d.–0.01	0.8	2.6	2.6	8.5	0.4
NEtFOSE	n.d.–0.01	n.d.–<IQL	0.7	2.5	2.2	8.3	0.3
PFOSA	n.d.	n.d.	0.2	n.l.	0.8	n.l.	0.6[d]

n.d., not detected; *n.l.*, not linear.
[a] Blanks were related to an average sample volume of 1160 m^3.
[b] Due to detectable method blanks, MQLs were defined as ten times the standard deviation of *column blanks* (n=4).
[c] As 6:2 PFOAc could not be determined in any sample, the corresponding chromatographic noise was integrated and quantified. The result times ten was considered to be the MQL.
[d] Due to very small analyte peak areas, the calibration was forced through the origin.
Details for the calculation of IDLs, IQLs and MQLs are given in the text.

of FTOHs in environmental air samples (Table 3), column blanks could also be influenced by the air volume (10 m^3) drawn through the sampling columns to avoid evaporative loss of the IS. Given the low blank levels, analyte concentrations in real samples were not blank-corrected.

Limits of detection and quantification IDLs, IQLs and MQLs as given in Table 2 were determined using different methods. The blank method was mostly not applicable due to the absence of several analytes in solvent and column blanks. The calibration method (following the German DIN 32645, which is the national equivalent to ISO) was applied using standard mixtures at very low concentrations (2.5, 5.0, 7.5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 pg/µL). However, the procedure most often used in chromatography is the evaluation of the signal-to-noise (S/N) ratio of standard solutions at very low concentration levels. In this study, an extrapolated concentration at a S/N of 3 was taken as the IDL. Correspondingly, a S/N of 10 was related to the IQL.

While IDLs and IQLs only depend on the instrumental sensitivity, MQLs include the whole procedure starting from sampling, and including sample extraction, extract concentration and determination. Furthermore, blank levels must be considered to obviate false-positive results. Given the very low method blanks, MQLs for most analytes were estimated using means of six real samples with lowest analyte concentrations and extrapolation to a S/N of 10 (Table 2). The MQL was only dominated by blank levels for 8:2 FTOH and 10:2 FTOH, where column blank contamination was found. Concerning these two analytes, MQLs were determined as ten times the standard deviation of column blanks (n=4).

Compared to previously reported methods, MQLs determined in our study were very low, as they ranged from 0.2 pg/m^3 (NMeFOSA) to 2.5 pg/m^3 (6:2 PFOAc). These levels correspond to MDLs of between 0.06 and 0.75 pg/m^3. The original analytical protocol developed by Martin et al. showed MDLs of 0.15 (10:2 FTOH) up to 6.2 pg/m^3 (NEtFOSE) [16]. Stock et al. reported MDLs of between 2 (FOSEs) and 14 pg/m^3 (6:2 FTOH) [17], while the method of Shoeib et al. (not including FTOHs) showed MDLs of 0.01 (NEtFOSA) up to 7.1 pg/m^3 (NMeFOSE) [31].

Recovery experiments All recovery experiments were performed in triplicate at two concentration levels each by spiking analyte mixtures at 20 and 80 ng absolute, respectively. Due to comparable findings at both spiking levels, results given in Fig. 1 were combined (PUF/XAD, n=6/GFF, n=8). Absolute recoveries were calculated by normalisation of the analyte areas to those of the

Table 3 Airborne PFAS concentrations (pg/m^3) and recoveries of the IS (%) determined in the gaseous and particulate phases of two sets of parallel air samples from an urban (Hamburg) and a rural (Waldhof) location in Northern Germany. Field blanks of the respective sampling periods are listed. Analyte concentrations are given in brackets if peak areas were smaller than those of the lowest calibration solution

		Hamburg (25–28/04/2005)			Waldhof (23–26/05/2005)		
		Concentration (pg/m^3)	Recovery of IS (%)	Blank (pg/m^3)	Concentration (pg/m^3)	Recovery of IS (%)	Blank (pg/m^3)
4:2 FTOH	gaseous phase	32, 29		n.d.	7.2, 11		n.d.
	particulate phase	n.d.			n.d.		
6:2 FTOH	gaseous phase	55, 56	57, 55	n.d.	29, 29	52, 42	n.d.
	particulate phase	n.d.	40, 48		n.d.	71, 71	
8:2 FTOH	gaseous phase	106, 110	91, 86	1.3	81, 88	77, 54	<1.0
	particulate phase	<1.0	56, 63		<1.0	108, 108	
10:2 FTOH	gaseous phase	29, 28	141, 154	1.1	27, 29	128, 80	<0.7
	particulate phase	<0.7, (0.8)	62, 67		<0.7	110, 112	
6:2 PFOAc	gaseous phase	n.d.		n.d.	n.d.		n.d.
	particulate phase	n.d.			n.d.		
NEtFOSA	gaseous phase	2.5, 2.6	84, 84	<0.3	(2.6), 3.2	86, 59	<0.3
	particulate phase	n.d.	113, 120		n.d.	139, 132	
NMeFOSA	gaseous phase	6.8, 7.2	63, 62	<0.2	5.1, 9.7	69, 32	<0.2
	particulate phase	<0.2	116, 126		<0.2	150, 144	
NMeFOSE	gaseous phase	22, 14		<0.4	4.2, 7.8		n.d.
	particulate phase	7.6, 15			4.7, 3.5		
NEtFOSE	gaseous phase	4.5, 2.6		0.3	5.8, 11		n.d.
	particulate phase	4.8, 8.5			15, 13		
PFOSA	gaseous phase	n.d.		n.d.	n.d.		n.d.
	particulate phase	n.d.			n.d.		

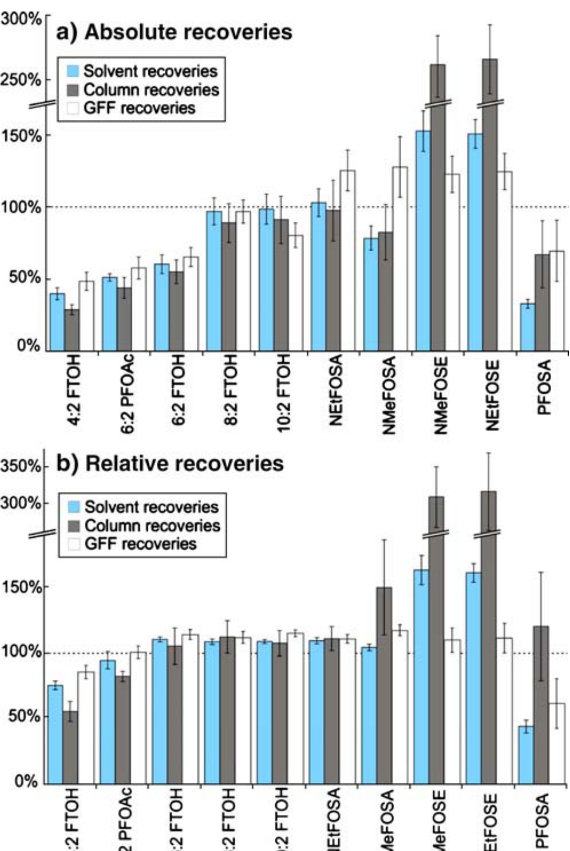

Fig. 1 Absolute (**a**) as well as IS-corrected relative analyte recoveries (**b**) determined at two concentration levels: 20 ng and 80 ng (n=3+3) by spiking into EtOAc (*solvent recoveries*) or onto PUF/XAD columns (*column recoveries*). *GFF recoveries* were determined at 20 ng or 80 ng (n=4+4). Details are given in the text

corresponding *RIS* (7:1 and 11:1, respectively) and quantification using the external two-point calibration curve (Fig. 1a). In this case, the RIS were used to correct for the injection volumes of the autosampler. Recovery experiments at two concentration levels showed absolute *solvent recoveries* of between 33% (PFOSA) and 153% (NMeFOSE), while absolute *column recoveries* were 29% (4:2 FTOH) up to 266% (NEtFOSE). *GFF recoveries* ranged from 49% (4:2 FTOH) to 125% (NEtFOSA and NEtFOSE).

By normalisation of the analyte areas to those of the corresponding *IS*, losses during extraction and extract concentration can be corrected, leading to enhanced accuracy and lower standard deviations. This is demonstrated by the IS-corrected relative recoveries given in Fig. 1b. Relative *solvent recoveries* were found to lie between 44% (PFOSA) and 164% (NMeFOSE), while relative *column recoveries* ranged from 56% (4:2 FTOH) to 151% (NMeFOSA) for most compounds (Fig. 1b). The *column recoveries* were only very high for NMeFOSE and NEtFOSE (311%–319%), where mass-labelled analogs were not available at the time of the study, pointing out the importance of appropriate mass-labelled IS for each individual analyte. Such signal enhancements of FOSEs have also been observed elsewhere [32] and probably lead to overestimation of those compounds in real samples.

Erney et al. characterised matrix enhancement effects concerning the analysis of pesticide residues in food by GC–MS [33]. The authors described the blocking of active sites in the GC system, especially in the injection liner, by matrix constituents as the main reason for the mentioned effect. Following this theory, the coextracted sample matrix increases analyte signals in comparison with solvent-only standard injections where the analytes themselves interact with the active sites. In our study, improved peak shapes in sample analyses compared with standard injections gave an indication that blocking of active sites by matrix constituents might have occurred. This is exemplified for NMeFOSE in Fig. 2. Among several ways to overcome or

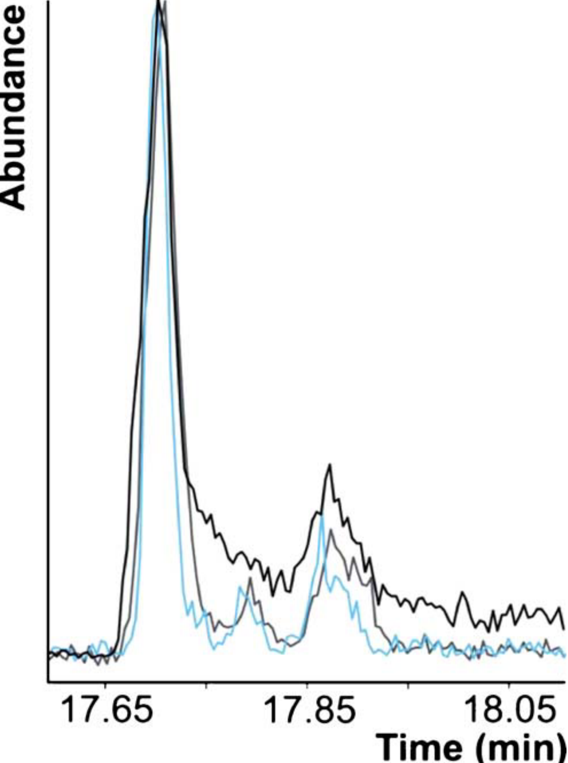

Fig. 2 Chromatograms of NMeFOSE (m/z 558.1) in a standard solution (*black*), as well as sample extracts from Hamburg (*blue*) and Waldhof (*grey*). The improved resolution of isomers in real samples could be attributed to the blocking of active sites in the chromatographic system by matrix constituents

reduce the matrix enhancement effect of up to >200%, Schenck et al. described the usage of matrix-matched standards, the application of an appropriate clean-up, or the use of similarly affected mass-labelled IS [34].

The matrix effects observed for FOSEs could be remediated by IS-correction using NMeFOSE [M+7] and NEtFOSE [M+9], now available from Wellington Laboratories Inc. (Guelph, Ontario, Canada). The same applies for the most volatile compounds 4:2 FTOH and 6:2 PFOAc, where results had to be IS-corrected using the less volatile 6:2 FTOH [M+4], so that losses during extraction and concentration were not fully accounted for (relative recoveries <100%, Fig. 1b). Thus, air concentrations of 4:2 FTOH were probably underestimated. Relative recoveries for those five analytes where mass-labelled analogues could be applied were around 100%, ensuring highly accurate results in air measurements. Regarding relative *GFF recoveries*, values of between 61% (PFOSA) and 115% (NMeFOSA) were determined. No signal enhancement for FOSEs was found in GFFs, leading to the conclusion that the specific matrix resulting from extraction of PUF/XAD columns with EtOAc was mainly responsible for matrix effects. Recoveries of the IS in real samples are given in Table 3.

Breakthrough experiments Figure 3 shows the results from the breakthrough experiments. Relatively high losses for the most volatile compounds were revealed. This holds especially for 4:2 FTOH, where a higher percentage of spiked analyte was found on the unspiked lower "breakthrough" column. When correcting using 6:2 FTOH [M+4], the 4:2 FTOH concentrations are thus underestimated (see

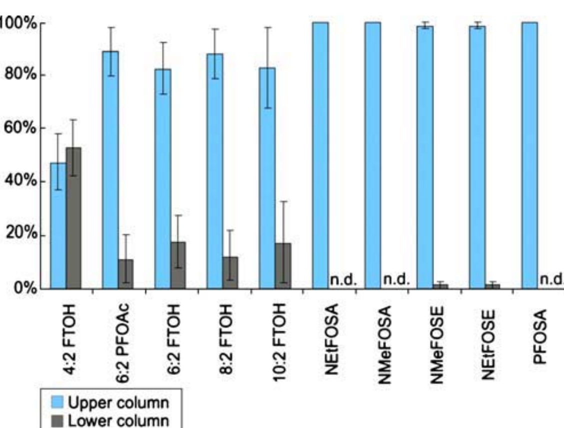

Fig. 3 Evaluation of the quantitative collection of the analytes in the gaseous phase by breakthrough experiments (n=2). Relative recoveries based on "upper column"+"lower column"=100% are given. The upper column (spiked with 40 ng of IS and 80 ng of a standard mixture) showed considerable breakthrough for FTOHs. The lower column (unspiked) was quantified externally

also discussion of recovery experiments above), underlining the importance of the application of the mass-labelled IS 4:2 FTOH [M+4] as soon as available.

Furthermore, moderate breakthrough could be found for the other FTOHs. In accordance with the trend of decreasing volatility with increasing chain length, the breakthrough of 6:2 FTOH was much lower than that of 4:2 FTOH, but higher than the breakthrough of 8:2 FTOH. Surprisingly, the breakthrough for 10:2 FTOH was similar to that of 6:2 FTOH. No explanation has been found for this phenomenon yet. The breakthrough of 6:2 PFOAc is comparable to that of 8:2 FTOH. Regarding FOSEs, breakthrough was minimal (2–3%), while PFOSA and both FOSAs could not be detected at all on the lower column.

The relatively high breakthrough of 4:2 FTOH leads to the assumption that a certain percentage of the spiked analyte is also lost from the lower column, as substantiated by the low absolute recoveries of 22 ng (spiking level 80 ng). Recoveries in the breakthrough experiments are directly linked to the relative recoveries described above, but are also influenced by the environmental air concentrations sampled during the experiment. This especially holds for 8:2 FTOH and 6:2 FTOH with the highest air concentrations (Table 3). Moreover, matrix effects resulting in signal enhancement of FOSEs, as described above, could also be seen in the breakthrough experiments, as absolute recoveries of NMeFOSE and NEtFOSE were very high: 206 and 193 ng (spiking level 80 ng, results not shown), respectively, despite relatively low environmental air concentrations (Table 3).

Referring to breakthrough of the IS, relative proportions of 18%, 9.1% and 11% of 6:2 FTOH [M+4], 8:2 FTOH [M+4], and 10:2 FTOH [M+4], respectively, were found on the unspiked lower column. Corresponding to the results for native FOSAs, breakthrough of the isotopically labelled FOSAs was very low, as only 1.3% NEtFOSA [M+5] and 0.9% NMeFOSA [M+3] were detected on the lower column.

Selectivity High method selectivity was ensured by monitoring several characteristic ions for each analyte. For FOSAs, where only one *m/z* could be monitored, qualitative confirmation was done in NCI mode as discussed above. Furthermore, a specific time window of elution (mean RT of standards ±0.5 s) and specific ratios of quantifier and qualifier ions (ratios determined in standard solutions ±20%) were considered. In addition, extensive QA/QC measures including blank experiments precluded false-positive and false-negative results.

Precision In order to evaluate the *instrumental precision*, within-day precision was tested by tenfold injection of the same calibration solution at 100 pg/μL, and it ranged from

4.2% (4:2 FTOH) to 7.4% (10:2 FTOH). Between-day precision at 200 pg/μL was shown to be between 5.5% (NMeFOSE) and 9.7% (PFOSA). For evaluation of *method precision*, environmental air samples were always taken in parallel. Despite the complexity of the analytical procedure, the gaseous phase concentration data (see Table 3) obtained from parallel samples usually deviated by less than 30%, demonstrating the excellent repeatability of the presented method.

Accuracy Due to the lack of certified reference materials, the accuracy of the method was investigated via the relative recovery experiments discussed above. Additionally, we performed an interlaboratory comparison of the quantification method between GKSS Research Centre Geesthacht and the Norwegian Institute for Air Research (NILU) in Tromso [32].

Interlaboratory comparison Two unknown standard mixtures were exchanged between GKSS and NILU. Concentrations of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE and PFOSA ranged from 20–250 pg/μL (low concentration mix, prepared at GKSS) and 100–900 pg/μL (high concentration mix, prepared at NILU), respectively. The solutions were analysed and quantified at both laboratories using their particular analytical methods.

Both laboratories used GC/PCI–MS approaches, but different instrumentation (NILU: Varian CP-3800 gas chromatograph/1200 triple quadrupole mass spectrometer; Varian, Palo Alto, CA, US), analytical methods and calibration models (NILU: 10, 25, 50, 100, 250, 500, 1000 and 2000 pg/μl, quadratic regression). Results from the interlaboratory comparison are given in Table 4. Of all the reported values of the interlab study, 82% were within ±30% of the theoretical values. However, some results revealed deviations from theoretical values of up to +180% (4:2 FTOH in the high concentration mix determined at GKSS). These discrepancies can be explained by the analytical challenges posed by volatile PFAS and the low concentrations in the test mixtures. The results from the interlaboratory comparison emphasise the need for further method improvement.

Environmental air samples Environmental air concentrations obtained from two sets of parallel samples from Northern Germany (Hamburg: urban; Waldhof: rural) are given in Table 3, together with field blanks of the respective sampling periods. Most analytes, except for 6:2 PFOAc and PFOSA, could be quantified in the gaseous phases of ambient air samples from both locations. The method thus proved applicable for the trace-analytical determination of FTOHs and FOSAs/FOSEs at an urban as well as a rural site in Northern Germany. A comprehensive sampling campaign at both locations is described in detail elsewhere [28], representing the first airborne PFAS data available for Europe.

Conclusions

The method originally developed by Martin et al. [16] for the determination of volatile PFAS in high-volume environmental air samples was further developed and validated here. An additional analyte was included: NMeFOSA. Moreover, the method was further optimised for quantitative determination of 4:2 FTOH as well as 10:2 FTOH at environmental levels. By means of recovery and breakthrough experiments, the imperative need to use adequate mass-labelled internal standard compounds in order to generate accurate concentration data was demonstrated. Further studies should include the mass-labelled IS 4:2 FTOH [M+4] (as soon as available), NMeFOSE [M+7] and

Table 4 Results from the interlaboratory comparison between GKSS, Geesthacht and NILU, Tromso. Two unknown standard mixtures were exchanged and analysed

	Low concentration mix (20–250 pg/μL)					High concentration mix (100–900 pg/μL)				
	Theoretical conc. (pg/μL)	GKSS (pg/μL)	Dev. (%)	NILU (pg/μL)	Dev. (%)	Theoretical conc. (pg/μL)	GKSS (pg/μL)	Dev. (%)	NILU (pg/μL)	Dev. (%)
4:2 FTOH	66.7	67.2	+1	69.9	+5	682	1900	+180	1226	+80
6:2 FTOH	–	<IDL		4.6		455	578	+27	365	−20
8:2 FTOH	100	85.8	−14	96.0	−4	227	235	+3	233	+2
10:2 FTOH	20.0	19.6	−2	32.7	+63	636	1529	+140	766	+20
NEtFOSA	167	142	−15	66.5	−60	227	285	+25	176	−23
NMeFOSA	233	205	−12	288	+23	409	424	+4	797	+95
NMeFOSE	33.3	28.6	−14	32.9	−1	909	1059	+16	710	−22
NEtFOSE	–	<IDL		26.9		455	421	−7	371	−18
PFOSA	40.0	34.7	−13	–	–	682	597	−12	–	–

NEtFOSE [M+9] in order to avoid significant under- or overestimation of environmental concentrations. Moreover, by optimising the ratio of the final extract volume (200 μL) to the injection volume (1 μL), a shortening of the sampling times could be achieved. Additionally, a clean-up should be considered in order to diminish matrix effects and to avoid early deterioration of GC injection liners and capillary columns encountered in relation to PUF/XAD extracts. In particular, FTOHs require further investigations, as they continue to be produced in increasing amounts, and have recently been shown to possess estrogen-like properties by promoting MCF-7 breast cancer cell proliferation [35].

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4. Publication II

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Urban versus Remote Air Concentrations of Fluorotelomer Alcohols and Other Polyfluorinated Alkyl Substances in Germany

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Neutral, volatile polyfluorinated alkyl substances (PFAS) were measured in environmental air samples at two different sites in Northern Germany in spring 2005. The sampling locations were chosen to cover a metropolitan and a rural site, the Hamburg city center, and Waldhof, a background monitoring site. An optimized and validated analytical protocol was used to analyze two sets of parallel high-volume air samples. For both sampling locations as well as for individual samples, field blanks were taken to monitor possible background contamination. Gas chromatography coupled to mass spectrometry using positive chemical ionization (GC/PCI–MS) was used for quantitative analyses. This article describes the first air concentration data of volatile PFAS outside North America reported in the peer-reviewed literature. The wide distribution of fluorotelomer alcohols (FTOHs), fluorinated sulfonamides, and sulfonamidoethanols (FOSAs/FOSEs) in German environmental air is presented. Furthermore, two volatile PFAS, i.e., N-methyl fluorooctane sulfonamide (NMeFOSA) and 4:2 FTOH, were determined for the first time in environmental air. Minimum–maximum ΣFTOH concentrations of 64–311 pg/m^3 (remote) up to 150–546 pg/m^3 (urban) and minimum–maximum ΣFOSA + FOSE concentrations between 12 and 54 pg/m^3 (remote) and 29 and 151 pg/m^3 (urban) were determined. 8:2 FTOH and 6:2 FTOH were found to be the predominant POPs determined in Waldhof so far. Blank contamination was found to be negligible. A significant correlation was found with the ambient temperature for the partitioning of airborne FOSEs between the gaseous and particulate phase ($R = 0.853$), whereas FTOHs and FOSAs were almost exclusively found in the gaseous phase. Furthermore, highest airborne PFAS concentrations were determined at relatively high ambient temperatures. Correlation coefficients (R) for ΣFTOH and ΣFOSA + FOSE concentrations with temperature were 0.954 and 0.968, respectively. Finally, the PFAS concentrations determined in this study are set into context with levels of "classical" persistent organic pollutants (POPs) in the same region and PFAS data available for North America.

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Introduction

In the course of the past years, ionic per- or polyfluorinated alkyl substances (PFAS) were detected in organisms from remote locations like the Canadian and European Arctic (*1–3*). Among these ubiquitously found compounds were perfluorooctane sulfonate (PFOS) and perfluorocarboxylates (PFCAs) like perfluorooctanoate (PFOA), which are known to barely be volatile. These findings resulted in two different theories concerning transportation pathways of ionic PFAS from highly industrialized production and emission areas to distant, "pristine" regions.

Either the moderately water-soluble compounds including shorter-chain PFCAs could be transported directly by sea currents or by means of sea-spray (*4*). This was supported by the determination of a suite of ionic PFAS in Arctic water samples (*5*). Alternatively, a suite of volatile, neutral precursors could undergo long-range atmospheric transport (LRAT) and be degraded in situ to form persistent PFAS in the Arctic environment. Possible atmospheric precursors include a number of fluorotelomer alcohols (FTOHs) as well as N-alkylated fluorooctane sulfonamides and sulfonamidoethanols (FOSAs/FOSEs). The second hypothesis is under extensive investigation and received some supporting evidence due to a number of biotic (*6–9*) and abiotic degradation studies, including smog chamber experiments (*10–12*), and the determination of neutral PFAS at ground level of the North American troposphere (*13–16*).

Smog chamber experiments showed an atmospheric lifetime of 20 d for FTOHs (*17*). Lifetimes of FOSAs/FOSEs have recently been estimated. As FOSAs/FOSEs could not be introduced into the experimental system in high enough quantities (*11*), the C_4 analogs were used for several studies. D'Eon et al. showed that fluoroalkyl sulfonamidoethanols have an atmospheric lifetime of 2 d and are rapidly degraded to the respective sulfonamides via N-dealkylation (*12*). However, via the longer-lived sulfonamides (lifetimes >20 d, ref *11*), FOSEs may contribute to the atmospheric PFAS burden transported to remote locations. LRAT of volatile precursors and degradation to form ionic, persistent PFAS can be an important mechanism in the global distribution of PFOS and PFOA (*18*).

Several data sets are available for the North American troposphere as well as for indoor air samples (*13–16, 19*). 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, *N*-ethyl fluorooctane sulfonamide (NEtFOSA), *N*-methyl fluorooctane sulfonamidoethanol (NMeFOSE), and *N*-ethyl fluorooctane sulfonamidoethanol (NEtFOSE) were found to be widely distributed in North American air samples (*13, 14*). Concentrations of total FOSAs/FOSEs ranged from below the method detection limit (MDL) to 1549 pg/m^3 and of total FTOHs from <MDL to 224 pg/m^3 (*14*). Shoeib et al. determined concentrations of ΣFOSEs in indoor air samples (up to 3615 pg/m^3) at levels about 10–100 times higher than in outdoor air (up to 41 pg/m^3, *15*). In another study, Shoeib et al. found ΣFOSE concentrations between 156 and 205 pg/m^3 in outdoor air (*16*). Boulanger et al. reported the determination of NEtFOSA and NEtFOSE in air over the Great Lakes at sum levels up to 3.2 pg/m^3 (*19*).

However, to the authors' knowledge, there are no existing volatile PFAS concentration data for Europe published in the peer-reviewed literature. The aim of this study was to investigate the occurrence of airborne PFAS in the gaseous and particulate phase of German air samples taken at a metropolitan site (Hamburg city center) as well as in a rural area (Waldhof). In order to ensure accurate results, the analytical protocol first described by Martin et al. (*13*) was

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further improved and validated as described in detail elsewhere (*20*). The application of the final method to the analysis of volatile PFAS in German ambient air is described. Special attention was paid to the evaluation of possible blank contamination from the analytical method and at the sampling sites. Furthermore, we focused on the influence of different ambient temperatures on airborne PFAS concentrations as well as the distribution of analytes between the gaseous and particulate phase and the two sampling sites. The data sets described here are compared to those published by North American research groups. Finally, volatile PFAS concentrations from our study are set into context with levels of other organic contaminants from the same area and time frame.

Experimental Section

The optimization, validation, and final analytical method used in this study are described in detail elsewhere (*20*). Briefly, high-volume air samples were collected on glass-fiber filters (GFF, particulate phase) and glass columns with a polyurethane foam (PUF)/XAD-2/PUF sandwich (gaseous phase). The analytical protocol was used to determine four fluorotelomer alcohols (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH), three fluorooctane sulfonamides (N-methyl fluorooctane sulfonamide (NMeFOSA), NEtFOSA and the non-alkylated perfluorooctane sulfonamide, PFOSA), two fluorooctane sulfonamidoethanols (NMeFOSE, NEtFOSE), as well as 3,3,4,4,5,5,6,6,7,7,8.8-tridecafluoro octyl acrylate (6:2 PFOAc). All standards were either purchased from Aldrich (Steinheim, Germany), Lancaster Synthesis (Frankfurt a.M., Germany), ABCR (Karlsruhe, Germany), and Wellington Laboratories Inc. (Guelph, Ontario, Canada), or donated by 3M, Germany (NMeFOSA/NMeFOSE) and the Mabury group at the University of Toronto, Canada (NEtFOSE, *20*).

Sampling columns were prepared in a clean lab at GKSS using a PUF slice of 6.5 cm diameter and 5 cm height, 25 g of Amberlite XAD-2 resin and another slice of PUF. PUF/XAD columns were cleaned by Soxhlet extraction using 500 mL of methanol (2 d) and subsequently with 500 mL of ethyl acetate (EtOAc) (2 d). The columns were dried with high-purity nitrogen and sealed in alumina coated polypropylene (PP) bags for transportation to the sampling locations. GFFs of 15 cm diameter were rinsed with EtOAc, heated overnight at 250 °C, individually wrapped in aluminum foil, and sealed in alumina coated PP bags.

Five mass-labeled internal standards (IS, 6:2 FTOH [M+4], 8:2 FTOH [M+4], 10:2 FTOH [M+4], NMeFOSA [M+3], and NEtFOSA [M+5], 40 ng in EtOAc) were spiked onto the upper PUF slice before sampling to correct for matrix effects as well as for breakthrough and losses during sampling, sample extraction, concentration, and analyses (*20*). Due to the non-availability of further mass-labeled IS at the time of the study, 6:2 FTOH [M+4] was also used as IS for 4:2 FTOH and 6:2 PFOAc due to similar retention times, while NEtFOSA [M+5] was assigned to the later eluting NMeFOSE, NEtFOSE, and PFOSA. PUF/XAD columns, which acted as passive samplers for 3.5 days (*individual blanks*) or the whole sampling period (*overall blanks*) at individual locations, were used as field blanks.

PUF/XAD columns were extracted using two cold column elution steps with EtOAc (300 mL/1 h infusion time and 200 mL/30 min), and the combined extracts were concentrated to 200 μL. GFFs were spiked with 40 ng of the IS and extracted in round-bottomed flasks using solvent soak with 50 mL EtOAc. The flask was placed on a mechanical shaker for 1 min. Subsequently, the extract was transferred to another flask and the procedure was repeated three more times (resulting in 200 mL EtOAc extract) with subsequent concentration of the combined extracts to 200 μL.

Quantitative analysis was performed using gas chromatography−mass spectrometry in the positive chemical ionization mode (GC/PCI−MS) using single ion monitoring (SIM). Furthermore, negative chemical ionization (NCI) was applied qualitatively (*20*). For this study, an Agilent (Böblingen, Germany) 6890 N gas chromatograph coupled to an HP 5973 mass-selective detector (MSD) was used. For separation of the analytes, a polar Varian CP-Wax 57 CB capillary column for glycols and alcohols (25 m × 0.25 mm × 0.2 μm) and an Agilent HP-INNOWax polyethylene glycol precolumn (~5 m × 0.25 mm × 0.2 μm) were used.

Two recovery internal standards (RIS) were spiked to final extracts just before GC/PCI−MS determination: 1H,1H-perfluoro-1-octanol (7:1 fluorinated alcohol, 7:1 FA) and 1H,-1H-perfluoro-1-dodecanol (11:1 FA). IS were used to normalize analyte areas before quantification using an external standard curve as described in (*20*), while RIS were applied to determine recoveries of the IS.

Sampling Locations. Sampling locations were chosen to cover an urban area with a presumably relatively high contaminant load (Hamburg) as well as a rural site without potential sources in the direct neighborhood (Waldhof). Waldhof is a background monitoring site of the German Federal Environmental Agency (UBA) and European Monitoring and Evaluation Program (EMEP) station. The sampling was conducted at the Max Planck Institute for Meteorology in the Hamburg city center (sample abbreviation HH) on a container deck at ~15 m height, and at the UBA site in Waldhof (located approximately 100 km south-east of Hamburg, sample abbreviation W) ~1.5 m above ground. At both sampling locations, the following meteorological data were available: air temperature and pressure, wind speed and direction, as well as the relative humidity.

Sampling Campaign in Hamburg and Waldhof. The sampling campaign was conducted from 25 April to 19 May, 2005 (3.5 weeks) in Hamburg (samples HH1−HH7), while the samples from Waldhof were taken from 19 May until 2 June, 2005 (2 weeks, samples W1−W4). Parallel samples were taken using high-volume air samplers at a flow rate of approximately 12−15 m^3/h for ~3.5 days in order to collect sample volumes between 850 and 1570 m^3 with a mean volume of 1160 (±214) m^3. For each sample, field blanks were taken by attaching open PUF/XAD columns close to the sampling sites during the sampling time (individual blanks). Furthermore, field blanks were taken for the whole sampling period in Hamburg and Waldhof, respectively (overall blanks).

Altogether, 14 samples (two parallels of seven samples), seven individual blanks, and one overall blank were collected in Hamburg, while for Waldhof, eight samples (two parallels of four samples), four individual blanks and one overall blank were obtained. After sampling, GFFs were sealed into test tubes, stored in alumina-coated PP bags together with PUF/XAD columns, and kept refrigerated on the way back to the laboratory. Samples were stored at −18 °C until elution, which was usually done within few days after sampling.

Results and Discussion

Field Blanks. Individual blank contamination values are given in the Supporting Information (Table S1). They were quantified externally since no IS were spiked. 4:2 FTOH, 6:2 PFOAc, and PFOSA were not detected in any field blanks. 6:2 FTOH was detected occasionally, but could not be quantified in any of the field blanks. NEtFOSA, NMeFOSA, NMeFOSE, and NEtFOSE ranged from not detected (n.d.) to 1.22 ng absolute in whole extracts. Taking into account the average sample volume of 1160 m^3, this corresponds to a maximum blank contribution of 1.1 pg/m^3 (NEtFOSA). 8:2 FTOH and 10:2 FTOH could be detected in all blanks at levels between below the method quantification limit (<MQL) as defined elsewhere

(*20*) and 1.56 ng (8:2 FTOH) absolute, corresponding to a maximum blank contribution of 1.3 pg/m^3 (see Table S1).

One high value in individual blanks showing 4.44 ng absolute for NMeFOSE was found, thus potentially contributing 3.8 pg/m^3 of this specific analyte to the corresponding sample (HH4). All the same, NMeFOSE concentrations determined in sample HH4 were in the lowest concentration range found in the course of the whole sampling period in Hamburg, and the HH overall blank showed NMeFOSE <MQL. This observation leads to the conclusion that the relatively high level of this analyte in the HH4 field blank did not correspond to actual contamination during sampling of HH4, but to packing of that particular PUF/XAD column.

In order to estimate possible contribution of blanks to real samples, peak areas of the analytes were compared to those of field blanks from the same sampling period. For FTOHs, blank areas were usually below 1% of the analyte areas in real samples with a maximum of 2.3%, so that contamination can be disregarded. For FOSAs/FOSEs, blank areas usually represented up to 4% of analyte areas. However, for samples HH4 (NEtFOSA, NMeFOSE), HH6 (NEtFOSA, NMeFOSE), and W4 (NEtFOSA, NMeFOSA), blank areas accounted for 11−34% of analyte areas. This relatively high blank contribution resulted from the very low FOSA/FOSE concentrations in these samples, which were close to the MQL. Another influencing factor might have been lower ambient temperatures during these particular sampling periods, resulting in enhanced adsorption of FOSAs/FOSEs to surface areas, as reported elsewhere (*13*).

Applying the setup used in this study, overall blanks did not show higher contamination levels than individual blanks. This observation leads to the conclusion that sampling time has less influence on blank contamination than the sampling material in individual manually packed PUF/XAD columns. Therefore, since field blanks did not show significant contamination, analyte concentrations were not blank-corrected.

Concentrations of Airborne PFAS in Germany. The presented study provides the first environmental concentration data for 4:2 FTOH and NMeFOSA and first airborne PFAS data outside North America. Furthermore, the improved analytical protocol allowed for the quantitative determination of 10:2 FTOH at environmental levels. Individual analyte concentrations determined in the gaseous and particulate phase of German environmental air samples are given in Table 1 together with IS recoveries. Recoveries of the IS were calculated by means of the area ratio of the IS to the respective RIS spiked prior to GC/PCI−MS analyses. They reflect the adjustment of analyte concentrations to breakthrough from the PUF/XAD columns, losses during sampling, sample elution, and extract concentration as well as to signal enhancements or suppression due to matrix effects observed in PUF/XAD extracts (*20*).

Mean concentrations of individual analytes at both locations are listed, with minimum and maximum concentrations given in brackets (Table 1). ΣFTOH and ΣFOSA + FOSE concentrations in individual samples are calculated as sums of mean concentrations of individual analytes in parallel samples (±error). ΣFTOH and ΣFOSA + FOSE concentrations for Hamburg and Waldhof, respectively, are calculated as means of sum concentrations in individual samples.

Except for 6:2 PFOAc and PFOSA, all analytes could be determined in the gaseous phase of German air samples. 6:2 PFOAc was not detected in any of the samples. PFOSA was detected occasionally, but at levels <MQL. A typical total ion chromatogram (TIC) of a standard mixture (A) as well as of the PUF/XAD extract (B) of a high-volume air sample (HH3) is given in the Supporting Information (Figure S1). NMeFOSE and NEtFOSE could be quantified in the particulate phase of all samples. 8:2 FTOH (<MQL), NMeFOSA (n.d.-<MQL) and 10:2 FTOH could be detected on GFFs, but quantification was possible only sporadically. 6:2 PFOAc, PFOSA, 4:2 FTOH, 6:2 FTOH, and NEtFOSA were not detected on any of the GFFs. The concentrations determined for GFFs are possibly underestimated, due to the known drawback of high-volume air sampling whereby revolatilization of particle-bound analytes from the filter and diffusion into the PUF/XAD columns may occur, especially at higher temperatures (*21*).

Parallel samples were in good agreement, illustrating the precision of the method. Despite the complex analytical protocol, only 13% of the gaseous phase concentration data obtained from parallel samples deviated by more than ±30%, reflecting the excellent repeatability, as described in more detail elsewhere (*20*). The most volatile IS, 6:2 FTOH [M + 4] showed low recoveries in the gaseous phase extracts of HH3 (17%/19%), W1 (16%/12%), and W3 (7%/6%), respectively (Table 1), probably attributable to high temperatures at the time the IS were spiked. Therefore, IS-corrected concentrations of 4:2 FTOH and 6:2 FTOH may be overestimated for these three samples. Furthermore, it should be taken into account that due to the non-availability of mass-labeled analogs for 4:2 FTOH, NMeFOSE, and NEtFOSE at the time of the study, concentrations for 4:2 FTOH might be underestimated, while FOSE concentrations are probably overestimated in PUF/XAD extracts of all samples (*20*).

Box-whisker plots of concentrations for individual analytes determined in Hamburg and Waldhof are given in Figure 1, including means and medians for the gaseous (A) and particulate (B) phase. ΣFTOH concentrations were by a factor of 4−5 higher than ΣFOSA + FOSE concentrations with 8:2 FTOH as the dominant analyte followed by 6:2 FTOH. This distribution pattern was the same at both sampling sites. Of the FOSAs/FOSEs, NMeFOSE was the prevailing compound in Hamburg, while NEtFOSE showed highest concentrations in Waldhof.

Two airborne PFAS concentrations were significantly higher in samples from the urban sampling site in Hamburg compared to the background site at Waldhof (Mann−Whitney U-test [p < 0.01]). Prior to application of this robust nonparametric test, concentrations were divided by the mean temperatures (in K) at the respective sampling periods for each site. 4:2 FTOH (gaseous phase) and NMeFOSE (particulate phase) showed significantly higher levels in the metropolitan area. This observation indicates the influence of possible point as well as diffuse sources at the urban site for these two compounds.

Two samples from Hamburg (HH2, HH3) showed very high concentrations for all PFAS investigated in this study (Table 1). This phenomenon might be related to wind coming mainly from south-east at that time, possibly over a point source. However, due to frequently changing wind conditions within the long sampling times of 3.5 days, no correlation could be found between the predominant wind directions and analyte levels. Additionally, low recoveries of 6:2 FTOH [M+4] in sample HH3 (Table 1) might cause an overestimation of IS-corrected concentrations of 4:2 FTOH and 6:2 FTOH (see discussion above). Further studies are required for establishing a relationship between air concentrations and back trajectories.

Comparison between PFAS in Environmental Air from Germany and North America. An overview of ΣFTOH and ΣFOSA + FOSE concentrations determined in this study and reported by North American research groups (*13*−*16*, *19*) is given in Table 2. It should be noted that other studies did not include the same analyte spectrum as covered by our investigations. Stock et al. (*14*). could not determine 10:2 FTOH, while both Martin et al. (*13*) and Stock et al. (*14*) did not include NMeFOSA in their studies addressing environmental air samples, so that ΣFOSA + FOSE concentrations represent NEtFOSA, NMeFOSE, and NEtFOSE only. Accordingly, ΣFTOH concentrations reported in other studies did

TABLE 1. Airborne PFAS Concentrations (pg/m³) determined in the Gaseous and Particulate Phase of Parallel Environmental Air Samples from an Urban (Hamburg, HH) and a Rural (Waldhof, W) Location in Germany[a]

		HH1	HH2[b]	HH3	HH4	HH5	HH6	HH7	mean (min-max)	W1	W2	W3	W4	mean (min-max)
4:2 FTOH	gaseous	32, 29	81, 60	115, 117	22, 28	33, 40	57, 50	47, 40	**54 (22–117)**	18, 24	7.2, 11	40, 45	3.3, 3.6	**19 (3.3–45)**
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.d.**	n.d.	n.d.	n.d.	n.d.	**n.d.**
6:2 FTOH	gaseous	55, 56	94, 94	145, 149	35, 42	33, 36	50, 46	42, 42	**66 (33–149)**	95, 86	29, 29	125, 114	18, 17	**64 (17–125)**
	recov. IS [%][c]	57, 55	n.a., 51	**17, 19**	56, 41	54, 53	39, 61	46, 43	46 ± 14	**16, 12**	52, 42	**7, 6**	47, 45	28 ± 20
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.d.**	n.d.	n.d.	n.d.	n.d.	**n.d.**
	recov. IS [%][d]	40, 48	19, 51	40, 37	32, 45	49, 56	49, 55	47, 50	44 ± 8	61, 57	71, 71	57, 57	51, 47	59 ± 8
8:2 FTOH	gaseous	106, 110	n.a., 275	204, 207	73, 82	62, 73	93, 110	84, 64	**119 (62–275)**	76, 66	81, 88	112, 108	37, 33	**75 (33–112)**
	recov. IS [%][c]	91, 86	n.a., n.a.	59, 67	75, 53	88, 72	83, 82	49, 70	73 ± 13	76, 80	77, 54	42, 37	96, 96	70 ± 23
	particulate	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	**<1.0**	<1.0	<1.0	<1.0	<1.0	**<1.0**
	recov. IS [%][d]	56, 63	42, 79	69, 66	57, 82	83, 81	73, 78	80, 82	71 ± 8	102, 102	108, 108	104, 104	78, 77	98 ± 13
10:2 FTOH	gaseous	29, 28	n.a., 93	55, 57	20, 26	19, 23	28, 35	24, 16	**35 (16–93)**	25, 22	27, 29	32, 26	12, 10	**23 (10–32)**
	recov. IS [%][c]	141, 154	n.a., n.a.	104, 106	98, 58	123, 84	125, 113	76, 117	108 ± 22	130, 140	128, 80	98, 105	141, 147	121 ± 24
	particulate	<0.7, (0.8)	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	**<0.7**	<0.7	<0.7	n.d.	n.d.	**<0.7**
	recov. IS [%][d]	62, 67	48, 72	60, 56	52, 76	78, 84	71, 79	76, 79	70 ± 11	91, 98	110, 112	110, 106	86, 84	100 ± 12
Σ FTOHs	**gaseous**	**223 ± 3.2**	**531 ± 15**	**524 ± 4.3**	**165 ± 10**	**160 ± 10**	**234 ± 14**	**179 ± 16**	**288 (150–546)**	**206 ± 11**	**151 ± 5.9**	**301 ± 10**	**67 ± 3.2**	**181 (64–311)**
	particulate	**n.q.**	**n.q.**	**n.q.**	**n.q.**	**n.q.**	**n.q.**	**n.q.**	**n.q.**	**n.q.**	**n.q.**	**n.q.**	**n.q.**	**n.q.**
NEtFOSA	gaseous	2.5, 2.6	5.9, 5.9	4.8, 5.0	(1.5, 1.6)	4.1, (2.0)	2.5, 2.3	(2.0, 1.3)	**3.1 (1.3–5.9)**	2.8, 2.6	(2.6), 3.2	3.4, 3.1	(1.8, 1.5)	**2.6 (1.5–3.4)**
	recov. IS [%][c]	84, 84	n.a., 71	75, 85	82, 83	107, 96	101, 95	66, 87	86 ± 13	83, 80	86, 59	63, 59	84, 82	74 ± 12
	particulate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.d.**	n.d.	n.d.	n.d.	n.d.	**n.d.**
	recov. IS [%][d]	113, 120	115, 127	96, 80	70, 101	102, 126	125, 117	96, 105	107 ± 18	137, 133	139, 132	138, 134	112, 112	130 ± 11
NMeFOSA	gaseous	6.8, 7.2	19, 20	15, 15	4.5, 4.1	7.3, 4.1	7.4, 6.3	5.0, 3.4	**9.0 (3.4–20)**	6.0, 6.5	5.1, 9.7	9.9, 11	3.8, 3.9	**7.0 (3.8–11)**
	recov. IS [%][c]	63, 62	n.a., 46	52, 64	84, 70	89, 78	75, 72	48, 71	66 ± 14	70, 66	69, 32	48, 43	65, 65	57 ± 14
	particulate	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	**<0.2**	<0.2	<0.2	<0.2	n.d.	**n.d.-<0.2**
	recov. IS [%][d]	116, 126	124, 138	102, 86	72, 104	106, 135	133, 126	100, 107	112 ± 20	149, 146	150, 144	150, 148	122, 120	141 ± 13
NMeFOSE	gaseous	22, 14	89, 88	71, 75	7.5, 6,6	4.9, 5.5	17, 13	6.1, 3.0	**30 (3.0–89)**	8.0, 9.0	4.2, 7.8	11, 11	(0.5, 0.6)	**6.5 (0.5–11)**
	particulate	7.6, 15	5.6, 6.0	2.3, 3.7	9.9, 9.9	9.8, 15	16, 17	18, 17	**11 (2.3–18)**	1.3, 0.9	4.7, 3.5	1.4, 1.5	3.3, 2.5	**2.4 (0.9–4.7)**
NEtFOSE	gaseous	4.5, 2.6	27, 25	15, 15	1.6, (1.2)	(1.1, 1.2)	3.4, n.d.	(1.3, 0.5)	**7.6 (0.5–27)**	8.0, 8.2	5.8. 11	23, 21	(<0.3, 0.5)	**11 (<0.3–23)**
	particulate	4.8, 8.5	3.4, 3.4	2.4, 8.6	6.3, 5.6	4.9, 7.5	11, 12	7.1, 8.3	**6.7 (2.4–12)**	1.9, 1.2	15, 13	3.0, 4.4	5.6, 3.3	**5.9 (1.2–15)**
Σ FOSAs/FOSEs	**gaseous**	**31.4 ± 5.8**	**140 ± 1.9**	**108 ± 2.7**	**14.3 ± 0.8**	**15.1 ± 2.7**	**27.3 ± 3.0**	**11.3 ± 2.6**	**50 (9–142)**	**25.6 ± 0.8**	**24.6 ± 5.4**	**46.5 ± 1.3**	**6.4 ± 0.3**	**26 (6–48)**
	particulate	**18.2 ± 6.1**	**9.2 ± 0.3**	**8.6 ± 4.5**	**15.9 ± 0.5**	**18.7 ± 4.1**	**27.9 ± 1.4**	**25.4 ± 0.8**	**18 (4–29)**	**2.7 ± 0.6**	**18.1 ± 2.0**	**5.2 ± 1.0**	**7.3 ± 1.7**	**8 (2–20)**

[a] Analyte concentrations are given in brackets if peak areas were smaller than those of the lowest calibration solution. Details on the calculation of sum concentrations are given in the text. Individual recoveries of the IS (%) are listed, mean recoveries are given with standard deviations (SD). n.d., not detected; n.a., not analyzed due to chromatographic problems; n.q., not quantifiable. [b] Recoveries of IS could not be calculated in some cases due to chromatographic problems concerning the RIS. [c] PUF/XAD columns were spiked with IS before sampling. [d] GFFs were spiked with IS before extraction.

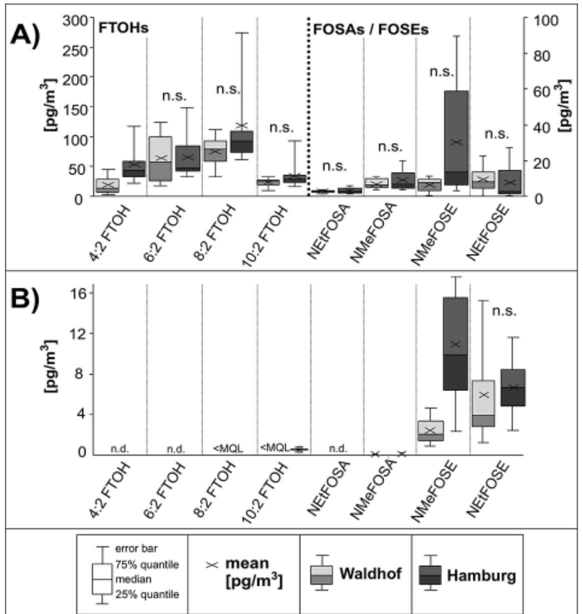

FIGURE 1. Box-whisker plots showing concentrations (pg/m^3) of volatile PFAS in (A) the gaseous (PUF/XAD) and (B) the particulate phase (GFF) of German air samples. Note different scales for FTOHs and FOSAs/FOSEs in the gaseous phase (A). Mean concentrations are indicated as a cross, while the boxes show medians as well as 25% and 75% percentiles. Waldhof is shown in lighter gray on the left for individual analytes, while Hamburg is displayed in darker gray on the right. Concentration differences between Hamburg and Waldhof, which are not significant (Mann−Whitney U-test [p < 0.01]), are indicated by "n.s."

not include 4:2 FTOH. Shoeib et al. determined FOSEs only (*15*) or FOSEs and NEtFOSA (*16*), respectively, in indoor as well as outdoor air. Boulanger et al. reported the determination of NEtFOSA and NEtFOSE at very low levels in air samples taken over Lake Erie and Lake Ontario close to Detroit and Toronto, respectively (*19*).

Compared to data published for North America, FTOH levels are slightly higher in Germany, while levels of FOSAs/FOSEs are much lower (Table 2). Further statistical analysis could not be carried out due to the insufficient amount of available data. However, the "European" pattern has also been reported in a recent study which analyzed air samples from the UK (*22*). Different use patterns as well as the influence of point or diffuse sources could be responsible for this observation. The high FOSA/FOSE levels in North America are especially striking in Griffin, Reno, and Toronto with average sum concentrations for the three investigated compounds of 95 up to 403 pg/m^3 (*14*), while in Hamburg, four FOSAs/FOSEs were determined at average sum concentrations of 68 pg/m^3. However, North American samples were taken in 2001 (*13, 14*), while our sampling campaign took place in 2005. Moreover, comparable or even higher FTOH than FOSA/FOSE concentrations were determined in Toronto for 2002, and especially 2003, as described by Stock et al. (*23*). These results are more in line with the European pattern and might indicate a trend toward increasing use of FTOHs in North America after the phase-out of the production of PFOS-based chemicals in 2002. However, non-use based factors like meteorological conditions, seasonality, and specific sampling locations may contribute to the observed differences. Shoeib et al. found rather high ΣFOSA + FOSE levels in outdoor air samples from Ottawa (collected during the winter of 2002/03), as average sum concentrations showed 171 pg/m^3, even if NEtFOSA was <MDL. All the same, they did not include FTOHs in their analyses (*16*).

Influence of Ambient Temperatures on PFAS Concentrations and the Gas/Particle Distribution. Martin et al. first described the different collection efficiency of airborne PFAS on GFF, PUF, and XAD-2 in dependence of temperature, which makes the use of the three sampling materials indispensable (*13*). Shoeib et al. investigated the gas/particle distribution of FOSEs and emphasized the importance of the gas/particle distribution of a chemical in the atmosphere which affects its deposition, degradation, overall transport, and fate (*15*). In this study, we investigated the influence of ambient temperatures on airborne concentrations of volatile PFAS and their distribution between the gaseous and particulate phase (Figure 2 and Figure S2 in the Supporting Information). Due to temperature differences during sampling between locations, data comparability for statistical analyses was achieved by standardization of concentration and temperature data from Hamburg and Waldhof. For this purpose, individual values were subtracted from means of the respective sampling location and divided by the respective standard deviation.

We present a significant correlation (p < 0.01) of ΣFTOH (R = 0.954) as well as ΣFOSA + FOSE concentrations (R = 0.968) with ambient temperature (Figure S2, Supporting Information). Furthermore, for FOSEs, the presented study revealed a significant correlation (p < 0.01) between ambient temperatures and the gas/particle distribution (R = 0.853). At lower mean temperatures, FOSEs were found mainly in

TABLE 2. Comparison of ΣFTOH and ΣFOSA+FOSE Concentrations with Literature Data (Minimum and Maximum Concentrations are Given in Brackets[a])

	location	inhabitants	ΣFTOHs (pg/m^3)	ΣFOSAs + FOSEs (pg/m^3)
Martin et al.[13]	Toronto, ON (n = 4)	2.480.000	171[b]	320[b]
	Long Point, ON (n = 2)	500	78[b]	111[b]
Stock et al.[14]	Griffin, GA (n = 5)	23.500	148 (49−224)	403 (57−1549)
	Cleves, OH (n = 3)	2.200	132 (103−181)	69 (<MDL−134)
	Long Point, ON (n = 3)	500	26 (<MDL−52)	48 (29−65)
	Toronto, ON (n = 3)	2.480.000	165 (113−213)	95 (31−211)
	Reno, NV (n = 3)	180.500	76 (51−93)	291 (157−491)
	Winnipeg, MB (n = 3)	685.900	11 (<MDL−18)	22 (15−32)
Shoeib et al.[15]	Toronto, ON (n = 2)	2.480.000	n.a.	33 (24−41)[c]
Shoeib et al.[16]	Ottawa, ON (n = 7)	780.000	n.a.	171 (156−205)[b,d]
Boulanger et al.[19]	Lake Erie (n = 5)		n.a.	2.0 (n.d.−3.2)[e]
	Lake Ontario (n = 3)		n.a.	1.3 (n.d.−1.9)[e]
this study	Hamburg (n = 7)	1.740.000	288 (150−546)	68 (29−151)
	Waldhof (n = 4)	20	181 (64−311)	34 (12−54)

[a] n.d., not detected; n.a., not analyzed; <MDL, below method detection limit. [b] Sum of mean values. [c] Analysis of FOSEs only. [d] Analysis of FOSEs and NEtFOSA only, with NEtFOSA <MDL. [e] Analysis of NEtFOSA and NEtFOSE only.

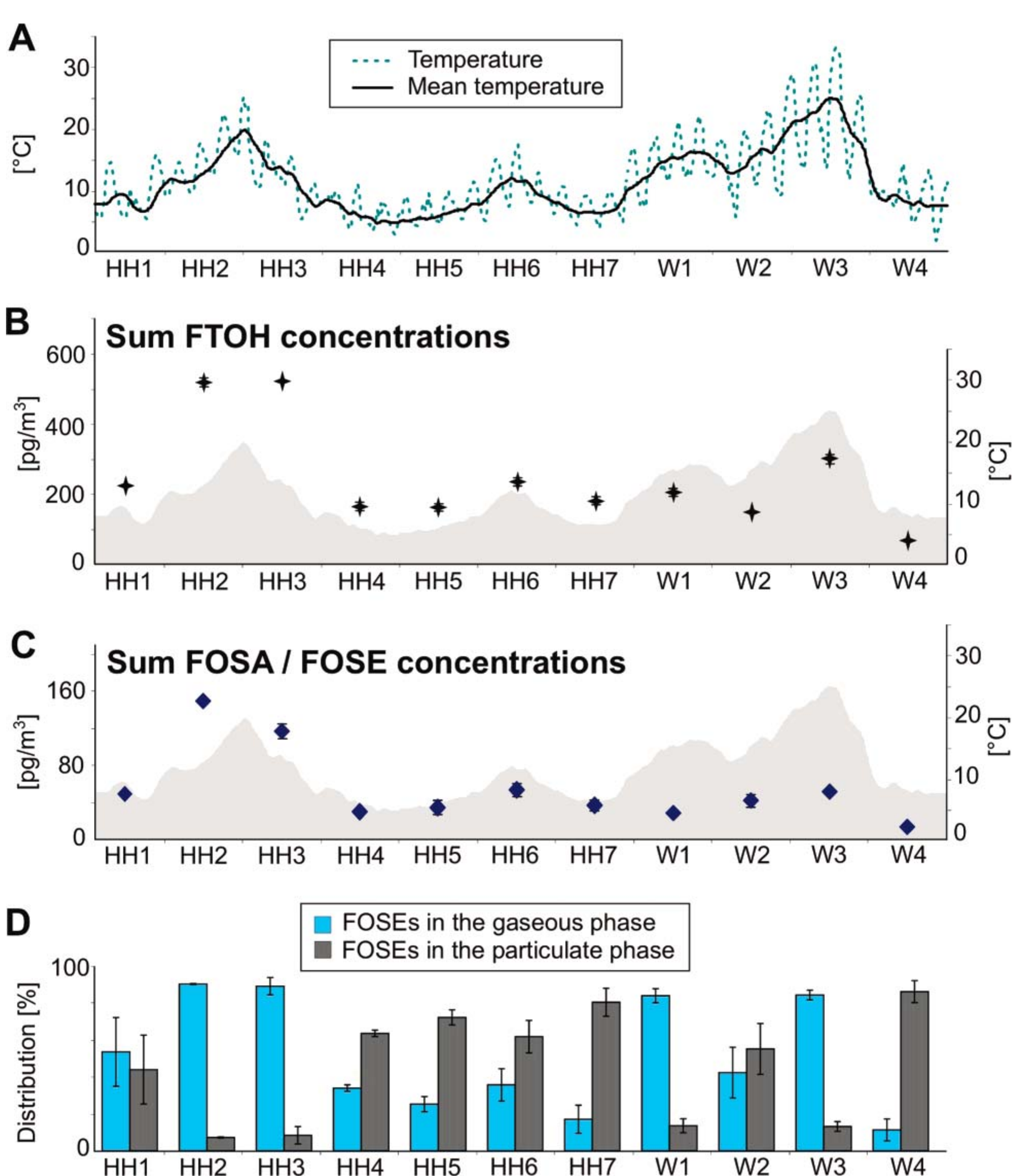

FIGURE 2. Ambient temperature (A), ΣFTOH (B), and ΣFOSA+FOSE (C) concentrations as well as the distribution of FOSEs between the gaseous and particulate phase (D) during the sampling campaign. FTOHs and FOSAs are almost exclusively found in the gaseous phase, while the distribution of FOSEs is correlated with ambient temperatures. Higher percentages are found in the gaseous phase at higher temperatures.

the particulate phase (HH4−HH7, W4; 9.2 ± 1.5 °C). At higher mean temperatures, >85% of FOSEs partitioned to the gaseous phase (HH2−HH3, W1, W3; 16.8 ± 3.3 °C). This phenomenon could partly be related to the significant revolatilization of particle-bound compounds from the filter at higher temperatures (*21*). Due to the long sampling times and rapidly changing conditions, no correlation could be found between analyte concentrations and other meteorological data.

Comparison of Airborne PFAS with Concentrations of Classical Persistent Organic Pollutants. Levels of airborne PFAS as given in Tables 1 and 2 were compared to concentration data of "classical" and further "new" persistent organic pollutants (POPs) from a similar region and time frame. By definition of the Stockholm Convention, POPs include polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins/-furans (PCDD/Fs), and organochlorine pesticides (OCPs) like hexachlorobenzene (HCB), chlordane, mirex, and para−para dichloro diphenyl trichloroethane (*pp*-DDT). These substances are long-lived in the environment, have the potential to undergo LRAT, and are bioaccumulated in food chains. Polybrominated diphenyl ethers (PBDEs),

hexachlorocyclohexane (HCH, incl. γ-HCH/lindane), as well as PFOS and other PFAS are classified as “candidate” POPs (*24*).

To compare airborne PFAS concentrations as described here with levels of classical as well as new and emerging POPs in the same region, a recent article dealing with a passive air sampling campaign throughout Europe in the summer of 2002 was referenced. Jaward et al. presented data of PCBs, selected OCPs (HCB, α- and γ-HCH, *pp*-DDT), and PBDEs from 22 countries (*25*). The German sampling sites included Waldhof. In the cited study, highest European concentrations for individual airborne POPs were determined for γ-HCH (9−390 pg/m^3), followed by PCB-28 (<5−230 pg/m^3), PCB-52 (1.6−210 pg/m^3), and *pp*-DDT (0.6−190 pg/m^3). Compared to other sampling locations across Europe, concentrations determined in Waldhof were in the lower concentration range. ΣPCB concentrations, *pp*-DDT, and ΣPBDE concentrations at German locations were 5−6 times lower than the maximum values determined in Russia (PCBs/*pp*-DDT) and the UK (PBDEs). Further locations in Germany (one rural site in Southern Germany and one urban location in Western Germany) showed similar levels as Waldhof. This is in line with our findings concerning most airborne PFAS, which showed similar concentration levels in Waldhof and Hamburg, respectively. However, the insufficient amount of data available for classical POPs in Waldhof impeded further use of statistical tests.

Considering individual compounds, concentrations of γ-HCH reported for Waldhof were between 40 and 52 pg/m^3, depending on the sampling rate used for calculations (3−4 m^3/d). The second highest concentrations were determined for HCB at 32−42 pg/m^3. Levels of individual PCBs in Waldhof are highest for PCB-149 at 6.7−8.8 pg/m^3. As to *pp*-DDT, Waldhof air concentrations were between 5.5 and 7.2 pg/m^3. By comparison with volatile PFAS data acquired in this study, mean 6:2 FTOH and 8:2 FTOH concentrations (Table 1) were slightly higher than γ-HCH concentrations. Maximum values of the predominant FTOHs were by a factor of 2−3 higher, making 6:2 FTOH and 8:2 FTOH the predominant POPs in Waldhof air. Compared to the concentrations determined for the prevalent PCB congener (PCB-149) and *pp*-DDT, mean concentrations of individual FTOHs were a factor of 2.5−12 higher. Levels were lower for FOSAs/FOSEs (Table 1). Mean concentrations were in the same range as PCB-149 and *pp*-DDT (factor 0.4−2.5), and they were 3−18 times lower than γ-HCH.

Sum concentrations of 29 PCBs and 8 PBDEs in Waldhof were 73−96 pg/m^3 and 9.7−13 pg/m^3, respectively, while this study showed means of 181 pg/m^3 for the sum of four FTOHs, underlining that FTOHs are the predominant POPs in Waldhof determined so far. Mean concentrations of ΣFOSAs/FOSEs were slightly higher than ΣPBDEs. Assuming a similar trend of relatively low concentrations of POPs in Germany compared to other European regions (as described by Jaward et al.), even higher FTOH concentrations are assumed to occur elsewhere. This is supported by recent data from the UK (*22*).

Overall Discussion and Recommendations. The optimized and validated analytical method (*20*) proved to be an excellent tool for quantification of PFAS at trace levels in environmental air samples. Outdoor air concentrations of NMeFOSA and 4:2 FTOH were determined for the first time. The analyses of parallel samples emphasized the precision of our analytical protocol. Our study showed the wide distribution of FTOHs and FOSAs/FOSEs at relatively high concentrations in German environmental air, thus supporting the atmospheric transport hypothesis of neutral, volatile precursors of PFCAs and PFOS to remote regions.

Future work should imperatively include the mass-labeled IS 4:2 FTOH [M+4] (as soon as available), NMeFOSE [M+7], and NEtFOSE [M+9] to avoid significant under- or overestimation of concentrations of the native analogs. Shorter sampling times would allow for correlations of PFAS concentrations with other meteorological data, e.g., wind direction, hence allowing for identification of possible point sources. This could be achieved by faster sampling using different column designs and thus lower backpressure or pumps with higher performance. Alternatively, sampling of lower air volumes could be considered. Moreover, airborne PFAS concentrations and their gas/particle distribution should be investigated at varying ambient temperatures throughout the whole year.

Research on deposition rates is desirable as only few data on PFAS in rainwater exist (*26, 27*). Regarding FTOHs, their relatively high vapor pressure and low water solubility are expected to preclude wet or dry deposition from the atmosphere (*26*). Nevertheless, particle-bound FOSEs and fluorotelomer acids (as atmospheric degradation products of FTOHs (*17*) with higher water-solubility and lower vapor pressure) might be more prone to wet or dry deposition. Research on bioconcentration factors, uptake routes as well as toxicological effects could link environmental concentrations of airborne PFAS to possible adverse effects. Endocrine disrupting effects of FTOHs have recently been shown by Maras et al. (*28*). In combination with continuing FTOH production in rising amounts, this makes research on airborne PFAS even more important.

Acknowledgments

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Supporting Information Available

Individual and overall field blanks from Hamburg and Waldhof, the TIC of a standard mixture and of the gaseous phase extract of sample HH3 as well as correlations of ambient temperatures with airborne PFAS concentrations and the distribution of FOSEs between the gaseous and particulate phase. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

Urban versus remote air concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany

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2) **Figure S1**. Total ion chromatograms (TIC) of a standard mixture at 200 pg/µL (A) and of the gaseous phase extract of sample HH3 (B).

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3) **Figure S2**. Correlations of ambient temperatures with airborne ΣFTOH (A) and ΣFOSA+FOSE concentrations (B) as well as the distribution of FOSEs between the gaseous and particulate phase (C).

Pag. S3

Table S1. Field blanks (pg/m^3) determined during the sampling campaign, including seven and four individual blanks from Hamburg (HH) and Waldhof (W), respectively, as well as one HH and W overall blank. Blank levels were referred to an average sample volume of 1160 m^3. One high value (HH4) is given in brackets.

	HH1	HH2	HH3	HH4	HH5	HH6	HH7	HH overall	W1	W2	W3	W4	W overall	all blanks
4:2 FTOH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.d.**	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.	<1.4	n.d.	**<1.4**	n.d.	n.d.	n.d.	<1.4	**<1.4**	**n.d.-<1.4**
8:2 FTOH	1.3	1.3	1.1	1.1	<1.0	<1.0	<1.0	**<1.0**	<1.0	<1.0	<1.0	<1.0	**<1.0**	**<1.0 -1.3**
10:2 FTOH	1.1	1.3	0.8	0.8	<0.7	0.8	<0.7	**<0.7**	0.7	<0.7	<0.7	<0.7	**<0.7**	**<0.7 -1.3**
6:2 PFOAc	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.d.**	n.d.	n.d.	n.d.	n.d.	**n.d.**	**n.d.**
NEtFOSA	<0.3	0.4	0.3	0.4	<0.3	1.1	0.5	**<0.3**	<0.3	<0.3	<0.3	0.4	**n.d.**	**n.d. -1.1**
NMeFOSA	<0.2	0.2	<0.2	0.3	n.d.	1.0	0.2	**<0.2**	<0.2	<0.2	<0.2	0.2	**n.d.**	**n.d.-1.0**
NMeFOSE	<0.4	0.7	<0.4	(3.8)	<0.4	<0.4	n.d.	**<0.4**	n.d.	n.d.	<0.4	n.d.	**<0.4**	**n.d.-0.7 (3.8)**
NEtFOSE	0.3	0.9	<0.3	n.d.	n.d.	n.d.	n.d.	**<0.3**	n.d.	n.d.	<0.3	n.d.	**<0.3**	**n.d.-0.9**
PFOSA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**n.d.**	n.d.	n.d.	n.d.	n.d.	**n.d.**	**n.d.**

n.d., not detected   <x, below the respective method quantification limit (MQL) as given in (*20*)

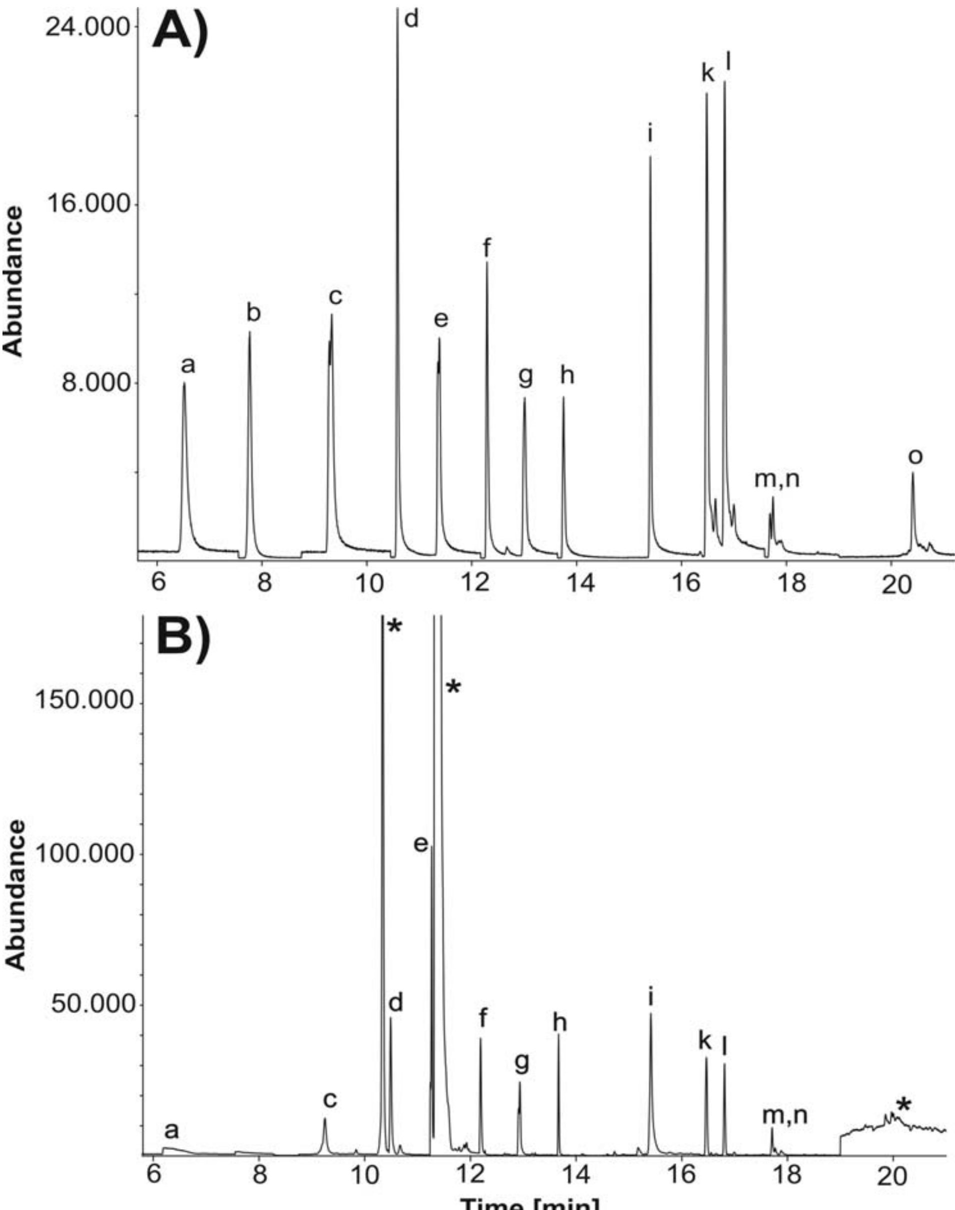

Figure S1. Total ion chromatograms (TIC) of a standard mixture at 200 pg/µL (A) and of the gaseous phase extract of sample HH3 (B). Analytes were identified as the following: a = 4:2 FTOH, b = 6:2 PFOAc, c = 6:2 FTOH [M+4] (IS) / 6:2 FTOH, d = 7:1 FA (RIS), e = 8:2 FTOH [M+4] (IS) / 8:2 FTOH, f = 9:1 FA (RIS), g = 10:2 FTOH [M+4] (IS) / 10:2 FTOH, h = 11:1 FA (RIS), i = 8:1 FA (RIS), k = NEtFOSA [M+5] (IS) / NEtFOSA, l = NMeFOSA [M+3] (IS) / NMeFOSA, m = NMeFOSE, n = NEtFOSE, o = PFOSA. Peaks indicated by a star (*) were part of the sample matrix and have not been identified.

S 2

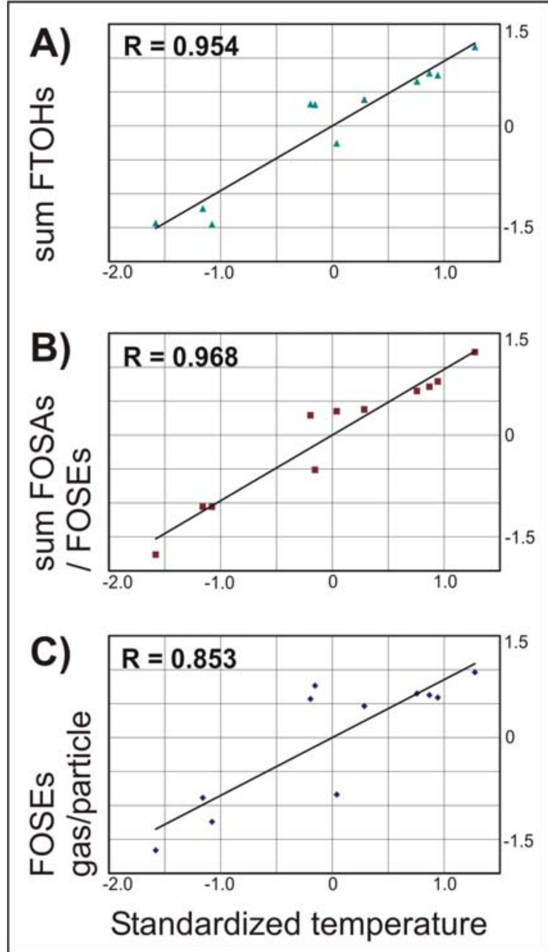

Figure S2. Correlations of ambient temperatures with airborne ΣFTOH (A) and ΣFOSA+FOSE concentrations (B) as well as the distribution of FOSEs between the gaseous and particulate phase (C). For statistical analysis, all values have been standardized. Details are given in the text.

5. Publication III

Latitudinal Gradient of Airborne Polyfluorinated Alkyl Substances in the Marine Atmosphere between Germany and South Africa (53° N–33° S)

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Neutral, volatile polyfluorinated alkyl substances (PFAS) were determined in high-volume air samples collected onboard the German research vessel *Polarstern* during cruise ANTXXIII-1 between Bremerhaven, Germany (53° N) and Capetown, Republic of South Africa (33° S) in fall 2005. An optimized and validated analytical protocol was used for the determination of several fluorotelomer alcohols (FTOHs) as well as *N*-alkylated fluorooctane sulfonamides and sulfonamidoethanols (FOSAs/FOSEs). Quantitative analyses were done by gas chromatography—mass spectrometry. This study provides the first concentration data of airborne PFAS from the Southern Hemisphere. Results indicate a strongly decreasing concentration gradient from the European continent toward less industrialized regions. The study confirms that airborne PFAS are mainly restricted to the Northern Hemisphere with a maximum concentration of 190 pg/m^3 (8:2 FTOH) in the first sample collected in the channel between the European mainland and the UK. However, south of the equator, trace amounts of several FTOHs and FOSAs with a maximum of 14 pg/m^3 (8:2 FTOH) could still be detected. Furthermore, a selection of ionic PFAS including perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) were determined in the particulate phase of high-volume air samples by liquid chromatography—mass spectrometry. Levels of ionic PFAS were almost 2 orders of magnitude lower than those of neutral PFAS, with maximum concentrations in the first sample of 2.5 pg/m^3 (PFOS) and 2.0 pg/m^3 (PFOA).

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Introduction

The ubiquitous detection of per- and polyfluorinated alkyl substances (PFAS) in many environmental compartments and even in biota from remote regions initialized intensive research on transportation pathways. Perfluorooctane sulfonate (PFOS), as well as perfluoroalkyl carboxylates (PFCAs) including perfluorooctanoate (PFOA), were detected in organisms from remote locations, e.g., polar bears from the Canadian and European Arctic (*1–3*). In view of the amphiphilic properties of ionic PFAS, two main transport hypotheses were proposed. Either neutral, volatile precursor compounds could undergo long-range atmospheric transport (LRAT) and be degraded *in situ* in remote regions (*4*), or alternatively, ionic PFAS could be transported directly by oceanic currents or by means of sea-spray (*5*). Both transport pathways have recently received some supporting empirical evidence.

The first hypothesis was supported by the ubiquitous detection of a suite of neutral, volatile precursors in North American (*6–9*) and European environmental air (*10*, *11*). Airborne precursor compounds of PFOS and PFCAs include fluorotelomer alcohols (FTOHs) as well as *N*-alkylated fluorooctane sulfonamides and sulfonamidoethanols (FOSAs/FOSEs). The plausibility of the LRAT theory was further supported by means of biodegradation (*12–15*) as well as smog chamber degradation studies (*16–18*) which showed that neutral, volatile PFAS can be degraded to form ionic PFAS. Second, a number of ionic PFAS were detected in Arctic water samples (*19*).

Two major manufacturing processes of PFAS are described. The production of FOSAs/FOSEs was associated with the process of electrochemical fluorination (ECF), which was in use since the 1950s, yielding an isomer mixture which is dominated by the linear isomer and additionally contains 15–30% branched isomers (*20*). However, 3M, which is the only major company known to have used ECF (*21*), phased out the production of PFOS-based chemicals as of the end of 2002. The C_8 product line has since been substituted by C_4 chemicals of similar structures, but which are believed to have limited bioconcentration potential and no known toxic effects. FOSAs/FOSEs were predominantly used as paper protectors, for water- and dirt-proofing in carpets, leather, and textiles, as performance chemicals (e.g., in aqueous film forming firefighting foams, AFFFs) (*22*), and as an insecticide (Sulfluramid). The second manufacturing process, telomerization, has been in use since the 1970s to produce exclusively linear compounds, including FTOHs. The production of FTOHs has continued to increase, particularly as precursors in the production of fluorinated polymers used in paper and carpet treatments, as well as in the production of paints, coatings, and adhesives (*12*, *16*).

Liquid chromatographic—mass spectrometric (LC—MS) methods have been published for the determination of FTOHs (*23*) and FOSAs/FOSEs (*24*). The simultaneous determination of FTOHs and FOSAs/FOSEs by gas chromatography coupled to mass spectrometry using positive chemical ionization (GC/PCI—MS) was first described by Martin et al. in 2002 (*6*). Recently, we published an improved and further validated analytical protocol (*25*).

The aim of this study was to investigate the inter-hemispherical gradient of neutral, volatile precursors of PFOS and PFCAs in environmental air, starting from the industrialized areas in Central Europe toward less urbanized regions in the Southern Hemisphere. To avoid the influence of possible point sources on land, air sampling was performed onboard the German research vessel *Polarstern*, representing

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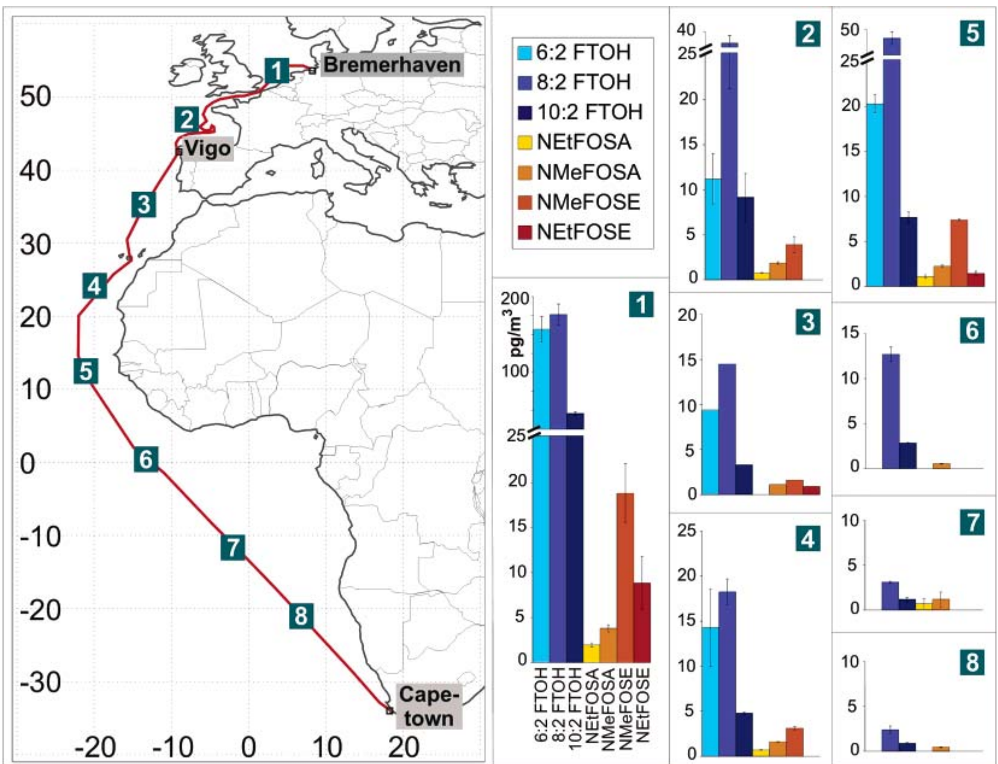

FIGURE 1. ***Polarstern*** **cruise ANTXXIII-1 between Bremerhaven, Germany (53° N) and Capetown, Republic of South Africa (33° S) in October/November, 2005. Airborne PFAS concentrations (pg/m³, means of duplicate samples) obtained from PUF/XAD extracts are given.**

an ideal platform for this study. A comparison with airborne PFAS data from a cruise between Sweden and Alaska (*26*) as well as with land-based measurements from Northern Germany (*10*) is given. Furthermore, glass-fiber filters (GFFs) used to collect analytes present in the particulate phase were subdivided and analyzed both for volatile PFAS as well as by LC−MS according to Berger and Haukas (*27*) to allow for the determination of ionic PFAS (including PFOS and PFCAs) in high-volume air samples. This study provides first evidence on the occurrence of airborne PFAS in environmental air samples from the Southern Hemisphere.

Experimental Section

Sampling Campaign. High-volume air samples were collected onboard the German research vessel *Polarstern* between Bremerhaven, Germany and Capetown, Republic of South Africa. The Atlantic transfer cruise ANTXXIII-1 (October 13 to November 17, 2005) was used to collect a set of eight samples along the cruise track as shown in Figure 1. Air samples were enriched on GFFs, which provided an estimate of the concentration in air associated with the particle phase, and polyurethane foam (PUF)/XAD-2/PUF columns, representing the concentration in air associated with the gaseous phase. The standards, chemicals, and materials used in this study are listed in Tables S1 and S2 of the Supporting Information. The optimized and validated analytical protocol for sampling, extraction, and GC/PCI−MS determination of neutral PFAS has been described in detail elsewhere (*25*).

Before sampling, 40 ng of the internal standards (IS, 6:2 FTOH [M + 4], 8:2 FTOH [M + 4], 10:2 FTOH [M + 4], *N*-methyl fluorooctane sulfonamide (NMeFOSA) [M + 3], *N*-ethyl fluorooctane sulfonamide (NEtFOSA) [M + 5], 10 μL of 4 ng/μL in ethyl acetate, EtOAc) were spiked onto the upper PUF slice of PUF/XAD columns. With the exception of the third sample, all air samples were taken in duplicate. To minimize the influence of the ship, high-volume pumps were operated on the observation deck close to the ship's bow at ~20 m above sea level. The pumps were operated for ~3.5 days per sample at a sampling rate of ~12−18 m³/h to collect sample volumes of 940−1790 m³ with a mean volume of 1250 (±268) m³. After sampling, GFFs were stored in fused test tubes and sealed together with the respective PUF/XAD column in alumina coated polypropylene bags stored at −30 °C. Subsequent to the cruise, samples were shipped back to Germany and extracted in a clean lab (class 10.000) within a few days after reception.

To check for possible background contamination, four field blanks (FBs) were taken. Two PUF/XAD columns were opened for several minutes and spiked with 40 ng of the IS batch (FB1 and FB2). Furthermore, two PUF/XAD columns were spiked with IS, attached close to the sampling site on the observation deck, and left for several days. One of these FBs was taken for the Northern Hemisphere (NHB, 13.10.-03.11.2005, 21 d), and the second one was taken for the Southern Hemisphere (SHB, 03.11.-14.11.2005, 11 d) including the inner tropical convergence zone (ITCZ). All blanks were stored and treated like real samples. In order to check for GFF blank contamination, four GFFs which had been prepared and stored together with the samples in the course of the cruise (travel blanks) were subdivided and extracted along with the samples.

As wind direction and speed may be main influencing factors of PFAS levels, air mass back trajectories were processed using the NOAA Air Resources Laboratory (ARL) HYSPLIT Online Transport and Dispersion Model (http://www.arl.noaa.gov/ready/hysplit4.html; *28*). The archived meteorological data set used was "global reanalysis 1948 − Dec 2005". Every 12 h during sampling, 6-day back trajectories were calculated and plotted (Figure 2).

Sample Extraction and Instrumental Analysis. In contrast to the analytical method as described in ref *25*, the

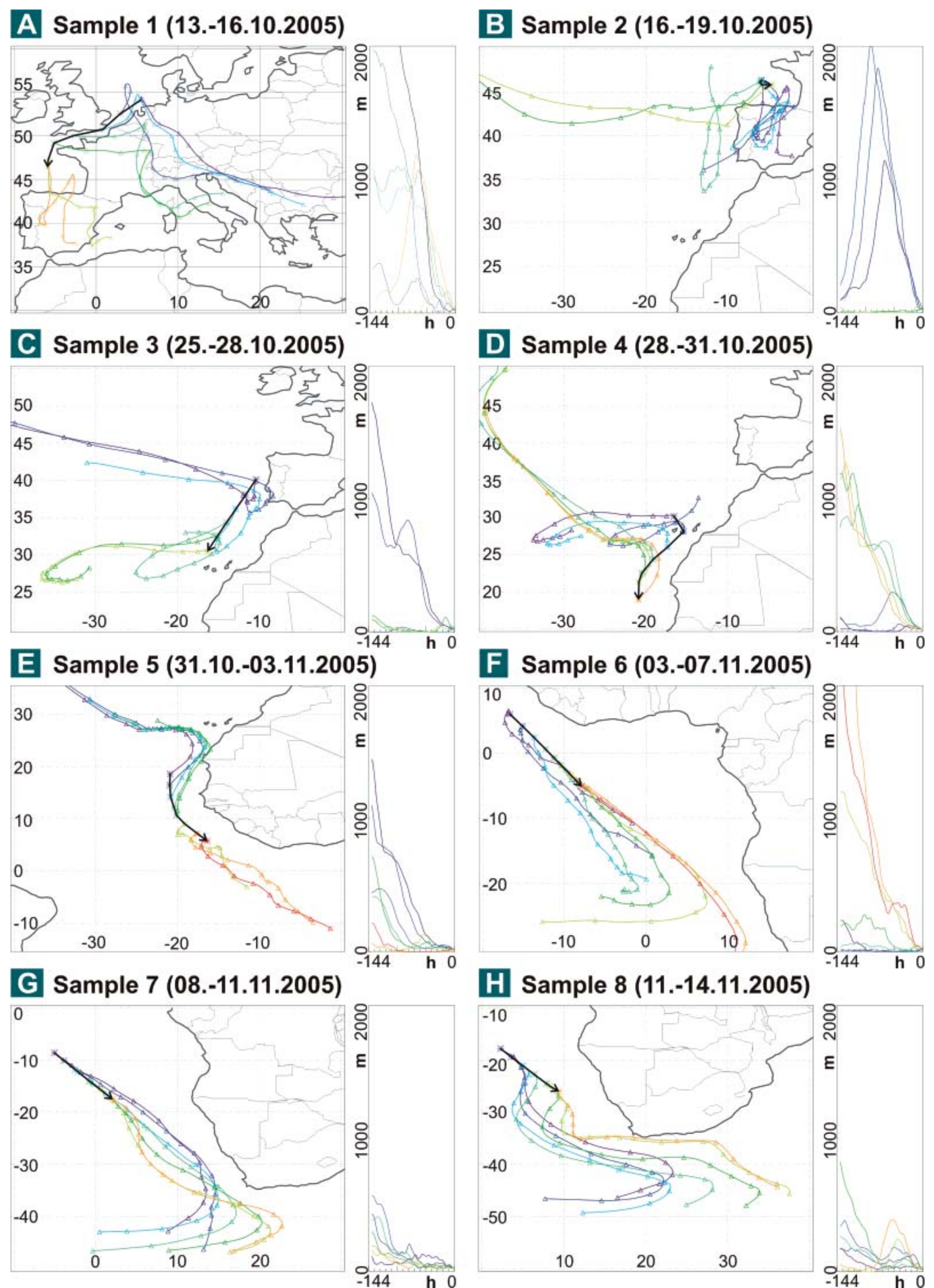

FIGURE 2. Back trajectories of the air samples taken during cruise ANTXXIII-1. Black arrows show the cruise of the *Polarstern* during collection of the respective samples. 6-day/144-hour back trajectories for the observation deck at 20 m height were calculated every 12 h during sampling. Triangles represent 12-hour markers of individual back trajectories to demonstrate transport velocities. Height profiles show the vertical origin of the air masses sampled in this study.

GFFs were cut in two parts. The first half of GFFs was spiked before extraction with the same batch of IS as used for PUF/XAD columns (see above). Extraction was done in four steps using 50 mL of EtOAc each (resulting in 200 mL of EtOAc extract) and placement on a mechanical shaker for 1 min, respectively. The combined extracts were concentrated by rotoevaporation and subsequently under high-purity nitrogen to 200 μL. PUF/XAD columns were extracted by cold-column elution with 300 mL + 200 mL EtOAc (1 h infusion time + 30 min). The combined extracts were concentrated to 200 μL. Both GFF and PUF/XAD extracts were spiked with the recovery internal standards (RIS, used to determine recoveries of the IS: 7:1 fluorinated alcohol (FA) and 11:1 FA, 10 μL of 4 ng/μL in EtOAc) prior to GC/PCI−MS analysis.

Analysis was done on an Agilent (Böblingen, Germany) 6890 N gas chromatograph coupled to an HP 5975 mass-selective detector with helium as carrier gas and methane as reagent gas. Quantification was done in the PCI mode by internal standard correction and external 2-point calibration as described in detail in ref *25* with confirmation of some analytes in the negative chemical ionization (NCI) mode. The method quantification limits (MQLs) of the GC−MS

TABLE 1. Field Blanks (FBs, pg/m^3) Taken during the Atlantic Cruise ANTXXIII-1 of the German Research Vessel *Polarstern* between Bremerhaven and Capetown (53° N−33° S)[a]

	FB1	FB2	NHB[b]	SHB[c]	all blanks
6:2 FTOH	n.d.	n.d.	n.d.	n.d.	n.d.
8:2 FTOH	<1.0	<1.0	1.2	n.d.	n.d.−1.2
10:2 FTOH	<0.7	<0.7	n.d.	n.d.	n.d.−<0.7
NEtFOSA	<0.3	0.4	n.d.	n.d.	n.d.−0.4
NMeFOSA	0.4	0.8	0.4	n.d.	n.d.−0.8
NMeFOSE	1.7	n.d.	n.d.	n.d.	n.d.−1.7
NEtFOSE	0.6	n.d.	n.d.	n.d.	n.d.−0.6

[a] Blank levels were referred to an average sample volume of 1250 m^3. Details are given in the text. n.d. = not detected. <*x* below the respective method quantification limit (MQL) as given in ref *25*. [b] Northern Hemisphere blank collected from October 13 to November 3, 2005 (21 d). [c] Southern Hemisphere blank collected from November 3 to 14, 2005 (11 d).

method given in ref *25* ranged from 0.2 pg/m^3 (NMeFOSA) to 1.4 pg/m^3 (6:2 FTOH).

The second half of GFFs was extracted with methanol (MeOH), followed by LC−MS determination of ionic PFAS, as described in ref *27*. The extraction was done in 7 mL glass vials using 6 mL of MeOH after the addition of 2 ng of the IS (perfluoro 3,7-dimethyl octanoic acid, PF-3,7-dimeOA, 20 μL of 0.1 ng/μL in MeOH). The vials were placed in an ultrasonic bath at room temperature for 30 min. Extracts were filtered over pre-cleaned cotton wool, concentrated in a RapidVap evaporation system (model 7900001, Labconco, Kansas City, MO) and subsequently under high-purity nitrogen to ~200 μL. The volume standard (5 ng of 3,5-bis-(trifluoromethyl)phenyl acetic acid, BTPA, 20 μL of 0.25 ng/μL in MeOH) was added before analysis. An 1100 series quaternary pump and autosampler (Agilent Technologies, Palo Alto, CA) were coupled to a time-of-flight (TOF) mass spectrometer (LCT, Micromass, Manchester, England) which was employed in the negative ion electrospray ionization ((−)ESI) mode. MQLs of the LC−MS method were defined as 10 times the standard deviation of the blanks (see below).

Results and Discussion

Blank Contamination. Results obtained from *Polarstern* FBs, related to an average sample volume of 1250 m^3, are given in Table 1. Both methods (PUF/XAD columns spiked and opened briefly (FB1, FB2) or spiked and left open close to the sampling sites for 21 (NHB) or 11 days (SHB), respectively) showed very low blank contamination. None of the analytes could be detected in SHB. 10:2 FTOH was detected in FB1 and FB2, but at levels below the MQL of 0.7 pg/m^3 (*25*), while 6:2 FTOH was not detected (n.d.) in any blank. 8:2 FTOH could only be quantified in the NHB at 1.2 pg/m^3. Given the relatively high 8:2 FTOH concentrations in samples from the Northern Hemisphere, blanks were negligible. FOSAs/FOSEs were detected occasionally, at maximum levels of 1.7 pg/m^3 (*N*-methyl fluorooctane sulfonamidoethanol (NMeFOSE), FB1). However, the nondetectability of NMeFOSE in FB2 (taken in parallel) indicates that blanks are not correlated with exposure times or actual contamination during transport or sampling, but are due to the specific manually packed PUF/XAD cartridges. Therefore, no blank correction was done. The GFF blanks revealed ionic PFAS concentrations up to 0.19 pg/m^3 (PFOA, results not shown). No blank-correction of the analyte concentrations was performed.

Concentrations of Neutral, Volatile PFAS. In this study, the IS were spiked to PUF/XAD columns before sampling, although this is not common practice in air analyses. In this way, the results were corrected for losses and matrix effects during the whole analytical process including sampling, sample extraction, extract concentration, and analysis. This is especially important regarding the distinct volatility of some of the investigated target compounds, particularly 6:2 FTOH and 8:2 FTOH, the observed breakthrough as described previously (*11*, *25*), as well as possible volatilization from the sampling media. As these sampling phenomena are expected to be temperature dependent, correction for each individual sample is indispensable for obtaining results with highest possible accuracy. The importance of this procedure is also reflected in the variation of IS recoveries between samples (see Table 2).

None of the neutral, volatile PFAS could be detected on any of the GFFs. Hence in the following, we discuss the gaseous phase concentrations of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH as well as FOSAs/FOSEs as given in Table 2/Figure 1. Furthermore, 6-day back trajectories (Figure 2) of the air masses sampled on the ship's observation deck at 20 m height were plotted every 12 h in order to discuss the PFAS concentration profiles observed in this study.

Sample 1 (13.-16.10.2005) taken in the channel between the European mainland and the UK showed very high concentrations of FTOHs, above all for 6:2 FTOH and 8:2 FTOH. However, the recovery of the IS 6:2 FTOH [M + 4] was very low (8%, see Table 2), thus possibly leading to an overestimation of the IS-corrected 6:2 FTOH concentration in the first sample. In a less pronounced way, this also holds for 8:2 FTOH with IS recoveries in sample 1 of 38 and 33%, respectively. In sample 2 from the Biscay area (16.-19.10.2005), airborne PFAS concentrations were already lower by a factor of 2−15. This observation can be explained by the back trajectories as air masses of sample 1 were primarily associated with air originating from the European mainland (Germany, France, Spain), while most of the air collected in sample 2 came over the Atlantic Ocean or over the Iberian Peninsula (see Figure 2A and B). In sample 3 (25.-28.10.2005), six of the investigated analytes could still be quantified at maximum concentrations of 15 pg/m^3 (8:2 FTOH), even though the sampled air almost exclusively originated from the open ocean (see Figure 2C). Extracted ion chromatograms of the respective quantifier m/z of sample 3 are given in Figure 3.

An interesting trend could be seen for the samples between Vigo, Spain and the equator. Concentrations of airborne PFAS increased from sample 3 to 4 (28.-31.10.2005) and reached a local maximum in sample 5 (31.10.-03.11.2005). This trend was consistent for all analytes and might be explained by rising ambient temperatures toward the equator (Table 2) as airborne PFAS levels were shown to correlate positively with temperature (*10*). As discussed above for the first sample, relatively low recoveries of 6:2 FTOH [M + 4] (12%/9%) and 8:2 FTOH [M + 4] (44%/24%) in sample 5 might lead to an overestimation of the respective compounds. Furthermore, back trajectories as given in Figure 2C−E revealed that sample 3 was least impacted by air masses traveling over land close to ground level. Contrarily, some of the air collected in samples 4 and 5 came over the Canary Islands or the African continent, respectively, close to ground level. Toward the end of sampling of sample 5, winds were already turning to southeast. After crossing the ITCZ at 3° N, air was mainly driven by southeast trade winds over the open Atlantic toward the ship (see Figure 2F−H), resulting in very low airborne PFAS concentrations.

Regarding FTOHs, 8:2 FTOH was found to be the dominating compound in air samples, followed by 6:2 FTOH. However, 6:2 FTOH was not determined in samples from the Southern Hemisphere even though 10:2 FTOH could still be quantified. This observation may be partly related to higher MQLs and lower recoveries of the most volatile compound 6:2 FTOH. Looking at FOSAs/FOSEs, the concentrations were about 1 order of magnitude lower than that of 8:2 FTOH. Interestingly, south of the equator, FOSEs were usually n.d. in the air samples. This can be explained by their shorter

TABLE 2. Individual Airborne PFAS Concentrations (pg/m³) and Recoveries of the IS (%) Determined in Duplicate Samples Taken Onboard the *Polarstern* during the ANTXXIII-1 Campaign[a]

	sample 1 13.-16.10.2005 54°N/5°E – 46°N/6°W, 15.8 °C (12.9–18.4 °C)	sample 2 16.-19.10.2005 46°N/6°W – 45°N/4°W, 16.5 °C (13.4–18.3 °C)	sample 3[b] 25.-28.10.2005 40°N/10°W – 30°N/16°W, 20.1 °C (17.0–24.2 °C)	sample 4 28.-31.10.2005 30°N/16°W – 18°N/20°W, 23.1 °C (21.8–24.8 °C)	sample 5 31.10.-03.11.2005 18°N/20°W – 6°N/16°W, 27.2 °C (24.6–30.0 °C)	sample 6 03.-07.11.2005 6°N/16°W – 4°S/8°W, 25.3 °C (22.2–27.5 °C)	sample 7 08.-11.11.2005 8°S/5°W – 17°S/2°E, 20.1 °C (18.1–22.5 °C)	sample 8 11.-14.11.2005 17°S/2°E – 26°S/9°E, 18.0 °C (17.4–18.7 °C)
6:2 FTOH	174, 140 (157)	14, 8.4 (11)	9.4	10, 19 (14)	21, 19 (20)	n.d.	n.d.	n.d.
recov. IS (%)	8, 8	47, 38	28	36, 14	12, 9	12, 15	34, 38	60, 54
8:2 FTOH	190, 163 (176)	36, 21 (29)	15	17, 20 (18)	35, 48 (42)	14, 12 (13)	3.2, 3.0 (3.1)	2.0, 2.8 (2.4)
recov. IS (%)	38, 33	78, 71	60	73, 45	44, 24	49, 38	65, 73	89, 80
10:2 FTOH	48, 44 (46)	12, 6.5 (9.2)	3.3	4.7, 4.9 (4.8)	8.3, 7.1 (7.7)	2.9, 2.8 (2.9)	1.4, 1.0 (1.2)	0.8, 1.0 (0.9)
recov. IS (%)	68, 47	96, 76	91	87, n.a.[c]	n.a.[c], n.a.[c]	77, 69	74, 75	100, 81
NEtFOSA	2.2, 1.7 (2.0)	0.8, 0.7 (0.8)	<0.3	0.7, 0.7 (0.7)	1.3, 0.9 (1.1)	<0.3, n.d.	1.3, <0.3	n.d.
recov. IS (%)	123, 102	146, 132	141	123, 98	131, 98	155, 97	124, 121	126, 128
NMeFOSA	4.2, 3.4 (3.8)	2.0, 1.7 (1.9)	1.1	1.6, 1.6 (1.6)	2.4, 2.1 (2.3)	0.5, 0.6* (0.6)	2.0, 0.4 (1.2)	0.4, 0.5 (0.5)
recov. IS (%)	111, 101	145, 132	135	82, 68	67, 54	144, 91	117, 115	124, 122
NMeFOSE	22, 16 (19)	4.8, 3.0 (3.9)	1.6	3.3, 2.9 (3.1)	7.5, 7.3 (7.4)	0.9*, n.d.	n.d.	n.d.
NEtFOSE	11.8, 5.9 (8.9)	n.d.	0.9*	n.d.	1.7*, 1.2* (1.5*)	n.d.	n.d.	n.d.

[a] Sampling dates, start and stop positions, and the mean temperatures (range) for individual samples are outlined. Mean concentrations of duplicate samples are given in brackets. Concentrations labeled with an asterisk (*) indicate a signal-to-noise (S/N) ratio close to 10. n.d. = not detected. <*x* below the respective method quantification limit (MQL) as given in ref *25*. [b] Due to problems with one of the high-volume pumps, parallel sampling of sample 3 was not possible. [c] Not analyzed due to chromatographic problems with the RIS.

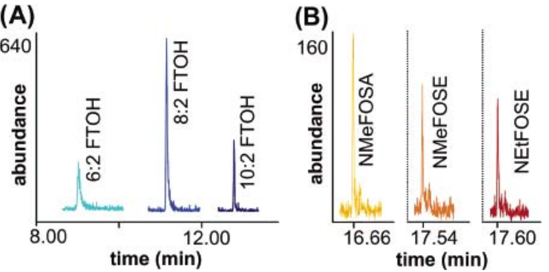

FIGURE 3. Extracted ion chromatograms of the quantifier *m/z* of neutral, volatile PFAS in sample 3 (see Table 2 for quantified concentrations). Three FTOHs (A) and three FOSAs/FOSEs (B) could be determined. Signals of branched isomers of FOSAs/FOSEs are barely visible just after the main signal.

atmospheric lifetimes compared to FOSAs (2 d in contrast to >20 d) as described by D'Eon et al. (*18*) and Martin et al. (*17*).

These first data of FTOHs and FOSAs/FOSEs from a latitudinal transect including air from the Southern Hemisphere show a distinctly decreasing concentration gradient from Central Europe toward Capetown. This indicates that no significant LRAT of these neutral, volatile PFAS emitted in the Northern Hemisphere occurs over the ITCZ. Atmospheric transport and subsequent transformation of FTOHs and FOSAs/FOSEs is not likely to be a mechanism delivering large amounts of persistent ionic PFAS such as PFOS and PFCAs toward Antarctica. Whether direct waterborne transport of PFOS and PFCAs might yield detectable quantities of these compounds in Southern remote locations should be evaluated in more detail.

Comparison with Other Ship-Based Airborne PFAS Measurements. The results described above can be compared to a suite of ship-based airborne PFAS measurements presented by Shoeib et al. (*26*). Daily samples of ~300 m³ were taken on the Swedish ice-breaker *Oden* between Gothenburg, Sweden and Barrow, Alaska in summer 2005. Shoeib et al. described the determination of 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, NMeFOSE, and *N*-ethyl fluorooctane sulfonamidoethanol (NEtFOSE) with method detection limits (MDLs) between 0.8 pg/m³ (10:2 FTOH) and 3.5 pg/m³ (8:2 FTOH). Highest mean gas-phase concentrations (pg/m³) were reported for 8:2 FTOH (11.4) and NMeFOSE (8.30), followed by 10:2 FTOH (6.27), 6:2 FTOH (2.65), and NEtFOSE (1.87). Our samples from the Southern Hemisphere with airborne PFAS concentrations between n.d. and 14 pg/m³ (Table 2) were in a range similar to those taken by Shoeib et al. during the crossing of the North Atlantic Ocean, with concentrations between n.d. and ~15 pg/m³. However, the high concentrations of 8:2 FTOH and 6:2 FTOH in *Polarstern* sample 1 (channel between the European mainland and the UK) are not reflected by the data from the *Oden* cruise which directly headed west after leaving Sweden.

Comparison with Land-Based Data from Northern Germany. Furthermore, the ship-based data collected on the *Polarstern* can be set into context with land-based measurements. As no simultaneous sampling could be performed, a sampling campaign in Northern Germany in spring 2005 (*10*) was used for comparison with sample 1 (channel between the European mainland and the UK). Even though the German sampling campaign was carried out in spring/summer and the *Polarstern* cruise took place in fall, temperatures during sampling on the *Polarstern* were in the upper range of the samples taken in Hamburg. In sample 1 of cruise ANTXXIII-1, FTOH concentrations were very high with up to 190 pg/m³ (mean 176 pg/m³) for 8:2 FTOH (Hamburg: mean 119, max. 275 pg/m³). Levels of 6:2 FTOH (mean 157 pg/m³) even exceeded those determined in the Hamburg city center where mean concentrations were 66 pg/m³ (max. 149 pg/m³). However, the concentration of 6:2 FTOH in sample 1 from the *Polarstern* was probably overestimated due to low IS recoveries (see above). 10:2 FTOH was found in comparable concentrations in Hamburg and onboard the *Polarstern*. Analogous to the German sampling campaign, NMeFOSE and NMeFOSA were the dominating FOSAs/FOSEs and showed levels comparable to those determined in Northern Germany. The ship-based measurements proved to provide valuable complementary information to ground-based measurements in Northern Europe since they show a large-scale distribution and can provide information about LRAT in areas not covered by present land-based measurements or future monitoring.

Concentrations of Ionic PFAS. The method described above for extraction of part of the GFFs with MeOH followed by LC–MS determination proved adequate to determine a suite of ionic PFAS on environmental airborne particles. Results are given in Table 3 together with MQLs (defined as 10 times the standard deviation of blanks, $n = 4$). 1H,1H,-

TABLE 3. Method Quantification Limits (MQLs, pg/m^3), Individual Ionic PFAS Concentrations (pg/m^3) and Recoveries of the IS PF-3,7-dimeOA (%) in the Particulate Phase of Air Samples from the Atlantic Cruise ANTXXIII-1 of the *Polarstern*[a]

	MQL[b]	sample 1	sample 2	sample 3[c]	sample 4	sample 5	sample 6	sample 7	sample 8
6:2 FTS	0.1	0.6, 0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxS	0.002	0.2, 0.3	0.04, 0.02	0.02	**0.05, 0.01**	0.02, 0.01	0.01, 0.03	n.d.	n.d.
PFOS	0.05	2.5, 2.4	0.5, 1.0	0.4	**1.9, 0.3**	0.3, 0.4	**1.0, 0.1**	**1.1, 0.05**	**0.05, 0.24**
PFHpA	0.6	n.d.	0.3*, 0.2*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOA	0.5	1.5, 2.0	1.3, 0.8	0.5	0.6, 0.6	0.7, 0.7	0.3*, 0.3*	n.d.	n.d.
PFNA	0.2	**n.d., 0.5**	0.5, 0.3	0.2	0.2, 0.2	0.3, 0.2	n.d.	n.d.	n.d.
PFDA	0.6	0.4*, 0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFUnA	0.02	n.d.	n.d.	n.d.	n.d.	0.1, 0.2	n.d.	n.d.	n.d..
PFDoA	0.14	0.12*, 0.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
recov. IS (%)	n.d.	83, 95	99, 81	65	55, 48	75, 67	69, 65	64, 61	70, 53

[a] Concentrations below the MQL are labeled with an asterisk (*). Bold concentrations highlight concentration differences larger than a factor of 3 between parallel samples. [b] MQL (pg/m^3) at 10 times the standard deviation of blanks ($n = 4$). [c] Due to problems with one of the high-volume pumps, parallel sampling of sample 3 was not possible.

2H,2H-Tetrahydro perfluorooctane sulfonate (6:2 FTS) was n.d. in particulate air samples except for sample 1. The method showed very low MQLs of perfluorohexane sulfonate (PFHxS) and PFOS, thus allowing for quantification of these sulfonates in most samples. Concerning PFCAs, PFOA and perfluorononanoate (PFNA) were determined in a number of samples, while perfluoroheptanoate (PFHpA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnA), and perfluorododecanoate (PFDoA) were detected only sporadically. Highest mean concentrations (if present) were found for PFOA (1.0 pg/m^3) and PFOS (0.9 pg/m^3). Maximum concentrations of PFOS, PFOA, PFNA, and PFHxS were 2.5, 2.0, 0.5, and 0.3 pg/m^3, respectively. In comparison to levels of neutral, volatile PFAS in the gaseous phase as given in Table 2, the concentrations of ionic PFAS on particles were very low. Highest concentrations of ionic PFAS were determined in the first two samples. However, the trend of increasing concentrations from samples 3 to 5 as discussed above for neutral, volatile PFAS could not be confirmed to the same extent for ionic PFAS.

The following analytes were also investigated, but not detected at levels >MQL (as given in brackets, pg/m^3): perfluorobutane sulfonate (PFBS, 0.02), perfluorodecane sulfonate (PFDS, 0.01), perfluorobutanoate (PFBA, 0.15), perfluoropentanoate (PFPA, 0.66), perfluorohexanoate (PFHxA, 0.04), perfluorotetradecanoate (PFTA, 0.07), and perfluorooctane sulfonamide (PFOSA, 0.09).

The first report on particle-bound PFOS in air samples was published by Sasaki et al. in 2003 and described PFOS levels between <MDL and 21.8 pg/m^3 in urban samples from Japan (*29*). The same group determined PFOA and PFOS in Japanese airborne dust at concentrations of 1.59 (rural) up to 919 pg/m^3 (urban) and between 0.46 (rural) and 9.80 pg/m^3 (urban), respectively (*30*). An investigation of the distribution of PFOA and PFOS on different particle sizes is described in ref *31*. Barton et al. described the determination of PFOA along the fence line of a manufacturing facility at <75−900 ng/m^3 (*32*). Recently, Barber et al. reported the determination of a selection of additional ionic PFAS in air samples collected in the UK at an urban and a semi-rural site. Among these were PFBS, PFHxS, PFOS, PFDS, and PFCAs of 6−11 carbon atoms chain length. Maximum values were reported for PFOA at up to 828 pg/m^3 (*11*). Comparing the results of our study, we found extremely low levels of ionic PFAS. PFOS concentrations were by a factor of ~50 lower than in the UK samples, while PFOA was ~200−800 times lower, thus indicating possible point or diffuse sources of ionic PFAS close to the UK sampling sites.

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Supporting Information Available

Details on the chemicals, standards, gases, and further materials used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53°N-33°S)

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1) **Table S1**. Standards and chemicals used in this study. All standards and solvents were used as received. A detailed description of the analytical protocol for neutral PFAS is given in (*25*). LC-MS conditions for ionic compounds are described in (*27*). Pag. S1

2) **Table S2**. Gases and materials used in this study. A detailed description of the analytical protocol for neutral PFAS is given in (*25*). Pag. S2

Table S1. Standards and chemicals used in this study. All standards and solvents were used as received. A detailed description of the analytical protocol for neutral PFAS is given in (*25*). LC-MS conditions for ionic compounds are described in (*27*).

	Supplier	Purity	Comments[a,b]
6:2 FTOH	Lancaster Synthesis, Frankfurt a.M., Germany	97%	
8:2 FTOH		97%	
10:2 FTOH		97%	
7:1 FA		98%	RIS
11:1 FA		90%	RIS
NEtFOSA	ABCR, Karlsruhe, Germany	95%	isomer mixture dominated by the linear isomer, containing 15-30% branched isomers (20)
6:2 FTOH [M+4]	Wellington Laboratories Inc., Guelph, Ontario, Canada	> 98%	IS
8:2 FTOH [M+4]		> 98%	IS
10:2 FTOH [M+4]		> 98%	IS
NEtFOSA [M+5]		> 98%	IS, linear isomer only
NMeFOSA [M+3]		> 98%	IS, linear isomer only
NMeFOSA	3M	n.a.	donation by 3M, isomer mixture dominated by the linear isomer, containing 15-30% branched isomers (20)
NMeFOSE		n.a.	
NEtFOSE	n.a.	n.a.	donation by the Mabury group, University Toronto, Canada, isomer mixture dominated by the linear isomer, containing 15-30% branched isomers (20)
PFOS	Fluka, Buchs, Switzerland	> 98%	potassium salt
PFOA		~ 95%	
PFDA		> 97%	
PFHxS	Interchim, Montluçon Cedex, France	98%	potassium salt
6:2 FTS		n.a.	
PFHpA	Sigma-Aldrich, Steinheim, Germany	99%	
PFNA		97%	
PFUnA		95%	
PFDoA		95%	
PF-3,7-dimeOA	ABCR, Karlsruhe, Germany	97%	IS
BTPA		98%	RIS
EtOAc	Merck, Darmstadt, Germany	Suprasolv®	
MeOH		Suprasolv®	
Na_2SO_4		for organic trace analysis	
NH_4OAc	Sigma-Adrich, Oslo, Norway	≥ 98%	

n.a. no information available.

[a] RIS, recovery internal standard, spiked before analyses.

[b] IS, internal standard, spiked before sampling (PUF/XAD) or sample extraction (GFF), respectively.

S1

Table S2. Gases and materials used in this study. A detailed description of the analytical protocol for neutral PFAS is given in (*25*).

	Supplier	Purity
nitrogen **helium** **methane**	Messer Griesheim/Air Liquide, Wittenberg, Germany	≥ 99.9995% ≥ 99,999% ≥ 99,9995%
SV 5.130/2-05 high-volume pumps	ISAP, Asendorf, Germany	n.a.
GF8 GFFs	Schleicher & Schuell/Whatman (Dassel, Germany)	n.a.
PUF	Klaus Ziemer GmbH, Langerwehe, Germany	n.a.
Amberlite XAD-2 resin	Supelco, Munich, Germany	n.a.
GC-precolumn: HP-INNOWax polyethylene glycol pre-column (~5 m x 0.25 mm x 0.2 µm)	Agilent, Böblingen, Germany	n.a.
GC-column: CP-Wax 57 CB capillary column for glycols and alcohols (25 m x 0.25 mm x 0.2 µm)	Varian, Darmstadt, Germany	n.a.
LC-column: Ace 3 C_{18}, 3 µm, 150 mm x 2.1 mm i.d.	Advanced Chromatography Technologies, Aberdeen, Scotland	n.a.

n.a. no information available.

S2

6. Additional studies

In addition to the work described in the three publications (***chapters 3-5***), several studies have been performed. Environmental air samples were taken during another scientific expedition on the research vessel Polarstern in summer, 2004 (ARKXX-1 Bremerhaven – Longyearbyen and ARKXX-2 Longyearbyen – Tromsø, ***6.1***). However, as this Arctic cruise took place in the very beginning of this work, the analytical protocol as used in this PhD thesis was not fully developed at that time. Furthermore, for comparison with the ship-based data, sampling was done at a European background site at Mace Head, West coast of Ireland (***6.2***). Finally, within the frame of a German-Norwegian project, a new and standardised sampling method for neutral, volatile PFAS was developed and applied to selected indoor and outdoor air samples (***6.3***).

6.1. Sampling campaign in the European Arctic

In the beginning of this PhD thesis, a sampling campaign was conducted in the European Arctic during Polarstern expedition ARKXX-1 (Figure 6), and continued on ARKXX-2 (Figure 7). The first cruise leg (Bremerhaven – Longyearbyen) was undertaken from 16th June to 16th July, 2004. It included a 10-day East-West transect on 75°N towards Greenland for oceanographic research and almost reached 80°N. On the second cruise leg (Longyearbyen – Tromsø), sampling was continued from 16th July to 29th August, 2004. Most of the time was spent between 80°N and 85°N, with the ship attached to an ice floe, drifting with the sea ice.

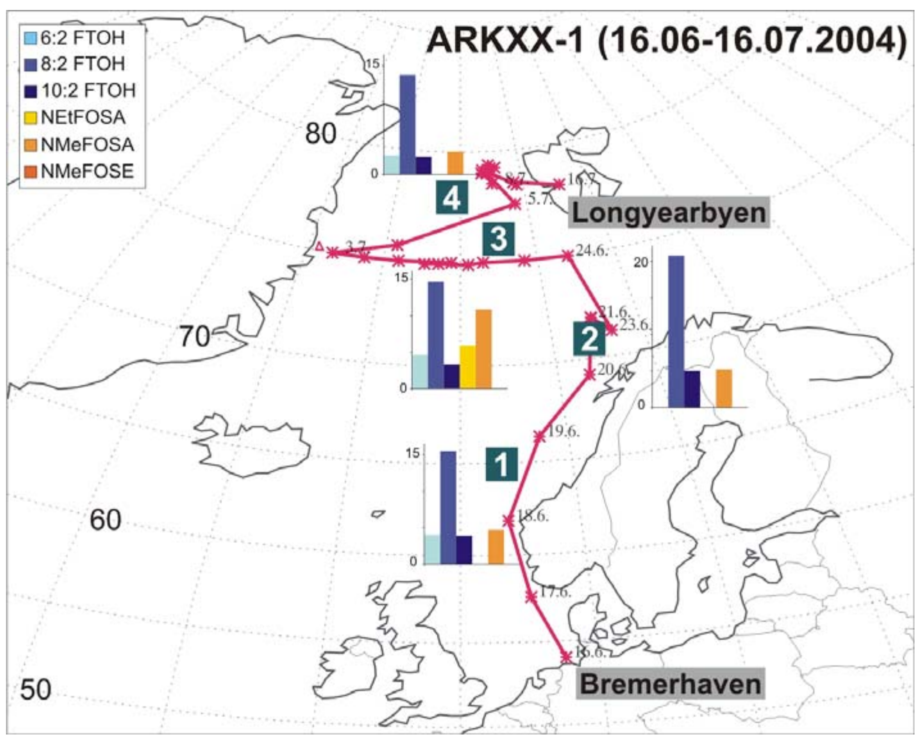

Figure 6. Cruise plot of Polarstern expedition ARKXX-1 (Bremerhaven – Longyearbyen), 16.06.-16.07.2004 and PFAS air concentrations (pg/m³).

Several drawbacks have to be taken into account for the samples collected on the first Polarstern expedition to the Arctic: First of all, no parallel sampling was possible as only one pump was available during the ARKXX expedition. Moreover, NEtFOSE was not yet available as a reference standard, so that it could not be included in field spike experiments. Furthermore, during ARKXX-1/2, only 8:2 FTOH [M+4] was available as IS and thus had to be used for

quantification of all target analytes. Finally, the sample elution was not yet optimised, so that the analytical protocol according to *Martin et al. 2002* was used. Sample elution was done in a primary elution step using 300 mL EtOAc / 1 hour infusion time, followed by four further steps with 200 mL EtOAc / 30 min each, thus resulting in an extract volume of ~1100 mL.

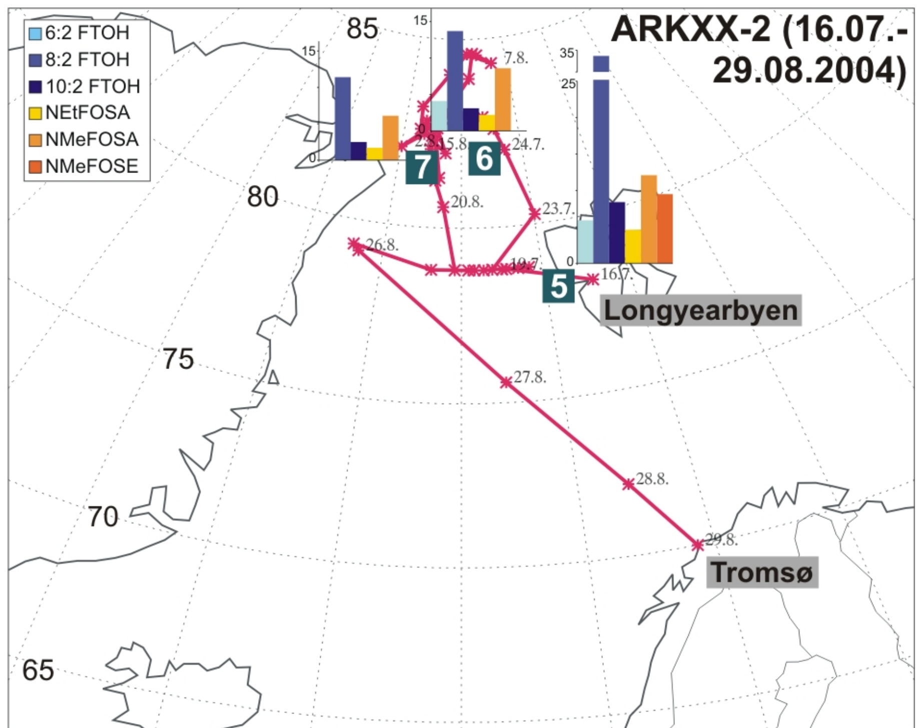

Figure 7. Cruise plot of Polarstern expedition ARKXX-2 (Longyearbyen – Tromsø), 16.07.-29.08.2004 and PFAS air concentrations (pg/m³).

Four samples were collected during the first cruise leg (ARKXX_1 – ARKXX_4), while three further samples were obtained on the second cruise leg (ARKXX_5 – ARKXX_7). Moreover, three field blanks were taken by attaching open PUF/XAD columns close to the sampling sites, which were left open for several days. Finally, one field spike was obtained from each cruise leg. For this experiment, a standard mixture (40 ng absolute, resulting in ~40 pg/m^3) was spiked onto the upper PUF slice before sampling of ~1000 m^3 of air. Results are given in Table 14.

None of the target analytes was detected in the particulate phase (GFF) of ARKXX samples. Referring to PFAS present in the gaseous phase (PUF/XAD), neither 4:2 FTOH nor 6:2 PFOAc or NEtFOSE could be detected in any of the samples. NMeFOSE was only detected once, just above the MQL. 6:2 FTOH was frequently detected, but close to a S/N of 10. Similarly, the determination of NEtFOSA and NMeFOSA was often close to the MQL. For 8:2 FTOH and 10:2 FTOH, results were obtained for most samples. However, in comparison with levels determined in Hamburg / Waldhof and in the beginning of Polarstern expedition ANTXXIII-1, levels were relatively low and showed little variance.

However, considering the ARKXX-1 cruise plot (Figure 6), the ship moved rapidly to the open sea far from the European continent. If wind back trajectories are taken into account (not shown), air masses were coming directly from the north (Svalbard) while passing by Norway, so that the air which was collected during sampling of ARKXX_1 can be considered as relatively 'clean'. Additionally, as concentrations of neutral, volatile PFAS have been shown to be positively correlated with ambient air temperatures (***publication II***), low levels were expected at air temperatures generally well below 5 °C.

Table 14. Concentrations of neutral, volatile PFAS (pg/m³) in air samples, field blanks (FB 1-3) and field spikes (Spike 1-2) collected during Polarstern expeditions ARKXX-1/2 in the European Arctic (summer 2004).

Sample	*Date*	*Volume (m³)*	*4:2 FTOH*	*6:2 PFOAc*	*6:2 FTOH*	*8:2 FTOH*	*10:2 FTOH*	*NEt-FOSA*	*NMe-FOSA*	*NMe-FOSE*
ARKXX_1	17.-21.06.	1115	n.d.	n.d.	(4.0)	15.5	3.9	n.d.	(4.7)	n.d.
ARKXX_2	21.-23.06.	664	n.d.	n.d.	n.d.	20.8	5.0	n.d.	(5.2)	n.d.
ARKXX_3	23.06.-04.07.	913	n.d.	n.d.	(4.6)	14.6	3.3	5.9	10.8	n.d.
ARKXX_4	04.-08.07.	911	n.d.	n.d.	(2.6)	13.6	2.4	n.d.	3.1	n.d.
ARKXX_5	11.-19.07.	1005	n.d.	n.d.	(5.9)	32.4	8.4	4.6	12.1	(9.5)
ARKXX_6	23.07.-02.08.	1150	n.d.	n.d.	(4.1)	13.7	3.1	(2.2)	8.6	n.d.
ARKXX_7	02.-15.08.	1026	n.d.	n.d.	n.d.	11.3	(2.5)	(1.7)	6.1	n.d.
FB 1	14.-15.07.	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FB 2	14.-15.07.	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FB 3	13.-15.08.	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Spike 1	08.-11.07.	917	15.6	41.4	73.1	94.4	63.9	249	245	519
Spike 2	15.-22.08.	948	18.2	50.1	68.3	70.2	63.2	336	314	546

IS-correction of all target analytes was done using 8:2 FTOH [M+4].
Values with a S/N close to 10 are given in brackets.

Surprisingly, highest concentrations of most target analytes observed during Polarstern expeditions ARKXX-1/2 were found in sample ARKXX_5 collected close to Longyearbyen, Svalbard. The presence of primary (synthesis) or secondary (application) PFAS manufacturing sites at Svalbard is extremely unlikely, so that the presence of point sources can be excluded. Therefore, diffuse sources resulting from the use of consumer products (e.g. outdoor clothes) seem to be an important factor for the observed relatively high PFAS levels. The concentrations of neutral, volatile PFAS determined during ARKXX-1/2 will be set into context with the Arctic data published by *Shoeib et al. 2006* in ***chapter 7***.

Field blanks did not show any of the investigated compounds at detectable levels. During field spike experiments, very variable recoveries were observed, ranging from 39.4 ± 3.7% (4:2 FTOH) to more than 1000% (NMeFOSE). Many different effects contribute to this observation. First of all, as 8:2 FTOH [M+4] was the only IS available for this study, a bias resulting from structural differences of the IS and the target analytes and thus varying physical-chemical parameters cannot be ruled out. Therefore, losses of the most volatile compounds as well as matrix enhancement of FOSAs / FOSEs were not fully accounted for by the IS. Furthermore, analytes present in environmental air were enriched during sampling of >900 m³, leading to elevated recoveries of the most abundant PFAS (i.e. 8:2 FTOH and 10:2 FTOH). Finally, for FOSAs / FOSEs, a strong signal enhancement due to the specific matrix resulting from elution of PUF/XAD with EtOAc (see ***publication I***) was observed. This matrix effect is supposed to be even stronger if larger EtOAc volumes are used (here: 1100 mL).

6.2. Sampling campaign at Mace Head, Ireland

For comparison with relatively high levels of neutral, volatile PFAS as observed in Northern Germany as well as with relatively low concentrations in the ship-based samples, air samples were taken at a European background site. Environmental air sampling was performed from March 16th to 30th, 2006 at Mace Head, European Monitoring and Evaluation Program (EMEP) and Global Atmospheric Watch (GAW) station on the West coast of Ireland. Being located in a zone with prevailing westerly wind directions, the site is assumed to be dominated by relatively 'clean' air coming over the open Atlantic Ocean. However, during the sampling period, the sampled air masses were coming predominantly from eastern (sample MH1) or north-eastern (sample MH2) directions, travelling over the UK. During sampling of MH3, the wind direction

turned, so that sample MH4 represents relatively 'clean' air masses which originated from the Atlantic Ocean or the Arctic (see air mass back trajectories in Figure 8).

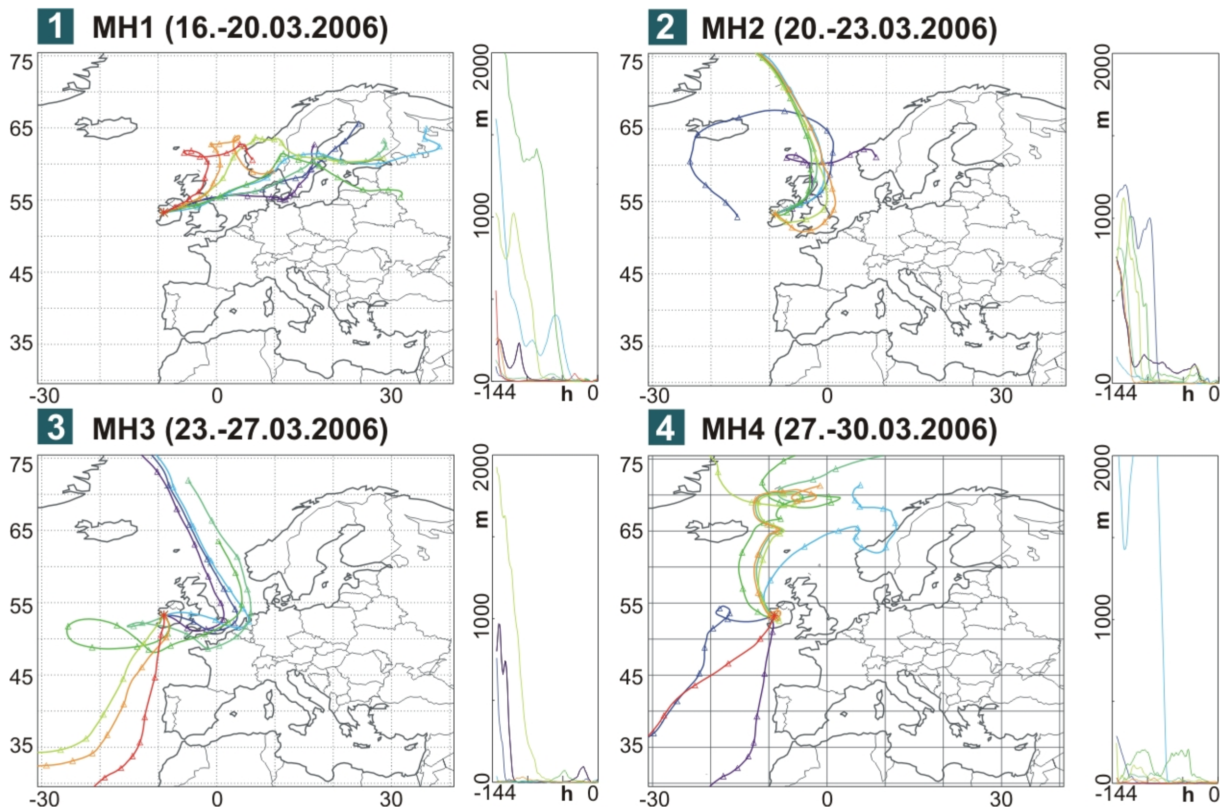

Figure 8. Back trajectories of air masses sampled at Mace Head (March 2006). 144-h back trajectories were calculated every 12 h during sampling. Triangles represent 12-h markers to demonstrate transport velocities. Height profiles show the vertical origin of the air masses.

For this sampling campaign, the fully developed and validated analytical protocol as described in ***publication I*** was applied. An overview of the concentration levels of neutral, volatile PFAS determined at Mace Head at given ambient temperatures is displayed in Table 15. Individual values of duplicate samples (not corrected for blank contamination) are given.

Table 15. Levels of neutral, volatile PFAS (pg/m³) determined in duplicate air samples taken at Mace Head, West coast of Ireland in March, 2006.

Sample Sampling date Mean temp.	***MH1*** 16.-20.03.2006 4.3 °C	***MH2*** 20.-23.03.2006 4.3 °C	***MH3*** 23.-27.03.2006 7.5 °C	***MH4*** 27.-30.03.2006 8.0 °C	***FB*** 16.-30.03.2006 6.3 °C
6:2 FTOH	8.4, 7.3	4.8, 6.1	12.4, 13.8	8.4, 6.6	n.d.
8:2 FTOH	19.1, 16.2	11.6, 11.6	35.3, 36.0	8.8, 9.3	2.1
10:2 FTOH	2.5, 2.3	2.5, 2.7	8.6, 8.1	2.4, 1.9	0.9
NEtFOSA	(<0.3), <0.3	<0.3, 0.5	0.3, (<0.3)	n.d.	n.d.
NMeFOSA	0.5, 0.5	0.6, 1.0	0.8, 0.7	(0.4, 0.4)	n.d.
NMeFOSE	(0.8), 0.7	n.d.	0.6, (0.7)	n.d.	n.d.
NEtFOSE	n.d., (<0.3)	n.d.	n.d.	n.d.	n.d.

Values with a S/N close to 10 are given in brackets.

Generally, Mace Head showed relatively low concentration levels of neutral, volatile PFAS. None of the target analytes could be detected in the particulate phase (GFFs) despite rather low ambient air temperatures. Regarding the gaseous phase (PUF/XAD) extracts, the concentrations of N-alkyl FOSAs / FOSEs were only quantified in selected samples, due to levels which were

often n.d. or <MQL, respectively. 6:2 FTOH, 8:2 FTOH and 10:2 FTOH could be quantified in all samples. Samples MH2 and MH4 showed lowest FTOH concentrations. If considering that the ambient air temperature during sampling of MH4 was relatively high, sampling of relatively 'clean' air can be assumed. This is confirmed by the respective air mass back trajectory as given in Figure 8 (4). In ***chapter 7***, the levels of neutral, volatile PFAS determined at Mace Head will be set into context with the ship-based data (ARKXX-1/2 and ANTXXIII-1).

6.3. Using solid-phase extraction (SPE) cartridges for the sampling of neutral, volatile PFAS in air

The sampling of neutral, volatile PFAS has so far been done using passive samplers with PUFs or using PUF/XAD in high-volume air samplers (see ***chapter 1.2.5***). However, the sampling equipment and setup depends very much on the laboratory performing the analyses, thus implicating a low comparability of results generated by different research groups. Therefore, a German-Norwegian project (German Academic Exchange Service (DAAD) D/05/51603, Research Council of Norway (NFR) project DAADppp) was performed at GKSS Research Centre Geesthacht and the Norwegian Institute for Air Research (NILU) in Tromsø, Norway. The aim of this study was to test the retention capacity of Isolute ENV+ SPE cartridges for airborne FTOHs and FOSAs / FOSEs in order to develop a simple and standardised method for the sampling of volatile PFAS, primarily in indoor air. This was done at NILU in January / February, 2006 as described in *Jahnke et al. 2006*. Furthermore, the new method was tested for environmental air samples in parallel with the established sampling protocol using PUF/XAD cartridges in Hamburg (April 2006).

In this study, an additional analyte was included: the fluorotelomer olefin 1H,1H,2H-perfluoro-1-dodecene (10:2 FT-ol, 97%, Figure 9) from Matrix Scientific (Columbia, SC, USA). Furthermore, 7:1 FA was used as IS, while 1,2,3,4-tetrachloronaphthalene (TCN) was applied as RIS. SPE cartridges used for the presented study were 5 g Isolute ENV+ columns (hydroxylated polystyrene-divinylbenzene copolymer, International Sorbent Technology, Hengoed, UK).

10:2 FT-ol

Figure 9. 10:2 fluorotelomer olefin.

In the general sampling procedure, Isolute ENV+ cartridges were pre-cleaned with 30 mL of EtOAc and subsequently dried using high-purity nitrogen. The IS (20 μL of 10 ng/μL 7:1 FA in EtOAc) was spiked directly onto the upper frit of the cartridge and the pump was started immediately afterwards. Due to the high back pressure of the sampling material, the flow rate using one SPE column was approx. 1.1 m^3/h. For the elution of analytes, 34 mL of EtOAc were added to each column, resulting in approx. 20 mL of eluent. Elution was done by gravitation and the extract was collected in a Turbovap (Zymark, Hopkinton, MA, USA) concentration flask. Several drops of isooctane were added to enhance recoveries in the solvent evaporation step. Concentrated extracts of around 200 μL were transferred to autosampler vials, and the RIS was added (20 μL of 2.5 ng/μL TCN in EtOAc).

Sample extracts were analysed using a Varian CP-3800 gas chromatograph coupled to a Varian 1200 triple quadrupole mass spectrometer (Varian, Palo Alto, CA, USA) operated in the PCI and NCI mode applying SIM. Separation was performed on a polar Varian CP-Wax 57 CB capillary column for glycols and alcohols (25 m x 0.25 mm x 0.2 μm). PCI at a source

temperature of 180 °C and a methane pressure of 6 Torr was used for quantification (one-point calibration at 200 pg/μL). NCI at a source temperature of 160 °C and a methane pressure of 6 Torr was used for confirmation of FOSAs which only generated one abundant *m/z* in PCI. Only the 10:2 FT-ol was quantified in NCI mode and confirmed by a second ion.

Fractionation experiments

In order to check how much EtOAc was needed for the elution of the target analytes from ENV+ cartridges, two fractionation experiments were performed. All analytes, including 7:1 FA, were spiked on a SPE column at 200 ng (20 μL of 10 ng/μL) and eluted with 4 × 10 + 40 mL EtOAc (1st experiment) or 5 × 3 mL of EtOAc (2nd experiment). Extract concentration was done as described above. The first fractionation experiment showed that no more than 3% of the eluted analytes were found after the first 10 mL fraction, while in the second experiment, most of the analytes were eluted in the first three 3 mL fractions. Quantitative elution was done using 34 mL of EtOAc, resulting in sample extracts of around 20 mL.

Recovery and blank experiments

For recovery experiments, two spiking levels were used: 40 ng (20 μL of 2 ng/μL), *n* = 3, and 200 ng (20 μL of 10 ng/μL), *n* = 3, of all analytes including the IS 7:1 FA. In order to determine blank contamination, three precleaned ENV+ cartridges were spiked with 200 ng of 7:1 FA only (20 μL of 10 ng/μL). After spiking, the pump was started immediately, and 0.1 m^3 of air was drawn through the cartridge before elution and extract concentration. Recovery experiments at two spiking levels showed volume standard corrected recoveries between 38% (10:2 FT-ol) and 117% (NEtFOSE) at the lower spiking level or 137% (NMeFOSE) at the higher spiking level, respectively (Figure 10). Only for 10:2 FTOH, recoveries were very high (390%). This signal enhancement could not be explained yet. Blank experiments did not show any of the target analytes at detectable concentrations.

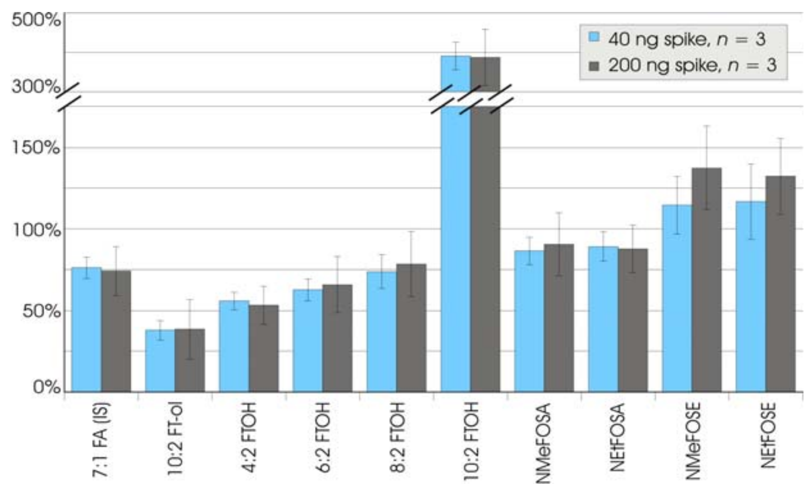

Figure 10. Elution recoveries [%] of neutral, volatile PFAS, determined by spiking experiments at two levels: 40 ng (n = 3) and 200 ng (n = 3).

100 m^3 experiment

All analytes including 7:1 FA were spiked onto an ENV+ cartridge before sampling of 100 m^3 office air in order to test the retention capacity for the target analytes sampling high indoor air volumes. Spiking of 200 ng absolute revealed the recoveries given in Table 16. As also described in ***publication I***, a strong signal enhancement for the FOSAs / FOSEs occurred. This can be

remediated by the application of adequate mass-labelled IS. However, the unnaturally high recoveries for 10:2 FTOH (see above) were not observed in this experiment.

Table 16. Recoveries [%] of 200 ng of the target analytes spiked onto a SPE cartridge, followed by sampling of 100 m³ office air.

	7:1 FA	10:2 FT-ol	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	NEt-FOSA	NMe-FOSA	NMe-FOSE	NEt-FOSE
Rec. [%]	35	29	17	30	53	143	264	328	434	414

Breakthrough experiment

A breakthrough experiment was performed using three ENV+ cartridges coupled in series. The upper column (spiked with 200 ng 7:1 FA) was employed in order to collect analytes present in indoor air, the middle cartridge was spiked with 200 ng of all analytes including 7:1 FA and the lower SPE column (spiked with 200 ng 7:1 FA) was used to trap and quantify the analytes that were not retained on the middle cartridge. A volume of 50 m^3 office air was drawn through the triple cartridge at a flow rate of 0.7 m^3/h. Except for 4:2 FTOH and NMeFOSA, all target analytes could be determined in the 50 m^3 office air sample, extracted from the upper SPE cartridge as shown in Table 17.

Table 17. Concentrations [pg/m³] of the target analytes determined on the upper SPE cartridge spiked with IS.

	10:2 FT-ol	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	NEt-FOSA	NMe-FOSA	NMe-FOSE	NEt-FOSE
Upper+IS	6	n.d.	177	853	898	188	n.d.	727	305

For the middle and lower SPE cartridge, recoveries were determined relative to the spiking level of 200 ng (Table 18). Virtually no breakthrough was observed. As in the 100 m^3 experiment, a signal enhancement can be seen for the FOSAs / FOSEs, but not as significant as in the former experiment. It can be concluded that the signal enhancement is matrix-related, so that the effect is stronger if higher sample volumes are taken. Additionally, in the 100 m^3 experiment, analytes present in the office air were sampled onto the spiked cartridge, thus enhancing recoveries. From the chromatogram of the extract of the upper column (50 m^3 office air sample), LODs as given in Table 19 were estimated at an extrapolated S/N of 3.

Table 18. Recoveries [%] of the target analytes on the middle SPE cartridge spiked with all target analytes and the lower column spiked with IS.

Rec. [%]	7:1 FA	10:2 FT-ol	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	NEt-FOSA	NMe-FOSA	NMe-FOSE	NEt-FOSE
Middle+Sp.	64	35	33	46	69	168	217	200	148	183
Lower+IS	51	n.d.	n.d.	0.3	n.d.	1	n.d.	n.d.	4	n.d.

Table 19. LODs [pg/m³] estimated using the 50 m³ office air sample (upper cartridge).

	10:2 FT-ol	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	NEt-FOSA	NMe-FOSA	NMe-FOSE	NEt-FOSE
LOD [pg/m³]	3	20	24	83	189	71	17	93	111

Paraglider experiment

ENV+ SPE cartridges were used to subsequently sample 20 m^3 office air and 20 m^3 of air in the same office, but with a paraglider laid out on the floor, which was suspected to be surface-

treated with PFAS. Before sampling, 200 ng of 7:1 FA were spiked onto the cartridges. The first sampling of 20 m^3 office air was performed to check for background contamination of the respective office and to evaluate if the very low sample volume was sufficient to determine airborne PFAS concentrations in indoor air. Again, all target analytes could be detected except for 4:2 FTOH and NMeFOSA. Subsequently, a paraglider was placed in the same office, and the 20 m^3 sampling was repeated. The second sample showed significantly elevated concentrations, especially for FTOHs (enhanced by up to a factor of 80 (8:2 FTOH), see Table 20).

Table 20. 20 m^3 office air and 20 m^3 air of the same office containing a paraglider. Values in ng/m^3.

	10:2 FT-ol	***4:2 FTOH***	***6:2 FTOH***	***8:2 FTOH***	***10:2 FTOH***	***NEt-FOSA***	***NMe-FOSA***	***NMe-FOSE***	***NEt-FOSE***
20m^3 office air	0.02	n.d.	0.25	0.42	1.66	0.16	n.d.	0.80	0.82
20 m^3 paraglider	0.02	(0.56)[a]	1.09	33.9	57.7	5.13	n.d.	2.57	1.02

[a] The concentration is given in brackets as the intensity ratio of the two monitored ions deviated from the ratio in the 4:2 FTOH standard.

Application to outdoor air in parallel with the 'classical' PUF/XAD high-volume sampling

In order to assess the applicability of the developed sampling method to environmental air samples, an additional sampling campaign was conducted at the MPI for Meteorology, Hamburg during two weeks from April 3rd to 18th, 2006. One high-volume air sampler was run with PUF/XAD columns, while a low-volume pump was equipped with a SPE cartridge. Both setups were run simultaneously to enable a comparison of the SPE approach to the 'classical' analytical protocol. In both cases, the mass-labelled IS (i.e. 6:2 FTOH [M+4], 8:2 FTOH [M+4], 10:2 FTOH [M+4], NMeFOSA [M+3], NEtFOSA [M+5]) were applied to preclude a bias of the concentration data due to IS-correction. Additionally, one low-volume SPE sample (HH5, 308 m^3) was collected over 11.5 days to facilitate quantification even of the lower concentrated FOSAs / FOSEs. Results (not corrected for blank contamination) are given in Table 21.

Table 21. Levels of neutral, volatile PFAS (pg/m^3) in Hamburg, April 2006. Sampling was done either using the 'classical' PUF/XAD columns or the newly developed SPE method. FOSEs were also detected in the particulate phase (GFFs).

Sample	***HH1***		***HH2***		***HH3***		***HH4***		***HH5***	***FB***
Sampling date	03.-06.04.2006		06.-10.04.2006		10.-13.04.2006		13.-18.04.2006		06.-18. 04.2006	03.-18. 04.2006
Mean temp.	4.2 °C		6.6 °C		5.8 °C		8.5 °C		7.1 °C	6.5 °C
Material	***PUF/XAD***	***SPE***	***PUF/XAD***	***SPE***	***PUF/XAD***	***SPE***	***PUF/XAD***	***SPE***	***SPE***	***PUF/XAD***
V (m^3)	1379	112	1591	138	1335	113	1776	175	308	
6:2 FTOH	15.3	36.3	18.8	16.5	23.9	26.5	26.1	17.3	16.3	(0.6)
8:2 FTOH	36.5	17.3	58.0	29.6	60.4	38.5	51.7	17.9	17.4	0.6
10:2 FTOH	15.9	9.2	22.9	9.1	14.2	9.8	13.0	8.5	9.8	0.5
NEtFOSA	0.5	n.d.	0.9	n.d.	0.8	n.d.	1.1	(0.7)	0.9	0.4
NMeFOSA	1.0	n.d.	1.6	n.d.	1.5	n.d.	2.6	2.5	2.1	0.8
NMeFOSE										
gas. phase	0.8	n.d.	5.3	(4.1)	2.6	(8.6)	7.5	(7.1)	9.3	n.d.
part. phase	(6.1)	n.a.	6.2	n.a	11.7	n.a.	n.a.	n.a.	n.a.	n.a.
NEtFOSE										
gas. phase	n.d.	n.d.	n.d.	n.d.	(0.4)	n.d.	(1.4)	n.d.	n.d.	n.d.
part. phase	(2.3)	n.a.	(2.8)	n.a.	(3.7)	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. not analysed.
Values with a S/N close to 10 are given in brackets.

During the sampling campaign, detectable FTOH levels were found even in the low-volume SPE samples. Contrarily, FOSAs could be quantified just above a S/N ratio of 10 only in samples of ≥175 m^3. NMeFOSE was detected just above a S/N ratio of 10 in most samples, whereas NEtFOSE was usually <MQL even in high-volume air samples.

No attempt was made to separate the gaseous and particulate phase in low-volume air samples. As to high-volume samples, high proportions of FOSEs were found in the particulate phase, corresponding to relatively low ambient air temperatures. Regarding NMeFOSE, 88%, 54% and 82% were found on GFFs. NEtFOSE was detected just above a S/N ratio of 10 in all three particulate phase samples, while it was mostly n.d. in PUF/XAD extracts. A ratio can only be calculated for sample HH3, where 91% of the total NEtFOSE were found on the GFF. Generally, PFAS concentrations were relatively constant during sampling in Hamburg in April, 2006 with only small variations. This may be attributable to stable meteorological conditions including similar ambient air temperatures as well as winds coming from invariable directions, so that the air which was sampled had travelled over similar regions (compare air mass back trajectories given in Figure 11).

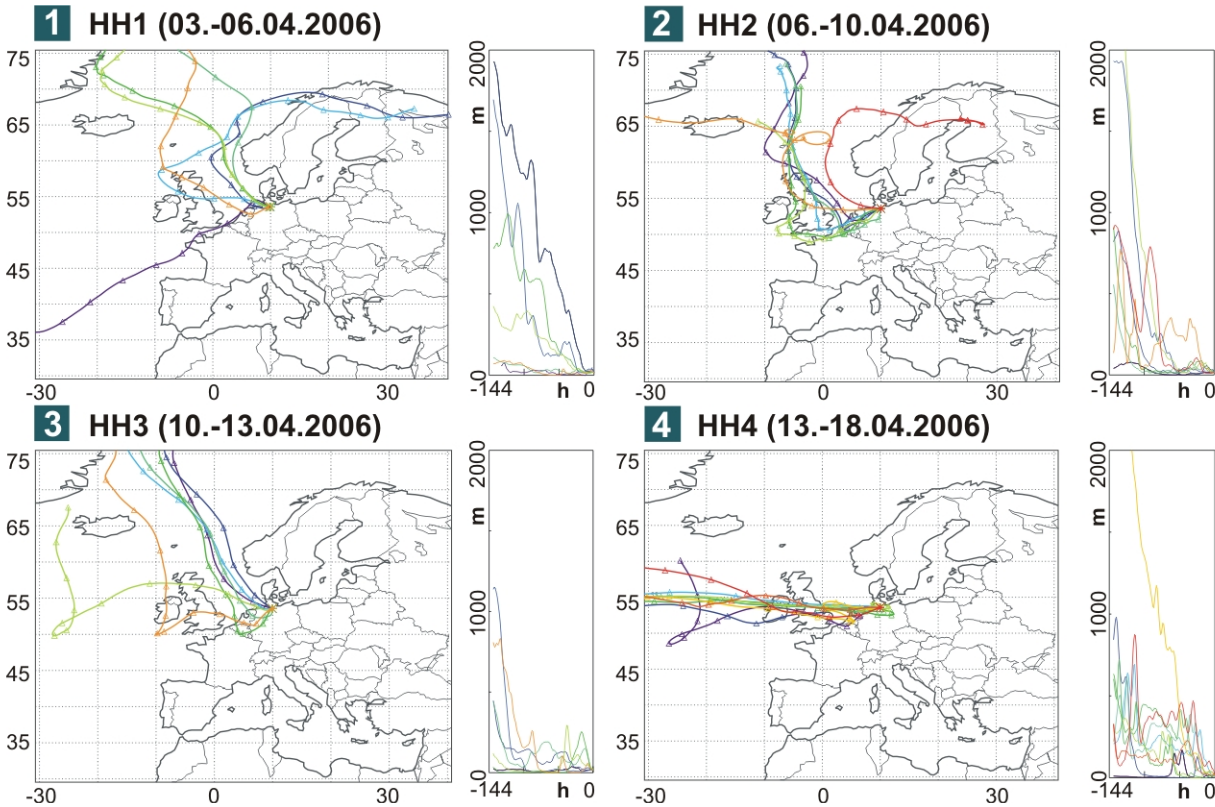

Figure 11. Back trajectories of air masses sampled in Hamburg (April 2006). 144-h back trajectories were calculated every 12 h during sampling. Triangles represent 12-h markers to demonstrate transport velocities. Height profiles show the vertical origin of the air masses.

FTOH levels from both high- and low-volume air samples were roughly in a similar range. Generally, SPE samples yielded lower concentrations than PUF/XAD samples. By comparison with levels of neutral, volatile PFAS determined in Hamburg in spring / summer 2005 (see ***publication II***), levels observed in 2006 were lower. This observation may be attributable to lower ambient air temperatures during sampling in April, 2006, as concentrations were shown to be positively correlated with temperature (***publication II***). If the samples from 2006 are set into context with samples HH4, HH5 and HH7 from 2005 (mean temperatures 7.9, 8.1 and 8.5 °C, respectively), the observed PFAS concentration ranges are comparable.

Conclusions

The presented study showed good retention capacity of Isolute ENV+ SPE cartridges for neutral, volatile PFAS (FTOHs and FOSAs / FOSEs) in indoor air. Advantages of the sampling design were the utilisation of commercially available SPE cartridges, the straightforward cleaning and extraction procedure as well as the low solvent and time consumption compared to the 'classical' sampling setup using PUF/XAD columns. Signal enhancement resulting in high recoveries of 10:2 FTOH and the FOSAs / FOSEs emphasised the importance of the application of adequate mass-labelled IS.

The determination of highly elevated airborne PFAS concentrations in the paraglider sample indicated that textiles surface-treated with (co-)polymers containing fluorochemicals might be a significant source of FTOHs and FOSAs / FOSEs to indoor and environmental air.

The applicability of the presented method to environmental air samples was tested in metropolitan Hamburg with assumed relatively high PFAS levels. As expected, due to the 10 to 100 times lower PFAS concentrations in outdoor air compared to indoor air (*Shoeib et al. 2004*), LODs of the SPE method were not low enough to regularly determine FOSAs / FOSEs at environmental levels in low-volume air samples. By application of a different pump or SPE cartridge design, higher air volumes could be sampled, optimising the method also for outdoor air.

7. Synthesis and Outlook

This chapter briefly summarises main results of the work performed in the course of this PhD thesis. An outlook of further PFAS studies currently being conducted at GKSS research centre Geesthacht GmbH concludes this dissertation.

Optimisation and validation of an analytical protocol (publication I)

The trace-analytical protocol for the identification and quantification of a suite of neutral, volatile PFAS in environmental air samples as published by *Martin et al. 2002* was optimised and fully validated. The following compounds were selected: four FTOHs (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH) as well as two FOSAs (NEtFOSA, NMeFOSA) and FOSEs (NMeFOSE, NEtFOSE). The original analytical protocol was thus extended by two further analytes, 4:2 FTOH and NMeFOSA, which were detected in environmental air samples. Two additional compounds were included in the analytical protocol, but not determined above the MQL in any of the environmental samples (PFOSA and 6:2 PFOAc).

The sampling procedure included the enrichment of the investigated compounds on GFFs (particulate phase) and glass columns filled with a PUF/XAD-2/PUF sandwich (gaseous phase) after spiking of five mass-labelled IS onto the upper PUF slice. High-volume air samples of approx. 1200 m^3 were taken in duplicate to investigate the repeatability of the method. At a sampling rate of 12-18 m^3/h, sampling took approx. 3.5 days. Sample extraction was done by cold column elution with EtOAc in two steps, and the combined extracts were concentrated to 200 μL. Two RIS were spiked to final extracts before analyses.

For quantification of the analytes, GC/PCI-MS was used. However, for NEtFOSA and NMeFOSA, where only one *m/z* could be detected in the PCI mode, confirmation was done in NCI mode. MQLs between 0.2 (NMeFOSA) and 2.5 pg/m^3 (6:2 PFOAc) were achieved, representing an improvement compared to the original protocol.

The optimisation and validation of the original protocol included numerous experiments like recovery tests, the evaluation of analyte breakthrough, matrix effects, an interlaboratory comparison of instrumental quantification between GKSS and NILU, Tromsø etc. Special emphasis was set on the evaluation of several mass-labelled compounds to be used as IS. Absolute analyte recoveries revealed significant signal enhancement of FOSEs in the specific PUF/XAD-derived matrix resulting from elution with EtOAc as well as considerable losses of the most volatile FTOHs during sampling, sample extraction and extract concentration. This lack of accuracy could be remediated by application of a suite of ^{13}C- and ^{2}H-labelled IS, so that IS-corrected relative recoveries were around 100% for most compounds. However, 4:2 FTOH [M+4] (not available yet), NMeFOSE [M+7] and NEtFOSE [M+9] remain to be included in the analytical protocol.

Sampling campaign in Northern Germany (publication II)

In order to test the optimised method in a region with urban background concentrations, the analytical procedure was applied in a first large sampling campaign. It was used to take duplicate sets of environmental air samples in metropolitan Hamburg (urban) and subsequently in Waldhof (rural), which is a background monitoring site of the German Federal Environmental Agency

(UBA) and EMEP. This campaign was carried out between April and June, 2005, and provided first concentration data of neutral, volatile PFAS outside North America.

Quantitative analysis of the samples revealed a wide distribution of FTOHs as well as FOSAs / FOSEs in German environmental air. The final analytical protocol allowed for the first determination of the most volatile compound, 4:2 FTOH, and NMeFOSA in environmental air. Concentrations of ∑FTOHs were almost one order of magnitude higher than ∑FOSAs+FOSEs. 8:2 FTOH was the dominating compound, followed by 6:2 FTOH. PFAS levels at the rural site, Waldhof, were in most cases not significantly lower than in metropolitan Hamburg, underlining the widespread distribution of PFAS in Northern Germany.

A significant positive correlation was found between the ambient air temperatures and concentration levels of neutral, volatile PFAS. This observation may be attributable to temporary deposition of PFAS at lower temperatures and revolatilisation when temperatures are higher. Furthermore, the study showed that FOSEs were distributed between the gaseous and particulate phase in dependence of ambient air temperatures, while FTOHs and FOSAs were found almost exclusively in the gaseous phase.

Comparison of airborne PFAS levels with 'classical' POPs

A comparison of PFAS concentrations with levels of several 'classical' and further 'new and emerging' POPs from a study conducted in Waldhof in 2002 was performed (see Table 22). *Jaward et al. 2004* presented data of PCBs, selected organochlorine pesticides (HCB, α- and γ-HCH, *pp*-DDT) and PBDEs from 22 countries across Europe. The German sampling sites included Waldhof.

Table 22. Comparison of air concentrations of neutral, volatile PFAS (publication II) with those of 'classical' POPs (Jaward et al. 2004) determined at the Waldhof site.

	Concentration [pg/m^3]	*Reference*
6:2 FTOH	17-125 (mean 64)	***publication II***
8:2 FTOH	33-112 (mean 75)	
∑FTOHs	64-311 (mean 181)	
∑FOSAs + FOSEs	14-52 (mean 34)	
γ-HCH	40-52	*Jaward et al. 2004*[a]
HCB	32-42	
pp-DDT	5.5-7.2	
PCB-149	6.7-8.8	
∑29 PCBs	73-96	
∑8 PBDEs	9.7-13	

[a] Values were derived from passive samplers [ng analyte / sampler] and the minimum / maximum air volume sampled (130 / 170 m^3, respectively). The sampling was done from June 15 to July 30, 2002 (6 weeks).

The comparison revealed that 8:2 FTOH and 6:2 FTOH were present at higher levels than γ-HCH, the predominant POP from the former study, thus underlining that PFAS are an important contaminant group. Further locations in Germany (one rural site in Southern Germany and one urban location in Western Germany) showed similar levels as Waldhof (*Jaward et al. 2004*). This is in line with our findings concerning most airborne PFAS, which showed similar concentration levels in Waldhof and Hamburg, respectively. However, the insufficient amount of data available for classical POPs in Waldhof impeded further use of statistical tests.

Considering individual compounds, concentrations of γ-HCH reported for Waldhof were between 40 and 52 pg/m^3, depending on the sampling rate used for calculations (3-4 m^3/d). The second highest concentrations were determined for HCB (32-42 pg/m^3), while levels of individual PCBs were highest for PCB-149 (6.7-8.8 pg/m^3). By comparison with volatile PFAS data acquired in this study, mean 6:2 FTOH and 8:2 FTOH concentrations (Table 22) are slightly higher than γ-HCH concentrations. Maximum values of the predominant FTOHs are by a factor of 2-3 higher, making 6:2 FTOH and 8:2 FTOH the predominant POPs investigated in Waldhof air so far.

Sum concentrations of 29 PCBs and eight PBDEs in Waldhof were lower than for the sum of four FTOHs, underlining that FTOHs are the predominant POP group in Waldhof determined so far. Mean concentrations of ∑FOSAs+FOSEs were slightly higher than ∑PBDEs. As *Jaward et al. 2004* described relatively low levels of airborne POPs in Germany compared to other European regions, even higher FTOH concentrations are assumed to occur elsewhere. This was supported by first data from the UK (*Berger et al. 2005a*).

Sampling campaign on the Polarstern, ARKXX-1/2

First ship-based concentration data of neutral, volatile PFAS were obtained by sampling during Polarstern expeditions ARKXX-1 and ARKXX-2 in the European Arctic in summer, 2004. Although several drawbacks have to be taken into account (as discussed in detail in ***chapter 6.1***, e.g. no parallel sampling, only 8:2 FTOH [M+4] available as IS), concentrations at relatively low levels could be reported.

NMeFOSE was not detected except for one sample, while NEtFOSE was not detected at all. The determination of 6:2 FTOH, NEtFOSA and NMeFOSA was frequently possible, although often close to a S/N of 10. 8:2 FTOH and 10:2 FTOH were determined in most samples at relatively constant levels throughout both cruise legs. No clearly decreasing trend was observed between Bremerhaven and Arctic regions. However, considering the cruise plot as given in ***chapter 6.1***, the ship moved rapidly towards the North. Air mass back trajectories (not shown) revealed that the air which was sampled while passing by Norway came from the polar region without having travelled over land. Surprisingly, the sample taken close to Longyearbyen, Svalbard showed highest levels of most target analytes, underlining the importance of possible diffuse sources.

Sampling campaign on the Polarstern, ANTXXIII-1 (publication III)

An additional sampling campaign applying the optimised analytical protocol took place on board of the German research vessel Polarstern of the Alfred-Wegener-Institute (AWI), Bremerhaven. The Atlantic transfer of the ice-breaker between Bremerhaven, Germany, and Capetown, Republic of South Africa, was used to collect parallel high-volume air samples along a latitudinal gradient from locations in Central Europe with supposedly many point and diffuse sources towards a less industrialised region. The scientific expedition ANTXXIII-1 was undertaken in October / November, 2005, providing first concentration data of neutral, volatile PFAS from the Southern Hemisphere.

The first sample taken in the North Sea and channel between the European continent and the UK confirmed the former results from Hamburg, as concentration levels were in the same range. In addition to field blanks taken on the ship, this comparison underlined that the ship

was a negligible contamination source for the investigated compounds. In the second sample from the Biscay region, levels of neutral, volatile PFAS were already about one order of magnitude lower than in the first sample.

Between Spain and the equator, increasing PFAS concentrations were found. This could be explained by higher ambient air temperatures towards the equator. After crossing of the ITC zone at 3°N, PFAS levels dropped, in some cases below the MDL. 6:2 FTOH and NEtFOSE were not found and NMeFOSE was only detected once, while 8:2 FTOH, 10:2 FTOH and NMeFOSA could still be determined in all samples from the Southern Hemisphere. Those results underlined that neutral, volatile PFAS are mainly restricted to the Northern Hemisphere due to their atmospheric lifetimes between 2 and >20 days. However, trace amounts of several analytes could still be detected and quantified south of the equator.

Comparison of ship-based measurements of airborne PFAS

Concentrations of neutral, volatile PFAS determined on the open Atlantic Ocean could be set into context with data from another sampling campaign in the Arctic as published by *Shoeib et al. 2006*. Their research group analysed air samples from the Atlantic Ocean taken on board of the Swedish ice-breaker Oden between Gothenburg, Sweden and Barrow, Alaska. The ship-based data from ARKXX-1/2 and ANTXXIII-1 as well as available from the literature are summarised in Table 23.

Table 23. Ship-based measurements of neutral, volatile PFAS (pg/m^3).

	Ship	ΣFTOHs	ΣFOSAs+FOSEs
ARKXX-1/2	Polarstern, North Atlantic	24.5[a]	10.6[a]
Shoeib et al. 2006	Oden, gaseous phase	20.4[b]	10.2[b,c]
	Oden, particulate phase	4.3	4.6
ANTXXIII-1, ***publication III***	Polarstern, English channel	379	33.4
	Polarstern, remote (Northern Hemisphere)	48.4	7.4
	Polarstern, remote (Southern Hemisphere)	7.7	1.1

[a] Mean of individual sum concentrations for each sample.
[b] Sum of mean values for each analyte over all samples.
[c] Analysis of NMeFOSE and NEtFOSE only.

Shoeib et al. 2006 determined both FTOHs and FOSAs / FOSEs in the particulate phase, while during the Polarstern expeditions, none of the target analytes was found on GFFs. Mean ∑FTOH levels of *Shoeib et al. 2006* and sampled during ARKXX-1/2 are comparable. As to expedition ARKXX-1/2, ∑FOSA+FOSE levels were represented mainly by NMeFOSA, while FOSEs were n.d. in most samples. However, *Shoeib et al. 2006* only investigated FOSEs, so that the reported sum concentrations did not include FOSAs.

Regarding expedition ANTXXIII-1, the first sample from the English channel was comparable to land-based measurements from central Europe. Samples ANTXXIII-1_2 to ANTXXIII-1_5 taken on the Northern Hemisphere were characterised by relatively high concentrations in comparison to ARKXX-1/2 and *Shoeib et al. 2006*, probably attributable to the crossing of temperate and tropical zones. In samples ANTXXIII-1_6 to ANTXXIII-1_8 from the Southern Hemisphere, FOSEs were mainly n.d., according to their relatively short atmospheric lifetimes (~2 days). NEtFOSA was only detected sporadically. However, 8:2

FTOH, 10:2 FTOH and NMeFOSA could be quantified in all samples with decreasing levels from tropical to temperate regions (see ***publication III***).

Airborne, particle-bound ionic PFAS (ANTXXIII-1)

Finally, the additional analysis of airborne, particle-bound ionic PFAS from halved GFFs (extracted with MeOH for HPLC/(-)ESI-TOF-MS analyses) from ANTXXIII-1 showed low but detectable levels (see Table 24). Highest concentrations were found for PFOS and PFOA in the first sample at 2.5 and 2.0 pg/m^3, respectively. 6:2 FTS, PFHxS and C_7-C_{12} PFCAs were additionally detected. Similar to neutral, volatile PFAS, the ionic compounds showed decreasing concentrations towards less industrialised regions (***publication III***) and were mostly <MQL in the last samples taken on the Southern Hemisphere.

Table 24. Concentration levels of airborne, particle-bound ionic PFAS (pg/m^3).

	Sasaki et al. 2003	***Harada et al. 2005***	***Harada et al. 2006***	***Boulanger et al. 2005a***	***Berger et al. 2005a***	***publication III***
	Japan	***Japan***	***Japan***	***Great Lakes***	***UK***	***ANTXXIII-1***
6:2 FTS					n.d.-9.7	<0.1-0.6
PFHxS					<5.9	<0.002-0.3
PFOS	n.d.-21.8	0.46-9.8	2.2-6.8	n.d.-8.1	<43.9-51.0	0.05-2.5
PFHpA					<6.3-14.4	<0.6
PFOA		1.59-919	15.2-320		226-828	<0.5-2.0
PFNA					<13.6	<0.2-0.5
PFDA					n.d.-14.3	<0.6
PFUnA					n.d.-<4.5	<0.02-0.2
PFDoA						<0.14-0.17

In comparison with levels of neutral, volatile PFAS, concentrations of ionic PFAS were about two orders of magnitude lower. Moreover, ship-based data of particle-bound, ionic PFAS were much lower than in land-based studies from the UK (*Berger et al. 2005a*). Several studies from Japan revealed very high PFOA levels (*Harada et al. 2005*, *Harada et al. 2006*). However, *Boulanger et al. 2005a* described similarly low PFOS concentrations above Lakes Ontario and Erie. Furthermore, Japanese dust samples showed relatively low PFOS levels (*Sasaki et al. 2003*, *Harada et al. 2005*, *Harada et al. 2006*).

Point sources seem to be an important factor if high concentrations of ionic, particle-bound PFAS are observed (compare e.g. *Berger et al. 2005a*). However, the very low levels determined during Polarstern expedition ANTXXIII-1 suggest that LRAT of ionic PFAS bound to particles is negligible compared to LRAT of neutral, volatile precursor compounds, which are found at much higher concentrations.

Sampling campaign at Mace Head, West coast of Ireland

A further sampling campaign was performed at Mace Head, which is an EMEP and Global Atmospheric Watch (GAW) station located on the West coast of Ireland. As the major wind direction brings air masses from the open Atlantic Ocean, the region is ideally suited to investigate European background levels of contaminants. Sampling took place in March, 2006, in order to generate European background concentrations for comparison with the Atlantic data from Polarstern expeditions ARKXX-1/2 and ANTXXIII-1 (see Table 25). However, in the beginning of the sampling period, the prevailing wind direction was from the east and turned during sampling of MH3 (see air mass back trajectories as given in ***chapter 6.2***).

Relatively high concentrations of neutral, volatile PFAS were found in sample MH3, possibly attributable to air masses travelling over the UK and Northern France. However, PFAS concentrations analysed in sample MH4 can be considered as European background levels as the sampled air masses mainly came over the open Atlantic Ocean. Even though ambient air temperatures were the highest observed during the two weeks of sampling at Mace Head, concentrations in sample MH4 were lowest, underlining that the collected air masses were relatively 'clean'.

Table 25. Sum concentrations of neutral, volatile FTOHs and FOSAs / FOSEs (pg/m³) determined at Mace Head, Ireland and on the research vessel Polarstern.

	Location	ΣFTOHs (pg/m³)	ΣFOSAs+FOSEs (pg/m³)
Mace Head	MH3, 'continental'	57.1	1.7
	MH4, 'maritime background'	18.7	0.4
ARKXX-1/2	Polarstern, North Atlantic	24.5	10.6
ANTXXIII-1, ***publication III***	Polarstern, remote (Northern Hemisphere)	48.4	7.4
	Polarstern, remote (Southern Hemisphere)	7.7	1.1

Development of a new sampling method for neutral, volatile PFAS

Within the framework of the Project-Based Personnel Exchange Programme of the German Academic Exchange Service (DAAD, D/05/51603) with the Norwegian Research Council (NFR, project DAADppp), a new and standardised sampling method for neutral, volatile PFAS was developed in January / February, 2006. The protocol used commercially available SPE cartridges to enrich neutral, volatile PFAS from air samples (see ***chapter 6.3***). The new sampling method was tested and applied to a small set of indoor air samples. Finally, the newly developed sampling setup was compared to the 'classical' analytical protocol using PUF/XAD in high-volume environmental air samples taken at the Max Planck Institute in Hamburg (April, 2006). Both sampling methods were run simultaneously to determine neutral, volatile PFAS in environmental air samples at an urban location.

The developed sampling method using Isolute ENV+ SPE cartridges revealed good results in terms of retention capacity combined with very low time and solvent consumption. However, only low-volume air sampling was possible with the current setup (1.1 m^3/h versus 12-18 m^3/h in high-volume air samples) due to the high back pressure of Isolute ENV+ SPE cartridges. Most of the target analytes could be detected in indoor air samples (20 m^3 of office air), except for 4:2 FTOH and NMeFOSA. Interestingly, the repeated sampling in the same office, but with a paraglider (which was suspected to be surface-treated with PFAS) laid out on the floor revealed significantly elevated concentrations of several neutral, volatile PFAS.

As expected, the application of the new protocol to outdoor air showed that concentrations of FOSAs / FOSEs were mostly too low to be detected at environmental levels in low-volume air samples. However, due to higher environmental concentrations, FTOHs could be quantified even in low-volume SPE samples. The data sets generated by both the classical and the newly developed analytical protocol were in a similar concentration range, but showed a relatively large distribution within the range. Generally, SPE extracts yielded lower concentration levels than PUF/XAD extracts.

Summary and Outlook

Prior to the PhD thesis at hand, no concentration data of neutral, volatile PFAS were available outside North America. This work helped to amplify information on the occurrence and distribution of PFAS in Europe, Arctic regions and the Southern Hemisphere and thus helps in the scientific discussion to estimate fluxes of airborne PFAS to remote locations such as the polar regions and to elucidate their worldwide occurrence.

Due to its actuality and importance, the research field dealing with per- and polyfluorinated compounds has been expanded recently at GKSS Research Centre Geesthacht. On the one hand, a follow-up PhD thesis was started in 2006, based on this work. The optimised and validated analytical protocol as described in ***publication I*** will be used and extended to further neutral, volatile PFAS. The method will then be used to generate two data sets (semi-rural / semi-urban) over a whole year to investigate changes in concentration levels throughout a seasonal cycle. Due to the correlation between airborne PFAS concentrations and ambient air temperatures, relatively low levels are expected during winter times. Airborne particles are going to be separated according to particle sizes using a cascade impactor. Furthermore, additional ship-based data will be collected. Finally, a transect between a point source and remote locations is planned.

On the other hand, a second PhD work presently being prepared at GKSS Research Centre Geesthacht will investigate PFAS levels in surface water and biota with a focus on the North and Baltic Sea. Currently, analytical methods using SPE or ion-pair extraction with MTBE and HPLC/(-)ESI-MS/MS determination are being developed and optimised for the determination of neutral and ionic PFAS in surface water (river and sea water) as well as liver and kidney tissue. A time trend analysis of archived seal livers (starting from 1960) will be the focus. Furthermore, studies of the bioconcentration potential of PFAS from water and biomagnification potential along food webs are planned.

Two additional diploma works (a) method development for water analysis and b) determination of octanol-air partition coefficients (log K_{OA}) for selected FTOHs, respectively) will be finished in the near future.

Several years ago, the levels of PFOS were in the focus of ongoing investigations. Soon thereafter, the target analyte spectrum was extended to the analysis of PFOA, PFHxS and PFOSA. The broadening of the compound spectrum has been ongoing, so that currently, about 50 analytes are included in the studies performed at GKSS Research Centre Geesthacht. In the long term it should be considered if the (additional) determination of non-target total organic fluorine as described by *Miyake et al. 2007* should be performed in order to obtain a complete picture of man-made organofluorine compounds in the marine environment.

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