GKSS
FORSCHUNGSZENTRUM
in der HELMHOLTZ-GEMEINSCHAFT

Atmospheric Distribution and Seasonality of Airborne Polyfluorinated Compounds: Spatial and Temporal Concentration Variations from Ship- and Land-Based Measurements in Northern Germany, the Atlantic Ocean, and Polar Regions

(Von der Fakultät Biologie/Chemie/Geowissenschaften der Universität Bayreuth im Jahr 2009 als Dissertation angenommene Arbeit)

Authoress:
A. Dreyer

ISSN 0344-9629

HELMHOLTZ
| GEMEINSCHAFT

wissen
schafft
nutzen

GKSS 2010/1

GKSS 2010/1

Atmospheric Distribution and Seasonality of Airborne Polyfluorinated Compounds: Spatial and Temporal Concentration Variations from Ship- and Land-Based Measurements in Northern Germany, the Atlantic Ocean, and Polar Regions

(Von der Fakultät Biologie/Chemie/Geowissenschaften der Universität Bayreuth im Jahr 2009 als Dissertation angenommene Arbeit)

Authoress:
A. Dreyer
(Institute of Coastal Research)

GKSS-Forschungszentrum Geesthacht GmbH · Geesthacht · 2010

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

Anforderungen/Requests:

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

ISSN 0344-9629

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

GKSS 2010/1

Atmospheric Distribution and Seasonality of Airborne Polyfluorinated Compounds: Spatial and Temporal Concentration Variations from Ship- and Land-Based Measurements in Northern Germany, the Atlantic Ocean, and Polar Regions

(Von der Fakultät Biologie/Chemie/Geowissenschaften der Universität Bayreuth im Jahr 2009 als Dissertation angenommene Arbeit)

Annekatrin Dreyer

249 pages with 54 figures and 66 tables

Abstract

In order to assess the distribution of per- and polyfluorinated compounds (PFC) in ambient air on temporal as well as spatial scales, air samples were taken during several sampling campaigns in 2007 and 2008. Permanent air monitoring stations close to Hamburg (Germany) as well as several research vessels operating in the Atlantic Ocean, the Southern Ocean, and the Baltic Sea were used as sampling platforms. Airborne PFC were sampled using glass fibre filters (particle-bound PFC) and a sandwich polyurethane foam and the polymer resin XAD-2 (gaseous PFC). Samples were extracted by acetone: methyl-tert-butyl ether (1:1) or methanol and detected by GC-MS or HPLC-MS/MS. Airborne PFC were detected in all of the collected air samples, even in Antarctica, with southern hemispheric concentrations being lower than those of the northern hemisphere which provides further evidence that this emerging group of contaminants is subject to atmospheric long-range transport from mainly northern hemispheric source regions towards remote areas. While the persistent perfluorinated acids (PFCA, PFSA) were only determined at concentrations below 1 pg m^{-3} in the particulate phase, their neutral volatile precursors (fluorotelomer alcohols (FTOH), fluorotelomer acrylates (FTA), perfluoroalkyl sulfonamides (FASA), and perfluoroalkyl sulfonamido ethanols (FASE)) occurred predominantly in the gas phase at concentrations that were usually two orders of magnitude higher and ranged from 4.5 pg m^{-3} in the Southern Ocean to 335 pg m^{-3} in source regions in ship-based samples and from 17 to 972 pg m^{-3} in land-based samples. Furthermore, PFC in ambient air varied strongly over time as observed during a 14 months lasting sampling campaign close to Hamburg. Emissions from nearby local sources as well as long-range transport of PFC emitted from diffuse sources west and southwest of the sampling sites were considered as explanation for the observed pattern.

Atmosphärische Verbreitung und Saisonalität von polyfluorierten Verbindungen in der Umgebungsluft: Zeitliche und räumliche Konzentrationsvariationen von Land- und Schiffsmessungen in Norddeutschland, dem Atlantischen Ozean und den Polarregionen

Zusammenfassung

Um die räumliche Verbreitung und zeitliche Variation der Konzentrationen von per- und polyfluorierte Verbindungen (PFC) in der Atmosphäre zu untersuchen, wurden Luftproben während verschiedener Probenahmekampagnen in den Jahren 2007 und 2008 genommen. Als Probenahmeplattformen dienten Dauermessstellen bei Hamburg (Deutschland) und verschiedene Forschungsschiffe, die in atlantischen und antarktischen Gewässern sowie in der Nord- und Ostsee operierten. Die Anreicherung von PFC aus der Luft erfolgete auf Glasfaserfiltern (partikuläre Phase) und geeigneten Adsorbtionsmaterialien (Gasphase), hier Polyurethanschaum und XAD-2. PFC wurden mit Aceton:Methyl-tert-butylether (1:1) oder Methanol extrahiert und mittels GC-MS oder HPLC-MS/MS detektiert. PFC konnten in allen Luftproben von der Arktis bis zur Antarktis nachgewiesen werden. Dabei waren die Konzentrationen in der Nordhemisphäre höher als in der Südhemisphäre. Die festgestellte weltweite Verbreitung von PFC in der Luft bestätigt, dass diese Gruppe von Chemikalien von hauptsächlich nordhemisphärischen Quellenregionen über weite Strecken in entlegene Gebiete transportiert werden kann. Während die perfluorierten Säuren (PFCA, PFSA) ausschließlich in geringen Konzentrationen (meist < 1 pg m^{-3}) in der partikulären Phase bestimmt wurden, lagen die Summenkonzentrationen ihrer volatilen Vorläufer (Fluortelomeralkohole (FTOH), Fluortelomeracrylate (FTA), Perfluoralkylsulfonamide (FASA), und Perfluoralkylsulfonamidoethanole (FASE)) zwischen 4.5 pg m^{-3} im antarktischen Ozean und 335 pg m^{-3} in Quellengebieten (marine Luft) und zwischen 17 und 972 pg m^{-3} (permanente Stationen bei Hamburg). Weiterhin wurden während einer 14monatigen Probenahmekampagne bei Hamburg starke Konzentrationsschwankungen von PFC in Luftproben beobachtet. PFC-Emissionen von nahe gelegenen lokalen Quellen sowie der Langstreckentransport von PFC, die von diffusen Quellen westlich und südwestlich von Hamburg emittiert wurden, schienen den Konzentrationsverlauf zu erklären.

Manuscript received / Manuskripteingang in TFP: 19. Januar 2010

Table of Contents

Study 1

List of Figures

List of Tables

Abbreviations

10:2 FTA	10:2 fluorotelomer acrylate
10:2 FTOH	10:2 fluorotelomer alcohol
12:2 FTOH	12:2 fluorotelomer alcohol
4:2 FTOH	4:2 fluorotelomer alcohol
6:2 FTA	6:2 fluorotelomer acrylate
6:2 FTOH	6:2 fluorotelomer alcohol
8:2 FTA	8:2 fluorotelomer acrylate
8:2 FTOH	8:2 fluorotelomer alcohol
ARL	Air Resources Laboratory
BAR	Barsbüttel (sampling site)
BDL	below detection limit
BFR	Bundesinstitut für Risikobewertung
BMG	Bundesministerium für Gesundheit
BQL	below quantification limit
c	concentration
DCM	dichloromethane
ECF	electrochemical fluorination
EEA	European Environmental Agency
ESI	electro spray ionization
EtFOSA	N-ethyl perfluorooctanesulfon amide
EtFOSE	N-ethyl-perfluorooctanesulfonamido ethanol
FASA	perfluoroalkylsulfon amides
FASE	perfluoroalkylsulfonamido ethanols
FB	filter blank
FldB	field blank
FTA	fluorotelomer acrylates
FTAL	fluorotelomer aldehydes
FTGly	fluorotelomer glycoxylate
FTOH	fluorotelomer alkohols
GC-MS	gas chromatography-mass spectrometry
GDAS	Global Data Assimilation System
GFF	glass fiber filters
GKSS	GKSS Research Center (sampling site)
HPLC-MS/MS	high performance liquid chromatography-tandem mass spectrometry
ITCZ	Intertropical Convergence Zone

KemI	Swedish Chemicals Inspectorate
LOD	limit of detection
LOQ	limit of quantification
LPDPF	liquid phase direct perfluorination
m/z	mass to charge ratio
MAK	maximum Occupational Air Concentration
MDL	method detection limit
Me_2FOSA	N,N-dimethylperfluorooctane sulfonamide
MeFBSA	N-methyl-perfluorobutane sulfonamide
MeFBSE	N-methyl-perflurobutane sulfonamido ethanol
MeFOSA	N-methyl-perfluorooctane sulfonamide
MeFOSE	N-methyl-perfluorooctane sulfonamido ethanol
MQL	method quantification limit
MTBE	methyl-tert-butyl ether
MW	molecular weight
n.a.	not analyzed
n.c.	not calculated
n.d.	not detected
n.q.	not quantified
NCEP	National Centers for Environmental Prediction
NCI	negative chemical ionization
NOAA	National Oceanic and Atmospheric Administration
OH	hydroxyl radicals
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
PCI	positive chemical ionization
PFAL	perfluorinated aldehydes
PFBA	perfluorobutanoate
PFBS	perfluorobutane sulfonate
PFC	poly- and perfluorinated compounds
PFCA	perfluorocarboxylates
PFDA	perfluorodecanoate
PFDoDA	perfluorododecanoate
PFDS	perfluorodecane sulfonate
PFDSi	perfluorodecane sulfinate
PFHpA	perfluoroheptanoate
PFHpDA	perfluoroheptadecanoate
PFHpS	perfluoroheptane sulfonate

PFHxA	perfluorohexanoate
PFHxDA	perfluorohexadecanoate
PFHxS	perfluorohexane sulfonate
PFHxSi	perfluorohexane sulfinate
PFNA	perfluorononanoate
PFOA	perfluorooctanoate
PFOcDA	perfluorooctadecanoate
PFOS	perfluorooctane sulfonate
PFOSA	perfluorooctane sulfonamide
PFOSi	perfluorooctane sulfinate
PFPA	perfluoropentanoate
PFPeDA	perfluoropentadecanoate
PFSA	perfluorosulfonates
PFSI	perfluorosulfinates
PFTeDA	perfluorotetradecanoate
PFTriDA	perfluorotridecanoate
PFUnDA	perfluoroundecanoate
POP	persistent organic pollutant
PTV Inlet	programmed temperature vaporizing inlet
PUF	polyurethane foam
Q	qualifier
R	recovery rate
S.B.	solvent blank
S.D.	standard deviation
S/N	signal to noise ratio
SIM	selected ion monitoring
TDI	tolerable daily intake
THF	tetrahydrofuran
TI	target ion
US-EPA	United States Environmental Protection Agency

Summary

Per- and polyfluorinated compounds (PFC) were recently identified as pollutants that are being observed worldwide in all environmental compartments. Some of these compounds, particularly perfluorinated carboxylates (PFCA) and sulfonates (PFSA), are considered as toxic and extraordinarily persistent substances that accumulate in humans as well as in wildlife. It was hypothesized that the atmospheric transport and degradation of volatile polyfluorinated PFCA and PFSA precursors may provide an explanation for the presence of non volatile persistent perfluorinated acids at locations remote from sources. Comprehensive studies about the occurrence of poly- and perfluorinated substances in air were lacking and gave reason for further investigations on the distribution of airborne PFC on temporal as well as spatial scales.

In order to be able to accurately detect PFC at low concentrations the analytical procedure was optimized. Basically, glass fibre filters and a sandwich polyurethane foam and the polymer resin XAD-2 were used to accumulate particle-bound and gaseous PFC, respectively. In previous studies, neutral volatile PFC were commonly extracted using ethyl acetate as extraction solvent and determined by gas chromatography - mass spectrometry. Ionic PFC were methanol-extracted and detected by high performance liquid chromatography - tandem mass spectrometry. Although previous analytical methods using this set-up were capable to detect airborne PFC, they were characterized by matrix problems that resulted in severe signal enhancement of several analytes. During this study's analyses it soon became evident that the matrix problem was rather a solvent problem. This was confirmed by experiments investigating the PFC recovery rates after the application of different extraction solvents. Whenever ethyl acetate was involved, PFC recovery rates remarkably exceeded 100 %, probably due to solvent impurities. Based on these results, the extraction solvent for gas-phase PFC was changed to a 1:1 mixture of acetone and methyl-tert-butyl ether. Additionally, chromatographic parameters were modified to achieve low detection limits. The optimized method was used to determine several fluorotelomer alcohols (FTOH), fluorotelomer acrylates (FTA), perfluoroalkyl sulfonamides (FASA), and perfluoroalkyl sulfonamido ethanols (FASE) in the gas and particulate phase as well as a set of PFCA and PFSA in the particulate phase.

Air concentrations of PFC were determined during several sampling campaigns in 2007 and 2008. Permanent air monitoring stations close to Hamburg (Germany) as well as several research vessels operating in the Atlantic Ocean, the Southern Ocean, and the Baltic Sea were used as sampling platforms. Generally, samples were taken in one to four days intervals during these campaigns. Airborne PFC occurred predominantly in the gas phase. While the persistent perfluorinated acids (PFCA, PFSA) were only determined at low concentrations in the particulate phase, their volatile neutral precursors (FTOH, FTA, FASA, FASE) occurred predominantly in the gas phase in concentrations that were usually two orders of magnitude higher. Only some FASA and FASE were observed in the particulate fraction, however, the average contribution did not exceed 20 %. Concentrations of gas-phase PFC varied between one and two orders of magnitude on temporal as well as on spatial scales. Total gas-phase concentrations ranged from 4.5 pg m^{-3} in the Southern Ocean to 335 pg m^{-3} in source regions in ship-based samples and from 17 to 972 pg m^{-3} in land-based samples. With about 80 % on average, the class of FTOH clearly dominated the gas-phase substance spectrum. The compound that was usually detected in highest concentrations was perfluorooctyl ethanol (8:2 FTOH) with a maximum concentration reaching 600 pg m^{-3} in the gas phase. Concentrations of individual particulate-bound precursors were usually below 1 pg m^{-3}.

During a 14 month lasting sampling campaign at two sites in the vicinity of Hamburg, PFC concentrations were observed to vary strongly over time. This reveals the limited interpretation potential of singular measurements. Concentration variations of precursor PFC were characterized by a fluctuating baseline and singular events of strongly enhanced PFC concentrations, probably due to emissions from local sources. The exclusion of these singular high concentration events from the time series resulted in a less interrupted concentration course where individual precursor concentrations were higher in summer than in winter. Temperature-dependent emissions of volatile PFC from diffuse sources to the gas phase were presumed to be responsible for this observation. Trajectory analysis revealed that the origin of sampled air was a driving parameter influencing the PFC levels of these samples. Elevated baseline concentrations of PFCA and PFSA precursors occurred, whenever air was arriving from industrialized and populated regions west and southwest of Hamburg. Trajectory, cluster, and correlation analyses performed on samples taken in the German Bight also confirmed that medium to long-distance transport of airborne PFC from south-westerly located source regions was an important factor determining the PFC level in northern Germany and the North Sea region. Airborne PFC were detected on a global scale in all of the collected air samples, even in Antarctica. PFC concentrations decreased from continental or coastal areas towards the open sea and from Central Europe towards the poles. Southern hemispheric concentrations of PFCA and PFSA precursors were significantly lower than those of the northern hemisphere. Atmospheric residence times of volatile PFC calculated on the basis of temporal and spatial concentrations variations were in the order of 20 to 60 days.

As comprehensively demonstrated in this thesis, the ubiquitous detection of airborne PFC as well as their residence time estimates give further evidence that this emerging group of contaminants is subject to atmospheric long-range transport from mainly northern hemispheric source regions towards remote areas.

Zusammenfassung

Per- und polyfluorierte Verbindungen (PFC) sind vielfältig verwendete chemische Substanzen, die mittlerweile weltweit und in allen Umweltmedien nachgewiesen werden konnten. Einige PFC, vor allem Perfluorcarboxylate (PFCA) und Perfluorsulfonate (PFSA), sind persistent, toxisch und reichern sich in Lebewesen, auch im Menschen, an. In einigen Studien wurde festgestellt, dass der atmosphärische Transport und Abbau von neutralen volatilen PFCA und PFSA Vorläufersubstanzen die Existenz dieser persistenten perfluorierten Säuren in quellenfernen Gebieten erklären könnte. Obwohl erste Einzelmessungen von volatilen PFC in Luftproben an verschiedenen Standorten einen atmosphärischen Transport bestätigten, fehlen bisher Studien, die die Verbreitung von poly- und perfluorierten Verbindungen umfassend darstellen. Aus diesem Grund wurde mittels intensiver Luftbeprobung die Variabilität der PFC-Konzentrationen auf räumlicher und zeitlicher Ebene untersucht.

Um PFC in Luftproben exakt und im Ultraspurenbereich bestimmen zu können, wurde basierend auf publizierten Verfahren die analytische Methode optimiert. Prinzipiell werden PFC in der Luft auf Glasfaserfiltern (partikuläre Phase) und geeigneten Adsorbtionsmaterialien (Gasphase), hier Polyurethanschaum und XAD-2, angereichert. In früheren Untersuchungen wurden neutrale volatile PFC vor allem mit Ethylacetat extrahiert und mittels Gaschromatographie - Massenspektrometrie detektiert. Diese Methode war jedoch durch starke matrixbedingte Störungen gekennzeichnet, die sich vor allem durch Signalverstärkung diverser Analyte äußerten. Während der vorliegenden Arbeiten wurde klar, dass das Matrixproblem auf das verwendete Extraktionsmittel zurückzuführen war. Experimente mit verschiedenen Extraktionsmitteln bestätigten, dass immer dann, wenn Ethylacetat verwendet worden ist, die Wiederfindungen von einigen polyfluorierten Substanzen auf weit über 100 % stiegen. Aufgrund der Ergebnisse dieser Experimente wurde das Extraktionsmittel für neutrale PFC von Ethylacetat auf Aceton:Methyl-tert-butylether (1:1) gewechselt. Weiterhin wurden chromatographische Parameter modifiziert, um niedrige Nachweisgrenzen zu erreichen. Die optimierte Methode wurde angewendet, um verschiedene PFC in Luftproben zu bestimmen. Darunter waren Fluortelomeralkohole (FTOH), Fluortelomeracrylate (FTA), Perfluoralkylsulfonamide (FASA), and Perfluoralkylsulfonamidoethanole (FASE) in der Gas- und Partikelphase sowie PFCA und PFSA in der partikulären Phase.

Die Luftkonzentrationen von PFC wurden in Proben aus verschiedenen Probenahmekampagnen der Jahre 2007 und 2008 bestimmt. Als Probenahmeplattformen dienten Dauermessstellen bei Hamburg (Deutschland) und verschiedene Forschungsschiffe, die in atlantischen und antarktischen Gewässern sowie der Nord- und Ostsee operierten. Die Luftproben wurden in Ein- bis Viertagesintervallen genommen. Polyfluorierte Verbindungen in der Luft lagen vor allem in der Gasphase vor. Die perfluorierten Säuren (PFCA, PFSA) wurden ausschließlich in geringen Konzentrationen in der partikulären Phase bestimmt. Im Gegensatz dazu waren die Gasphasenkonzentrationen ihrer neutralen volatilen Vorläufer (FTOH, FTA, FASA, FASE) bis zu zwei Größenordnungen höher. Nur einige FASA und FASE wurden auch in der partikulären Phase detektiert. Durchschnittlich lag dieser Anteil unter 20 %. Die Gasphasenkonzentrationen von PFC variierten zwischen ein und zwei Größenordnungen auf räumlicher und zeitlicher Ebene. PFC Summenkonzentrationen in Luftproben, die auf Forschungsschiffen genommen wurden, variierten zwischen 4.5 pg m^{-3} im antarktischen Ozean und 335 pg m^{-3} in Quellengebieten. Die Summenkonzentrationen in Luftproben von den permanenten Stationen bei Hamburg lagen zwischen 17 und 972 pg m^{-3}. Mit durchschnittlich mehr als 80 % dominierten die FTOH das Substanzspektrum in der Gasphase. Perfluoroctylethanol (8:2 FTOH) war die Einzelsubstanz, die in höchsten Konzentrationen vorgefunden wurde. Die Einzelstoffkonzentrationen in der partikulären Phase lagen meist unter 1 pg m^{-3}.

Während einer 14monatigen Probenahmekampagne an zwei Dauermessstationen bei Hamburg wurden die zeitlichen Variationen von PFC Konzentrationen untersucht. Die beobachteten starken Schwankungen über diesen Zeitraum verdeutlichten die limitierte Aussagekraft von Einzelmessungen. Der Konzentrationsverlauf der volatilen PFCA- und PFSA-Vorläuferverbindungen war durch eine fluktuierende Grundlinie gekennzeichnet, die durch einzelne, unregelmäßig vorkommende Ereignisse stark erhöhter Konzentrationen unterbrochen wurde. Diese Hochkonzentrationsereignisse könnten durch lokale Quellen verursacht worden sein. Die Bereinigung der Zeitreihen von diesen Einzelereignissen führte zu weniger gestörten Konzentrationsverläufen, bei denen die Konzentrationen der Vorläuferverbindungen in den Sommermonaten höher als die in den Wintermonaten waren. Wir vermuten, dass temperatur-abhängige Emissionen von diffusen Quellen für diesen beobachteten Konzentrationsverlauf verantwortlich sind. Die Luftmassenherkunft hatte einen starken Einfluss auf die PFC Konzentrationen dieser Luftproben. Die Untersuchung der Luftmassenherkunft mittels Trajektorien ließ auf westlich und südwestlich von Hamburg gelegene Quellenregionen mit hoher Bevölkerungs- und Industriedichte schließen.

Trajektorien-, Korrelations- und Clusteranalysen von Luftproben aus der Deutschen Bucht bestätigten, dass Mittel- bis Langstreckentransport einen wichtigen Einfluss auf das detektierte PFC Niveau in Luftproben aus Norddeutschland und der Nordsee hat. Poly- und perfluorierte Verbindungen konnten in allen Luftproben von der Arktis bis zur Antarktis nachgewiesen werden. Dabei nahmen Konzentrationen von kontinentalen und küstennahen Regionen zur offenen See und von Mitteleuropa zu den Polen ab. Die Einzelstoffkonzentrationen waren in der Nordhemisphäre signifikant höher als in der Südhemisphäre. Auf Grundlage der zeitlichen und räumlichen Konzentrationsvariationen konnten atmosphärische Verweilzeiten für die analysierten PFC berechnet werden. Diese lagen im Bereich von 20 bis 60 Tagen.

Die Ergebnisse dieser Arbeit liefern neue Erkenntnisse über atmosphärisch transportierte PFC. Sowohl die atmosphärischen Verweilzeiten als auch die festgestellte weltweite Verbreitung von PFC in der Luft bestätigen, dass diese Gruppe von Chemikalien von hauptsächlich nordhemisphärischen Quellenregionen über weite Strecken in entlegene Gebiete transportiert werden können.

EXTENDED SUMMARY

1. Introduction

1.1. Rationale

Fluorine is a key element in modern chemistry. In recent years, there was hardly another element that chemistry contributed to the progress in numerous fields to the same extent as fluorine did (Röschenthaler, 2008). The group of poly- and perfluorinated organic compounds (PFC) is one example of many other substance classes containing one or more fluorine atoms. Due to their thermal and chemical stability as well as their surface activity, PFC or PFC-containing products are applied in a variety of industrial and consumer products or household agents and thus are a part of everyday life. Recently, it has become evident that those PFC properties that are beneficial for their use as well as the extensive application of PFC itself resulted in serious environmental problems. Most of the PFC are extremely persistent in the environment and those PFC that do degrade, the so called precursor PFC, finally yield the persistent compounds (Prevedouros et al., 2006). Some PFC have been identified to be toxic (Lau et al., 2007) and bioaccumulative (Conder et al., 2008) and wildlife monitoring studies revealed the worldwide distribution of PFC, even to remote regions such as the Arctic (Houde et al., 2006). Given these aspects, PFC were classified as “new” chemicals of emerging environmental concern and partly being scrutinized for possible persistent organic pollutant (POP)-like behavior according to the Stockholm Convention (KemI, 2005).

One key issue for a compound’s classification or legislative regulation efforts is its potential for long-range environmental transport. Oceanic transport is known to contribute significantly to the PFC contamination of remote regions (Wania, 2007). In contrast, the importance of long-range atmospheric transport of precursor PFC for the overall PFC contamination of these ecosystems is less known. Analysis of the atmospheric transport of precursor PFC is also of particular interest against the background of legislative regulations which aim to restrict manufacturing and use of selected persistent PFC but not of their volatile precursors. In order to better understand the atmospheric transport pathway it is essential to study the distribution of airborne PFC. Particularly, the description of PFC air concentration variations on temporal and spatial scales provides valuable information.

1.2. Background

Per- and polyfluorinated compounds are substances that contain an alkyl chain of typically four or more carbon atoms where all or most of the hydrogen atoms are replaced by fluorine (Prevedouros et al., 2006). Due to the strength of the carbon-fluorine bond this replacement causes the stability of the alkyl chain (Key et al., 1997). Additionally, PFC also contain a more reactive functional group, e.g. an carboxyl, sulfonyl, or alcohol moiety, or their derivatives. Together with the fluorinated chain these functional groups dictate the compound's characteristic physical, chemical, and toxicological properties. Several hundred of these PFC are known today (Jensen et al., 2008), those, that will be focused on in this study are presented in table I. They comprise ionic substances such as perfluoroalkyl carboxylates (PFCA), -sulfonates (PFSA) or -sulfinates (PFSI) as well as neutral compounds like fluorotelomer alcohols (FTOH), fluorotelomer acrylates (FTA) perfluoroalkyl sulfonamides (FASA), and -sulfonamido ethanols (FASE).

PFC are surface-active compounds. Lowering the surface tension much more than other surfactants at relatively low concentrations, they repel water, grease and dirt, and are therefore used as detergents or impregnating agents in numerous industrial or consumer products (Jensen et al., 2008; Kissa, 2001). Specifically, PFC are being applied as emulsifiers and processing aids in the manufacture of inert fluoropolymers such as polytetrafluoro ethylene (PTFE) or foaming hydrocarbons, in various coatings (wetting or grease resistance, leveling, spreading, anti-blocking) for textiles, carpets, upholstery, or paper and packaging, in floor and shoe polishes, personal care products, lubricants, corrosion inhibitors, paints, dyes, specialty inks, electrical insulation, micro electronics, fire fighting foams, or pesticides (Begley et al., 2005; Buck, 2008; Ellis and Mabury, 2003; Jensen et al., 2008; Johns and Stead, 2000; Paul et al., 2009; Prevedouros et al., 2006). Trade names like Teflon®, Scotchgard®, Baygard®, Gore-Tex®, Zonyl®, or Stainmaster® are just some well known examples of PFC containing products. Generally, the eight-carbon chemicals (perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and its derivatives) have been most effective in commercial uses and therefore were heavily applied in the past (Lau et al., 2007; Prevedouros et al., 2006). All of the applications and products mentioned above contribute to the PFC contamination of the environment, either directly during manufacturing, use, and disposal, or indirectly by washout or evaporation of unbound residuals left from the manufacturing process (Dinglasan-Panlilio and Mabury, 2006).

Table I: Overview about poly-and perfluorinated compounds analyzed in this study.

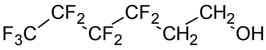
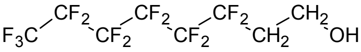
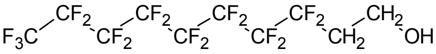
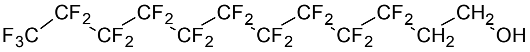
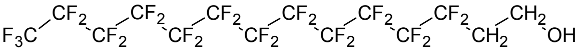
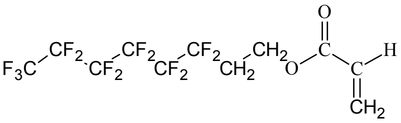
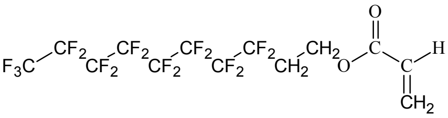
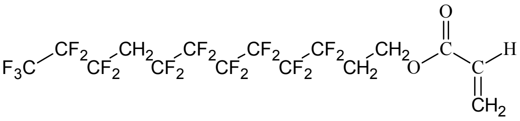
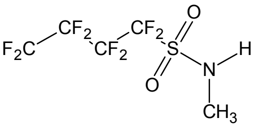
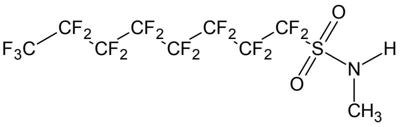
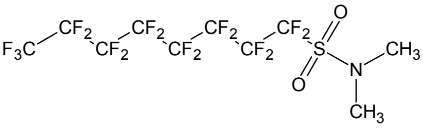
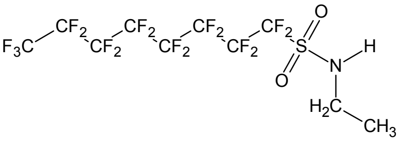
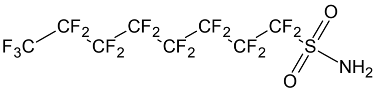
Analytes	Acronym	Structure
Fluorotelomer alcohols (FTOH)		
4:2 fluorotelomer alcohol	4:2 FTOH	
6:2 fluorotelomer alcohol	6:2 FTOH	
8:2 fluorotelomer alcohol	8:2 FTOH	
10:2 fluorotelomer alcohol	10:2 FTOH	
12:2 fluorotelomer alcohol	12:2 FTOH	
Fluorotelomer acrylates (FTA)		
6:2 fluorotelomer acrylate	6:2 FTA	
8:2 fluorotelomer acrylate	8:2 FTA	
10:2 fluorotelomer acrylate	10:2 FTA	
Perfluoroalkyl sulfonamides (FASA)		
N-methyl-perfluorobutane sulfonamide	MeFBSA	
N-methyl-perfluorooctane sulfonamide	MeFOSA	
N,N-dimethylperfluorooctane sulfonamide	Me_2FOSA	
N-ethyl perfluorooctane sulfonamide	EtFOSA	
perfluorooctane sulfonamide	PFOSA	

Table I: cont.

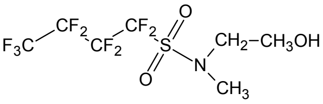
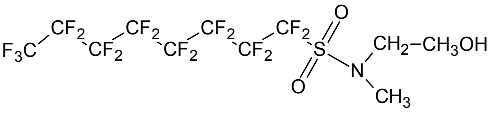
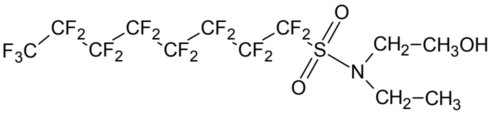
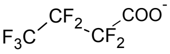
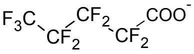
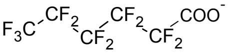
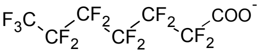
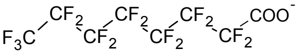
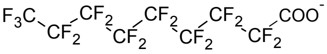
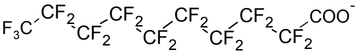
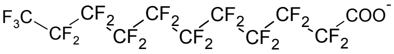
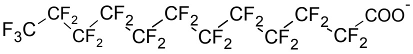
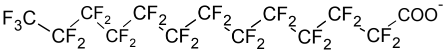
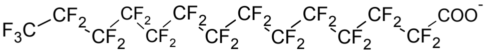
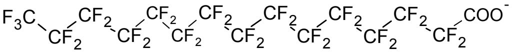
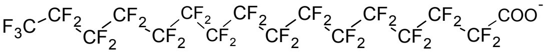
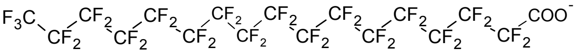
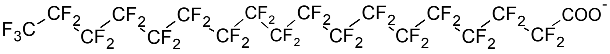
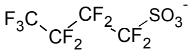
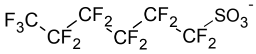
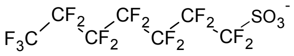
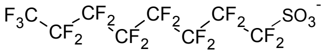
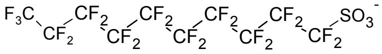
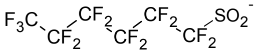
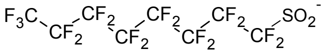
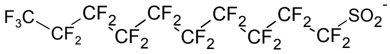
Analytes	Acronym	Structure
Perfluoroalkylsulfonamido ethanols (FASE)		
N-methyl-perflurobutane sulfonamido ethanol	MeFBSE	
N-methyl-perfluorooctane sulfonamido ethanol	MeFOSE	
N-ethyl-perfluorooctane sulfonamido ethanol	EtFOSE	
Perfluoroalkyl carboxylates (PFCA)		
perfluorobutanoate	PFBA	
perfluoropentanoate	PFPA	
perfluorohexanoate	PFHxA	
perfluoroheptanoate	PFHpA	
perfluorooctanoate	PFOA	
perfluorononanoate	PFNA	
perfluorodecanoate	PFDA	
perfluoroundecanoate	PFUnDA	
perfluorododecanoate	PFDoDA	
perfluorotridecanoate	PFTriDA	
perfluorotetradecanoate	PFTeDA	
perfluoropentadecanoate	PFPeDA	
perfluorohexadecanoate	PFHxDA	
perfluoroheptadecanoate	PFHpDA	
perfluorooctadecanoate	PFOcDA	

Table I: cont.

Analytes	Acronym	Structure
	Perfluoroalkyl sulfonates (PFSA)	
perfluorobutane sulfonate	PFBS	
perfluorohexane sulfonate	PFHxS	
perfluoroheptane sulfonate	PFHpS	
perfluorooctane sulfonate	PFOS	
perfluorodecane sulfonate	PFDS	
	Perfluoroalkyl sulfinates (PFSI)	
perfluorohexane sulfinate	PFHxSi	
perfluorooctane sulfinate	PFOSi	
perfluorodecane sulfinate	PFDSi	

PFC are being produced since the late 1940s (Paul et al., 2009; Prevedouros et al., 2006). The total historical worldwide production of PFOA was estimated to be 3600-5700 t (Prevedouros et al., 2006). Paul et al. (2009) estimated the total production of perfluorooctane sulfonyl fluoride that was used to produce PFOS and its derivatives to be 96000 t or 122500 t including unusable wastes. The production of PFC increased within the past 50 years. Whereas in 1979, a total of 200 t fluorosurfactants were produced (Shoeib et al., 2004), the production of PFOS in 2000 or PFOA in 2003 alone was estimated to be above 3500 and 500 t, respectively (Lau et al., 2004). Fluorotelomer alcohol production increased from zero in 1960 (Smithwick et al., 2006) over 5000-6000 t a^{-1} in 2000-2002 (Ellis and Mabury, 2003) to currently 11000-14000 t a^{-1} (Dinglasan-Panlilio and Mabury, 2006).

PFC were mainly produced by Simons electrochemical fluorination (ECF) or fluorotelomerization. During ECF, hydrogen fluoride is used to replace hydrogen with fluorine atoms of hydrogen-containing organic substances (Simons, 1949). This process yields linear and branched isomers and impurities of different chain length (De Silva and Mabury, 2004; Giesy and Kannan, 2002; Kissa, 2001). In contrast, fluorotelomerisation, a polymerisation process that involves the reaction of perfluoroalkyl iodides with perfluorinated alkenes such as tetrafluoroethylen, forms straight-chain substances only (Kissa, 2001).

Fluorotelomer alcohols which generally have the form $CF_3(CF_2)_n(CH_2)_2OH$ (n=odd numbered) and are named (n+1):2 FTOH are products of this process. A third, however less often used synthesis to produce fluorocarbons is liquid phase direct perfluorination (LPDPF) which uses a hydrogen-containing starting material that is dissolved in a perhalogenated liquid medium (De Silva and Mabury, 2004).

1.3. Environmental Concerns

Since the late 1990s, an increasing number of scientific studies pointed at the potential environmental problems involved with PFC and brought these chemicals in the focus of international public environmental concern. Several PFC are considered as toxic and extraordinarily persistent substances that contaminate and accumulate in humans as well as wildlife all over the world. Today, the awareness of producers as well as political stakeholders for appropriate action concerning these compounds is reflected by voluntary commitments of the fluorochemical industry and regulation efforts of political institutions. Examples are the voluntary phase out of PFOS-based compounds by its main producer 3M in 2002 or the commitment of PFC producing companies to reduce PFOA emissions by 95 % until 2010 (US-EPA, 2006) as well as several restrictions concerning manufacturing, marketing, and use of PFOS by the United States Environmental Protection Agency or the European Community (European Community, 2006; US-EPA, 2002).

1.3.1. Persistence

Perfluorinated acids have no known route of biotic or abiotic degradation in the environment (Martin et al., 2004; US-EPA, 2002). Although thermal degradation of PFCA and PFSA was observed at temperatures above 360-500 °C (Powley et al., 2005; US-EPA, 2000) and PFCA were degraded by a technical photochemical system (Hori et al., 2005), perfluorinated acids resist degradation by acids, bases, oxidants, reductants, photolytic processes, microbes, and metabolic processes at environmental conditions (US-EPA, 2000). This is due to the strong carbon-fluorine bond, the presence of three pairs of non-bonding electrons around each fluorine atom, and the effective shielding of carbon by the fluorine atoms (Kissa, 2001). Consequently, these fluorosurfactants as well as other fluorinated alkyl substances are stable under conditions that degrade their hydrocarbon analogues (Kissa, 2001).

In contrast to the fully fluorinated acids, partially fluorinated compounds such as FTOH, FTA, FASA, or FASE can undergo metabolic and atmospheric degradation. Biotic breakdown of FTOH and FASA was demonstrated in various studies using microbial systems (Dinglasan et al., 2004; Wang et al., 2005) or *in-vitro* cultures (Martin et al., 2005; Tomy et al., 2004). Several studies gave evidence for abiotic degradation of partially fluorinated compounds in the atmosphere (see section 1.4), mostly using smog chambers as experimental approach (Butt et al., 2009; D'Eon et al., 2006; Ellis et al., 2004; Hurley et al., 2004b; Martin et al., 2006; Solignac et al., 2007; Sulbaek Andersen et al., 2005). Although yields were below 100 %, all of these processes resulted in the formation of PFCA and PFSA.

Based on smog chamber experiments, atmospheric lifetimes of FTA and FASE were estimated to be approximately 1 to 2 days, those of FTOH and FASA were estimated to be higher than 20 days which is sufficient to reach remote locations (Butt et al., 2009; D'Eon et al., 2006; Ellis et al., 2003). Estimates of atmospheric FTOH residence times based on field measurements were even higher (Piekarz et al., 2007). Atmospheric lifetimes of PFCA with respect to reaction with OH radicals were estimated to be approximately 130 days (Hurley et al., 2004a). However, the major atmospheric removal mechanism is supposed to be wet and dry deposition which probably occurs on a time scale of the order of 10 days.

1.3.2. Bioaccumulation

Numerous biomonitoring studies from all over the world revealed the bioaccumulation and bioconcentration potential of several PFSA and PFCA (Bossi et al., 2005; Butt et al., 2008; Butt et al., 2007a; Haukas et al., 2007; Houde et al., 2006; Martin et al., 2003; Powley et al., 2008; Smithwick et al., 2005; Tao et al., 2006). Bioaccumulation of PFC varies species and sex dependent (Hundley et al., 2006; Kennedy et al., 2004; Kudo et al., 2001; Olsen et al., 2009). For example, the half-life time of PFOA was 5.6 days for male rats whereas that of female rats was only 2 hours (Kudo et al., 2002). PFOA half-life times in monkeys were observed to be between 20 to 30 days (Kennedy et al., 2004). In contrast, Olsen et al. (2007) reported mean PFOA and PFOS human serum half-life times of 3.8 and 5.4 years, respectively, revealing that humans excrete PFC rather slowly leading to enhanced accumulation of these substances. Time trends of PFC concentrations observed in biota roughly followed their production trends (Berger et al., 2007; Bossi et al., 2005; Butt et al., 2007b; Smithwick et al., 2006). Generally, protein-rich tissues such as liver and blood were the primary repositories where perfluorinated acids accumulated, usually with concentrations that were orders of magnitude higher than those in other biological compartments (Ahrens et al., in press; Jones et al., 2003; Martin et al., 2003; Powley et al., 2008; Van de Vijver et al., 2005). For example, concentrations of PFOS and PFOA in liver from Arctic polar bears ranged from 263-6340 and 3-57 ng g^{-1}, respectively (Martin et al., 2004; Smithwick et al., 2005). Smithwick et al. (2005) observed that PFOS concentrations in polar bear liver were even higher than those of several polychlorinated biphenyls (PCB) in fatty tissue. Human blood concentrations of PFOS and PFOA ranged between <1 to 116 ng mL^{-1} and <1 to 256 ng mL^{-1}, respectively (Kannan et al., 2004) and reached up to 10600 (PFOS) and 6160 (PFOA) in occupationally exposed persons (Olsen et al., 2003). The analysis of human breast milk revealed that PFC are also being accumulated in this compartment at concentrations below 1 ng mL^{-1} and are thus being transferred to newborns (Kaerrman et al., 2007; Tao et al., 2008a; Tao et al., 2008b; Voelkel et al., 2008).

Overall, PFSA were observed to be more bioaccumulative than PFCA of the same fluorinated chain length (Houde et al., 2006; Martin et al., 2003; Ohmori et al., 2003). For example, bioaccumulation factor means of perfluorononanoate (PFNA) and PFOS (both have eight fluorinated carbon atoms) were 900 and 1800 L kg^{-1}, respectively (Conder et al., 2008). Furthermore, bioconcentration and bioaccumulation were directly related to the fluorinated chain length, i.e. they increased with increasing number of fluorinated carbon atoms (Conder et al., 2008). In bioconcentration experiments performed by Martin et al. (2003), PFSA and PFCA comprising of less than six or seven carbon atoms, respectively, did not accumulate in any of the investigated tissues. Similarly, Conder et al. (2008) concluded that perfluorinated acids below these carbon chain lengths are not considered to be bioaccumulative according to regulatory criteria.

Several studies revealed biomagnification of PFCA and PFSA (Conder et al., 2008; Haukas et al., 2007; Houde et al., 2006). Biomagnification factors of PFCA and PFSA appeared to be in the same order of magnitude, an apparent relationship between fluorinated carbon chain length and biomagnification was not observed (Conder et al., 2008).

1.3.3. Toxicity

Numerous studies on the toxicity of PFC, especially of PFOS and PFOA, have been performed on various species in the past; however, little is known about the human toxicity. Basically, the acute toxicities of PFCA and PFSA on various species are moderate but increase with chain length (Jensen and Leffers, 2008; Mulkiewicz et al., 2007). Fluorotelomer acids (FTCA), intermediates in the degradation of FTOH to PFCA, were observed to be more toxic than the PFCA themselves (Phillips et al., 2007). The primary target organ of PFC toxicity was the liver although toxic and/or carcinogenic effects have also been reported for other organs such as the thyroid gland or testicles (Fromme et al., 2006). PFOS and PFOA were associated with liver enlargement and hepatocarcinogenesis in rodents and nonhuman primates which were probably caused by peroxisome proliferation (Kennedy et al., 2004; Lau et al., 2007). Both substances induced peroxisome proliferation, either by activating the peroxisome proliferator-activated receptor-alpha (PPAR-α) or by perturbing lipid metabolism and transport (Berthiaume and Wallace, 2002; Lau et al., 2007). The longer the perfluoroalkyl chain of PFCA and PFSA the higher was the accumulation of the compound and thus the potency to induce peroxisome proliferation (Kudo et al., 2000; Kudo et al., 2006; Lau et al., 2007). Peroxisome proliferation and hepatotoxicity in FTOH-fed mice was also described since these precursors readily form PFOA (Kudo et al., 2005). Gap junctional intercellular communication, a process by which cells exchange ions, small molecules or second messages, is involved in normal growth, development and may also play a role in carcinogenesis. Perfluorooctane sulfonates and a number of fluorinated compounds structurally related to PFOS have been demonstrated to inhibit gap junctional intercellular communication *in vitro* and *in vivo* (Hu et al., 2002). This effect was dependent on the length of the fluorinated carbon chain but not likely by the nature of the functional group (Hu et al., 2002; Lau et al., 2007).

Developmental toxicity of perfluoroalkyl acids and their derivatives was reviewed by Lau et al. (Lau et al., 2007; Lau et al., 2004). Dose-dependent increased morbidity and mortality of newborns was observed in rats after prenatal PFOS exposure during pregnancy. Organ development, growth, and weight gain were hindered as well. Precursors such as FASE metabolizing to PFOS were observed to cause similar developmental toxicity as PFOS (Luebker et al., 2005). Prenatal exposure to PFOA resulted in birth weight reduction and neonatal mortality with similar patterns as those obtained for PFOS (Lau et al., 2007).

Yang et al. (2002; 2000) reported the immunotoxic potential of PFOA which was found suppressing the inflammatory response. Several PFCA and PFOS were observed to disrupt thyroid hormones and alter steroid hormone biosynthesis (Lau et al., 2007). Estrogen-like properties were described for PFOS and FTOH (Austin et al., 2003; Maras et al., 2006).

Results from animal studies were extrapolated to evaluate the human health risks. It was suggested that the health risks for the general, non-occupationally exposed population is likely to be low (Fromme et al., 2007; Fromme et al., 2006; Midasch and Angerer, 2006).

Trudel et al. (2008) and Vestergren et al. (2008) estimated that the greatest portion of the chronic exposure to PFOS and PFOA was likely to result from the intake of contaminated foods including drinking water. The contribution of consumer products was expected to be minor. The relative importance of precursor-based PFOA and PFOS for the general population was estimated to be below 10 % (Vestergren et al., 2008). Based on toxicological studies and exposure estimates the tolerable daily intake (TDI) of PFOA and PFOS in Germany was set to 0.1 $\mu g\,kg^{-1}\,d^{-1}$ (BfR, 2006). The German long-term limit for PFOA in drinking water was established at 0.1 $\mu g\,L^{-1}$ (BMG, 2006) and the maximum occupational air concentration (MAK) of PFOA at 0.005 $mg\,m^{-3}$ (DFG, 2005).

1.3.4. Long-Range Transport

First indications for long-range transport of PFC were presented in a study on the global distribution of PFOS in wildlife liver and blood samples (Giesy and Kannan, 2001). Since then, PFC, mainly PFSA and PFCA, have been detected in hundreds of biota samples from the high Arctic to Antarctica revealing their presence at locations remote from sources (Bossi et al., 2005; Butt et al., 2007b; De Silva and Mabury, 2004; Houde et al., 2006; Kallenborn et al., 2004; Martin et al., 2004; Smithwick et al., 2005; Smithwick et al., 2006; Tao et al., 2006).

PFCA and PFSA, particularly those of chain lengths less than ten carbon atoms, have been detected globally in rivers and oceans and therefore are considered to be significantly transported over long distances via this aqueous pathway (Caliebe et al., 2004; McLachlan et al., 2007; So et al., 2007; Wei et al., 2007; Yamashita et al., 2008; Zushi et al., 2008). Concentration of PFOS and PFOA ranged from 8.6 and 52 $pg\,L^{-1}$ in ocean surface water (Yamashita et al., 2008) to 4385 and 3640 $ng\,L^{-1}$ in river surface water (Skutlarek et al., 2006), respectively. Thousand-fold higher PFOS concentrations were observed in a river following a spill of PFC containing fire fighting foams (Moody et al., 2001). It is estimated that the majority of PFCA and PFSA is emitted directly to the water phase during manufacturing and use (Paul et al., 2009; Prevedouros et al., 2006). Perfluorooctanoate that reaches the Arctic via oceanic transport is calculated to be between 2 and 23 $t\,a^{-1}$ (Armitage et al., 2006; Prevedouros et al., 2006; Wania, 2007). Being dissolved in the water phase or enriched at the water surface, these ionic PFC may also be transferred to the air in marine aerosols (Prevedouros et al., 2006). However, atmospheric removal by wet and dry deposition is expected to occur in the order of a few days (Hurley et al., 2004a).

Atmospheric transport and degradation of PFCA and PFSA precursors is considered as another main long-range transport mechanism. However, its importance is discussed controversially. Basically, PFCA and PFSA precursors like FTOH, FTA, FASA, or FASE are thought to be emitted to the atmosphere during their manufacturing, the production of fluoropolymers (Paul et al., 2009; Prevedouros et al., 2006), and more importantly by diffuse sources during use and disposal (Barber et al., 2007; Dinglasan-Panlilio and Mabury, 2006; Paul et al., 2009; Sinclair et al., 2007). Precursors are more volatile than PFCA and PFSA (Goss et al., 2006; Kaiser et al., 2005; Krusic et al., 2005; Lei et al., 2004) and therefore are more likely to undergo atmospheric long-range transport. Being in the atmosphere, these volatile compounds are degraded to PFCA and PFSA by hydroxyl (OH) radical initiated oxidation (see section 1.4) (Butt et al., 2009; D'Eon et al., 2006; Ellis et al., 2004; Ellis et al., 2003; Martin et al., 2006). Precursors were detected in air in several studies in North America, Europe, Asia, and the Atlantic Ocean (Barber et al., 2007; Jahnke et al., 2007b; Jahnke et al., 2007c; Kim and Kannan, 2007; Oono et al., 2008a; Piekarz et al., 2007; Primbs et al., 2008; Shoeib et al., 2006; Stock et al., 2007; Stock et al., 2004) and modelling results reveal the ubiquitous atmospheric distribution of FTOH and its degradation products (Wallington et al., 2006). Concentrations of airborne PFC frequently reported in literature are presented in tables II and III. The actual extent to which the atmospheric transport and degradation of precursors contribute to the PFCA and PFSA contamination of remote regions is still unclear. Some studies estimated that this pathway is less important than oceanic transport, mainly due to the low PFCA and PFSA yield of the degradation reactions and too low historic precursor emissions (Prevedouros et al., 2006; Wania, 2007). Several recent studies estimated the Arctic deposition of perfluorooctanoate from FTOH oxidation to be between 50 and 500 kg a^{-1} (Schenker et al., 2008; Wallington et al., 2006; Wania, 2007; Yarwood et al., 2007) whereas an earlier estimate by Ellis et al. (2004) assumed an approximate flux of 0.1-10 t a^{-1} of PFCA to the Arctic. Nevertheless, the presence of PFCA and PFSA in glacial ice caps that received their contamination solely from the atmosphere (Young et al., 2007), in air and lake water of remote mountains (Loewen et al., 2008), or the occurrence of precursor degradation intermediates in precipitation (Loewen et al., 2005; Scott et al., 2006), Arctic sediments, and air particles (Stock et al., 2007) reveal that the atmospheric transport and degradation of precursors considerably contributes to the PFCA and PFSA contamination of remote locations.

Table II: Mean outdoor air concentrations of frequently analyzed PFC (gas phase, pg m^{-3}). BDL: below detection limit. BQL: below quantification limit. n.a.: not analyzed.

Reference	Location	Character	n	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	MeFBSA	MeFOSA	EtFOSA	MeFBSE	MeFOSE	EtFOSE
Martin et al. (2002)[a]	Toronto, Canada	urban	4	BDL.	87	55	29	n.a.	n.a.	n.a.	14	n.a.	101	206
	Long Point, Canada	rural	2	BDL.	29	32	17	n.a.	n.a.	n.a.	BDL	n.a.	35	76
Shoeib et al. (2004) [a]	Cleves,OH, USA	urban	3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	24	9.1
Stock et al. (2004) [a]	Griffin,GA, USA[b]	rural	3	n.a.	<40	>100	BQL	n.a.	n.a.	n.a.	10	n.a.	>300	<20
	Cleves,OH, USA	rural	3	n.a.	65	65	BQL	n.a.	n.a.	n.a.	45	n.a.	20	BDL
	Long Point,ON, Canada	rural	3	n.a.	25	BDL	BDL	n.a.	n.a.	n.a.	10	n.a.	10	25
	Toronto,ON, Canada	urban	3	n.a.	80	80	BDL	n.a.	n.a.	n.a.	BDL	n.a.	80	<40
	Reno,NV, USA	semi-urban	3	n.a.	40	40	BQL	n.a.	n.a.	n.a.	>50	n.a.	BDL	<200
	Winnipeg,MB, Canada	urban	3	n.a.	BDL	10	BDL	n.a.	n.a.	n.a.	BDL	n.a.	20	BDL
Boulanger et al. (2005)	Lake Erie, Canada	semi-urban	5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.5	n.a.	n.a.	0.3
	Lake Ontario, Canada	semi-urban	3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.5	n.a.	n.a.	0.3
Shoeib et al. (2005)	Ottawa	urban	7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	BDL	n.a.	83	88
Shoeib et al. (2006)	Canadian Arctic	remote	20	n.a.	2.6	11	6.3	n.a.	n.a.	n.a.	n.a.	n.a.	8.3	1.9
	Toronto	urban	3	n.a.	18	40	21	n.a.	n.a.	n.a.	n.a.	n.a.	4.2	1
Piekarz et al. (2007)	MBO, OR, USA	remote	34	n.a.	4.6	24	15	n.a.	n.a.	n.a.	<3.2	n.a.	<11	<1.3
Jahnke et al. (2007b)	Hamburg, Germany	urban	14	54	66	119	35	n.a.	n.a.	9.0	3.1	n.a.	41	14
	Waldhof, Germany	rural	8	19	64	75	23	n.a.	n.a.	7.0	2.6	n.a.	8.9	17

[a] gas and particle phase was not separately analyzed. [b] carpet manufacturing close by. [c] fluoropolymer production facility close by.

Table II: cont.

Reference	Location	Character	n	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	MeFBSA	MeFOSA	EtFOSA	MeFBSE	MeFOSE	EtFOSE
Jahnke et al. (2007c)	Atlantic (Europe)	ocean, mixed	2	n.a.	157	176	46	n.a.	n.a.	3.8	2	n.a.	19	8.9
	Atlantic (Spain)	ocean	2	n.a.	11	29	9.2	n.a.	n.a.	1.9	0.8	n.a.	3.9	BDL
	Atlantic (Spain, North Africa)	ocean	1	n.a.	9.4	15	3.3	n.a.	n.a.	1.1	<0.3	n.a.	1.6	0.9
	Atlantic (North Africa)	ocean	2	n.a.	14	18	4.8	n.a.	n.a.	1.6	0.7	n.a.	3.1	BDL
	Atlantic (North Africa)	ocean	2	n.a.	20	42	7.7	n.a.	n.a.	2.4	1.1	n.a.	7.4	1.5
	Atlantic (Central Africa)	ocean	2	n.a.	BDL	13	2.9	n.a.	n.a.	0.6	<0.3	n.a.	0.9	BDL
	Atlantic (Central Africa)	ocean	2	n.a.	BDL	13	1.2	n.a.	n.a.	1.2	1.3	n.a.	BDL	BDL
	Atlantic (Southern Africa)	ocean	2	n.a.	BDL	3.1	0.9	n.a.	n.a.	0.5	BDL	n.a.	BDL	BDL
Barber et al. (2007)	Hazelrigg, UK^{c} (spring)	semi-rural	2	0.7	81	102	75	n.a.	n.a.	5.5	7.9	n.a.	24	9.2
	Manchester, UK (spring)	urban	2	3	187	237	65	n.a.	n.a.	6.1	9.6	n.a.	24	6.1
	Kjeller, Norway (fall)	rural	1	<0.1	12	34	17	n.a.	n.a.	5.5	5	n.a.	49	30
	Hazelrigg, UK^{c} (fall)	semi-rural	10	26	32	67	21	21	0.2	<5.3	<3.7	<2.5	<54	66
	Manchester, UK (fall)	urban	2	<16	612	237	62	62	0.4	<5.3	<3.7	<2.5	54	<2.2
	Mace Head, Ireland (spring)	remote	4	1.4	5.0	11	7.8	7.8	0.1	<4.9	<1.6	14.5	9.6	<52
Stock et al. (2007)	Canadian Arctic	remote	10	n.a.	<14	<9.1	<1.5	n.a.	n.a.	n.a.	<11	<25	<30	<27
Oono et al. (2008b)	Kaihan, Japan	urban	24	n.a.	31	1190	137	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Oono et al. (2008a)	Japan	mixed	19	n.a.	18	90	19	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

[a] gas and particle phase was not separately analyzed. [b] carpet manufacturing close by. [c] fluoropolymer production facility close by.

Table III: Mean outdoor air concentrations of frequently analyzed PFC (particle phase, pg m^{-3}). BDL: below detection limit.

Reference	Location	Character	n	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE	PFHxA	PFHpA	PFOA	PFNA	PFOS
Sasaki et al. (2003)	Fukuchiyama City, Japan	urban	12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.7
	Oyamazaki Town, Japan	urban	12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	6.7
Harada et al. (2005)	Oyamazaki, Japan	urban	12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	372	n.a.	5.6
	Morioka, Japan	urban	8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.0	n.a.	0.7
Boulanger et al. (2005)	Lake Erie, Canada	semi-urban	5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.3
	Lake Ontario, Canada	semi-urban	2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.3
Shoeib et al. (2006)	Canadian Arctic	remote	20	3.5	0.8	n.a.	n.a.	3.5	1.1	n.a.	n.a.	n.a.	n.a.	n.a.
	Toronto	urban	3	0.7	1.1	n.a.	n.a.	4.2	1.0	n.a.	n.a.	n.a.	n.a.	n.a.
Jahnke et al. (2007b)	Hamburg, Germany	urban	14	<1.0	<0.7	<0.2	BDL	11	6.7	n.a.	n.a.	n.a.	n.a.	n.a.
	Waldhof, Germany	rural	8	<1.0	<0.7	BDL	BDL	2.4	5.9	n.a.	n.a.	n.a.	n.a.	n.a.
Barber et al. (2007)	Hazelrigg, UK [a] (spring)	semi-rural	2	<1.1	<1.1	<1.1	0.4	12.1	6.9	<56	14	552	<14	<45
	Manchester, UK (spring)	urban	2	5.8	2.7	1.5	0.7	24	11	<26	8.2	341	<27	46
	Kjeller, Norway (fall)	rural	1	<0.3	<0.4	<0.4	0.71	3.6	3.4	0.5	0.9	1.5	0.1	1
	Hazelrigg, UK [a] (fall)	semi-rural	10	8.5	<0.5	<9.1	<6.5	<1.8	6.9	107	1.6	101	0.9	1.6
	Manchester, UK (fall)	urban	2	<1.8	<0.5	<9.1	<6.5	<1.8	<4.3	<34	0.2	16	0.8	7.1
	Mace Head, Ireland (spring)	remote	4	<1.9	<0.5	<4.7	<2.9.	<18.9	<7.5	<14	<0.001	8.9	<3.3	<1,8
Kim and Kannan (2007)	Albany, NY, USA	urban	8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.4	2.0	0.1	0.6
Stock et al. (2007)	Canadian Arctic	remote	10	<5.2	<4	n.a.	<5.6	<15	<22	n.a.	n.a.	n.a.	n.a.	n.a.

[a] fluoropolymer production facility close by.

1.4. Atmospheric Chemistry of PFC

The atmospheric degradation of PFC was investigated in several studies using smog chamber experiments (Butt et al., 2009; D'Eon et al., 2006; Ellis et al., 2004; Hurley et al., 2004a; Hurley et al., 2005; Martin et al., 2006; Sulbaek Andersen et al., 2005). Since they appeared to be virtually non degradable, the atmospheric chemistry of perfluorinated acids themselves was reported to be of minor importance (Hurley et al., 2004a). Removal of these acids from the atmosphere depended rather on wet and dry deposition, which readily occurs in the order of several days, than on gas-phase reactivity. In contrast to PFCA and PFSA, partially fluorinated compounds can be significantly degraded in the atmosphere, usually by OH radical initiated reactions. An overview about the atmospheric degradation of these substances to the persistent acids is presented in figure I.

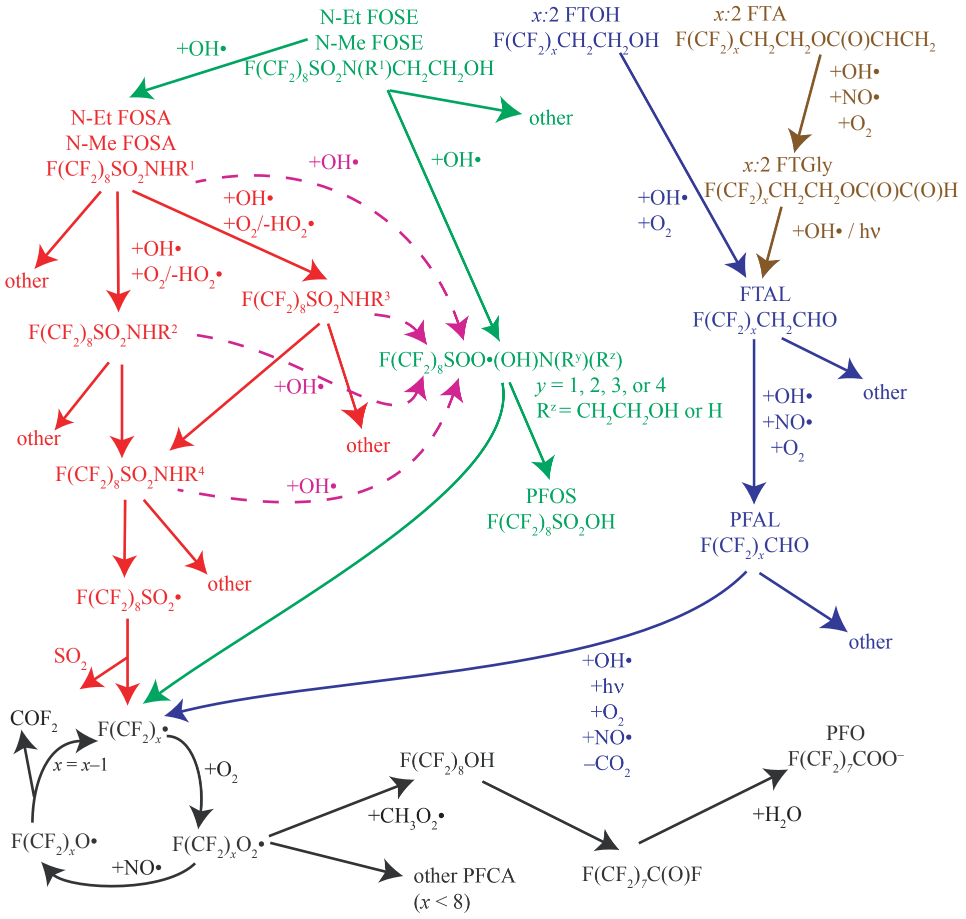


Figure I: Summary of the most important reactions occurring during the atmospheric degradation of FASA, FASE, FTA, and FTOH in air. FTAL: fluorotelomer aldehydes. PFAL: perfluorinated aldehydes. FTGly: fluorotelomer glycoxylate. R^1: methyl or ethyl substitutes. R^2-R^4: various substitutes of intermediate degradation products. Scheme adapted from Schenker et al. (2008), modified.

Generally, the degradation of precursor substances (D'Eon et al., 2006; Ellis et al., 2004; Hurley et al., 2004b; Martin et al., 2006; Sulbaek Andersen et al., 2005; Wallington et al., 2006) can be distinguished into two parts. First, as revealed by red, purple, green, blue, and brown colors in figure I, various OH radical initiated reactions at the compounds' functional group lead to the formation of $F(CF_2)_x$ radicals. As side product, PFSA may be produced from FASE oxidation during these reactions (green color). Second, PFCA are formed (black color). PFCA of equal chain length are formed directly from the $F(CF_2)_x$ radicals by reaction with alkyl peroxi radicals; PFCA of chain lengths shorter than *x* are formed after exiting the unzipping cycle during which the chain length is reduced by sequential loss of COF_2. Whereas the first part of the degradation scheme is different for PFOS-based and FTOH precursors, the second part (black colors) is the same. More reactions than those presented in figure I might occur during the degradation of precursor compounds, e.g. oxidations at the R^1 chain of FASA and FASE (D'Eon et al., 2006; Martin et al., 2006) or photolysis (Wallington et al., 2006) and hydration (Sulbaek Andersen et al., 2006) reactions at the perfluorinated aldehyde (PFAL), an intermediate of the FTOH and FTA breakdown. However, to which exact extent PFCA and PFSA are formed during precursor degradation remains unclear. D'eon et al. (2006) reported approximate yields of PFBS and PFCA from EtFBSE oxidation of 1 and 10 %, respectively. The PFCA yields from FTOH and FTA degradation were between 1 and 10 % (Butt et al., 2009; Ellis et al., 2004; Hurley et al., 2004b). Overall, yields of perfluorinated acids were larger in the absence of NO_x than in the presence of NO_x (Butt et al., 2009; Ellis et al., 2004; Sulbaek Andersen et al., 2005).

1.5. Research Objectives

There are still many unknowns concerning environmental fate, distribution, and sources of PFC, especially in the perspective of volatile and semi-volatile substances that can be atmospherically degraded to persistent perfluorinated acids and are today heavily applied to replace those PFC that were restricted or phased out. Therefore, the focus of this work is on airborne PFC. Concentrations of airborne PFC were assumed to decrease along gradients from source regions to remote or marine areas where they were expected to be present at low concentrations. Furthermore, since the degradation of precursor PFC is dependent on OH radicals and thus radiation, seasonal concentration variations were hypothesized. Thus, in order to improve the understanding of atmospherically transported PFC, it is essential to investigate their atmospheric distribution and concentration variations on temporal and spatial scales using a validated and accurate analytical method possessing low limits of detection. Specifically, the objectives of this thesis were:

1. The improvement of existing analytical methods. The analyte spectra ought to be expanded in order to cover an increased number of relevant PFC, especially those that are used as replacements of restricted compounds. Their detection limits had to be decreased that sampling duration could be reduced to increase temporal as well as spatial resolution of PFC concentrations. The insufficient chromatographic separation of several compounds had to be improved. Previously existing methods were characterized by highly enhanced recovery rates of certain analytes. These response enhancements had to be overcome, particularly for those substances where compound specific mass-labeled internal standards were not available.

2. The elucidation of temporal concentration changes of polyfluorinated compounds in ambient air. Studies describing the occurrence and distribution of (semi-)volatile polyfluorinated compounds in ambient air only display a snapshot of PFC air concentrations; emission events, seasonality, or fluctuations in the highly dynamic atmospheric system are not accounted for. The knowledge about concentration variations in dependence of distinct atmospheric conditions is of importance in order to compare the results of different studies. Therefore the aim of this study was to determine and characterize seasonal variations of PFC concentrations. Additional parameters that potentially influence PFC concentrations, such as air mass history, meteorological or air quality parameters, and nearby sources, should be considered as well.

3. The assessment of concentration variations of polyfluorinated compounds in ambient air at a regional scale. Studies concerning concentration variations of airborne PFC along spatial gradients only covered large scales with large sampling intervals so far (Jahnke et al., 2007c; Shoeib et al., 2006), mostly due to methodological drawbacks. Small scale changes of PFC air concentrations are unclear though. Thus, an aim of this thesis was to obtain new information on the spatial atmospheric distribution of polyfluorinated compounds on a regional scale in Northern Germany and the German North Sea as well as the identification of source regions for that area.

4. The description of concentration variations of polyfluorinated compounds in ambient air at a global scale. The transport and degradation of volatile PFCA and PFSA precursors may significantly contribute to the contamination of remote ecosystems. Although the worldwide distribution of polyfluorinated precursor compounds and their atmospheric transport has been

modeled already (Schenker et al., 2008; Wallington and Nielsen, 2002), analytical data on a global scale are rare. Only two studies described concentrations of a few PFC along large spatial gradients in the North Atlantic and Canadian Archipelago as well as along a transect from Germany to South Africa (Jahnke et al., 2007c; Shoeib et al., 2006). Therefore one key objective of this thesis was the assessment of the occurrence of airborne PFC on a global scale from the Arctic to Antarctica. Spatial gradients of PFC concentrations should be assessed and hemispheric (background) levels be defined. It should be elucidated if PFCA and PFSA precursors really reach these remote regions and thus may contribute to their presence in wildlife there.

2. Experimental

2.1. Sampling

Samples were taken with high volume air samplers. The sampling duration varied in dependence on the expected concentration level or accessibility of the site and was generally between one and four days. Land-based sampling was conducted at two sites located in the vicinity of Hamburg, Germany from 2nd April 2007 to 1st June 2008. The site Barsbüttel (BAR), an air monitoring site of the Environmental Agency, is situated approximately 20 km east of Hamburg (1770000 inhabitants) at 53°34’14’’ N and 10°12’55’’ E. The GKSS site is located about 40 km southeast of the city centre of Hamburg close to the city of Geesthacht (30000 inhabitants) at 53°24’26’’ N, 10°25’20’’ E. Both sites have a semi-rural character.

Ship-based samples were taken at the observation deck of different research vessels (RV Polarstern, RV Maria S. Merian, RV L’Atalante, RV Atair) during several sampling campaigns in the Baltic Sea, the Atlantic, and Southern Ocean along north-south and east-west transects as well as in coastal areas (figure II; Atair 155, German Bight, North Sea, 09/2007; MSM05/1, Las Palmas, Spain - St. John’s, Canada, 04/2007; MSM05/6, Longyearbyen, Norway - Kiel, Germany, 08/2007; MSM08/3, Rostock, Germany - Tallinn, Estonia - Kiel, Germany, 06/2008; AntXXIV-1 and AntXXV-1, Bremerhaven, Germany - Cape Town, South Africa, 11/2007, 11/2008; AntXXV-2, Cape Town, South Africa - Neumayer Station, Antarctica - Cape Town, South Africa, 12/2008; L’Atalante leg 2 MARSÜD, Recife, Brazil - Dakar, Senegal, 01/2008).

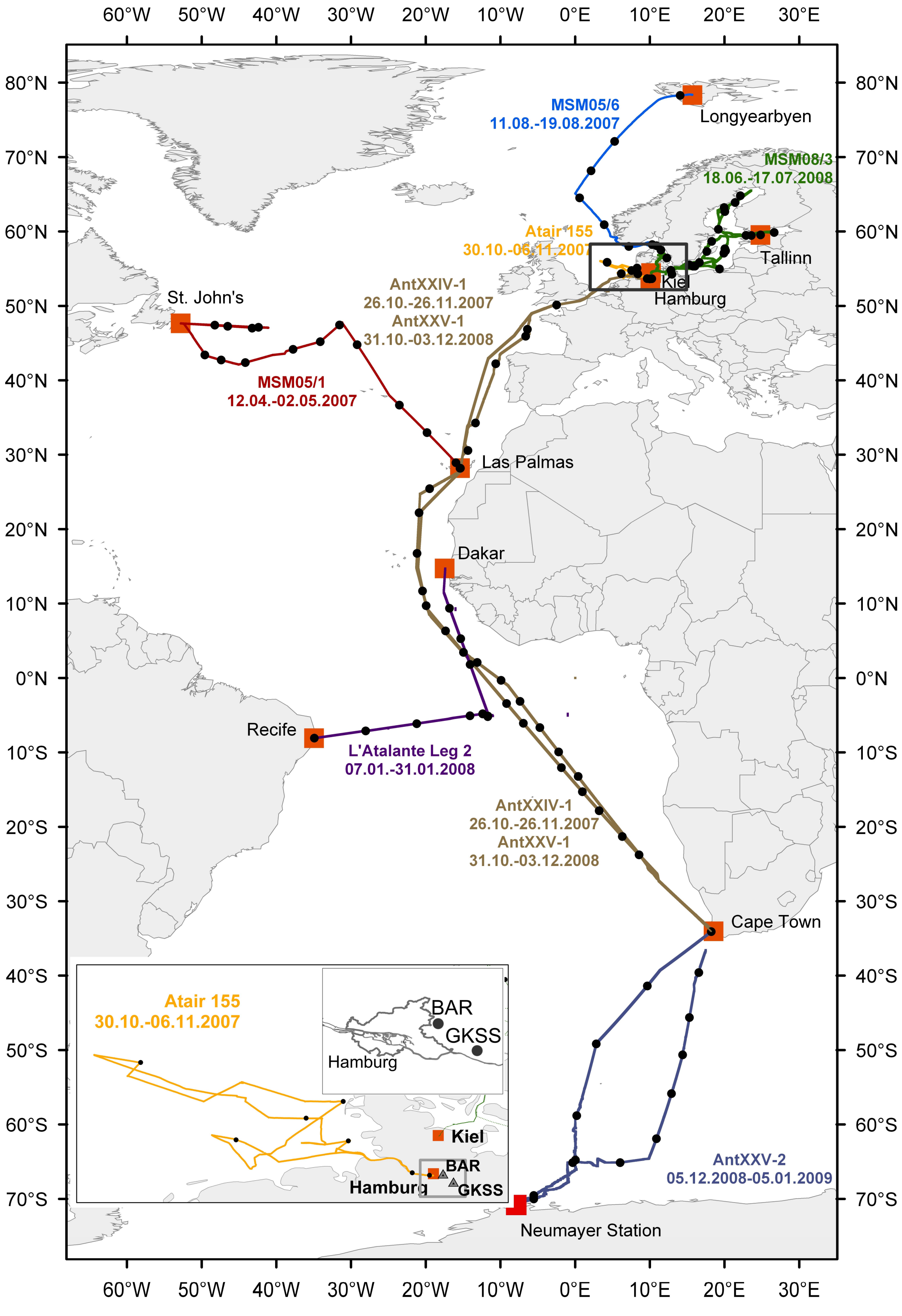


Figure II: Overview about sampling campaigns discussed in this thesis. Black dots mark the positions where the sampling started. Sampling was conducted between this and the following point (for directions see text). Barsbüttel (BAR) and GKSS were stationary sites where samples were taken for 14 months.

To minimize ship-borne contamination air samplers were controlled by a computer connected to the ship's meteorological system assuring that the sampling was interrupted when relative winds were arriving from the rear of the ship. The average sampling rate for land- and ship-based samples was about 450 m^3d^{-1}. Airborne PFC were enriched on glass fiber filters (particle-bound PFC) and cartridges filled with a sandwich of polyurethane foam (PUF) and Amberlite XAD-2 (gaseous PFC). Prior to the sampling, 50 µL of an internal standard solution containing mass-labeled PFC were spiked directly onto the upper PUF disk to account for gas-phase analytes' losses during sampling and sample preparation. Samples were sealed air tight and stored at -20 °C until analysis in the laboratory.

2.2. Extraction

The extraction procedure of gas-phase PFC was evaluated thoroughly (study 1) because signal enhancements up to 300 % had frequently been observed in the analyses of (semi-)volatile polyfluorinated compounds using ethyl acetate as solvent (Barber et al., 2007; Jahnke et al., 2007a; Jahnke et al., 2007d). Recovery enhancements mainly affected FASA and FASE but were also observed for long-chain FTOH. These increased recoveries were generally explained by matrix effects that resulted in higher detection efficiencies in samples compared to standard solutions (Jahnke et al., 2007a; Schenck and Lehotay, 2000). However, enhanced recoveries observed in solvent blanks have not been explained (Jahnke et al., 2007a). This is of importance since it may lead to false estimates of environmental concentrations of critical analytes, particularly if compound specific mass-labeled internal standards are not available as it was in previous studies.

In order to improve the extraction method of gas-phase PFC, nine different solvents were investigated for their potential to induce signal enhancement. The solvents were chosen because of similar polarity compared to ethyl acetate, their application in other studies, and/or general laboratory use for the extraction of semi-polar compounds. Polyfluorinated compounds containing solutions were spiked at different concentration levels to 50 mL of each solvent. After evaporation, measurement, and quantification, the analytes' recovery rates were calculated. As expected, recovery rates of certain PFC using ethyl acetate as solvent were up to 300 %. This was attributed to ethyl acetate impurities, primarily acetic acid. In contrast to ethyl acetate and other solvents, recovery rates of dichloromethane (DCM), methyl-tert-butyl ether (MTBE), and acetone were close to 100 % (figure III). The evaluation of their extraction efficiency in comparison to ethyl acetate revealed that all of these solvents were suited to extract gas-phase PFC. For most analytes, recovery rates using acetone, MTBE and DCM as solvents were comparable to or partly even higher than those of the established solvent ethyl acetate.

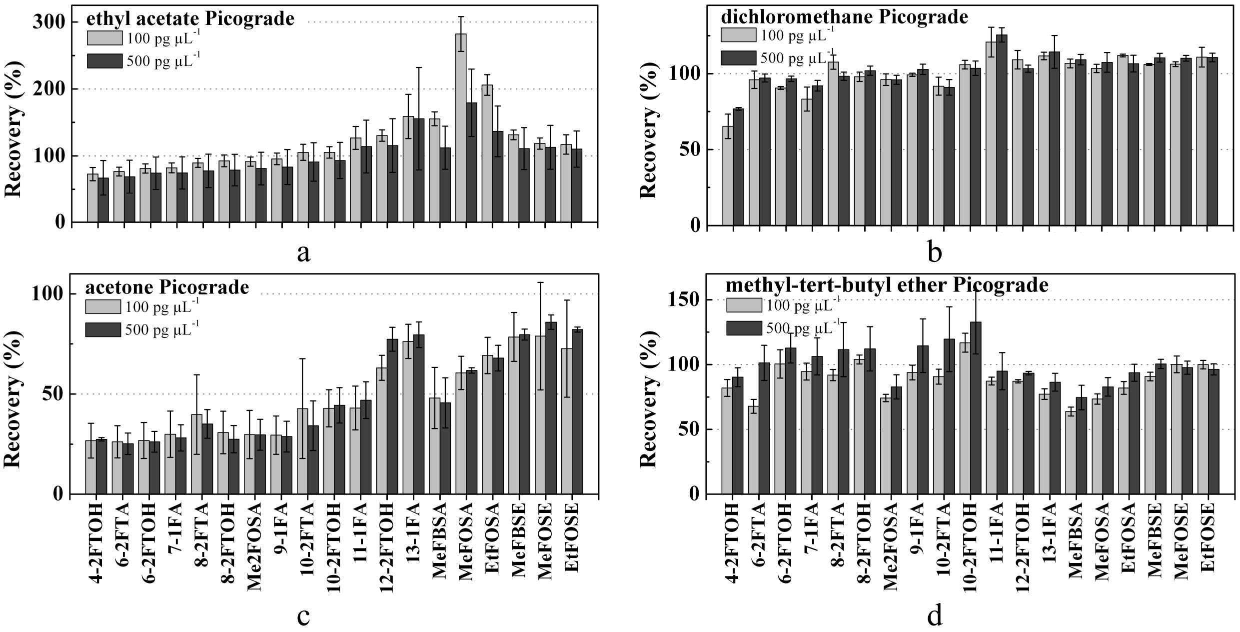


Figure III: Average recovery rates of PFC after the evaporation of 50 mL solvent. Error bars are standard deviations. a: ethyl acetate. b: dichloromethane. c: acetone. d: methyl tert-butyl ether.

A mixture of acetone and MTBE (1:1; v:v) was chosen as alternative solvent to replace ethyl acetate. Recovery rates using this solvent mixture were mostly between 50 and 100 % and the mixture appeared to extract the analytes more efficiently than DCM (figure 1-5 and 1-6). The use of DCM also led to a higher matrix background within the samples, making the solvent less suitable for extraction. The relative polarity of MTBE is slightly lower, the one of acetone little higher than that of ethyl acetate, providing a broad range of polarity that furthermore supported the mixture's suitability. Boiling points of MTBE and acetone are lower than that of ethyl acetate, allowing a more gentle evaporation of the solvent during sample preparation and thus potentially resulting in higher recovery rates of the most volatile compounds. Detailed information on these experiments are presented in study 1 of the cumulative studies section.

Finally, the optimized method for the extraction of gas-phase analytes was as follows. Cartridges were extracted thrice with acetone:MTBE 1:1 (v:v). Solvent was filled into the cartridges until the entire sandwich was covered. For the extraction, the solvent was allowed to soak into the adsorption material for 1hour (extraction step 1 and 2) and ½ hour (extraction step 3). After each extraction step, the solvent drained into a flask and the remaining solvent in the cartridge was blown out with nitrogen. The combined solvent (approximately 500 mL) was evaporated using rotary evaporators and a gentle stream of preheated nitrogen. An injection standard was added prior to the measurement.

Particle-bound PFC were extracted using fluidized bed extraction. Mass-labeled internal standards were added to the filters prior to the extraction. Neutral volatile PFC were extracted with acetone:MTBE 1:1 (v:v), ionic PFC with methanol as extraction solvent. Injections standards were used to correct for instrumental irregularities.

2.3. Instrumental Analysis & Quantification

Quantification of volatile neutral PFC (FTOH, FTA, FASA, FASE) was performed by gas chromatography-mass spectrometry (GC-MS) with positive chemical ionization (PCI) using the selected ion monitoring (SIM) mode. For confirmation, samples were also run in negative chemical ionization (NCI) mode. Instrumental parameters, particularly concerning the injection, the inlet, and the capillary column were optimized thoroughly to obtain optimum instrumental performance. The final GC-MS parameters are given in detail in study 1. Methanol-extracted polyfluorinated compounds (PFCA, PFSA, PFSI) were determined by high performance liquid chromatography - tandem mass spectrometry (HPLC-MS/MS) using electrospray ionization (ESI). Instrumental specifications concerning HPLC-MS/MS measurements are described in detail by Ahrens et al. (2007).

Quantification was based on peak areas. Analyte concentrations were calculated with the internal standards method using a seven point calibration. Internal standards were used to correct for analyte losses. Whole method average recovery rates for analytes in the gas phase ranged between 21+/-27 % (^{13}C 4:2 FTOH, n=127) and 68+/-32 % (MeFOSE D_7, n=173) for ship-based samples and 25+/-17 % (^{13}C 4:2 FTOH, n=113) and 60+/-19% (EtFOSE D_9, n=243) for land-based samples. Average recovery rates for particle-bound analytes were between 41+/-15 % (^{13}C 4:2 FTOH, n=117) and 123+/-76 % (^{13}C PFUnDA, n=43) for ship-based samples and between 22+/-15 % (^{13}C 4:2 FTOH, n=85) and 95+/-64 % (^{13}C PFUnDA, n=238). Compounds were classified as not detected (n.d.) with signal to noise ratio (S/N) below 3 and not quantified (n.q.) with S/N below 10. Based on the signal to noise ratio, the instrumental limits of detection (LOD) were between 0.2 pg and 8.2 pg, the instrumental limits of quantification (LOQ) were between 0.4 pg and 16.4 pg. Method detection limits (MDL) were typically below 1 pg m^{-3}.

2.4. Quality Assurance & Quality Control

Since polyfluorinated materials are often applied in laboratory equipment, it was crucial to take severe precautionary measures to avoid contamination. Sample preparation was performed in a clean lab (class 10000). Perfluorinated materials or fluorinated polymers were avoided during sampling, sample preparation, and instrumental detection. Prior to the sampling, PUF/XAD-2/PUF cartridges were cleaned with MTBE:acetone and acetone for 24 hours using Soxhlet extraction. Filters were heated at 300°C for at least 24 hours. Barrier septa, that are free of PFC were used for the detection of ionic PFC at the HPLC-MS/MS. Silicon-Teflon septa were used for GC-MS measurements (vials), however, pre-tests showed no contamination with (semi-)volatile polyfluorinated compounds. The glassware was machine-washed, heated at 250 °C for twelve hours, and washed with the applied solvent before use. Mass-labeled injection standards and internal standards were used to correct for losses and irregularities during sampling and analysis. Standard solutions were only used at room temperature. A seven point calibration was run with each set of samples (6-8 samples) measured. Field, solvent, and filter blanks were frequently taken to determine possible contamination of the entire method.

2.5. Air Mass Back Trajectories

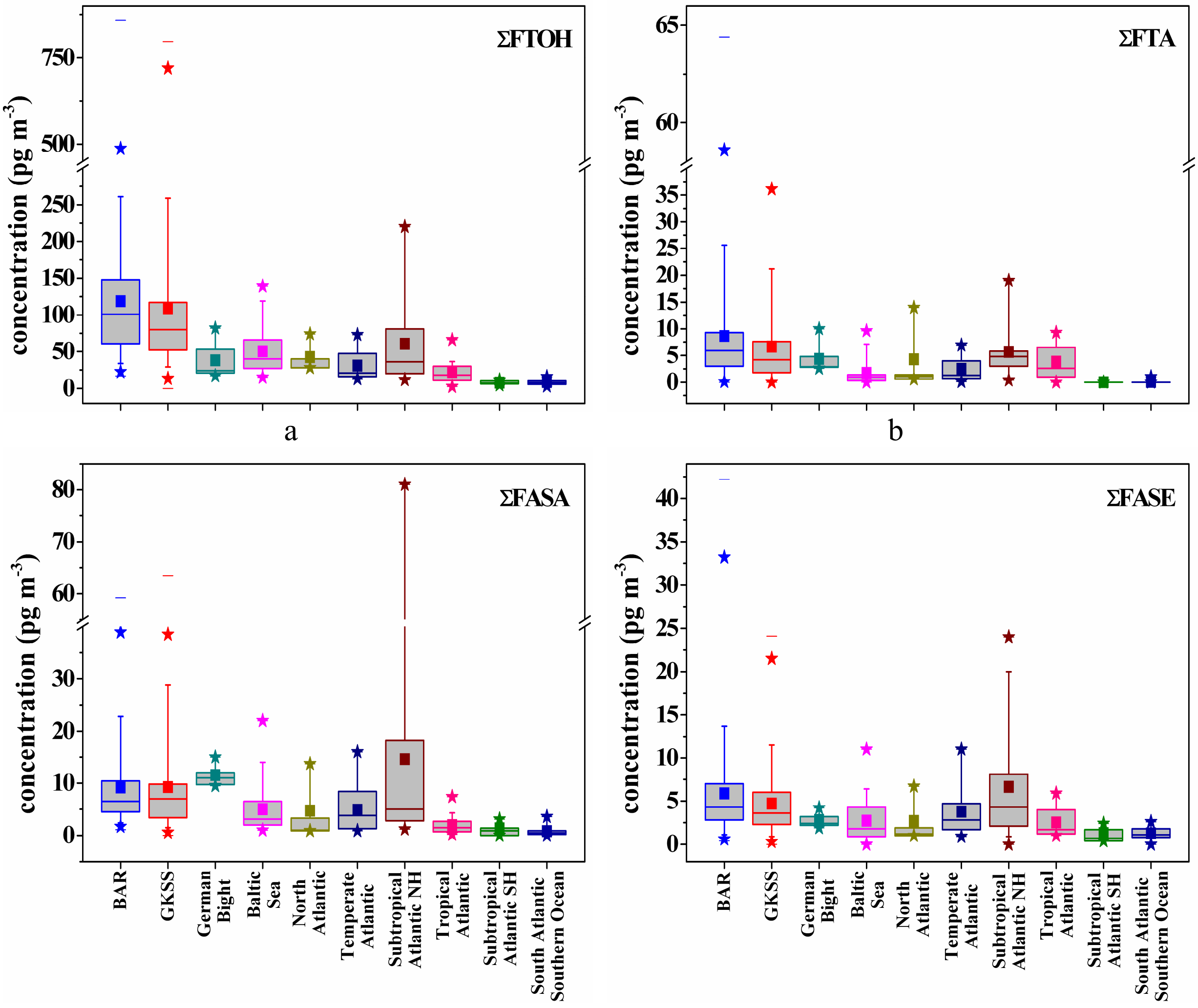
Seven days air mass backward trajectories were calculated with the model Hysplit 4.8 using NCEP's Global Data Assimilation System (GDAS) data with 1 degree latitude/longitude resolution provided by NOAA-Air Resources Laboratory (Draxler and Rolph, 2003). Trajectories were calculated for intervals of three and six hours. The sampling height was set as arrival height. In order to verify the origin of air masses obtained by these computations, back trajectories were also calculated exemplarily for arrival heights of 100 and 500 m using GDAS data as well as for the sampling height using NCEP's reanalysis data. The observed differences were in the range of the trajectories' uncertainty. To obtain main air mass pathways for the BAR and GKSS site, cluster analysis of trajectories was performed with Hysplit 4.8. Detailed information on this issue is presented in study 2.

3. Results & Discussion

3.1. Synopsis of PFC Concentrations in Ambient Air

Neutral precursor PFC were detected almost exclusively in the gas phase which is corroborated by octanol-air partition coefficients determined for these substances (Dreyer et al., 2009; Goss et al., 2006; Thuens et al., 2008). Only FASA and FASE were observed on particles. On average, the particle-phase contribution of these compounds did not exceed 20 %. Figure IV summarizes gas-phase concentrations of FTOH, FTA, FASA, and FASE. Concentrations of gas-phase PFC varied between one and two orders of magnitude on temporal as well as on spatial scales. Total gas-phase concentrations ranged from 4.5 pg m^{-3} in the Southern Ocean to 335 pg m^{-3} in source regions in ship based samples and from 17 to 972 pg m^{-3} in land-based samples. Gas-phase concentrations of PFC observed at Barsbüttel and GKSS were comparable to those determined at similar (Jahnke et al., 2007b) or other urban sites in Europe (Barber et al., 2007) or North America (Martin et al., 2002; Shoeib et al., 2006; Stock et al., 2004; Stock et al., 2005) and were at least one order of magnitude higher than marine PFC concentrations in the northern hemisphere published by Shoeib at al. (2006). Ship-based PFC concentrations were in the same range as those determined in studies covering similar locations (Jahnke et al., 2007c; Shoeib et al., 2006). With about 80 % on average, FTOH were the dominant class of PFC, followed by FASA, FASE, and FTA. In gas-phase samples 8:2 FTOH was usually observed in highest concentrations. The gas-phase PFC composition corroborates results of other studies in Europe and the Atlantic Ocean (Barber et al., 2007; Jahnke et al., 2007c; Shoeib et al., 2006).

Concentrations of individual particle-bound precursors were usually below 1 pg m^{-3}. Maximum particle-phase concentrations were reached for MeFOSE in the port of Hamburg (9 pg m^{-3}). MeFOSA and MeFOSE were the compounds that were most frequently observed. In contrast to other studies (Barber et al., 2007; Shoeib et al., 2006), FTOH were not detected in the particle fraction. Of ionic PFC, PFOS, PFBA, PFHxA, PFOA, PFNA, and PFDA were quantified most frequently in the particle fraction. Other ionic PFC detected occasionally were PFBS, PFHxS, PFPA, PFUnDA, PFDoDA, and PFTriDA. Particle-phase concentrations of ionic PFC were below < 1 pg m^{-3} on average. Maximum concentrations were observed for PFOS (13 pg m^{-3}) and PFOA (6 pg m^{-3}) in samples taken close to Hamburg or in the German Bight. Since sorption of gaseous PFCA to the glass fiber filters has been demonstrated by Arp and Goss (2008) particle-phase concentrations may be biased. Because of the low concentrations and the uncertainties involved during sampling and analysis, particle-phase PFC were not taken into account for further discussions.



a b

c d

Figure IV: Box-Whisker plots of gas-phase concentrations (pg m^{-3}) of ΣFTOH, ΣFTA, ΣFASA, and ΣFASE from studies 2-4 summarized for selected regions. —: minimum/maximum. ★: 1/99 percentile. Whiskers: 5/95 percentile. Box: 25/75 percentile and median. ■: mean.

3.2. Temporal Concentration Variations of PFC in Ambient Air

Significant variations of PFC gas-phase concentrations were observed in time series of 14 months at two locations (BAR, GKSS) in the vicinity of Hamburg revealing the limited interpretation potential of singular measurements (study 2). The concentration courses over time were characterized by fluctuating baselines that were interrupted by short singular and unevenly distributed events of high PFC concentrations. This is exemplarily presented for

8:2 FTOH in figure V. High concentration events were observed more often in summer than in winter, they did not necessarily occur at the same time at both sampling sites, and did not reveal any compound-specific fingerprint or correlation to meteorological or air quality parameters. Therefore, this suggests that these events give evidence for different nearby sources of airborne PFC with pulsing emission patterns and point-source like character.

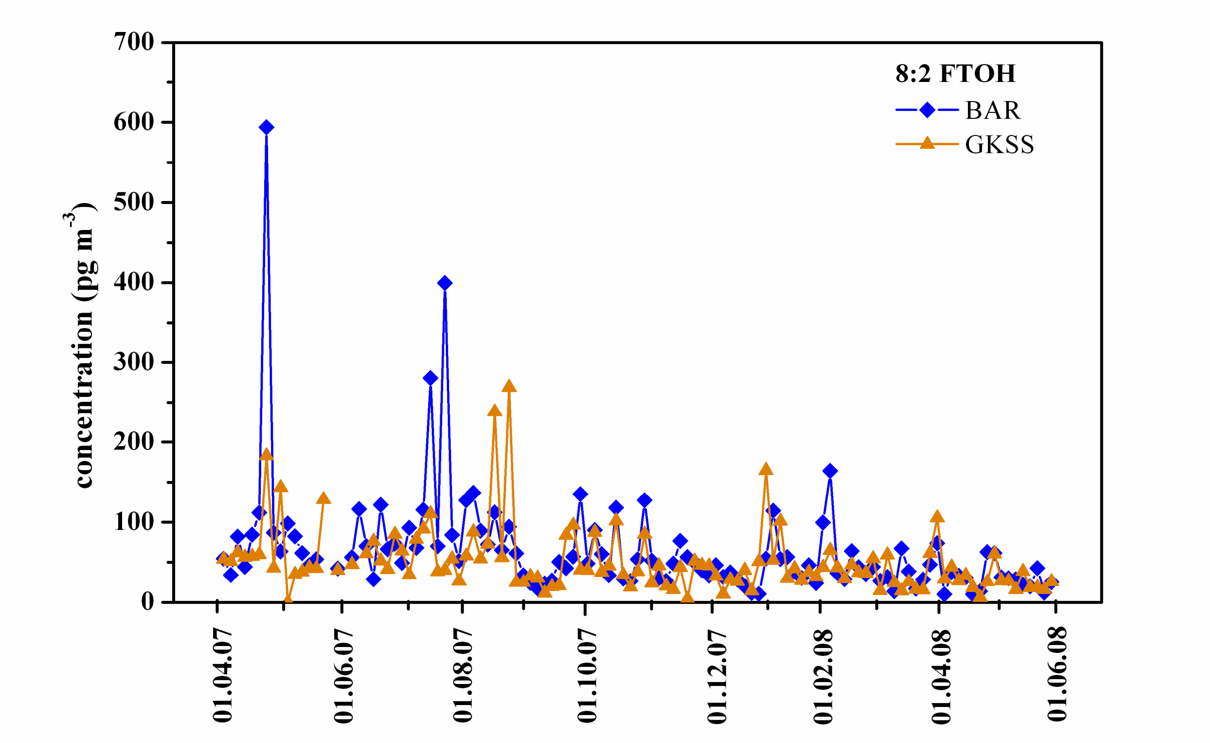


Figure V: Gas-phase concentrations (pg m^{-3}) of 8:2 FTOH at Barsbüttel (blue) and GKSS (orange) over the 14 months sampling period. Strongly elevated concentrations are supposed to result from nearby sources. In contrast, fluctuations of "baseline" concentrations appear to depend on diffuse sources and air mass origin.

High concentration events were excluded for the analysis of seasonal PFC concentration variations. Averages of smoothed concentrations of individual PFC decreased in the order of summer > spring, fall > winter and were most pronounced for the substances found in high concentrations. However, as correlation and trajectory analyses reveled, PFC concentrations varied rather dependent on the air mass origin (see section 3.4) than on seasonality. In winter, the lower planetary boundary layer height as well as reduced degradation by OH radicals should have led to increased PFC concentrations during the winter season as it was observed by Barber et al. (2008). This suggests that temperature dependent emissions of volatile PFC from diffuse sources, for instance residual PFC present in products that are currently in use

(Dinglasan-Panlilio and Mabury, 2006; Kaiser et al., 2004), were the reasons for this observation. Depending on the air mass origin, samples were influenced by these sources to different degrees. Enhanced deposition in winter due to increased PFC partitioning to particles may additionally explain the observed concentration differences for FASA or FASE but not for FTOH since these were not observed on particles.

3.3. Spatial Concentration Distribution of PFC in Ambient Air

Although the number of detected substances varied, precursor PFC were determined in all air samples, even in Antarctica. The distribution of PFC in ambient air on a global scale is exemplarily presented for 8:2 FTOH in figure VI (study 4, figures S4-2 – S4-7). These results clearly demonstrate the long-range atmospheric transport potential of this group of chemicals. Concentrations and occasionally PFC composition varied in dependence of the location, i.e. distance to source regions, and air mass history (see section 3.4). Consequently, PFC concentrations decreased from continental or coastal areas towards the open sea and from the northern hemispheric mid latitudes (Central Europe) towards the north and the south. Overall and marine background concentrations of precursors were lower in the southern hemisphere than in the northern hemisphere (table 4-2). Lowest concentrations in the southern hemisphere were observed in Antarctic air. There, the only PFC detected significantly above the field blanks were 8:2 FTOH and 10:2 FTOH. They were observed in concentrations of about 2 pg m^{-3}. Lowest PFC concentrations in the northern hemisphere were determined in marine air masses that were sampled in temperate regions in the middle of the Atlantic Ocean. There, ΣFTOH concentrations were around 15 pg m^{-3}. ΣFASA concentrations were around 1 pg m^{-3}, ΣFASE concentrations were below 3.5 pg m^{-3}, and ΣFTA concentrations were below 1 pg m^{-3}. In contrast, arctic air sampled close to Svalbard, Norway, was characterized by around twice as high PFC concentrations. These elevated concentrations probably reveal the more concentrated human activity in that region compared to the open ocean. The spatial distribution of volatile PFC obtained in our studies are consistent with findings of other authors (Jahnke et al., 2007c; Shoeib et al., 2006) as well as for persistent organic pollutants such as PCB, PBDE or organochlorine pesticides in similar regions (Choi et al., 2008; Jaward et al., 2004a; Jaward et al., 2004b; Luek et al., 2008; Montone et al., 2005).

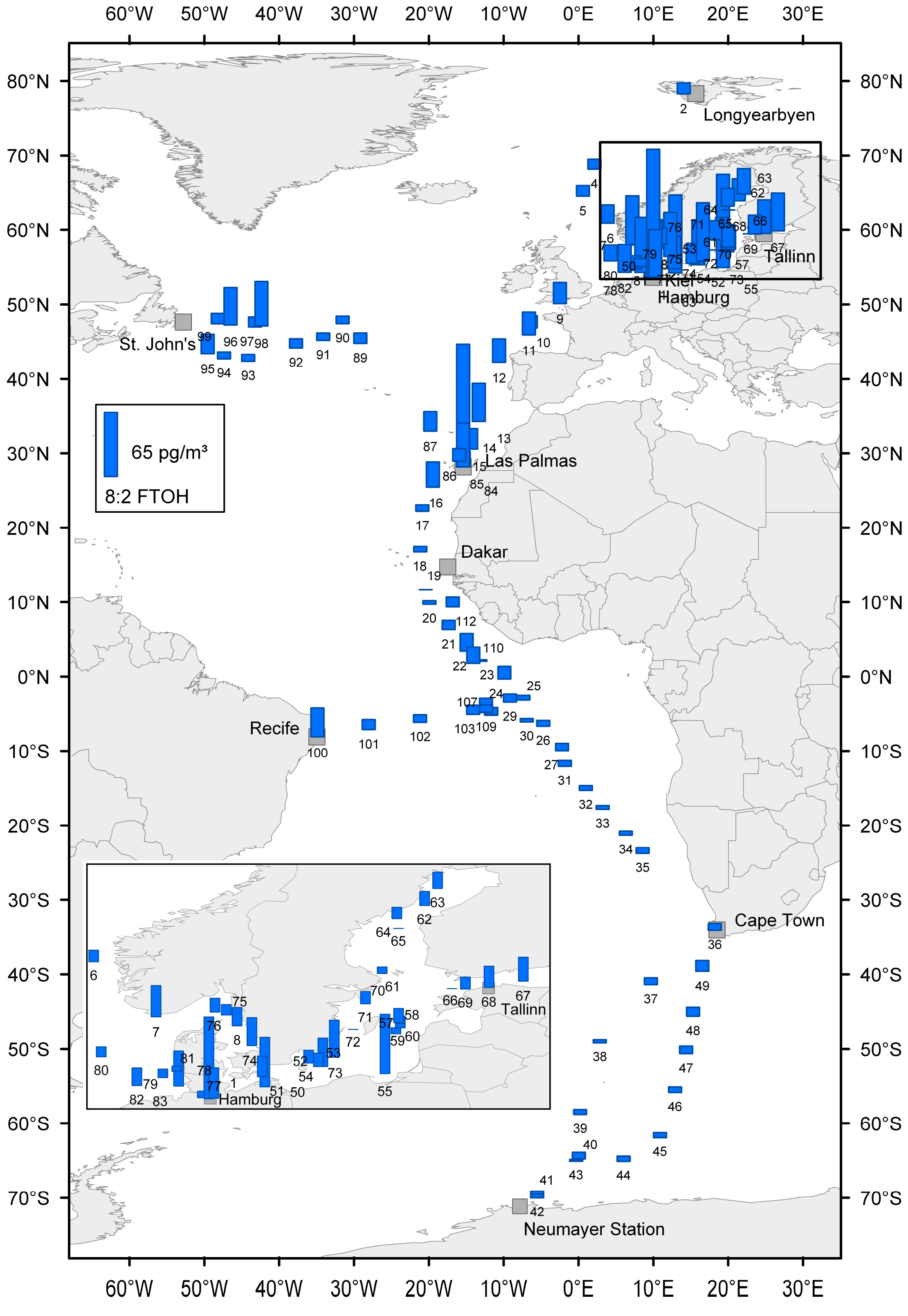


Figure VI: Spatial distribution of 8:2 FTOH gas-phase concentrations (pg m^{-3}) determined during several cruises in the Baltic Sea, the Atlantic and Southern Ocean. Note that the close-up of the Baltic Sea region is not to scale.

3.4. Influence of Air Mass Origin on Concentrations of PFC

As pointed out above, PFC concentrations were strongly influenced by the origin of the air mass that was sampled. Detailed analyses on this issue were conducted in study 2 and 3 using air mass back trajectories. These analyses revealed that gas-phase PFC levels at Barsbüttel increased whenever air was arriving close to ground and at low velocities from surrounding and southwestern directions (figure VII). Air masses that originated in northern and northwestern directions, particularly those traveling at high velocities, were significantly less contaminated with PFC. These results were supported by regional PFC concentration variations investigated during a field campaign on the research vessel Atair in the German Bight and its coastal regions (study 3). The regional differences of PFC air concentrations were likely due to the varying degree air masses had passed coastal and/or terrestrial areas. During this cruise lowest concentrations of volatile PFC were observed when air masses originated completely from marine regions (figure VIIIb). Quite the opposite was observed when sampled air masses had passed Southern UK, the Netherlands, and highly industrialized areas of Germany, regions that are known to be point sources for other inorganic and organic pollutants (EEA, 2008). Under these conditions, PFC concentrations significantly increased at land-based and ship-based sites (figure VIIIa). Elevated PFC gas-phase concentrations of air masses arriving from Central Europe were also observed by Barber et al. (2008). Similarly, other authors noted the importance of long-distance transport from continental Europe (mainly southwestern directions) for the pollution of the North Sea areas (Bjorseth et al., 1979; Lunde and Bjorseth, 1977; Preston and Merrett, 1991). Correspondingly, figure 4-3 illustrates that comparable transport events commonly occurred in various areas during all sampling campaigns.

Of course, air mass back trajectories do not explain the entire concentration variability that is observed in real samples. Although they offer important information on the air mass history, trajectory analyses may neither account for local phenomena nor provide sufficiently high resolution to be applicable to all samples. For instance, this was observed for a sample taken close to land in the German Bight. Elevated concentrations in that sample might be explained by local winds from southwesterly located coastal regions which were observed by onboard measurements but were not shown by the trajectories. Hence, it is important to monitor and thoroughly mind meteorological conditions throughout field campaigns.

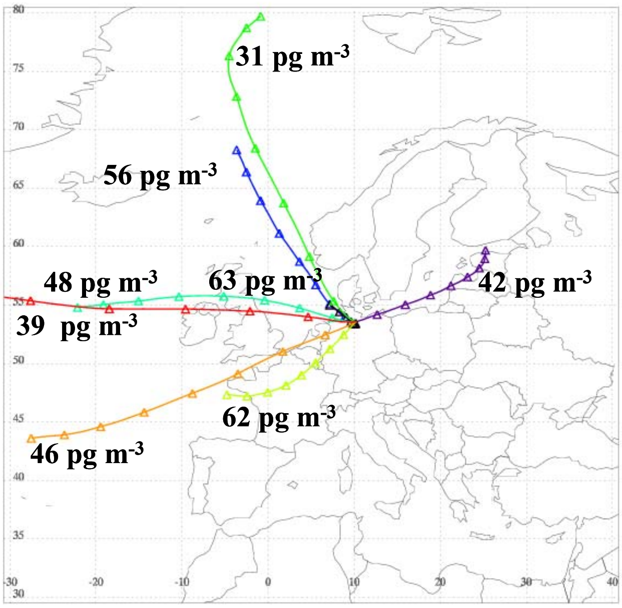


Figure VII: Average concentrations of 8:2 FTOH at Barsbüttel in dependence on main air mass origins. The main air mass origins are represented by average trajectories that are based on cluster analyses of 96 hours back trajectories for the 14 months sampling period. Triangles present the location of the air mass parcel in twelve hours intervals. Cluster means of 8:2 FTOH concentrations (also see table 2-1) were peak event-corrected and calculated from individual sample concentrations of those samples that were assigned to the corresponding cluster. Further details of results and cluster analysis are given in study 2.

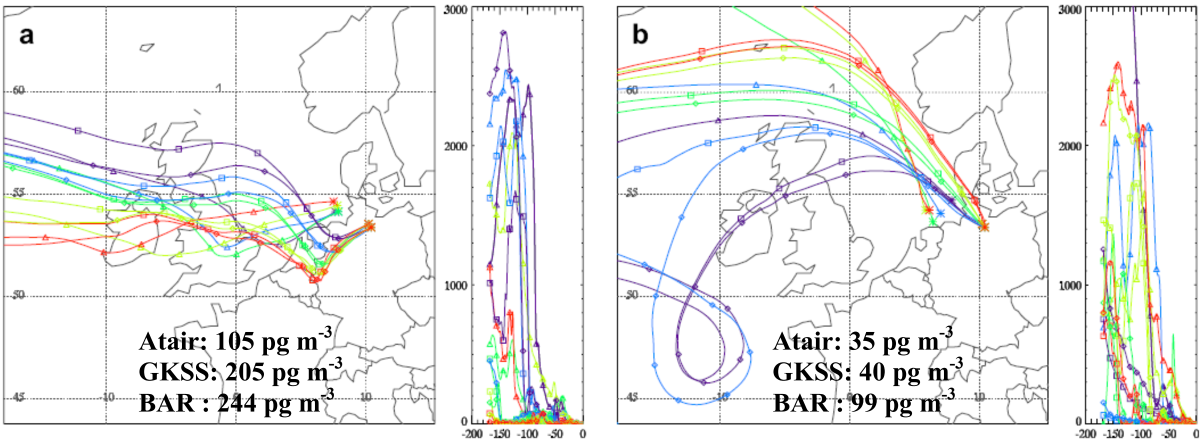


Figure VIII: Total gas-phase PFC concentrations as a function of air mass history expressed as back trajectories of selected samples. a: High concentration scenario. Prior to being sampled, air passed populated and/or industrialized areas of The Netherlands and western Germany. b: Low concentrations scenario. Air masses arrived from marine regions. Trajectories were calculated for 3 hours intervals. Asterisks mark the location of the sampling site or the ship's positions, respectively. Triangles, squares, and rhombs show the position of the air parcel in twelve hours intervals for Atair, Barsbüttel, and GKSS samples, respectively. Trajectory heights are presented as well. Further details are given in study 3.

3.5. Atmospheric Residence Times

An important parameter that influences the transport of a substance and hence is crucial for its ability to be transported to remote areas over long distances in the atmosphere is the substance's atmospheric life or residence time. The large spatially and temporally resolved data set of this thesis enabled the calculation of atmospheric residence times using the two indirect methods suggested by Junge (1974) and Manchester-Neesvig and Andren (1989). The Junge method was already applied to obtain atmospheric residence times of several compounds such as methyl bromide (Colman et al., 1998), mercury (Slemr et al., 1981), PCB (Anderson and Hites, 1996; Manchester-Neesvig and Andren, 1989; Panshin and Hites, 1994), or recently FTOH (Piekarz et al., 2007). Applying the Junge method, we calculated the atmospheric residence times separately using the temporal (14 months time series at land-based sites) and the spatial approach (ship-based samples, study 4). Since it is based on the partitioning of gas-phase chemicals to the particle phase, the method by Manchester-Neesvig and Andren (1989) was only applied to those analytes where partitioning to particles was actually observed.

Atmospheric residence times of precursor PFC are given in table IV. They varied between the different approaches up to a factor of 2, in case of EtFOSE by a factor of 3.5. Residence times calculated for FTOH were between those estimated by Piekarz (2007) using the Junge method (50 d, 80 d, and 70 d, for 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively) and atmospheric lifetimes of 20 days determined in smog chamber studies (Ellis et al., 2003). Atmospheric residence times of FASA and FASE were in the same range as lifetimes determined in smog chamber studies (D'Eon et al., 2006; Martin et al., 2006), except for MeFBSE (2 days, D'Eon et al. 2006). Atmospheric residence times calculated for FTA were one order of magnitude above those estimated by Butt et al. (2009). However, limitations of the indirect methods estimating the atmospheric residence times should be taken into account. Samples that were collected at different locations do not reflect potential seasonal changes. In ship-based samples FASA and FASE were often observed in concentrations close to the detection limit. Partitioning of FASA and FASE is in contradiction to the Junge-method's assumption of one uniformly distributed sink (Junge, 1974). Furthermore, the analytical method to detect trace amounts of PFC might not be as precise as required to get accurate residence times. Considering these limitations, atmospheric residence times determined here are in good agreement to those observed in other studies. Most importantly, these results further demonstrate that the persistence of volatile precursor PFC in the atmosphere is sufficient to allow long-range transport. Therefore long-range transport may contribute significantly to the contamination of remote regions with persistent PFCA and PFSA.

Table IV: Atmospheric residence times (τ) in days based on the Junge relation and the partitioning ratio of a gaseous substance to particles. n.c.: not calculated, due to lack of data.

	τ (Junge relation; d)		τ (partitioning ratio; d)	
	ship samples	**BAR samples**	**ship samples**	**BAR samples**
4:2 FTOH	n.c.	n.c.	n.c.	n.c.
6:2 FTOH	39	52	n.c.	n.c.
8:2 FTOH	56	48	n.c.	n.c.
10:2 FTOH	66	46	n.c.	n.c.
12:2 FTOH	48	26	n.c.	n.c.
6:2 FTA	33	30	n.c.	n.c.
8:2 FTA	33	33	n.c.	n.c.
10:2 FTA	23	30	n.c.	n.c.
MeFBSA	39	40	n.c.	n.c.
MeFOSA	46	53	36	n.c.
Me_2FOSA	n.c.	n.c.	n.c.	n.c.
EtFOSA	27	55	57	n.c.
PFOSA	n.c.	n.c.	n.c.	n.c.
MeFBSE	42	50	66	n.c.
MeFOSE	46	49	30	35
EtFOSE	38	53	15	n.c.

3.6. Where Did They Come From? – A Discussion About Sources of Atmospheric PFC

A variety of products and processes may contribute to the emission of polyfluorinated compounds to the atmosphere. The majority of PFC are emitted as persistent perfluorinated acids to the water phase (Paul et al., 2009; Prevedouros et al., 2006). Direct emission of PFCA and PFSA to the air is rather particle-related and thus subject of fast deposition (Barton et al., 2006). In contrast to the persistent ionic PFC, volatile and semi-volatile PFCA and PFSA precursors are readily emitted to the air during manufacturing of fluorochemicals and fluorochemical-containing polymers (Paul et al., 2009; Prevedouros et al., 2006). More importantly, emissions from application or volatilization of volatile and semi-volatile polyfluorinated compounds which have been found in commercial and industrial fluoropolymers, surfactants, and other agents (Dinglasan-Panlilio and Mabury, 2006; Fiedler et al., submitted; Jensen et al., 2008; Paul et al., 2009) contribute to the diffuse air contamination. With the data obtained in this thesis, distinct PFC sources, particularly for PFCA and PFSA precursors, cannot be identified. Nevertheless, some basic conclusions about PFC sources influencing this data set can be drawn.

Single events of significantly enhanced concentrations of volatile PFC were observed during the analysis of the time series at Barsbüttel and GKSS (study 2). Since these events were irregular and occurred on very short time scales, unknown sources located in short distance to the sampling sites were assumed to be responsible for these observations. Detailed investigation about potential contributors is underway in an ongoing diploma project. Evidence for a distinct local source of certain precursor PFC was also observed in the ship yard of Las Palmas, Spain (study 4). Sampling was conducted at the research vessel Maria S. Merian while it was waiting for repair in the shipyard. Around the sampling site, many other ships were refurbished; their (underwater) coatings were ground off and/or renewed. In these samples very high PFC concentrations (ΣPFC 335 pg m^{-3}) were observed and with an EtFOSA contribution of 20 % also an unusual PFC gas-phase composition. Further indications that paints or dyes may contain and release certain precursors were obtained in samples taken at the research vessel L'Atalante in the tropical Atlantic. In some samples of that cruise, unusually high concentrations of MeFBSE were detected after painting works on a deck below the sample inlet.

Despite of these incidents, this study's data suggest that emissions from diffuse PFC sources like application, volatilization, or distant manufacturing were rather responsible for the concentration variations observed. This assumption was not only based on trajectory analyses as described above but also on correlation and fingerprint analyses. Fiedler et al. (submitted) investigated FTOH fingerprint ratios of several PFC containing products. However, ratios observed in samples described in this thesis revealed that there must have been far more than those sources. Our results were confirmed by a study of Piekarz et al. (2007) applying trajectory analyses and FTOH concentration ratios to identify PFC source regions at the American west coast. We identified source regions in the Gulf of Finland around Helsinki, Finland and Tallinn, Estonia as well as in Central Europe in an area roughly covering northern parts of Belgium, The Netherlands, Southern UK, and north-western Germany (study 2-4). For the identification of additional regions, the spatial and temporal resolution of ship- and land-based samples was too low. Results were particularly convincing for the latter source region which is known for point sources of other inorganic and organic pollutants such as

NO_x, SO_x, hydrofluorocarbons, or polycyclic aromatic hydrocarbons (PAH) (EEA, 2008). Moreover, several facilities producing fluorochemicals such as Dyneon, Clariant, or Atofina are located in that area (Hekster et al., 2002), among them is one of the two largest production sites of the company 3M located in Antwerp, Belgium (Paul et al., 2009). Whenever air masses arrived from that densely populated and industrialized region, elevated air concentrations of PFCA and PFSA precursors were observed. Increasing concentrations of these volatile PFC in air masses arriving from this central European region were also determined by Barber et al. (2008).

Several studies reported PFC air concentrations to be higher at urban than at rural sites (Barber et al., 2007; Primbs et al., 2008; Stock et al., 2004). Based on these studies one might assume that, overall, Hamburg acts as significant PFC source. However, it was not possible to completely evaluate the PFC air contamination potential of the city of Hamburg, mainly because the sampling set up was not sufficiently suited for this purpose. Concentrations of volatile PFC in samples taken in the port of Hamburg which is located in the city centre did not differ from those determined in samples of Barsbüttel and GKSS at the same time. Taken these results into account, the source strength of Hamburg appears to be rather small. This finding was also confirmed by Jahnke et al. (2007b) who did not observe distinct concentration differences of airborne PFC between the city of Hamburg and the remote sampling site at Waldhof located approximately 100 km southeast of Hamburg. Based on the results of study 2 and 3, the origins of airborne PFC appeared to be rather from temperature dependent diffuse sources and/or medium to long-distance atmospheric transport from highly populated and industrialized areas southwest and west of Hamburg than from the city itself.

The ubiquitous presence of volatile PFCA and PFSA precursors in air demonstrates the global presence of PFC emitting sources. Although atmospheric lifetimes of volatile PFC are long enough to enable their long-range transport they appear to be not sufficiently long to pass the Intertropical Convergence Zone (ITCZ) where exchange processes occur in the order of a year. Thus, polyfluorinated compounds detected south of the ITCZ must have been emitted from sources located in the southern hemisphere. Since PFC concentrations were higher in the northern than in the southern hemisphere it is evident that southern hemispheric PFC sources are less significant and that PFC are applied more heavily in the northern hemisphere, probably due to the relatively high degree of industrialization and prosperity there.

4. Conclusion

Applying an optimized analytical method, polyfluorinated substances were detected in every air sample from the Arctic to Antarctica. While PFCA and PFSA were determined in low concentrations in the particle phase, their neutral precursors occurred in concentrations that were usually two orders of magnitude higher. Fluorotelomer alcohols were the precursor compounds observed in highest concentrations and proportions, followed by FASE, FASA, and FTA. Precursors were predominantly detected in the gas phase corroborating recent studies on octanol-air partition coefficients. Regardless of the substance or the location, PFC concentrations of the sampled air mainly depended on the air mass origin. Generally, PFC concentrations significantly increased when air masses were arriving from densely populated and/or industrialized regions. Concentrations of gas-phase PFC were observed to vary strongly over the year without revealing a distinct temperature dependence or significant seasonality. Nevertheless, concentrations of volatile PFC were higher in summer than in winter time, probably due to varying emissions from diffuse sources. On the contrary, abruptly occurring singular events of high concentrations were most likely caused by local sources that were characterized by a point-source pattern. This demonstrated that measurements covering long periods are necessary and provide valuable tools to assess concentration variations. Overall, studies cumulated in this thesis underline that volatile and semi-volatile PFCA and PFSA precursors are being transported over long distances in the atmosphere. Due to their volatility and long atmospheric residence times, these compounds are able to reach remote ecosystems such as the Arctic or Antarctica via that pathway where they may serve as an important source of persistent, bioaccumulative, and toxic perfluorinated acids. Although studies in this thesis cannot resolve the extent to which atmospheric transport contributes to the PFCA and PFSA contamination of remote regions, they provide substantial new data and information that had never been obtained before to that extend, both temporally and spatially. These data significantly help to validate environmental fate models of polyfluorinated compounds.

In contrast to data of PFCA and PFSA in the water phase, information on airborne PFC is still limited. Analytical efforts to determine volatile precursors in air have yet to be extended. As it was performed for the water phase (Van Leeuwen et al., 2006), additional intercomparison studies to compare sampling and analytical techniques of airborne PFC like that presented by Dreyer et al. (2008) have to be carried out. To further improve our understanding of the atmospheric transport and degradation of volatile PFC, additional analytical methods should be applied. Methods should be less solvent and time consuming than the procedure applied in these studies. Temporal resolution is to be decreased further. New accumulation and analytical techniques such as thermodesorption might be suited to achieve these goals. Atmospheric processing of aerosols may have an important influence on the PFC degradation process that occurs in the atmosphere and should be considered in future studies. Furthermore, the deposition behavior of PFC, particularly of PFCA and PFSA is only poorly understood and studied up to now and should therefore be subject of future research as well. Source identification and characterization will have to continue. This includes the evaluation of individual diffuse and point sources as well as the assessment and characterization of source regions. Estimates of source strengths or emission factors will provide crucial information for environmental fate studies. The collection of new information will finally help scientists and political stakeholders to asses those PFC that are not subject to regulation efforts today.

References

Ahrens, L.; Plaßmann, M.; Temme, C.; Ebinghaus, R. 2007. Determination of per- and polyfluorinated alkyl compounds using liquid chromatography tandem mass spectrometry in water samples. *Organohalogen Compounds*, *69*, 2804-2807.

Ahrens, L.; Siebert, U.; Ebinghaus, R. in press. Total body burden and tissue distribution of polyfluorinated compounds in habor seals (Phoca vitulina) from the German Bight. *Marine Pollution Bulletin*.

Anderson, P. N.; Hites, R. A. 1996. OH Radical Reactions: The major removal pathway for polychlorinated biphenyls from the atmosphere. *Environmental Science & Technology*, *30*, 1756-1763.

Armitage, J.; Cousins, I. T.; Buck, R. C.; Prevedouros, K.; Russell, M. H.; MacLeod, M.; Korzeniowski, S. H. 2006. Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. *Environmental Science & Technology*, *40*, 6969-6975.

Arp, H. P. H.; Goss, K. U. 2008. Irreversible sorption of trace concentrations of perfluorocarboxylic acids to fiber filters used for air sampling. *Atmospheric Environment*, *42*, 6869-6872.

Austin, M. E.; Kasturi, B. S.; Barber, M.; Kannan, K.; MohanKumar, P. S.; MohanKumar, S. M. J. 2003. Neuroendocrine effects of perfluorooctane sulfonate in rats. *Environmental Health Perspectives*, *111*, 1485-1489.

Barber, J. L.; Berger, M. L.; Chaemfa, C.; Huber, S.; Jahnke, A.; Temme, C.; Jones, K. C. 2007. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *Journal of Environmental Monitoring*, *9*, 530-541.

Barber, J. L.; Chaemfa, C.; Jones, K. C.; Huber, S. 2008. Seasonal variability in atmospheric concentrations of polyfluorinated chemicals (PFCs) at 2 sites in the UK. *1st International Workshop Fuorinated Surfactants - New Developments, http://pft.fh-fresenius.de/, Idstein, Germany*.

Barton, C. A.; Butler, L. E.; Zarzecki, C. J.; Flaherty, J.; Kaiser, M. 2006. Characterizing perfluorooctanoate in ambient air near the fence line of a manufacturing facility: Comparing modeled and monitored values. *Journal of the Air & Waste Management Association*, *56*, 48-55.

Begley, T. H.; White, K.; Honigfort, P.; Twaroski, M. L.; Neches, R.; Walker, R. A. 2005. Perfluorochemicals: Potential sources of and migration from food packaging. *Food Additives and Contaminants*, *22*, 1023-1031.

Berger, U.; Verreault, J.; Gabrielsen, G. W. 2007. Spatial and temporal trends of perfluorinated compounds in herring gull eggs from northern Norway. *SETAC Europe 27th Meeting, Porto, Portugal*, *Poster*.

Berthiaume, J.; Wallace, K. B. 2002. Perfluorooctanoate, perflourooctanesulfonate, and N-ethyl perfluorooctanesulfonamido ethanol; peroxisome proliferation and mitochondrial biogenesis. *Toxicology Letters*, *129*, 23-32.

BfR 2006. Hohe Gehalte an perfluorierten organischen Tensiden (PFT) in Fischen sind gesundheitlich nicht unbedenklich. *Stellungnahme Nr. 035/2006 des Bundesinstituts für Risikobewertung vom 27. Juli 2006.*

Bjorseth, A.; Lunde, G.; Lindskog, A. 1979. Long-Range Transport of Polycyclic Aromatic-Hydrocarbons. *Atmospheric Environment*, *13*, 45-53.

BMG 2006. Vorläufige Bewertung von Perfluorierten Tensiden (PFT) im Trinkwasser am Beispiel ihrer Leitsubstanzen Perfluoroktansäure (PFOA) und Perfluorsulfonsäure (PFOS). *Stellungnahme der Trinkwasserkommission des Bundesministeriums für Gesundheit (BMG) beim Umweltbundesamt vom 21.06.06 überarbeitet am 13.7.06.*

Bossi, R.; Riget, F. F.; Dietz, R. 2005. Temporal and spatial trends of perfluorinated compounds in ringed seal (Phoca hispida) from Greenland. *Environmental Science & Technology*, *39*, 7416-7422.

Boulanger, B.; Peck, A. M.; Schnoor, J. L.; Hornbuckle, K. C. 2005. Mass budget of perfluorooctane surfactant in Lake Ontario. *Environmental Science & Technology*, *39*, 74-79.

Buck, R. C. 2008. The Chemistry, Properties, and Uses of commercial fluorinated Surfactants - A Primer. *1st International Workshop Fuorinated Surfactants - New Developments*, *Idstein, Germany*. http://pft.fh-fresenius.de/.

Butt, C. M.; Mabury, S. A.; Kwan, M.; Wang, X.; Muir, D. C. G. 2008. Spatial trends of perfluoroalkyl compounds in ringed seals (Phoca hispida) from the Canadian Arctic. *Environmental Toxicology and Chemistry*, *27*, 542-553.

Butt, C. M.; Mabury, S. A.; Muir, D. C. G.; Braune, B. M. 2007a. Prevalence of long-chained perfluorinated carboxylates in seabirds from the canadian arctic between 1975 and 2004. *Environmental Science & Technology*, *41*, 3521-3528.

Butt, C. M.; Muir, D. C. G.; Stirling, I.; Kwan, M.; Mabury, S. A. 2007b. Rapid response of arctic ringed seals to changes in perfluoroalkyl production. *Environmental Science & Technology*, *41*, 42-49.

Butt, C. M.; Young, C. J.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. 2009. Atmospheric chemistry of 4:2 fluorotelomer acrylate [C4F9CH2CH2OC(O)CH=CH2]: kinetics, mechanisms, and products of chlorine-atom- and OH-radical-initiated oxidation. *Journal of Physical Chemistry A*, *113*, 3155-3161.

Caliebe, C.; Gerwinski, W.; Hühnerfuss, H.; Theobald, N. 2004. Occurrence of perfluorinated organic acids in the water of the North Sea. *Organohalogen Compounds*, *66*, 4024-4028.

Choi, S.-D.; Baek, S.-Y.; Chang, Y.-S.; Wania, F.; Ikonomou, M. G.; Yoon, Y.-J.; Park, B.-K.; Hong, S. 2008. Passive Air Sampling of Polychlorinated Biphenyls and Organochlorine Pesticides at the Korean Arctic and Antarctic Research Stations: Implications for Long-Range Transport and Local Pollution. *Environmental Science & Technology*, *42*, 7125-7131.

Colman, J. J.; Blake, D. R.; Rowland, F. S. 1998. Atmospheric residence time of CH3Br estimated from the Junge spatial variability relation. *Science (Washington, D. C.)*, *281*, 392-396.

Conder, J. M.; Hoke, R. A.; De Wolf, W.; Russell, M. H.; Buck, R. C. 2008. Are PFCAs bioaccumulative? A critical review and comparison with regulatory lipophilic compounds. *Environmental Science & Technology*, *42*, 995-1003.

D'Eon, J. C.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. 2006. Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, C4F9SO2N(CH3)CH2CH2OH: Kinetics and mechanism of reaction with OH. *Environmental Science & Technology*, *40*, 1862-1868.

De Silva, A. O.; Mabury, S. A. 2004. Isolating isomers of perfluorocarboxylates in polar bears (Ursus maritimus) from two geographical locations. *Environmental Science & Technology*, *38*, 6538-6545.

DFG 2005. MAK- und BAT-Werte-Liste 2005. *Wiley-VCH Verlag, Weinheim*.

Dinglasan-Panlilio, M. J. A.; Mabury, S. A. 2006. Significant residual fluorinated alcohols present in various fluorinated materials. *Environmental Science & Technology*, *40*, 1447-1453.

Dinglasan, M. J. A.; Ye, Y.; Edwards, E. A.; Mabury, S. A. 2004. Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. *Environmental Science & Technology*, *38*, 2857-2864.

Draxler, R. R.; Rolph, G. D. 2003. HYSPLIT (HYbrid Single-Particle Langerian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). *NOAA Air Resources Laboratory, Silver Spring, MD.*

Dreyer, A.; Barber, J. L.; Ebinghaus, R.; Fiedler, S.; Harner, T.; Jones, K. C.; Schramm, K.-W.; Shoeib, M. 2008. Field Intercomparison on the determination of airborne volatile and semi-volatile polyfluorinated organic compounds. *1st International Workshop Fluorinated Surfactants - New Developments, http://pft.fh-fresenius.de/, Idstein, Germany*, *Poster*.

Dreyer, A.; Langer, V.; Ebinghaus, R. 2009. Determination of octanol-air partition coefficients (K_{OA}) of fluorotelomer acrylates, perfluoroalkyl sulfonamides, and perfluoroalkylsulfonamido ethanols. *Journal of Chemical and Engineering Data*, *54,* 3022-3025.

EEA 2008. The European Pollutant Emission Register (EPER). *http://www.eper.ec.europe.eu*.

Ellis, D. A.; Mabury, S. A. 2003. Chemical ionization pathways of polyfluorinated chemicals - A connection to environmental atmospheric processes. *Journal of the American Society for Mass Spectrometry*, *14*, 1177-1191.

Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. 2004. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environmental Science & Technology*, *38*, 3316-3321.

Ellis, D. A.; Martin, J. W.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. 2003. Atmospheric lifetime of fluorotelomer alcohols. *Environmental Science & Technology*, *37*, 3816-3820.

European Community 2006. Directive 2006/122/EC of the European Parliament and of the Council. *Official Journal of the European Union*, *L 372*, 32-34.

Fiedler, S.; Pfister, G.; Schramm, K.-W. submitted. Poly- and perfluorinated compounds in household consumer products. *Environmental Science & Technology*, *es-2008-03109g*.

Fromme, H.; Midasch, O.; Twardella, D.; Angerer, J.; Boehmer, S.; Liebl, B. 2007. Occurrence of perfluorinated substances in an adult German population in southern Bavaria. *International Archives of Occupational and Environmental Health*, *80*, 313-319.

Fromme, H.; Schlummer, M.; Ungewiss, J.; Roscher, E. 2006. Umweltmedizinische Bedeutung perfluorierter Kohlenwasserstoffe (PFC). *Materialien zur Umweltmedizin*, *Band 16*, 97-124.

Giesy, J. P.; Kannan, K. 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environmental Science & Technology*, *35*, 1339-1342.

Giesy, J. P.; Kannan, K. 2002. Perfluorochemical surfactants in the environment. *Environmental Science & Technology*, *36*, 146A-152A.

Goss, K. U.; Bronner, G.; Harner, T.; Monika, H.; Schmidt, T. C. 2006. The partition behavior of fluorotelomer alcohols and olefins. *Environmental Science & Technology*, *40*, 3572-3577.

Harada, K.; Nakanishi, S.; Saito, N.; Tsutsui, T.; Koizumi, A. 2005. Airborne perfluorooctanoate may be a substantial source contamination in Kyoto area, Japan. *Bulletin of Environmental Contamination and Toxicology*, *74*, 64-69.

Haukas, M.; Berger, U.; Hop, H.; Gulliksen, B.; Gabrielsen, G. W. 2007. Bioaccumulation of per- and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web. *Environmental Pollution*, *148*, 360-371.

Hekster, F. M.; De Voogt, P.; Pijnenburg, A. M. C. M.; Laane, R. W. P. M. 2002. Perfluorinated Substances - Aquatic environmental Assessment. *Report RIKZ/2002.043*.

Hori, H.; Yamamoto, A.; Hayakawa, E.; Taniyasu, S.; Yamashita, N.; Kutsuna, S. 2005. Efficient decomposition of environmentally persistent perfluorocarboxylic acids by use of persulfate as a photochemical oxidant. *Environmental Science & Technology*, *39*, 2383-2388.

Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. G. 2006. Biological monitoring of polyfluoroalkyl substances: A review. *Environmental Science & Technology*, *40*, 3463-3473.

Hu, W. Y.; Jones, P. D.; Upham, B. L.; Trosko, J. E.; Lau, C.; Giesy, J. P. 2002. Inhibition of gap junctional intercellular communication by perfluorinated compounds in rat liver and dolphin kidney epithelial cell lines in vitro and sprague-dawley rats in vivo. *Toxicological Sciences*, *68*, 429-436.

Hundley, S. G.; Sarrif, A. M.; Kennedy, G. L. 2006. Absorption, distribution, and excretion of ammonium perfluorooctanoate (APFO) after oral administration to various species. *Drug and Chemical Toxicology*, *29*, 137-145.

Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. 2004a. Atmospheric chemistry of perfluorinated carboxylic acids: Reaction with OH radicals and atmospheric lifetimes. *Journal of Physical Chemistry A*, *108*, 615-620.

Hurley, M. D.; Misner, J. A.; Ball, J. C.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A.; Andersen, M. P. S. 2005. Atmospheric chemistry of CF3CH2CH2OH: Kinetics, mechanisms and products of Cl atom and OH radical initiated oxidation in the presence and absence of NOX. *Journal of Physical Chemistry A*, *109*, 9816-9826.

Hurley, M. D.; Wallington, T. J.; Andersen, M. P. S.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. 2004b. Atmospheric chemistry of fluorinated alcohols: Reaction with Cl atoms and OH radicals and atmospheric lifetimes. *Journal of Physical Chemistry A*, *108*, 1973-1979.

Jahnke, A.; Ahrens, L.; Ebinghaus, R.; Berger, U.; Barber, J. L.; Temme, C. 2007a. An improved method for the analysis of volatile polyfluorinated alkyl substances in environmental air samples. *Analytical and Bioanalytical Chemistry*, *387*, 965-975.

Jahnke, A.; Ahrens, L.; Ebinghaus, R.; Temme, C. 2007b. Urban versus remote air concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany. *Environmental Science & Technology*, *41*, 745-752.

Jahnke, A.; Berger, U.; Ebinghaus, R.; Temme, C. 2007c. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53 degrees N-33 degrees S). *Environmental Science & Technology*, *41*, 3055-3061.

Jahnke, A.; Huber, S.; Ternme, C.; Kylin, H.; Berger, U. 2007d. Development and application of a simplified sampling method for volatile polyfluorinated alkyl substances in indoor and environmental air. *Journal of Chromatography A*, *1164*, 1-9.

Jaward, F. M.; Barber, J. L.; Booij, K.; Dachs, J.; Lohmann, R.; Jones, K. C. 2004a. Evidence for dynamic air-water coupling and cycling of persistent organic pollutants over the open Atlantic Ocean. *Environmental Science & Technology*, *38*, 2617-2625.

Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. 2004b. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environmental Science & Technology*, *38*, 34-41.

Jensen, A. A.; Leffers, H. 2008. Emerging endocrine disrupters: perfluoroalkylated substances. *International Journal of Andrology*, *31*, 161-169.

Jensen, A. A.; Poulsen, P. B.; Bossi, R. 2008. Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. *Survey of Chemical Substances in Consumer Products, Danish Ministry of the Environment*, *No. 99*.

Johns, K.; Stead, G. 2000. Fluoroproducts - the extremophiles. *Journal of Fluorine Chemistry*, *104*, 5-18.

Jones, P. D.; Hu, W. Y.; De Coen, W.; Newsted, J. L.; Giesy, J. P. 2003. Binding of perfluorinated fatty acids to serum proteins. *Environmental Toxicology and Chemistry*, *22*, 2639-2649.

Junge, C. E. 1974. Residence time and variability of tropospheric trace gases. *Tellus*, *26*, 477-488.

Kaerrman, A.; Ericson, I.; van Bavel, B.; Darnerud, P. O.; Aune, M.; Glynn, A.; Lignell, S.; Lindstroem, G. 2007. Exposure of perfluorinated chemicals through lactation: levels of matched human milk and serum and a temporal trend. *Environmental Health Perspectives*, *115*, 226-230.

Kaiser, M. A.; Cobranchi, D. P.; Kao, C. P. C.; Krusic, P. J.; Marchione, A. A.; Buck, R. C. 2004. Physicochemical properties of 8-2 fluorinated Telomer B alcohol. *Journal of Chemical and Engineering Data*, *49*, 912-916.

Kaiser, M. A.; Larsen, B. S.; Kao, C. P. C.; Buck, R. C. 2005. Vapor pressures of perfluorooctanoic, -nonanoic, -decanoic, -undecanoic, and -dodecanoic acids. *Journal of Chemical and Engineering Data*, *50*, 1841-1843.

Kallenborn, R.; Berger, U.; Järnberg, U. 2004. Perfluorinated alkylated substances (PFAS) in the nordic environment. *TemaNord 2004*, *255*, Nordic Council of Ministers. http://sft.no/nyheter/dokumenter/pfas_nmr2004.pdf.

Kannan, K.; Corsolini, S.; Falandysz, J.; Fillmann, G.; Kumar, K. S.; Loganathan, B. G.; Mohd, M. A.; Olivero, J.; Van Wouwe, N.; Yang, J. H.; Aldous, K. M. 2004. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. *Environmental Science & Technology*, *38*, 4489-4495.

KemI 2005. Proposal for listing Perfluorooactane sulfonate (PFOS) in Annex A of the Stockholm Convention on Persistent Organic Pollutants. *Swedish Chemicals Inspectorate (KemI), Sweden: http://www.pops.int/documents/meetings/poprc/meeting_docs/en/POPRC1-INF9-b.pdf.*

Kennedy, G. L.; Butenhoff, J. L.; Olsen, G. W.; O'Connor, J. C.; Seacat, A. M.; Perkins, R. G.; Biegel, L. B.; Murphy, S. R.; Farrar, D. G. 2004. The toxicology of perfluorooctanoate. *Critical Reviews in Toxicology*, *34*, 351-384.

Key, B. D.; Howell, R. D.; Criddle, C. S. 1997. Fluorinated organics in the biosphere. *Environmental Science & Technology*, *31*, 2445-2454.

Kim, S. K.; Kannan, K. 2007. Perfluorinated acids in air, rain, snow, surface runoff, and lakes: Relative importance of pathways to contamination of urban lakes. *Environmental Science & Technology*, *41*, 8328-8334.

Kissa, E. 2001. Fluorinated Surfactants and Repellents; *2nd ed.; Marcel Dekker: New York*.

Krusic, P. J.; Marchione, A. A.; Davidson, F.; Kaiser, M. A.; Kao, C. P. C.; Richardson, R. E.; Botelho, M.; Waterland, R. L.; Buck, R. C. 2005. Vapor pressure and intramolecular hydrogen bonding in fluorotelomer alcohols. *Journal of Physical Chemistry A*, *109*, 6232-6241.

Kudo, N.; Bandai, N.; Suzuki, E.; Katakura, M.; Kawashima, Y. 2000. Induction by perfluorinated fatty acids with different carbon chain length of peroxisomal beta-oxidation in the liver of rats. *Chemico-Biological Interactions*, *124*, 119-132.

Kudo, N.; Iwase, Y.; Okayachi, H.; Yamakawa, Y.; Kawashima, Y. 2005. Induction of hepatic peroxisome proliferation by 8-2 telomer alcohol feeding in mice: Formation of perfluorooctanoic acid in the liver. *Toxicological Sciences*, *86*, 231-238.

Kudo, N.; Katakura, M.; Sato, Y.; Kawashima, Y. 2002. Sex hormone-regulated renal transport of perfluorooctanoic acid. *Chemico-Biological Interactions*, *139*, 301-316.

Kudo, N.; Suzuki-Nakajima, E.; Mitsumoto, A.; Kawashima, Y. 2006. Responses of the liver to perfluorinated fatty acids with different carbon chain length in male and female mice: In relation to induction of hepatomegaly, peroxisomal beta-oxidation and microsomal 1-acylglycerophosphocholine acyltransferase. *Biological & Pharmaceutical Bulletin*, *29*, 1952-1957.

Kudo, N.; Suzuki, E.; Katakura, M.; Ohmori, K.; Noshiro, R.; Kawashima, Y. 2001. Comparison of the elimination between perfluorinated fatty acids with different carbon chain length in rats. *Chemico-Biological Interactions*, *134*, 203-216.

Lau, C.; Anitole, K.; Hodes, C.; Lai, D.; Pfahles-Hutchens, A.; Seed, J. 2007. Perfluoroalkyl acids: A review of monitoring and toxicological findings. *Toxicological Sciences*, *99*, 366-394.

Lau, C.; Butenhoff, J. L.; Rogers, J. M. 2004. The developmental toxicity of perfluoroalkyl acids and their derivatives. *Toxicology and Applied Pharmacology*, *198*, 231-241.

Lei, Y. D.; Wania, F.; Mathers, D.; Mabury, S. A. 2004. Determination of vapor pressures, octanol-air, and water-air partition coefficients for polyfluorinated sulfonamide, sulfonamidoethanols, and telomer alcohols. *Journal of Chemical and Engineering Data*, *49*, 1013-1022.

Loewen, M.; Halldorson, T.; Wang, F. Y.; Tomy, G. 2005. Fluorotelomer carboxylic acids and PFOS in rainwater from an urban center in Canada. *Environmental Science & Technology*, *39*, 2944-2951.

Loewen, M.; Wania, F.; Wang, F. Y.; Tomy, G. 2008. Altitudinal transect of atmospheric and aqueous fluorinated organic compounds in western Canada. *Environmental Science & Technology*, *42*, 2374-2379.

Luebker, D. J.; Case, M. T.; York, R. G.; Moore, J. A.; Hansen, K. J.; Butenhoff, J. L. 2005. Two-generation reproduction and cross-foster studies of perfluorooctanesulfonate (PFOS) in rats. *Toxicology*, *215*, 126-148.

Luek, J.; Dickhut, R. M.; Cochran, M.; Geisz, H. N. 2008. Persistent organic pollutants in air over the Atlantic and Southern Oceans. *SETAC North America 29th Meeting, Tampa, USA, Poster*.

Lunde, G.; Bjorseth, A. 1977. Polycyclic aromatic-hydrocarbons in long-range transported aerosols. *Nature*, *268*, 518-519.

Manchester-Neesvig, J. B.; Andren, A. W. 1989. Seasonal variation in the atmospheric concentration of polychlorinated biphenyl congeners. *Environmental Science &Technology*, *23*, 1138-1148.

Maras, M.; Vanparys, C.; Muylle, F.; Robbens, J.; Berger, U.; Barber, J. L.; Blust, R.; De Coen, W. 2006. Estrogen-like properties of fluorotelomer alcohols as revealed by MCF-7 breast cancer cell proliferation. *Environmental Health Perspectives*, *114*, 100-105.

Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. 2006. Atmospheric chemistry of perfluoroalkanesulfonamides: Kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. *Environmental Science & Technology*, *40*, 864-872.

Martin, J. W.; Mabury, S. A.; O'Brien, P. J. 2005. Metabolic products and pathways of fluorotelomer alcohols in isolated rat hepatocytes. *Chemico-Biological Interactions*, *155*, 165-180.

Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. 2003. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (Oncorhynchus mykiss). *Environmental Toxicology and Chemistry*, *22*, 196-204.

Martin, J. W.; Muir, D. C. G.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. 2002. Collection of airborne fluorinated organics and analysis by gas chromatography/chemical ionization mass spectrometry. *Analytical Chemistry*, *74*, 584-590.

Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C. G.; Mabury, S. A. 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environmental Science & Technology*, *38*, 373-380.

McLachlan, M. S.; Holmstrom, K. E.; Reth, M.; Berger, U. 2007. Riverine discharge of perfluorinated carboxylates from the European continent. *Environmental Science & Technology*, *41*, 7260-7265.

Midasch, O.; Angerer, J. 2006. Pilot study on the perfluorooctanesulfonate and perfluorooctanoic acid exposure of the general population. *Epidemiology*, *17*, S176-S176.

Montone, R. C.; Taniguchi, S.; Boian, C.; Weber, R. R. 2005. PCBs and chlorinated pesticides (DDTs, HCHs, and HCB) in the atmosphere of the southwest Atlantic and Antarctic oceans. *Marine Pollution Bulletin*, *50*, 778-782.

Moody, C. A.; Kwan, W. C.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. 2001. Determination of Perfluorinated Surfactants in Surface Water Samples by Two Independent Analytical Techniques: Liquid Chromatography/Tandem Mass Spectrometry and 19F NMR. *Analytical Chemistry*, *73*, 2200-2206.

Mulkiewicz, E.; Jastorff, B.; Skladanowski, A. C.; Kleszczynski, K.; Stepnowski, P. 2007. Evaluation of the acute toxicity of perfluorinated carboxylic acids using eukaryotic cell lines, bacteria and enzymatic assays. *Environmental Toxicology and Pharmacology*, *23*, 279-285.

Ohmori, K.; Kudo, N.; Katayama, K.; Kawashima, Y. 2003. Comparison of the toxicokinetics between perfluorocarboxylic acids with different carbon chain length. *Toxicology*, *184*, 135-140.

Olsen, G. W.; Burris, J. M.; Ehresman, D. J.; Froehlich, J. W.; Seacat, A. M.; Butenhoff, J. L.; Zobel, L. R. 2007. Half-life of serum elimination of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in retired fluorochemical production workers. *Environmental Health Perspectives*, *115*, 1298-1305.

Olsen, G. W.; Chang, S.-C.; Noker, P. E.; Gorman, G. S.; Ehresman, D. J.; Lieder, P. H.; Butenhoff, J. L. 2009. A comparison of the pharmacokinetics of perfluorobutanesulfonate (PFBS) in rats, monkeys, and humans. *Toxicology*, *256*, 65-74.

Olsen, G. W.; Logan, P. W.; Hansen, K. J.; Simpson, C. A.; Burris, J. M.; Burlew, M. M.; Vorarath, P. P.; Venkateswarlu, P.; Schumpert, J. C.; Mandel, J. H. 2003. An occupational exposure assessment of a perfluorooctanesulfonyl fluoride production site: biomonitoring. *AIHA Journal*, *64*, 651-659.

Oono, S.; Harada, K. H.; Mahmoud, M. A. M.; Inoue, K.; Koizumi, A. 2008a. Current levels of airborne polyfluorinated telomers in Japan. *Chemosphere*, *73*, 932-937.

Oono, S.; Matsubara, E.; Harada, K. H.; Takagi, S.; Hamada, S.; Asakawa, A.; Inoue, K.; Watanabe, I.; Koizumi, A. 2008b. Survey of airborne polyfluorinated telomers in Keihan area, Japan. *Bulletin of Environmental Contamination and Toxicology*, *80*, 102-106.

Panshin, S. Y.; Hites, R. A. 1994. Atmospheric concentrations of polychlorinated biphenyls in Bermuda. *Environmental Science & Technology*, *28*, 2001-2007.

Paul, A. G.; Jones, K. C.; Sweetman, A. J. 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. *Environmental Science & Technology*, *43*, 386-392.

Phillips, M. M.; Dinglasan-Panlilio, M. J. A.; Mabury, S. A.; Solomon, K. R.; Sibley, P. K. 2007. Fluorotelomer acids are more toxic than perfluorinated acids. *Environmental Science & Technology*, *41*, 7159-7163.

Piekarz, A. M.; Primbs, T.; Field, J. A.; Barofsky, D. F.; Simonich, S. 2007. Semivolatile fluorinated organic compounds in Asian and western U.S air masses. *Environmental Science & Technology*, *41*, 8248-8255.

Powley, C. R.; George, S. W.; Russell, M. H.; Hoke, R. A.; Buck, R. C. 2008. Polyfluorinated chemicals in a spatially and temporally integrated food web in the Western Arctic. *Chemosphere*, *70*, 664-672.

Powley, C. R.; Michalczyk, M. J.; Kaiser, M. A.; Buxton, L. W. 2005. Determination of perfluorooctanoic acid (PFOA) extractable from the surface of commercial cookware under simulated cooking conditions by LC/MS/MS. *Analyst*, *130*, 1299-1302.

Preston, M. R.; Merrett, J. 1991. The distribution and origins of the hydrocarbon fraction of particulate material in the North-Sea atmosphere. *Marine Pollution Bulletin*, *22*, 516-522.

Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. 2006. Sources, fate and transport of perfluorocarboxylates. *Environmental Science & Technology*, *40*, 32-44.

Primbs, T.; Piekarz, A.; Wilson, G.; Schmedding, D.; Higginbotham, C.; Field, J.; Simonich, S. M. 2008. Influence of Asian and Western United States urban areas and fires on the atmospheric transport of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and fluorotelomer alcohols in the Western United States. *Environmental Science & Technology*, *42*, 6385-6391.

Röschenthaler, G.-V. 2008. Fluor - ein Element für (fast) alle Fälle. *Münchner Beiträge zur Abwasser-, Fischerei- und Flussbiologie*, *59*, 11-33.

Sasaki, K.; Harada, K.; Saito, N.; Tsutsui, T.; Nakanishi, S.; Tsuzuki, H.; Koizumi, A. 2003. Impact of airborne perfluorooctane sulfonate on the human body burden and the ecological system. *Bulletin of Environmental Contamination and Toxicology*, *71*, 408-413.

Schenck, F. J.; Lehotay, S. J. 2000. Does further clean-up reduce the matrix enhancement effect in gas chromatographic analysis of pesticide residues in food? *Journal of Chromatography A*, *868*, 51-61.

Schenker, U.; Scheringer, M.; Macleod, M.; Martin, J. W.; Cousins, I. T.; Hungerbuhlert, K. 2008. Contribution of volatile precursor substances to the flux of perfluorooctanoate to the arctic. *Environmental Science & Technology*, *42*, 3710-3716.

Scott, B. F.; Spencer, C.; Mabury, S. A.; Muir, D. C. G. 2006. Poly- and perfluorinated carboxylates in north American precipitation. *Environmental Science & Technology*, *40*, 7167-7174.

Shoeib, M.; Harner, T.; Ikonomou, M.; Kannan, K. 2004. Indoor and outdoor air concentrations and phase partitioning of perfluoroalkyl sulfonamides and polybrominated diphenyl ethers. *Environmental Science & Technology*, *38*, 1313-1320.

Shoeib, M.; Harner, T.; Vlahos, P. 2006. Perfluorinated chemicals in the Arctic atmosphere. *Environmental Science & Technology*, *40*, 7577-7583.

Shoeib, M.; Harner, T.; Wilford, B. H.; Jones, K. C.; Zhu, J. P. 2005. Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: Occurrence, partitioning, and human exposure. *Environmental Science & Technology*, *39*, 6599-6606.

Simons, J. H. 1949. Electrochemical process for the production of fluorocarbons. *Journal of the Electrochemical Society*, *95*, 47-67.

Sinclair, E.; Kim, S. K.; Akinleye, H. B.; Kannan, K. 2007. Quantitation of gas-phase perfluoroalkyl surfactants and fluorotelomer alcohols released from nonstick cookware and microwave popcorn bags. *Environmental Science & Technology*, *41*, 1180-1185.

Skutlarek, D.; Exner, M.; Farber, H. 2006. Perfluorinated surfactants in surface and drinking water. *Environmental Science and Pollution Research*, *13*, 299-307.

Slemr, F.; Seiler, W.; Schuster, G. 1981. Latitudinal distribution of mercury over the Atlantic Ocean. *Journal of Geophysical Research, Sect. C: Oceans and Atmospheres*, *86*, 1159-1166.

Smithwick, M.; Mabury, S. A.; Solomon, K. R.; Sonne, C.; Martin, J. W.; Born, E. W.; Dietz, R.; Derocher, A. E.; Letcher, R. J.; Evans, T. J.; Gabrielsen, G. W.; Nagy, J.; Stirling, I.; Taylor, M. K.; Muir, D. C. G. 2005. Circumpolar study of perfluoroalkyl contaminants in polar bears (Ursus maritimus). *Environmental Science & Technology*, *39*, 5517-5523.

Smithwick, M.; Norstrom, R. J.; Mabury, S. A.; Solomon, K.; Evans, T. J.; Stirling, I.; Taylor, M. K.; Muir, D. C. G. 2006. Temporal trends of perfluoroalkyl contaminants in polar bears (Ursus maritimus) from two locations in the North American Arctic, 1972-2002. *Environmental Science & Technology*, *40*, 1139-1143.

So, M. K.; Miyake, Y.; Yeung, W. Y.; Ho, Y. M.; Taniyasu, S.; Rostkowski, P.; Yamashita, N.; Zhou, B. S.; Shi, X. J.; Wang, J. X.; Giesy, J. P.; Yu, H.; Lam, P. K. S. 2007.

Perfluorinated compounds in the Pearl River and Yangtze River of China. *Chemosphere*, *68*, 2085-2095.

Solignac, G.; Mellouki, A.; Le Bras, G.; Yujing, M.; Sidebottom, H. 2007. The gas phase tropospheric removal of fluoroaldehydes (CxF2x +1CHO, x=3, 4, 6). *Physical Chemistry Chemical Physics*, *9*, 4200-4210.

Stock, N. L.; Furdui, V. I.; Muir, D. C. G.; Mabury, S. A. 2007. Perfluoroalkyl contaminants in the canadian arctic: Evidence of atmospheric transport and local contamination. *Environmental Science & Technology*, *41*, 3529-3536.

Stock, N. L.; Lau, F. K.; Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. 2004. Polyfluorinated telomer alcohols and sulfonamides in the north American troposphere. *Environmental Science & Technology*, *38*, 991-996.

Stock, N. L.; Muir, D.; Mabury, S. A. 2005. Airborne perfluorinated sulfonamides and telomer alcohols in Toronto: a long-term study. *Fluoros, Toronto*, *Poster*.

Sulbaek Andersen, M. P.; Nielsen, O. J.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. 2005. Atmospheric chemistry of 4 : 2 fluorotelomer alcohol (n-C4F9CH2CH2OH): Products and mechanism of Cl atom initiated oxidation in the presence of NOx. *Journal of Physical Chemistry A*, *109*, 1849-1856.

Sulbaek Andersen, M. P.; Toft, A.; Nielsen, O. J.; Hurley, M. D.; Wallington, T. J.; Chishima, H.; Tonokura, K.; Mabury, S. A.; Martin, J. W.; Ellis, D. A. 2006. Atmospheric chemistry of perfluorinated aldehyde hydrates (n-CxF2x+1CH(OH)2, x = 1, 3, 4): hydration, dehydration, and kinetics and mechanism of Cl atom and OH Radical initiated oxidation. *Journal of Physical Chemistry A*, *110*, 9854-9860.

Tao, L.; Kannan, K.; Kajiwara, N.; Costa, M. M.; Fillmann, G.; Takahashi, S.; Tanabe, S. 2006. Perfluorooctanesulfonate and related fluorochemicals in albatrosses, elephant seals, penguins, and Polar Skuas from the Southern Ocean. *Environmental Science & Technology*, *40*, 7642-7648.

Tao, L.; Kannan, K.; Wong, C. M.; Arcaro, K. F.; Butenhoff, J. L. 2008a. Perfluorinated compounds in human milk from Massachusetts, USA. *Environmental Science & Technology*, *42*, 3096-3101.

Tao, L.; Ma, J.; Kunisue, T.; Libelo, E. L.; Tanabe, S.; Kannan, K. 2008b. Perfluorinated compounds in human breast milk from several Asian countries, and in infant formula and dairy milk from the United States. *Environmental Science & Technology*, *42*, 8597-8602.

Thuens, S.; Dreyer, A.; Sturm, R.; Temme, C.; Ebinghaus, R. 2008. Determination of the octanol-air partition coefficient (K_{OA}) of fluorotelomer alcohols. *Journal of Chemical and Engineering Data*, *53*, 223-227.

Tomy, G. T.; Tittlemier, S. A.; Palace, V. P.; Budakowski, W. R.; Braekevelt, E.; Brinkworth, L.; Friesen, K. 2004. Biotransformation of N-ethyl perfluorooctanesulfonamide by rainbow trout (Onchorhynchus mykiss) liver microsomes. *Environmental Science & Technology*, *38*, 758-762.

Trudel, D.; Horowitz, L.; Wormuth, M.; Scheringer, M.; Cousins, I. T.; Hungerbuhler, K. 2008. Estimating consumer exposure to PFOS and PFOA. *Risk Analysis*, *28*, 807-807.

US-EPA 2000. Sulfonated perfluorochemicals in the environment: sources, dispersion, fate and effects. *EPA docket*, EPA-HQ-OPPT-2002-0043-0005. http://www.rulemaking.com/browse/fdms/document/EPA-HQ-OPPT-2002-0043.

US-EPA 2002. Perfluoroalkyl Sulfonates; Significant New Use Rule; Final Rule and Supplemental Proposed Rule. *Federal Register*, *67*.

US-EPA 2006. 2010/15 PFOA Stewardship Program. http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html.

Van de Vijver, K. I.; Hoff, P.; Das, K.; Brasseur, S.; Van Dongen, W.; Esmans, E.; Reijnders, P.; Blust, R.; De Coen, W. 2005. Tissue distribution of perfluorinated chemicals in harbor seals (Phoca vitulina) from the Dutch Wadden Sea. *Environmental Science & Technology*, *39*, 6978-6984.

Van Leeuwen, S. P. J.; Karrman, A.; Van Bavel, B.; De Boer, J.; Lindstrom, G. 2006. Struggle for quality in determination of perfluorinated contaminants in environmental and human samples. *Environmental Science & Technology*, *40*, 7854-7860.

Vestergren, R.; Cousins, I. T.; Trudel, D.; Wormuth, M.; Scheringer, M. 2008. Estimating the contribution of precursor compounds in consumer exposure to PFOS and PFOA. *Chemosphere*, *73*, 1617-1624.

Voelkel, W.; Genzel-Boroviczeny, O.; Demmelmair, H.; Gebauer, C.; Koletzko, B.; Twardella, D.; Raab, U.; Fromme, H. 2008. Perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA) in human breast milk: results of a pilot study. *International Journal of Hygiene and Environmental Health*, *211*, 440-446.

Wallington, T. J.; Hurley, M. D.; Xia, J.; Wuebbles, D. J.; Sillman, S.; Ito, A.; Penner, J. E.; Ellis, D. A.; Martin, J.; Mabury, S. A.; Nielsen, O. J.; Andersen, M. P. S. 2006. Formation of C7F15COOH (PFOA) and other perfluorocarboxylic acids during the atmospheric oxidation of 8 : 2 fluorotelomer alcohol. *Environmental Science & Technology*, *40*, 924-930.

Wallington, T. J.; Nielsen, O. J. Atmospheric chemistry and environmental impact of hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs). In *The Handbook of Environmental Chemistry*; Neilson, A. H., Ed.; Springer: Berlin, 2002; Vol. 3, Part N Organofluorines, pp 85-102.

Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Capka, V.; Berti, W. R.; Gannon, J. T. 2005. Fluorotelomer alcohol biodegradation - Direct evidence that perfluorinated carbon chains breakdown. *Environmental Science & Technology*, *39*, 7516-7528.

Wania, F. 2007. A global mass balance analysis of the source of perfluorocarboxylic acids in the Arctic ocean. *Environmental Science & Technology*, *41*, 4529-4535.

Wei, S.; Chen, L. Q.; Taniyasu, S.; So, M. K.; Murphy, M. B.; Yamashita, N.; Yeung, L. W. Y.; Lam, P. K. S. 2007. Distribution of perfluorinated compounds in surface seawaters between Asia and Antarctica. *Marine Pollution Bulletin*, *54*, 1813-1818.

Yamashita, N.; Taniyasu, S.; Petrick, G.; Wei, S.; Gamo, T.; Lam, P. K. S.; Kannan, K. 2008. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. *Chemosphere*, *70*, 1247-1255

Yang, Q.; Abedi-Valugerdi, M.; Xie, Y.; Zhao, X. Y.; Moller, G.; Nelson, B. D.; DePierre, J. W. 2002. Potent suppression of the adaptive immune response in mice upon dietary exposure to the potent peroxisome proliferator, perfluorooctanoic acid. *International Immunopharmacology*, *2*, 389-397.

Yang, Q.; Xie, Y.; Depierre, J. W. 2000. Effects of peroxisome proliferators on the thymus and spleen of mice. *Clinical and Experimental Immunology*, *122*, 219-226.

Yarwood, G.; Kemball-Cook, S.; Keinath, M.; Waterland, R. L.; Korzeniowski, S. H.; Buck, R. C.; Russell, M. H.; Washburn, S. T. 2007. High-resolution atmospheric modeling of fluorotelomer alcohols and perfluorocarboxylic acids in the north American troposphere. *Environmental Science & Technology*, *41*, 5756-5762.

Young, C. J.; Furdui, V. I.; Franklin, J.; Koerner, R. M.; Muir, D. C. G.; Mabury, S. A. 2007. Perfluorinated acids in arctic snow: New evidence for atmospheric formation. *Environmental Science & Technology*, *41*, 3455-3461.

Zushi, Y.; Takeda, T.; Masunaga, S. 2008. Existence of nonpoint source of perfluorinated compounds and their loads in the Tsurumi River basin, Japan. *Chemosphere*, *71*, 1566-1573.

Contributions to the Included Studies

Study 1: An Optimized Method Avoiding Solvent-Induced Response Enhancement in the Analysis of Volatile and Semi-Volatile Polyfluorinated Alkylated Compounds Using Gas Chromatography-Mass Spectrometry

Authors: Annekatrin Dreyer, Christian Temme, Renate Sturm, Ralf Ebinghaus

A. Dreyer	85 %	concept, laboratory work, data evaluation and discussion, manuscript preparation
C. Temme	5 %	data discussion, comments on the manuscript
R. Sturm	5 %	data discussion, comments on the manuscript
R. Ebinghaus	5 %	comments on the manuscript

Study 2: Annual Time Series of Air Concentrations of Polyfluorinated Compounds

Authors: Annekatrin Dreyer, Volker Matthias, Christian Temme, Ralf Ebinghaus

A. Dreyer	80 %	concept, laboratory work, data evaluation and discussion, manuscript preparation
V. Matthias	10 %	trajectory analyses, data discussion, comments on the manuscript
C. Temme	5 %	concept, comments on the manuscript
R. Ebinghaus	5 %	concept, comments on the manuscript

Study 3: Polyfluorinated Compounds in Ambient Air from Ship- and Land-Based Measurements in Northern Germany

Authors: Annekatrin Dreyer, Ralf Ebinghaus

A. Dreyer	95 %	concept, field & laboratory work, data evaluation and discussion, manuscript preparation
R. Ebinghaus	5 %	concept, comments on the manuscript

Study 4: Polyfluorinated Compounds in the Atmosphere of the Atlantic and Southern Ocean: Evidence for a Global Distribution

Authors: Annekatrin Dreyer, Ingo Weinberg, Christian Temme, and Ralf Ebinghaus

A. Dreyer	80 %	concept, arrangement of sampling campaigns, field & laboratory work, data evaluation and discussion, manuscript preparation
I. Weinberg	10 %	field & laboratory work, comments on the manuscript
C. Temme	5 %	concept, comments on the manuscript
R. Ebinghaus	5 %	concept, comments on the manuscript

CUMULATIVE STUDY

Study 1

An Optimized Method Avoiding Solvent-Induced Response Enhancement in the Analysis of Volatile and Semi-Volatile Polyfluorinated Alkylated Compounds Using Gas Chromatography-Mass Spectrometry

Annekatrin Dreyer, Christian Temme, Renate Sturm, Ralf Ebinghaus

Journal of Chromatography A (2008), 1178, pp 199-205

An Optimized Method Avoiding Solvent-Induced Response Enhancement in the Analysis of Volatile and Semi-Volatile Polyfluorinated Alkylated Compounds Using Gas Chromatography-Mass Spectrometry

Annekatrin Dreyer, Christian Temme, Renate Sturm, and Ralf Ebinghaus

Institute for Coastal Research, GKSS Research Centre Geesthacht, Max Planck Str. 1, 21502 Geesthacht, Germany

Abstract

A method for the analysis of airborne (semi-)volatile polyfluorinated alkyl substances (PFAS) was optimized to avoid solvent-induced response enhancements as observed using ethyl acetate as extraction solvent (recoveries up to 300 %, likely due to acetic acid as impurity). Of nine solvents tested, only the use of acetone, DCM, MTBE, and acetone:petroleum ether 1:1 (v:v) resulted in recoveries below 100 % and acetone:MTBE 1:1 (v:v) was chosen as suited extraction solvent. An appropriate GC capillary column and the application of mass-labeled internal standards appeared to be essential for these analyses. Instrumental LOD of <0.2 (Me_2FOSA, EtFOSA D_5, MeFOSA D_3) to 8.2 (PFOSA) pg and LOQ of 0.4 (Me_2FOSA, EtFOSA D_5, MeFOSA D_3) pg to 16.4 (PFOSA) pg were determined.

Keywords

Fluorotelomer alcohols; FTOH, perfluoroalkyl sulfonamides, perfluoroalkylsulfonamido ethanols, PFAS, PFC, matrix effect, acetic acid

1. Introduction

Perfluorocarboxylic and -sulfonic acids such as PFOA and PFOS belong to the group of polyfluorinated organic compounds that have been distributed globally in the past due to extensive industrial application and consumer use (Berger, 2004; Giesy and Kannan, 2001;

Martin et al., 2004; Prevedouros et al., 2006; Smithwick et al., 2006; Young et al., 2007; Young et al., 2005). Atmospheric transport and subsequent degradation of volatile and semi-volatile precursor compounds like fluorotelomer alcohols (FTOH), perfluorinated sulfonamides (FASA) and perfluorinated sulfonamido ethanols (FASE) to the persistent acids, is assumed to be a main transport mechanism (Barber et al., 2007; Ellis et al., 2004; Jahnke et al., 2007b; Martin et al., 2002; Shoeib et al., 2006; Wallington et al., 2006).

FTOH, FASA, and FASE have been analysed in air samples of laboratory (smog-chamber studies, determination of partitioning coefficients) (D'Eon et al., 2006; Ellis et al., 2004; Goss et al., 2006; Hurley et al., 2005; Lei et al., 2004; Martin et al., 2006) and environmental studies (Barber et al., 2007; Berger et al., 2005; Jahnke et al., 2007b; Shoeib et al., 2006; Shoeib et al., 2005). In general, substances in air were concentrated on XAD-2 (smog chamber studies) (Ellis et al., 2004), polyurethane foam (PUF, active and passive air sampling) (Shoeib et al., 2004; Shoeib et al., 2005), or a sandwich of both, usually PUF/XAD-2/PUF (active air sampling) (Barber et al., 2007; Jahnke et al., 2007a; Jahnke et al., 2007b; Martin et al., 2002; Shoeib et al., 2006). As common extraction solvent (in combination or alone), ethyl acetate was used (Barber et al., 2007; Ellis et al., 2004; Jahnke et al., 2007a; Jahnke et al., 2007c; Martin et al., 2002; Stock et al., 2004), however, acetone:petroleum ether (Shoeib et al., 2006) and methanol (Ellis et al., 2004) were also applied. Highly enhanced recoveries, partly exceeding 200 %, mainly of FASA and FASE but also for longer chain FTOH was a problem frequently observed in the analyses of (semi-)volatile polyfluorinated compounds using ethyl acetate as solvent (Barber et al., 2007; Berger et al., 2005; Jahnke et al., 2007a; Jahnke et al., 2007c). These increased recoveries were generally explained by matrix effects, i.e. that co-eluting parts of the sample matrix block active sites in the measurement system (usually GC-MS) leading to higher detection efficiencies in samples compared to standard solutions (Jahnke et al., 2007a; Schenck and Lehotay, 2000). However, enhanced recoveries observed in solvent blanks have not been explained (Jahnke et al., 2007a). This is of great importance since environmental concentrations of critical analytes might be overestimated if compound-specific mass-labeled internal standards were not used or were not available at the time of the studies. It is also noteworthy that some authors applied native compounds as standards for volume correction, e.g. 11:1 FA, which might result in enhanced recoveries as well (Jahnke et al., 2007a).

In this paper we present an optimized method for the analysis of gas-phase fluorotelomer alcohols, fluorotelomer acrylates, perfluorinated sulfonamides, and perfluorinated sulfonamido ethanols. By comparison of different extraction solvents we show that the choice of solvent for extraction should be thoroughly made to avoid adverse effects such as solvent-induced response enhancement as observed with ethyl acetate. Furthermore, we give evidence for the importance of appropriate mass-labeled internals standards to be used in the analysis of these (semi-)volatile substances.

2. Experimental

2.1. Chemicals

Standards, native compounds: perfluorobutyl ethanol (4:2 FTOH, 97 %, Aldrich, Munich, Germany), perfluorohexyl ethanol (6:2 FTOH, 97 %, Lancaster Synthesis, Frankfurt, Germany), perfluorooctyl ethanol (8:2 FTOH, 97 %, Lancaster Synthesis, Frankfurt, Germany), perfluorodecyl ethanol (10:2 FTOH, 97 %, Lancaster Synthesis, Frankfurt, Germany), perfluorododecyl ethanol (12:2 FTOH, DuPont), perfluoroheptyl methanol (7:1 FA, 97 %, Lancaster Synthesis, Frankfurt, Germany), perfluorononyl methanol (9:1 FA, 98 %, Lancaster Synthesis, Frankfurt, Germany), perfluoroundecyl methanol (11:1 FA, >90 %, Lancaster Synthesis, Frankfurt, Germany), perfluorotridecyl methanol (13:1 FA, 96 %, Lancaster Synthesis, Frankfurt, Germany), perfluorohexyl ethylacylate (6:2 FTA, 97 %, Aldrich, Munich, Germany), perfluorooctyl ethylacylate (8:2 FTA, 97 %, Fluorochem, UK), perfluorodecyl ethylacylate (10:2 FTA, 97 %, Fluorochem UK), n-methyl perfluorobutane sulfonamide (MeFBSA, 3M, USA), n-methyl perfluorooctane sulfonamide (MeFOSA, 3M, USA), n-ethyl perfluorooctane sulfonamide (EtFOSA, 95 %, ABCR, Karlsruhe, Germany), perfluorooctane sulfonamide (PFOSA, 3M, USA), dimethylperfluorooctane sulfonamide (Me_2FOSA, 98 %, Wellington Laboratories, Guelph, Canada), n-methyl perfluorobutane sulfonamido ethanol (MeFBSE, 3M, USA), n-methyl perfluorooctane sulfonamidoethanol (MeFOSE, 3M, USA), n-ethyl perfluorooctane sulfonamido ethanol (EtFOSE, Mabury group, University of Toronto, Canada). All native FOSAs/FOSEs were a mixture of linear and branched isomers at a ratio of approximately 70:30 (Jahnke et al., 2007a).

Internal standards, mass-labeled compounds: 2-Perfluorohexyl-(1,1-$^2H_2$)-(1,2-$^{13}C_2$)-ethanol (^{13}C 6:2 FTOH), 2-Perfluorooctyl-(1,1-$^2H_2$)-(1,2-$^{13}C_2$)-ethanol (^{13}C 8:2 FTOH), 2-Perfluorodecyl-(1,1-$^2H_2$)-(1,2-$^{13}C_2$)-ethanol (^{13}C 10:2 FTOH), methyl-D_3-perfluorooctane sulfonamid (D_3 MeFOSA), ethyl-D_5-perfluorooctane sulfonamid (D_5 EtFOSA), methyl-D_7-perfluorooctane sulfonamido ethanol (D_7 MeFOSE), ethyl-D_9-perfluorooctane sulfonamido ethanol (D_9 MeFOSE; all > 98 %, Wellington Laboratories, Guelph, Canada).

Internal standards for volume corrections, mass-labeled compounds: hexachlorobenzene $^{13}C6$ (^{13}C HCB, 97 %, Dr. Ehrensdorfer, Augsburg, Germany), 1,3,5-trichlorobenzene D_3 (TCB D_3, 98 %, Aldrich, Munich, Germany).

Solvents: ethyl acetate (SupraSolv, Merck, Darmstadt, Germany), acetone, ethyl acetate, toluene, butan-2-one, methyl-tert-butyl ether (MTBE), dichloromethane (DCM), tetrahydofuran (THF), petroleum ether (all Picograde, Promochem, Wesel, Germany).

2.2. Sample Preparation

Recovery experiments on solvents: Since it was observed that ethyl acetate lead to unusually high recoveries of some polyfluorinated compounds, different solvents (acetone, toluene, MTBE, DCM, butanone, acetone:petroleum ether 1:1 (v:v), and THF) were applied and evaluated in addition to ethyl acetate (Picograde and SupraSolv). The solvents were chosen because of similar polarity compared to ethyl acetate, their use in literature, and/or general laboratory use for semi-polar compounds. 100 µL of a standard solution containing 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 6:2 FTA, 8:2 FTA, 10:2 FTA, 7:1 FA, 9:1 FA, 11:1 FA, 13:1 FA, MeFOSE, EtFOSE, MeFOSA, EtFOSA, MeFBSA, MeFBSE, and Me_2FOSA in ethyl acetate were spiked at two concentration levels (100 pg μL^{-1}, 500 pg μL^{-1}) to 50 mL of each solvent. The solvents were firstly evaporated to about 1 mL using rotary evaporators and then to 200 µL using a gentle stream of nitrogen. Fifty µL of HCB (500 pg μL^{-1}) were added as injection standard prior to the measurement to correct for volume differences. In addition to these experiments, 100 µL of the analyte standard solution, at the same two concentration levels, and 50 µL of HCB were added to 100 µL of each solvent directly within the vial. All experiments were performed in triplicate.

Extraction experiments: To evaluate the extraction efficiency of three pre-selected solvents (acetone, MTBE, and DCM) in comparison to ethyl acetate, glass cartridges (Orbo Tubes 6000 Supelco, Munich, Germany) industrially filled with 25 g XAD-2 between two 6 cm polyurethane foam (PUF) plugs, were spiked with 50 µL of a standard solution containing 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 6:2 FTA, 8:2 FTA, 10:2 FTA, MeFOSE, EtFOSE, MeFOSA, EtFOSA, MeFBSA, MeFBSE, Me2FOSA, and PFOSA (200 pg μL^{-1}). As internal standard 50 µL of a solution containing ^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH, D_3 MeFOSA, D_5 EtFOSA, D_7 MeFOSE, and D_9 MeFOSE (200 pg μL^{-1}) were added. Solvent was filled into the cartridges until the entire sandwhich was covered with solvent. For the extraction, the solvent was allowed to soak for 1 hour (first extraction) and ½ hour (second extraction). After each extraction step, the remaining solvent in the cartridge was blown out using nitrogen. All cartridges were extracted twice and the solvent (approximately 350 mL) was evaporated with ethyl acetate as keeper to 150 µL using rotary evaporators and nitrogen. Fifty µL of the injection standard containing TCB D_3 and ^{13}C HCB (500 pg µL^{-1}) were added prior to the measurement to correct for volume differences. Experiments were performed in triplicate.

Confirmation of the quality of the chosen extraction solvent: Since it turned out that a mixture of acetone and MTBE might be a suitable alternative to ethyl acetate, 50 mL MTBE:acetone 1:1 (v:v) and two PUF/XAD-2/PUF cartridges were spiked with 50 µL of a standard solution containing 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 6:2 FTA, 8:2 FTA, 10:2 FTA, MeFOSE, EtFOSE, MeFOSA, EtFOSA, MeFBSA, MeFBSE, Me2FOSA, and PFOSA (200 pg µL^{-1}). Additionally the method was applied to two real samples which were collected at a site close to Hamburg within 3 days in June 2006 using high volume air samplers (about 1500 m³. 50 µL of the solution containing ^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH, D_3 MeFOSA, D_5 EtFOSA, D_7 MeFOSE, and D_9 MeFOSE (200 pg µL^{-1}) were added to all samples for correction of analyte recoveries. All cartridges were extracted twice with MTBE:acetone 1:1 (v:v) as described above. The solvent was evaporated with ethyl acetate as keeper to 150 µL using rotary evaporators and nitrogen. Fifty µL of the injection standard containing TCB D_3 and ^{13}C HCB (500 pg µL^{-1}) were added prior to the measurement to correct for volume differences.

2.3. Instrumental Analysis & Quantification

Quantification was performed by gas chromatography-mass spectrometry with positive chemical ionization (PCI) using the selected ion monitoring (SIM) mode. For confirmation, samples were also run in negative chemical ionization (NCI) mode. The 6890 GC (Agilent Technologies, Waldbronn, Germany) was equipped with a PTV inlet and coupled to a 5975 inert MS (Agilent Technologies, Waldbronn, Germany). The following previously optimized instrumental conditions were used: injection volume: 2 µL; injection mode: pulsed splitless; pulse pressure: 40 psi, initial inlet temperature 60 °C hold for 0.10 min; heating rate: 400 °C min^{-1} to 270 °C hold for 20.00 min; oven temperature program: initial oven temperature 50 °C hold for 2 min, 3 °C min^{-1} to 70 °C hold for 0 min, 10.00 °C min^{-1} to 130 °C hold for 0 min, 20 °C min^{-1} to 220 °C hold for 0 min, 120 °C min^{-1} to 275 °C hold for 5 min, 10 °C min^{-1} to 270 °C hold for 10 min; transferline temperature: 250 °C; column flow: 1.5 mL min $^{-1}$; carrier gas: He; reactant gas: CH_4; ion source temperature (PCI): 300 °C;

quadrupole temperature (PCI) 150 °C; ion source temperature (NCI): 150 °C; quadrupole temperature (NCI) 150 °C. The capillary column was thoroughly chosen in separate experiments (also see supplemental information), finally analytes were separated on a Supelcowax10 (Supelco, Munich, Germany) capillary column, 0.25 mm i.d., 0.25 µm film thickness, 60 m and 30 m for the evaluation of pure solvents, 60 m for the remaining experiments.

Recoveries of analytes spiked to 50 mL of pure solvents were calculated using standard solutions of the equal concentration levels in the same solvent. For quality assurance a five point calibration was measured with each set of solvent and used for control calculations of evaporated and not evaporated samples.

Quantification was based on peak areas. Analyte concentrations in the extraction experiments were calculated using a seven point calibration. Internal standards were used to correct for analyte losses. Based on the signal to noise ratio, the limit of detection was between 0.2 pg (various analytes) and 8.2 pg (PFOSA), the limit of quantification was between 0.4 pg (various analytes) and 16.4 pg (PFOSA, also see supplemental information).

2.4. Quality Assurance & Quality Control

All experiments were performed in a clean lab (class 10.000). Perfluorinated materials or fluorinated polymers were avoided. Silicon-Teflon septa were used for measurements (vials), however, extensive pre-tests showed no contamination with (semi-)volatile polyfluorinated compounds. The glassware was machine-washed, heated at 250 °C for twelve hours, and washed with the used solvent before use. Standard solutions were only used at room temperature. If not mentioned differently, mass-labeled injection standards and internal standards were used to correct for losses and irregularities during analysis and measurement. For each compound, one target ion (PCI) and one qualifier ion (PCI and/or NCI) were measured for the GC-MS identification of the compounds. If not mentioned differently, a seven point calibration was run with each set of samples measured. Linearity of the GC-MS measurements was determined as described in DIN 32645 (1994). Blank samples were measured to determine possible cross contamination of the entire method. No signals were found.

3. Results & Discussion

3.1. Recovery Experiments on Solvents

The recoveries of analytes spiked to 50 mL solvents are shown in figure 1-1. Recoveries varied among solvents. They were lowest for the most volatile analytes and increased with decreasing volatility. For some solvents (ethyl acetate, butanone, THF), recovery rates far above 100 % were achieved for analytes, generally of molecular weights above 400 g mol^{-1} which eluted relatively late. Analytes spiked to the solvent ethyl acetate resulted in recoveries between about 60 and 300 %. Except for MeFOSA, recoveries using ethyl acetate Picograde were slightly but not significantly lower than for ethyl acetate SupraSolv. Only the use of acetone, DCM, MTBE, and acetone:petroleum ether 1:1 resulted in analyte recoveries below or close to 100 %. No clear difference was found between both concentration levels tested. Analytes in pure (not evaporated) solvents showed no signal enhancements.

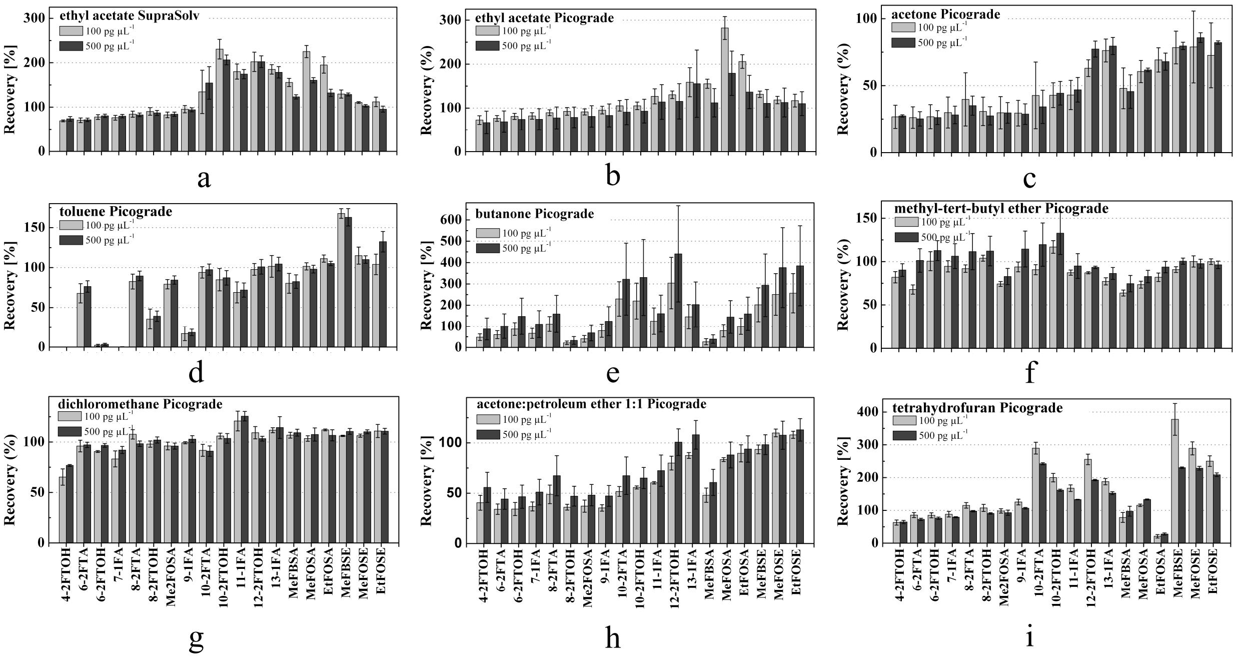


Figure 1-1: Average analyte recoveries (n=3) of different solvents at concentrations of 100 pg µL^{-1} and 500 pg µL^{-1}. Error bars are standard deviations. The analytes were measured using a 30 m Supelcowax10 capillary column and are aligned according to their retention time. a: ethyl acetate SupraSolv, b: ethyl acetate Picograde, c: acetone, d: toluene, e: butanone, f: methyl tert-butyl ether, g: dichloromethane, h: acetone:petroleum ether 1:1 (v:v), i: tetrahydrofuran. Note the differences in the ordinates' scale.

For some solvents, calculated recoveries were far above 100 % because analyte responses were strongly enhanced. This finding appeared unusual since no real-sample matrix was present in these experiments. In environmental samples the so called matrix effect is a well known problem. Co-extracted sample compounds block active sites in the GC-MS system and thus lead to greater analyte detection efficiency in the sample compared to the calibration standard (Schenck and Lehotay, 2000). However, in the recovery experiments performed here, no real-sample matrix was present and the solvent was the only matrix. Potential contamination leading to these effects was not discovered. Signal enhancement of MeFOSE and EtFOSE was also observed by other authors (Barber et al., 2007; Berger et al., 2005; Jahnke et al., 2007a). Some of these authors explained the presence of matrix effects only for real samples and PUF/XAD-2/PUF cartridges by the theory mentioned above, solvent-induced response enhancements observed for ethyl acetate were not further investigated (Jahnke et al., 2007a). The results clearly lead to two major consequences: Firstly, mass-labeled standards to correct for the high recovery rates should be applied whenever possible, which was already pointed out by Jahnke et al. (2007a) and Martin et al. (2002). The use of perfluoroalkyl methanols (X:1 FA) as used by some authors (Jahnke et al., 2007a; Martin et al., 2002) as correction substances is not advisable since these compounds are prone to strongly enhanced responses, however to different degrees compared to other analytes of interest. Secondly, solutions have to be found to overcome this problem since mass-labeled standards are not available for all analytes determined in this and other studies. This means that the reason for the solvent-induced response enhancement using ethyl acetate as extraction solvent has to be found and proper measures to avoid it are to be applied. Alternatively, another extraction solvent has to be chosen and its suitability in the analysis of (semi-)volatile polyfluorinated compounds is to be validated.

Figure 1-2 indicates a possible reason for enhanced analyte recoveries using ethyl acetate. A large peak with the mass to charge ratio (m/z) 61 was co-eluting with recovery-enhanced polyfluorinated compounds starting with 11:1 FA. The beginning of the m/z 61 peak was dependent on the column length and column quality. Since a freshly cut column was used for the measurements presented in figure 1-2 the peak started relatively late. With used columns, it already started at about the retention time of 8:2 FTOH.

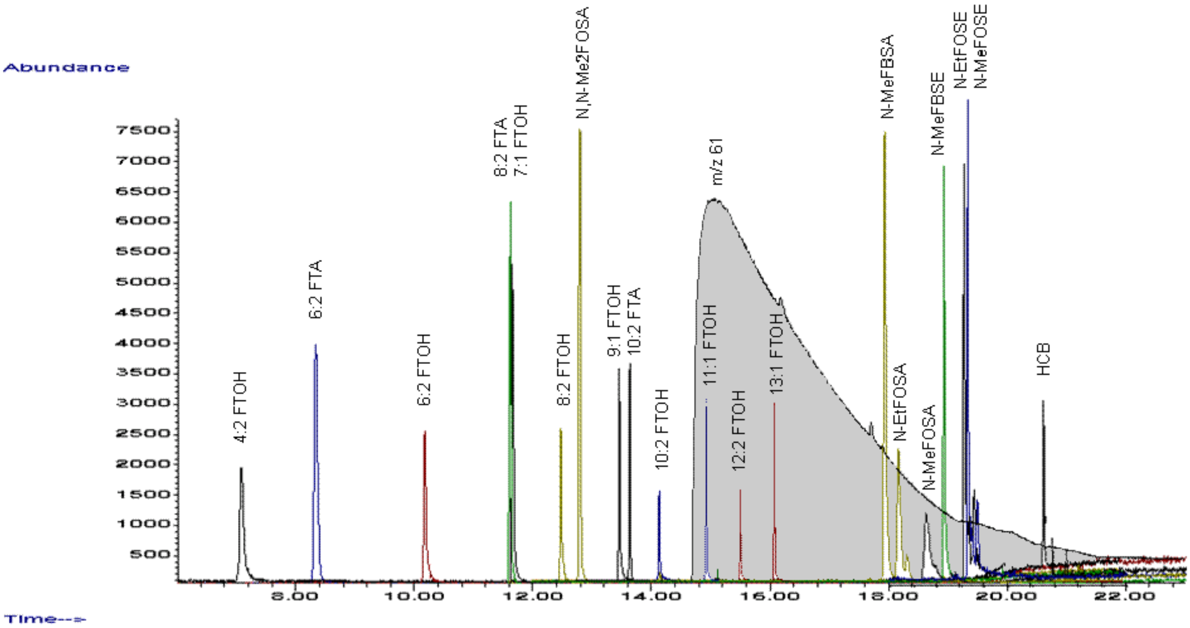


Figure 1-2: SIM chromatogram of polyfluorinated compounds and acetic acid (m/z 61, $CH_3CO(OH_2)^+$) measured in evaporated ethyl acetate SupraSolv using a 30 m Supelcowax10 capillary column. Note: abundance of m/z 61 x 100. m/z 61 was also detected in scan measurements.

The m/z 61 peak was assigned to acetic acid ($CH_3CO(OH_2)^+$ in PCI measurements), which is a common impurity of ethyl acetate (titrated acid < 0.0008 mass equivalents g^{-1}). Its presence was also validated in EI measurements. Due to the higher boiling point of acetic acid (118 °C) compared to ethyl acetate (77 °C), it is concentrated in the process of solvent evaporation to concentrations exceeding 50 pg μL^{-1} (figure 1-3) .The acetic acid might interfere with active sites of liner, column, and/or ion source of the GC-MS and thus lead to higher detection efficiencies of co-eluting analytes in the evaporated solvent compared to not evaporated solvent. Furthermore, acetic acid is a major decomposition product of ethyl acetate during chemical ionization (Jelus et al., 1974) and therefore might lead to interferences within the ion source (Schenck and Lehotay, 2000).

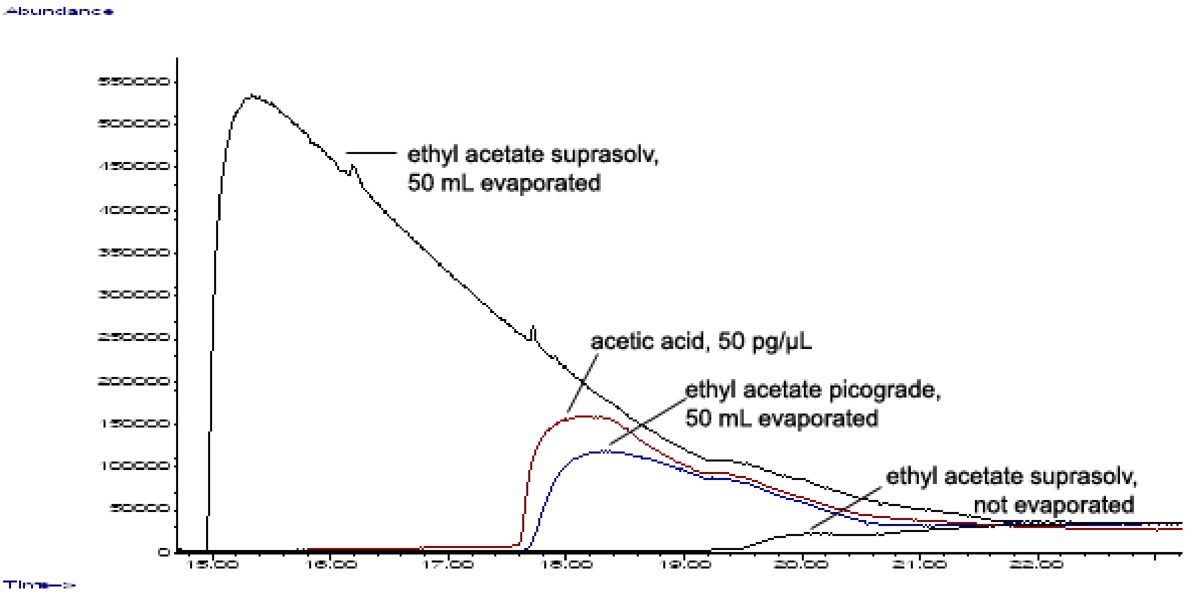


Figure 1-3: SIM chromatograms of acetic acid (m/z 61, $CH_3CO(OH_2)^+$) in evaporated ethyl acetate SupraSolv, evaporated ethyl acetate Picograde, ethyl acetate SupraSolv that did not undergo evaporation, and an acetic acid standard solution (50 pg µL^{-1}) in ethyl acetate using a 30 m Supelcowax10 capillary column.

Figure 1-4 shows that the use of a 60 m column instead of a 30 m column resulted in recoveries below 100 % for all analytes with ethyl acetate SupraSolv as solvent. This is explained by the enhanced separation of substances using the 60 m column. The acetic acid (m/z 61) peak was still present taking the 60 m column; however, it was situated right between the group of polyfluorinated alcohols and sulfonamides and therefore expressed no influence on the analytes. Hence, the use of a 60 m capillary column solves the problem of recoveries above 100 % using ethyl acetate as extraction solvent, however, the high acid concentrations in the samples shortens the lifetime of the capillary column significantly. As we showed, some other solvents did not show problematic recoveries. Therefore, we suggest a change of solvent instead (see below).

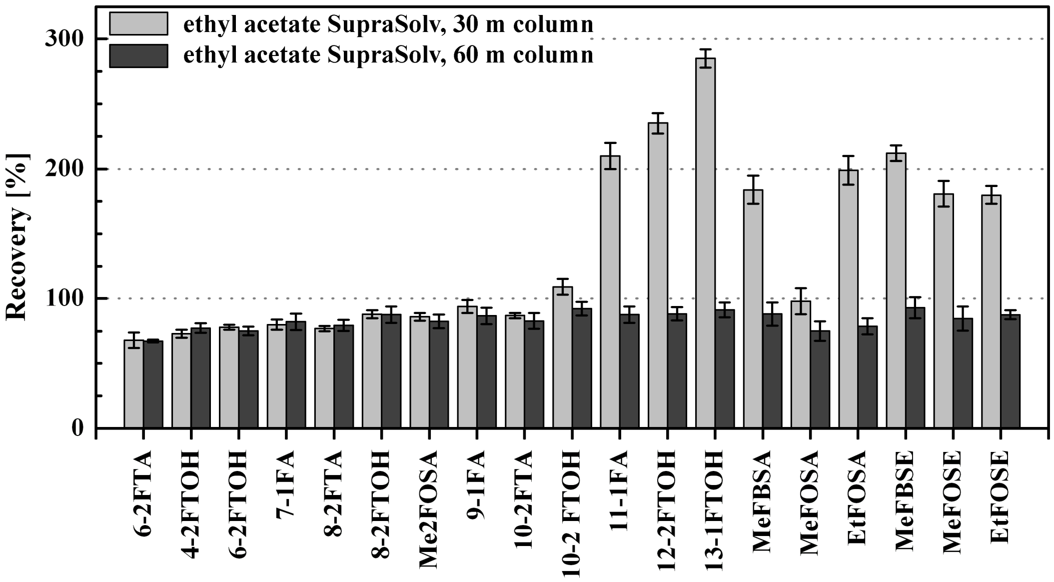


Figure 1-4: Recoveries of polyfluorinated compounds after the evaporation of 50 mL ethyl acetate SupraSolv using a 30 m and a 60 m Supelcowax10 capillary column.

3.2. Extraction Experiments

The following experiments were run on 60 m Supelcowax10 columns. The efficiency of the four pure solvents, which showed good results in the recovery experiments before (ethyl acetate SupraSolv, acetone, MTBE, DCM) to extract (semi-)volatile polyfluorinated compounds spiked to PUF/XAD-2/PUF cartridges is shown in figure 1-5. In general, all of the solvents were efficient to extract the analytes. For most analytes, recoveries using acetone, MTBE and DCM as solvents were comparable to or partly even higher than those of the established solvent ethyl acetate. We decided on taking a mixture of acetone and MTBE (1:1; v:v) as alternative solvent for ethyl acetate, since recoveries appeared to be more reproducible than those of DCM. Besides the higher toxicity compared to acetone and MTBE the use of DCM also led to more matrix background within the samples, making the solvent less suitable for extraction. The relative polarity of MTBE is slightly lower, the one of acetone little higher than that of ethyl acetate SupraSolv, giving a broader range of polarity for extraction and hence underlining the suitability of the mixture. Boiling points of MTBE and acetone (55.2 and 56.6 °C, respectively) are lower than that of ethyl acetate (77 °C), allowing a more gentle evaporation of the solvent during sample preparation and thus potentially resulting in higher recovery rates of the most volatile compounds (e.g. 4:2 FTOH, boiling point: 65 °C). The final confirmation of the suitability of acetone:MTBE 1:1 (v:v) is presented in figure 1-6. Recovery rates of almost all analytes were between 50 and 100 %.

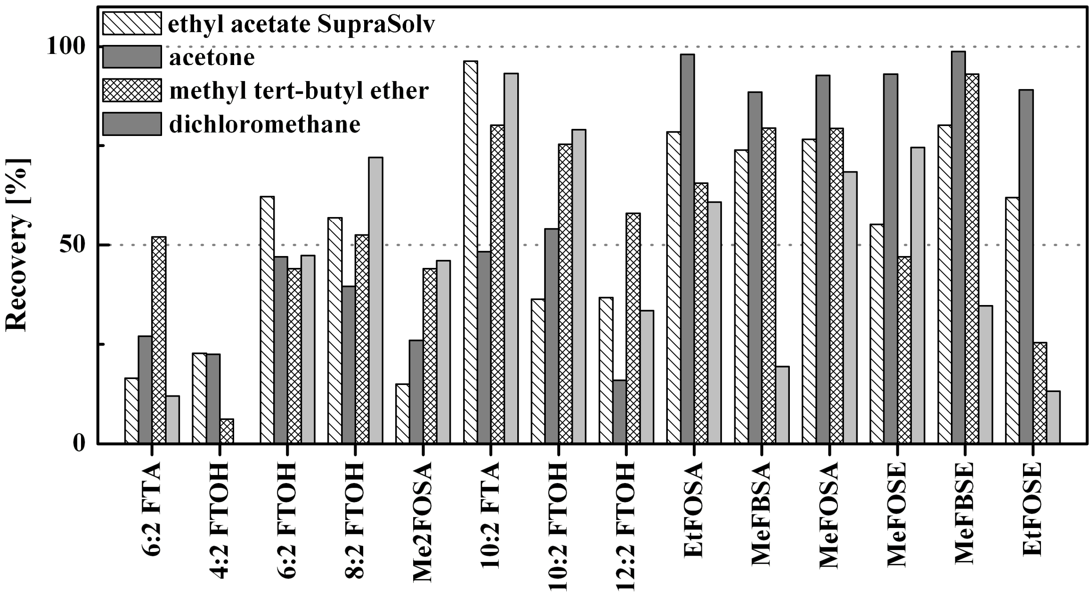


Figure 1-5: Average relative recoveries (n=3) of volatile and semi-volatile polyfluorinated compounds spiked to PUF/XAD-2/PUF cartridges using ethyl acetate SupraSolv, acetone, MTBE, and DCM as extraction solvents. Samples were measured using a 60 m Supelcowax10 capillary column.

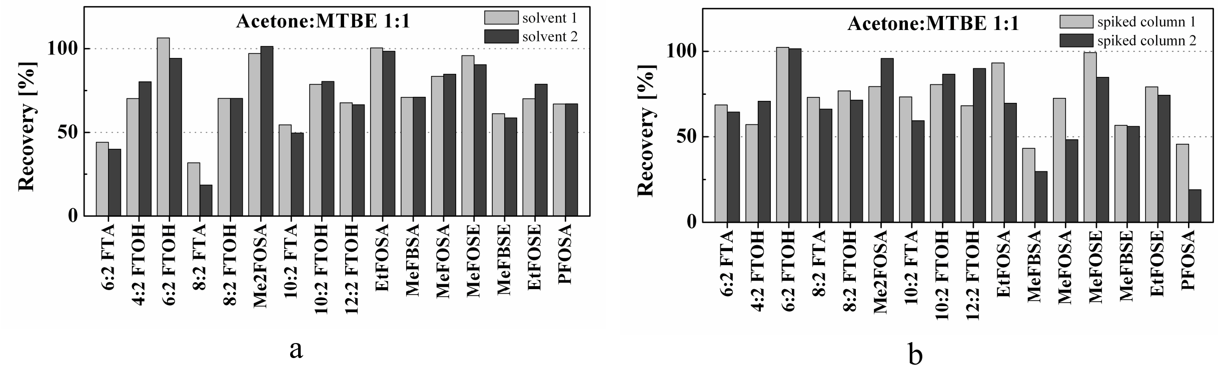


Figure 1-6: Relative recovery rates of (semi-)volatile fluorinated compounds using acetone:MTBE 1:1 (v:v) as extraction solvent. a: recoveries of analytes spiked to 50 mL acetone:MTBE 1.1 (v:v). b: recoveries of analytes spiked to PUF/XAD-2/PUF cartridges and extracted with acetone:MTBE 1:1 (v:v). Samples were measured using a 60 m Supelcowax10 capillary column.

The method was applied to real samples. Concentrations of target analytes are shown in table 1-1. 8:2 FTA and 10:2 FTA were found in low concentrations in these environmental samples. 8:2 FTOH showed maximum concentrations of all FTOH determined, which is consistent with previous results of other authors (Barber et al., 2007; Jahnke et al., 2007a; Jahnke et al., 2007b; Shoeib et al., 2006). 12:2 FTOH was found in low environmental concentrations comparable to those determined by Barber et al. (2007), 4:2 FTOH could not be detected. MeFBSA and MeFBSE were detected in similar concentrations than their C8 analogues and were comparable to results of Barber et al. (2007). Overall, environmental concentrations of ΣFTOH were higher than those of ΣFASA+FASE, or ΣFTA, confirming previous results of sampling in European environments (Barber et al., 2007; Jahnke et al., 2007a; Jahnke et al., 2007b) in contrast to some results of sampling in American environments (Martin et al., 2002; Shoeib et al., 2006; Stock et al., 2004). Interestingly, we observed Me_2FOSA, which is used as injection standard by various groups (Barber et al., 2007; Shoeib et al., 2006), in environmental samples. The occurrence of Me_2FOSA was confirmed by NCI measurements. Blank samples of pure solvents and PUF/XAD-2/PUF cartridges revealed no contamination. Carry-over within the GC-MS was not found to occur. Hence, we suggest the use of other, if possible mass-labeled injection standards for volume correction.

Table 1-1: Concentrations of volatile and semi-volatile compounds in air samples at a site close to Hamburg. Values in brackets: concentrations were below the smallest calibration standard. n.d.: analytes were not detected.

	gas-phase concentration (pg m^{-3})			gas-phase concentration (pg m^{-3})	
analyte	**sample 1**	**sample 2**	**analyte**	**sample 1**	**sample 2**
6:2 FTA	(0.2)	(0.2)	**12:2 FTOH**	7	12.4
4:2 FTOH	n.d.	n.d.	**EtFOSA**	2	2.3
6:2 FTOH	16	26	**MeFBSA**	4.7	5
8:2 FTA	(0.9)	(1.2)	**MeFOSA**	5.4	6.9
8:2 FTOH	97	104	**MeFOSE**	1.9	2.3
Me_2FOSA	0.2	0.2	**MeFBSE**	2.6	2.9
10:2 FTA	0.4	0.6	**EtFOSE**	0.4	0.6
10:2 FTOH	28	37	**PFOSA**	(0.4)	0.8

Overall, we optimized a method for the analysis of airborne volatile and semi-volatile polyfluorinated organic compounds such as FTOH, FTA, FASA, and/or FASE to avoid solvent-induced analyte response enhancements. Two possibilities to overcome the major problem of strongly enhanced recovery rates using ethyl acetate were shown: Firstly, using a 60 m capillary GC column reduce the risk of enhanced responses. Secondly, an maybe more important, solvent-induced response enhancement is avoided by changing the extraction solvent, e.g. to acetone:MTBE 1:1 (v:v). Three extraction steps involving about 500 mL solvent are most suited (see also the supporting information). We recommend a combination of these two measures. We want to emphasize again the use and thorough choice of mass-labeled compounds for recovery and volume correction.

Supplemental Information

Supplemental information is available, further elucidating some aspects of the method optimization, its validation, and the search for internal standards.

Acknowledgements

Annekatrin Dreyer was funded by the Scholarship Program of the German Federal Environmental Foundation (Deutsche Bundesstiftung Umwelt, DBU). Sabine Thüns and Armando Caba helped with analyses and valuable thoughts.

References

Barber, J. L.; Berger, M. L.; Chaemfa, C.; Huber, S.; Jahnke, A.; Temme, C.; Jones, K. C. 2007. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *Journal of Environmental Monitoring*, *9*, 530-541.

Berger, U. 2004. Perfluoroalkylated substances (PFAS) in water samples: An improved analytical method and results from Nordic samples. *SETAC Europe, Prague, Czech Republic, Poster*.

Berger, U.; Barber, J. L.; Jahnke, A.; Temme, C.; Jones, K. C. 2005. Analysis of fluorinated alkyl compounds in air samples from England. *Fluoros*, *Toronto, Canada*.

D'Eon, J. C.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. 2006. Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, C4F9SO2N(CH3)CH2CH2OH: Kinetics and mechanism of reaction with OH. *Environmental Science & Technology*, *40*, 1862-1868.

DIN 1994. DIN 32645: Chemische Analytik: Nachweis-, Erfassungs- und Bestimmungsgrenze, Ermittlung unter Wiederholungsbedingungen, Begriffe, Verfahren, Auswertung*; Beuth Verlag*.

Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. 2004. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environmental Science & Technology*, *38*, 3316-3321.

Giesy, J. P.; Kannan, K. 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environmental Science & Technology*, *35*, 1339-1342.

Goss, K. U.; Bronner, G.; Harner, T.; Monika, H.; Schmidt, T. C. 2006. The partition behavior of fluorotelomer alcohols and olefins. *Environmental Science & Technology*, *40*, 3572-3577.

Hurley, M. D.; Misner, J. A.; Ball, J. C.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A.; Andersen, M. P. S. 2005. Atmospheric chemistry of CF3CH2CH2OH: Kinetics, mechanisms and products of Cl atom and OH radical initiated oxidation in the presence and absence of NOX. *Journal of Physical Chemistry A*, *109*, 9816-9826.

Jahnke, A.; Ahrens, L.; Ebinghaus, R.; Berger, U.; Barber, J. L.; Temme, C. 2007a. An improved method for the analysis of volatile polyfluorinated alkyl substances in environmental air samples. *Analytical and Bioanalytical Chemistry*, *387*, 965-975.

Jahnke, A.; Ahrens, L.; Ebinghaus, R.; Temme, C. 2007b. Urban versus remote air concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany. *Environmental Science & Technology*, *41*, 745-752.

Jahnke, A.; Huber, S.; Ternme, C.; Kylin, H.; Berger, U. 2007c. Development and application of a simplified sampling method for volatile polyfluorinated alkyl substances in indoor and environmental air. *Journal of Chromatography A*, *1164*, 1-9.

Jelus, B. L.; Michnowi.J; Munson, B. 1974. Studies in Chemical Ionization Mass-Spectrometry - Mechanisms in Ester Spectra. *Journal of Organic Chemistry*, *39*, 2130-2131.

Lei, Y. D.; Wania, F.; Mathers, D.; Mabury, S. A. 2004. Determination of vapor pressures, octanol-air, and water-air partition coefficients for polyfluorinated sulfonamide, sulfonamidoethanols, and telomer alcohols. *Journal of Chemical and Engineering Data*, *49*, 1013-1022.

Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. 2006. Atmospheric chemistry of perfluoroalkanesulfonamides: Kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. *Environmental Science & Technology*, *40*, 864-872.

Martin, J. W.; Muir, D. C. G.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. 2002. Collection of airborne fluorinated organics and analysis by gas chromatography/chemical ionization mass spectrometry. *Analytical Chemistry*, *74*, 584-590.

Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C. G.; Mabury, S. A. 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environmental Science & Technology*, *38*, 373-380.

Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. 2006. Sources, fate and transport of perfluorocarboxylates. *Environmental Science & Technology*, *40*, 32-44.

Schenck, F. J.; Lehotay, S. J. 2000. Does further clean-up reduce the matrix enhancement effect in gas chromatographic analysis of pesticide residues in food? *Journal of Chromatography A*, *868*, 51-61.

Shoeib, M.; Harner, T.; Ikonomou, M.; Kannan, K. 2004. Indoor and outdoor air concentrations and phase partitioning of perfluoroalkyl sulfonamides and polybrominated diphenyl ethers. *Environmental Science & Technology*, *38*, 1313-1320.

Shoeib, M.; Harner, T.; Vlahos, P. 2006. Perfluorinated chemicals in the Arctic atmosphere. *Environmental Science & Technology*, *40*, 7577-7583.

Shoeib, M.; Harner, T.; Wilford, B. H.; Jones, K. C.; Zhu, J. P. 2005. Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: Occurrence, partitioning, and human exposure. *Environmental Science & Technology*, *39*, 6599-6606.

Smithwick, M.; Norstrom, R. J.; Mabury, S. A.; Solomon, K.; Evans, T. J.; Stirling, I.; Taylor, M. K.; Muir, D. C. G. 2006. Temporal trends of perfluoroalkyl contaminants in polar bears (Ursus maritimus) from two locations in the North American Arctic, 1972-2002. *Environmental Science & Technology*, *40*, 1139-1143.

Stock, N. L.; Lau, F. K.; Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. 2004. Polyfluorinated telomer alcohols and sulfonamides in the north American troposphere. *Environmental Science & Technology*, *38*, 991-996.

Wallington, T. J.; Hurley, M. D.; Xia, J.; Wuebbles, D. J.; Sillman, S.; Ito, A.; Penner, J. E.; Ellis, D. A.; Martin, J.; Mabury, S. A.; Nielsen, O. J.; Andersen, M. P. S. 2006. Formation of C7F15COOH (PFOA) and other perfluorocarboxylic acids during the atmospheric oxidation of 8 : 2 fluorotelomer alcohol. *Environmental Science & Technology*, *40*, 924-930.

Young, C. J.; Furdui, V. I.; Franklin, J.; Koerner, R. M.; Muir, D. C. G.; Mabury, S. A. 2007. Perfluorinated acids in arctic snow: New evidence for atmospheric formation. *Environmental Science & Technology*, *41*, 3455-3461.

Young, C. J.; Muir, D. C. G.; Koerner, R. M.; Mabury, S. A. 2005. Atmospheric Flux of Perfluorinated Acids into the high Arctic. *Fluoros, Toronto*, *Poster*.

Supporting Information

The supporting information covers the following topics:

14 pages, 7 tables, 6 figures

Mass Fragments of Volatile & Semi-Volatile Polyfluorinated Substances Analyzed in This Study

Table S1-1: Mass fragments of compounds analyzed in this study. m/z: mass to charge ratio. MW: Molecular Weight. TI: target ion. Q: qualifier ion. PCI: positive chemical ionization mode. NCI: negative chemical ionization mode. The mass-labeled internal standards were used to correct native substances as follows: [a]: 4:2 FTOH, 6:2 FTOH, 6:2 FTA; [b]: 8:2 FTOH, 8:2 FTA, Me$_2$FOSA; [c]: 10:2 FTOH, 10:2 FTA, 12:2 FTOH; [d]: EtFOSA; [e]: MeFOSA, MeFBSA; [f]: EtFOSE, PFOSA; [g]: MeFOSE, MeFBSE.

analyte	MW	m/z TI	m/z Q1 (PCI)	m/z Q2(NCI)
4:2 FTOH	264	265.0	227.0	-
6:2 FTOH	364	365.0	327.0	-
8:2 FTOH	464	465.0	427.0	-
10:2 FTOH	564	565.0	527.0	-
12:2 FTOH	664	665.1	627.0	-
7:1 FA	400	401.0	345.0	-
9:1 FA	500	501.0	445.0	-
11:1 FA	600	601.0	545.0	-
13:1 FA	700	701.0	645.0	-
6:2 FTA	418	419.0	447.1	-
8:2 FTA	518	519.1	547.1	-
10:2 FTA	618	619.1	647.1	-
EtFOSA	527	528.0	508.0	507.0
EtFOSE	571	554.0	572.1	508.0
MeFOSA	513	514.0	494.0	493.0
MeFOSE	557	540.0	558.0	494.0
MeFBSA	313	314.0	294.0	292.9
MeFBSE	357	340.0	358.0	293.2
Me2FOSA	527	528.0	444.0	483.0
PFOSA	499	500.0	381.0	478.9
^{13}C 6:2 FTOH[a]	368	369.1	331.0	-
^{13}C 8:2 FTOH[b]	468	469.0	431.0	-
^{13}C 10:2 FTOH[c]	568	569.0	531.0	-
EtFOSA D$_5$[d]	532	533.1	-	511.9
MeFOSA D$_3$[e]	516	517.0	-	495.9
EtFOSE D$_9$[f]	580	563.1	581.1	514.0
MeFOSE D$_7$[g]	564	547.1	565.1	497.9

Instrumental Limits of Detection (LOD) and Limits of Quantification (LOQ) of Environmentally Relevant Target Analytes and Mass-Labeled Internal Standards Analyzed in This Study

Table S1-2: Limits of detection (LOD) and limits of quantification (LOQ) based on the signal to noise ratios and on DIN32645 (1994). A substance was detectable with S/N exceeding 3 and quantifiable with S/N exceeding 10.

analyte	LOD (S/N) (pg µL^{-1})	LOQ (S/N) (pg µL^{-1})	LOD (DIN) (pg µL^{-1})	LOQ (DIN) (pg µL^{-1})
6:2 FTA	0.1	0.2	7	25
4:2 FTOH	0.8	1.1	6	20
6:2 FTOH ^{13}C	0.8	1.0	38	142
6:2 FTOH	0.9	1.1	6	20
8:2 FTA	0.1	0.2	4	13
8:2 FTOH ^{13}C	0.9	1.1	42	167
8:2 FTOH	0.8	1.0	8	28
Me_2FOSA	< 0.1	0.1	9	29
10:2 FTA	0.1	0.2	4	15
10:2 FTOH ^{13}C	0.4	0.8	60	203
10:2 FTOH	0.8	1.0	9	30
12:2 FTOH	0.8	1.0	26	87
EtFOSA D_5	< 0.1	0.1	12	44
EtFOSA	0.1	0.2	5	17
MeFBSA	0.1	0.2	6	22
MeFOSA D_3	< 0.1	0.1	51	173
MeFOSA	0.1	0.2	3	10
MeFOSE D_7	0.2	0.4	36	137
MeFOSE	0.1	0.2	10	35
EtFOSE D_9	0.2	0.4	46	156
MeFBSE	0.1	0.2	5	18
EtFOSE	0.2	0.4	7	22
PFOSA	4.1	8.2	10	34

Choice of the GC Capillary Column

The following four different capillary GC columns, each 30 m x 0.25 mm x 0.25 µm in size, were tested for their suitability for the measurement of polyfluorinated alcohols, sulfonamides, and sulfonamido ethanols: Varian CP-Wax 57 CB, used by (Jahnke et al 2007), Optima 210, Optima 17, Supelcowax 10. A standard solution containing 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, MeFOSE, EtFOSE, MeFOSA, and EtFOSA at two different concentration levels (800 pg μL^{-1}, 20 pg μL^{-1}) was injected and measured with the method described in the paper. Suitability for the analysis of volatile and semi-volatile polyfluorinated compounds was evaluated in terms of separation, analyte signal to noise ratio, and column bleeding (table S1-3). Since analyte separation was much better, column bleeding much lower, and the allowed maximum temperature higher (higher heating to clean GC column) using the Supelcowax 10 column this one was chosen for further analyses. Note that the solvent-induced response enhancements did depend only upon the column length, not upon the column type.

Table S1-3: Characteristics of four capillary columns evaluated for the analysis of (semi-)volatile polyfluorinated substances.

	Varian CP Wax 57 CB	Optima 210	Optima 17	Supelcowax10
manufacturer	Varian	Macherey/Nagel	Macherey/Nagel	Supelco
phase	bonded polyethylenglycol	trifluoropropyl-methylpolysiloxane (50 % trifluoropropyl)	phenyl-methylpolysiloxane (50 % phenyl)	bonded polyethylenglycol
suited for	polar analytes such as alcohols or halogenated compounds	polar analytes in environmental analyses, among others FTOH	medium polar analytes such as steroids or pesticides	polar compounds such as alcohols, fatty acid methylester
maximum temperature	240	280	300	280
separation of PFC	good	good for FTOH only	good	very good
S/N	high	low	very low	high
column bleeding	high	high	Low	low

Search for Suitable Injection Standards

Extensive search was performed to find a suitable standard for volume corrections. The proper standard was to meet the following demands: give a strong and reliable signal in the PCI mode, elute from the GC column in the range of the fluorinated analytes, not subject to signal enhancement due to typical matrix effects. Table S1-4 shows a list of compounds tested. Finally, mass-labeled tichlorobenzene (TCB) and hexachlorobenzene (HCB) were chosen. They reduced the standard deviation of multi measurements significantly (95 %, t-test) at concentrations of 200 pg µL^{-1} and 40 pg µL^{-1}. The difference was not significant anymore at 1 pg µL^{-1} (Table S1-5, S1-6, S1-7).

Table S1-4: Substances evaluated for their suitability as injection standard. MW: molecular weight. BP: boiling point. RT: retention time of peak. m/z: mass/charge ratio. TI: target ion.

compound name	MW (g/mol)	PB (°C)	RT in analytes range?	general remarks	m/z TI (PCI)
1,3,5-trichlorobenzene D_3	181	220	Yes	not found in environmental samples, no matrix influence	184
2,4,5-trichlorophenol	198	246	Yes	no matrix influence	197
2,4 dichloro-phenoxyacetate	221	160	no peak	-	-
3,4-dichlorophenol	163	210	No	too late	163
7:1 FA	400	161	Yes	signal enhancement in env. samples	401
9:1 FA	500	193	Yes	signal enhancement in env. samples	501
11:1 FA	600	228	Yes	signal enhancement in env. samples	601
13:1 FA	700	260	Yes	signal enhancement in env. samples	701
acenaphthene D_{10}	154	280	No	too late	165
acenaphthylene	152	280	Yes	low abundance	153
decanol	158	233	No	m/z too low	97
dichloprop	221	160	no peak	-	-
dinitrobenzol	168	303	No	too late	139; 169
diuron	233	180	no peak	-	-
endrin	381	245	No	too late	349
ethion	385	165	Yes	break down into 3 peaks	199; 215, …
fenitrothion	277	140	Yes	break down into 2 peaks	157; 168
fenthion	278	210	Yes	break down into several peaks	157, 185, …
fluorene	166	295	Yes	low abundance	167

Table S1-4: cont.

compound name	MW (g/mol)	PB (°C)	RT in analytes range?	general remarks	m/z TI (PCI)
hexachlorobenzene $^{13}C6$	190	231	Yes	not found in environmental samples, no matrix influence,	291
hexanol D_{13}	115	158	Yes	m/z too low	85
linuron	249	185	no peak	-	-
malathion	303	156	No	bad peak shape (very broard)	161
metolachlor	284	100	Yes	break down into several peaks	180, 218, …
octanol D_{17}	147	194	Yes	m/z low, m/z 130 is released by XAD-2	125, 130
parathionmethyl	263	154	no peak	-	-
PCB 49	286	343	No	too late	293
PCB 6	215	306	No	too late	223
PCB 65	286	345	No	too late	293
PCB 70	286	362	no peak	-	-
pentachorophenol	266	300	no peak	-	-
pentafluorophenol	184	143	Yes	bad peak shape (very broard)	185
phenylethanol	122	220	Yes	m/z 105 is released by XAD-2	105
profluralin	347	393	No	too late	348
teflubenzuron	381		No	too late	158
tefluthrin	419	156	no peak	-	-
terbutylazine	230	373	No	too late	194
toluensulfonamide	171	221	no peak	-	-

Table S1-5: Analyte standard deviations of multi measurement of a 200 pg µL^{-1} standard solution. A: peak area. S.D.: standard deviation.

	S.D. A(analyte) (%)	S.D. A(analyte)/A(TCB) (%)	S.D. A(analyte)/A(HCB) (%)
6:2 FTA	4.8	1.5	1.2
4:2 FTOH	4.6	1.2	0.9
6:2 FTOH ^{13}C	4.8	1.4	1.2
6:2 FTOH	4.6	1.4	1.3
8:2 FTA	4.8	1.9	1.7
8:2 FTOH ^{13}C	4.8	2.0	1.8
8:2 FTOH	4.2	1.5	1.4
10:2 FTOH ^{13}C	4.3	2.1	2.0
10:2 FTOH	4.5	1.9	2.0
12:2 FTOH	6.6	3.2	2.9
EtFOSA D_5	4.4	1.3	1.3
EtFOSA	3.7	1.4	2.0
MeFBSA	3.9	0.8	1.2
MeFOSA D_3	4.4	1.3	1.3
MeFOSA	5.1	1.9	1.9
MeFOSE D_7	5.5	2.2	2.2
MeFOSE	6.4	3.1	3.0
EtFOSE D_9	5.5	2.2	2.2
MeFBSE	4.5	1.1	1.2
EtFOSE	5.2	1.9	1.8
PFOSA	9.0	6.7	6.7

Table S1- 6: Analyte standard deviations of multi measurement of a 40 pg µL^{-1} standard solution. A: peak area. S.D.: standard deviation.

	S.D. A(analyte) (%)	S.D. A(analyte)/A(TCB) (%)	S.D. A(analyte)/A(HCB) (%)
6:2 FTA	3.5	1.1	2.4
4:2 FTOH	3.3	1.3	1.7
6:2 FTOH ^{13}C	4.2	2.1	2.5
6:2 FTOH	3.9	1.6	3.5
8:2 FTA	4.7	2.2	3.5
8:2 FTOH ^{13}C	5.3	2.9	3.4
8:2 FTOH	5.4	3.7	5.0
10:2 FTA	5.7	3.6	5.3
10:2 FTOH ^{13}C	6.8	5.0	5.9
10:2 FTOH	6.4	4.6	6.1
12:2 FTOH	7.6	5.5	6.8
EtFOSA D_5	4.5	2.2	3.5
EtFOSA	4.7	2.6	4.2
MeFBSA	3.9	1.5	2.0
MeFOSA D_3	4.8	2.4	2.5
MeFOSA	3.3	1.4	3.1
MeFOSE D_7	4.1	1.9	2.1
MeFOSE	4.0	2.2	1.7
EtFOSE D_9	4.9	2.9	2.0
MeFBSE	3.6	1.4	1.6
EtFOSE	4.5	2.3	1.8
PFOSA	5.7	4.3	3.5

Table S1-7: Analyte standard deviations of multi measurement of a 1 pg µL^{-1} standard solution. A: peak area. S.D.: standard deviation.

	S.D. A(analyte) (%)	S.D. A(analyte)/A(TCB) (%)	S.D. A(analyte)/A(HCB) (%)
6:2 FTA	3.8	2.2	2.2
4:2 FTOH	9.6	8.8	8.7
6:2 FTOH ^{13}C	16.6	16.4	17.6
6:2 FTOH	13.5	12.3	12.6
8:2 FTA	7.1	7.0	7.1
8:2 FTOH	17.7	16.6	16.3
10:2 FTA	9.7	8.0	7.5
EtFOSA D_5	4.5	3.8	4.0
EtFOSA	6.0	4.8	5.1
MeFBSA	5.3	4.9	5.1
MeFOSA D_3	6.6	5.7	5.8
MeFOSA	5.3	4.2	4.3
MeFOSE D_7	8.5	8.1	7.7
MeFOSE	20.2	22.1	22.5
EtFOSE D_9	11.4	10.2	10.1
MeFBSE	11.9	13.1	13.4
EtFOSE	10.7	11.4	10.9

Identification of Acetic Acid in Ethyl Acetate and Its Implications on the Recovery of FTOH

The following experiments were performed to verify that acetic acid is concentrated when ethyl acetate was evaporated. Pure ethyl acetate SupraSolv, 50 mL ethyl acetate SupraSolv evaporated to 250 µL, and 250 µL ethyl acetate SupraSolv + acetic acid were measured in the Scan mode using a 30 m Supelcowax 10 capillary column. As shown in figure S1-1 to S1-3, acetic acid is not detectable in pure ethyl acetate, but in evaporated ethyl acetate and ethyl acetate + acetic acid. Figure S1-4 shows the impact of 1 µL acetic acid added to 250 µL of a FTOH standard solution. It is clearly shown, that recoveries of 8:2 FTOH and compounds eluting later are response enhanced. FASE and FASA were not determined in these measurements.

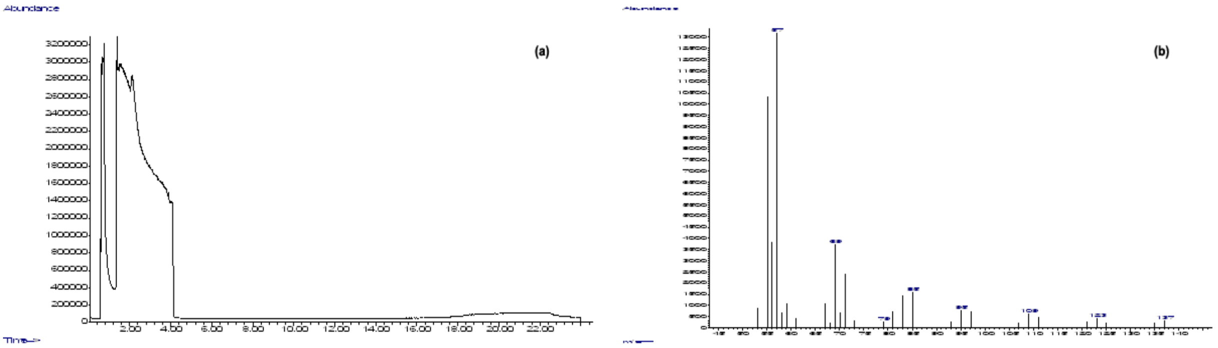


Figure S1-1: Total ion chromatogram (a) and scan (b) of pure ethyl acetate SupraSolv measured on a 30 m Supelcowax 10 capillary column.

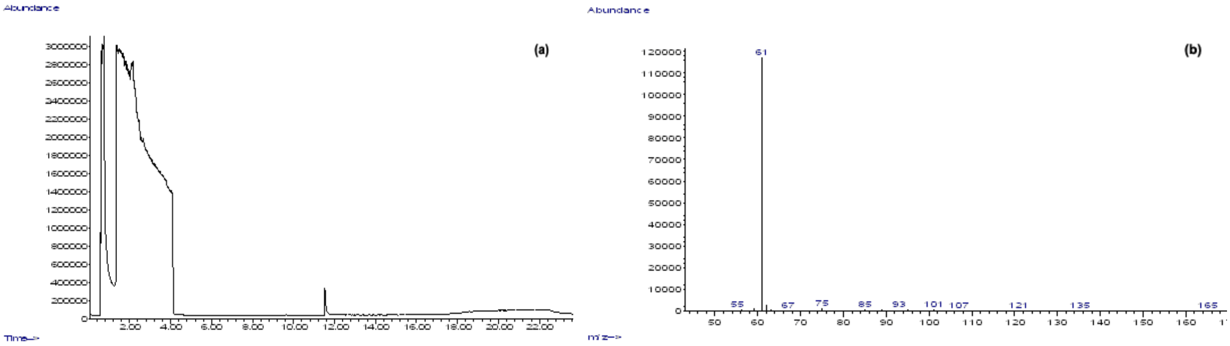


Figure S1-2: Total ion chromatogram (a) and scan (b) of evaporated ethyl acetate SupraSolv measured on a 30 m Supelcowax 10 capillary column.

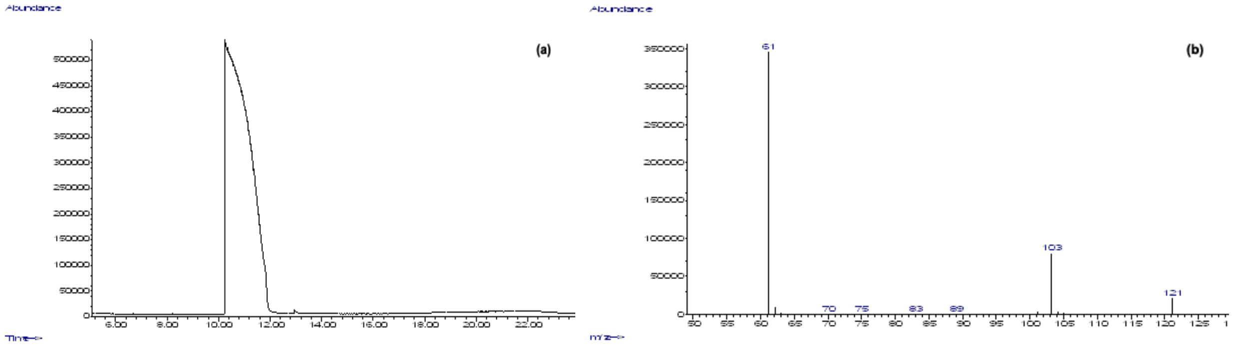


Figure S1-3: Total ion chromatogram (a) and scan (b) of acetic acid added to pure pure ethyl acetate SupraSolv measured on a 30 m Supelcowax 10 capillary column.

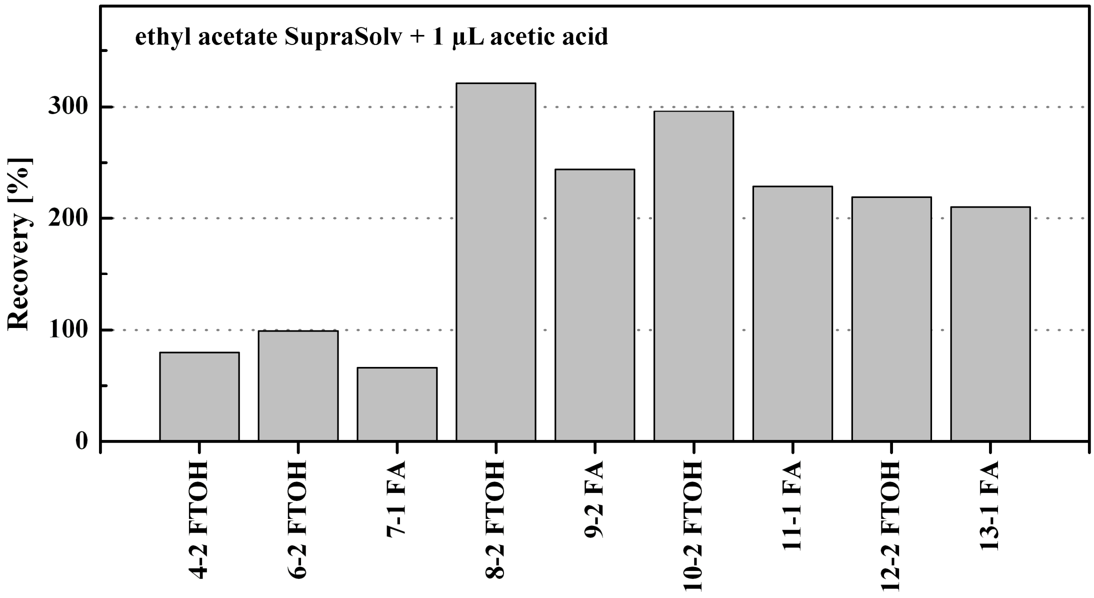
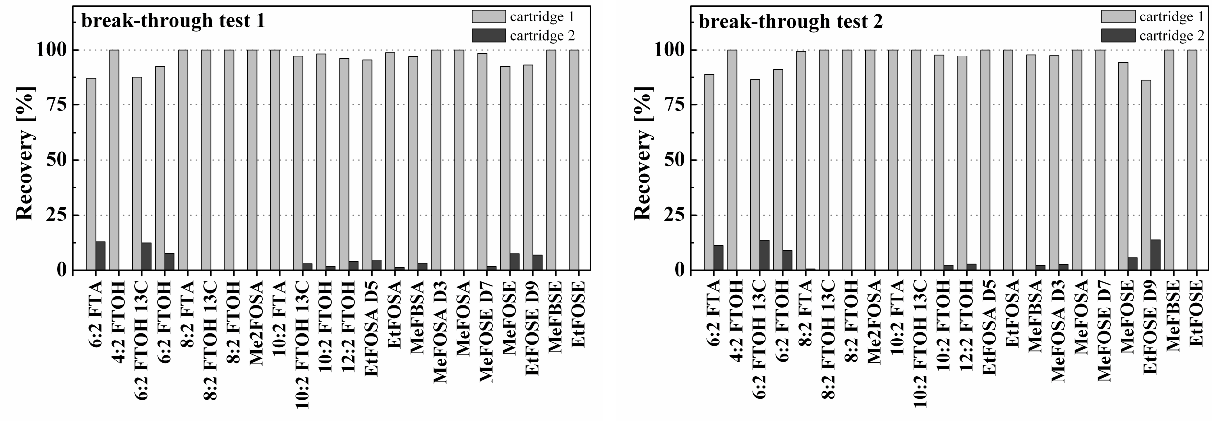


Figure S1-4: Recovery rates of certain PFC after in a standard solution based on ethyl acetate fortified with 1 µL acetic acid.

Break-Through Experiments

Break-through experiments were performed to test the sampling efficiency of the industrially manufactured cartridges containing PUF/XAD-2/PUF (Orbo Tubes 6000, Supelco, Munich, Germany) which were applied for the first time in the determination of volatile and semi-volatile polyfluorinated organic compounds using high volume air samplers. For this purpose, a cartridge was spiked with a solution containing ^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH, D_3 MeFOSA, D_5 EtFOSA, D_7 MeFOSE, and D_9 MeFOSE (200 pg µL^{-1}) prior sampling. Behind this cartridge, a second PUF/XAD-2/PUF cartridge was introduced to adsorb analytes that have not been retained by the first one during the sampling procedure. The duration of the sampling was 3 days (about 1500 m^3). After sampling, columns were extracted with acetone:MTBE 1:1 (v:v). For the extraction, the solvent was allowed to soak for 1hour (first extraction) or ½ hour (second and third extraction). After each extraction step, remaining solvent in the cartridge was blown out using nitrogen. The solvent was evaporated to 150 µL using rotary evaporators and a gentle stream of nitrogen. Fifty µL containing TCB D_3 and ^{13}C HCB (500 pg µL^{-1}) were added prior measurement at the GC-MS. The experiment was performed in parallel.

As the break-through experiments show (figure S1-5), break-through of 5 % or more occurs only for the most volatile polyfluorinated analytes. Thus, their environmental concentrations will be underestimated. For the remaining substances, no or only very little break-through occurs.



a b

Figure S1-5: Break-through experiment of two parallel air samples (a, b).

Determination of the Number of Extraction Steps

In this experiment the number of extraction steps to fully extract volatile and semi-volatile poly fluorinated compounds from a PUF/XAD-2/PUF cartridge was determined. One cartridge was spiked with 50 µL of a solution containing 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 6:2 FTA, 8:2 FTA, 10:2 FTA, 7:1 FA, 9:1 FA, 11:1 FA, 13:1 FA, MeFOSE, EtFOSE, MeFOSA, EtFOSA, MeFBSA, MeFBSE, and Me_2FOSA ($c = 200$ pg μL^{-1}) and 50 µL of the internal standard solution containing ^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH, D_3 MeFOSA, D_5 EtFOSA, D_7 MeFOSE, and D_9 MeFOSE (200 pg μL^{-1}) to correct for analyte losses. Additionally, two real samples were taken using high volume air samplers. Cartridges were spiked with 50 µL of the internal standard solution prior to the sampling. After sampling columns were extracted with acetone:MTBE 1:1 (v:v) five times. For the extraction, the solvent was allowed to soak for 1hour (first and second extraction) or ½ hour (third to fifth extraction). After each extraction step, remaining solvent in the cartridge was blown out using high purity nitrogen. The five fractions were collected separately and evaporated to 150 µL using rotary evaporators and a gentle stream of nitrogen. Fifty µL containing ^{13}C TCB and ^{13}C HCB (500 pg μL^{-1}) were added prior to the measurement at the GC-MS.

As figure S1-6 shows, the highest proportion of polyfluorinated analytes elutes with the first extraction step. However, significant proportions for most analytes are also found in extraction 2 and especially for the perfluoroalkyl sulfonamides in extraction 3 as well. Generally, higher proportions of analytes in the second and third extraction step are found for real samples, emphasizing the use of real samples for these experiments. Overall, we decided on three extraction steps for the desorption of (semi-volatile) polyfluorinated organic compounds from the PUF/XAD-2/PUF sandwich. This involves the use of about 500 mL MTBE:acetone 1:1.

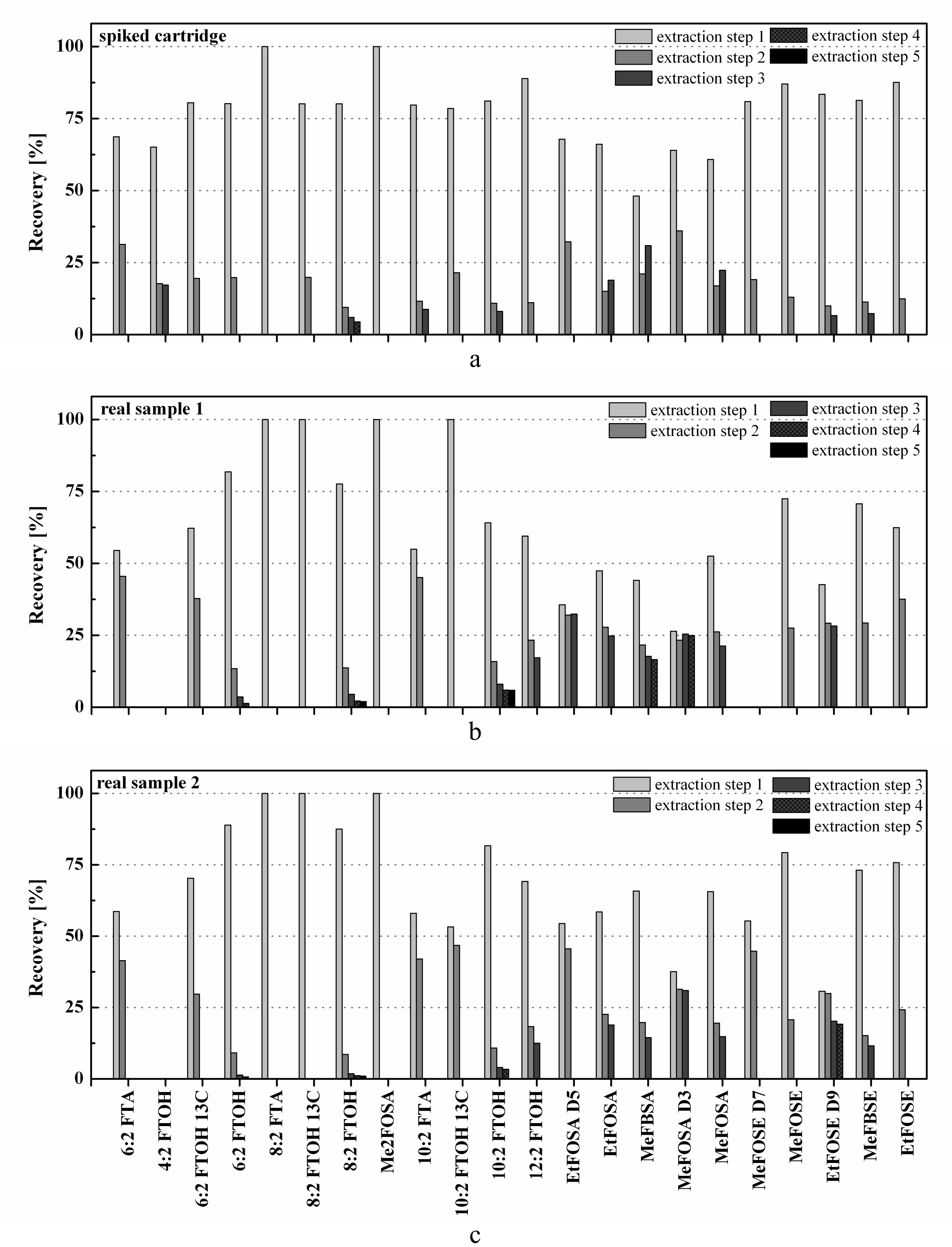


Figure S1-6: Analyte Recoveries of five extraction steps. a: spiked cartridge. b: real sample 1. c: real sample 2. 4:2 FTOH was not detected in environmental samples.

References

DIN 32645. 1994. Chemische Analytik: Nachweis-, Erfassungs- und Bestimmungsgrenze, Ermittlung unter Wiederholungsbedingungen, Begriffe, Verfahren, Auswertung; Beuth Verlag.

Jahnke, A.; Ahrens, L.; Ebinghaus, R.; Berger, U.; Barber, J. L.; Temme, C. 2007. An improved method for the analysis of volatile polyfluorinated alkyl substances in environmental air samples. Analytical and Bioanalytical Chemistry. 387. 965-975

Study 2

Annual Time Series of Air Concentrations of Polyfluorinated Compounds

Annekatrin Dreyer, Volker Matthias, Christian Temme, Ralf Ebinghaus

Environmental Science & Technology (2009) 43,4029-4036

Annual Time Series of Air Concentrations of Polyfluorinated Compounds

Annekatrin Dreyer, Volker Matthias, Christian Temme, and Ralf Ebinghaus

GKSS Research Centre, Max Planck Str. 1, 21502 Geesthacht, Germany

Abstract

Per- and polyfluorinated organic compounds (PFC) in air were determined in samples taken at two sites in the vicinity of Hamburg, Germany over a period of 14 months. PUF/XAD-2/PUF cartridges and glass fiber filters were applied for the collection of airborne PFC. A set of volatile, neutral PFC such as fluorotelomer alcohols (FTOH) or perfluorinated sulfonamides and ionic, non-volatile PFC like perfluorinated carboxylates (PFCA) and sulfonates (PFSA) were determined using GC-MS and HPLC-MS/MS. Backwards trajectory analysis was performed to elucidate the origin of the air mass parcels sampled. PFC were predominantly detected in the gas phase. A fluctuating baseline of north German background levels and singular events of high concentrations were characteristic for the time series of all analytes and both locations. The origin of sampled air was the driving parameter influencing the PFC levels. Elevated PFC concentrations occurred in air arriving from industrialized and populated regions west and southwest of Hamburg. Maximum individual PFC concentrations reached 600 pg m^{-3} (8:2 FTOH) in the gas phase and 13 pg m^{-3} (perfluorooctane sulfonate, PFOS) in the particle phase. The class of FTOH clearly dominated the gas-phase substance spectrum. The compound that was detected in highest concentrations was 8:2 FTOH. Individual gas-phase PFC concentrations were higher in summer than in winter. Temperature-dependent emissions of (semi-)volatile PFC from diffuse sources to the gas phase are presumed to be responsible for this observation.

1. Introduction

Long-chain perfluorinated carboxylates (PFCA) and -sulfonates (PFSA) such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) have been found to be persistent, bioaccumulative, and entailing toxic properties (Beach et al., 2006; Giesy and Kannan, 2002; Haukas et al., 2007; Houde et al., 2006; Prevedouros et al., 2006). Furthermore, global distribution to remote regions caused by extensive industrial application and consumer use has been demonstrated for these compounds classes (Bossi et al., 2005; Giesy and Kannan, 2001; Prevedouros et al., 2006; Tao et al., 2006; Wei et al., 2007; Young et al., 2007). Although some main industrial producers committed to phase out the production of persistent and bioaccumulative long-chain PFCA and PFSA and legislative restrictions exist concerning manufacturing, marketing, and use of PFOS and its derivatives (European Community, 2006; US-EPA, 2002), less persistent polyfluorinated compounds such as fluorotelomer alcohols (FTOH), fluorotelomer acrylates (FTA), short chain acids or their derivatives are still being produced as substitutes or intermediates in large quantities. For example, the amount of globally produced telomere alcohols increased from 5-6.5 t a^{-1} in 2000-2002 to 11-14 t a^{-1} which is perhaps related to the withdrawal by 3M of their POSF based products in 2000-2002 (Dinglasan-Panlilio and Mabury, 2006).

Several studies revealed that perfluorinated acids can be transported over long distances within the water phase (Caliebe et al., 2004; McLachlan et al., 2007; Wei et al., 2007; Yamashita et al., 2008). Atmospheric transport of PFCA and PFSA as observed by some authors (Barber et al., 2007; Dreyer and Ebinghaus, 2009) appears to be of minor importance to explain contamination of remote regions due to efficient scavenging by wet and dry deposition (Hurley et al., 2004). In contrast to PFSA and PFCA, volatile and semi-volatile polyfluorinated compounds such as perfluorinated sulfonamides (FASA), perfluorinated sulfonamido ethanols (FASE), FTOH, or FTA undergo significant atmospheric long-range transport (Barber et al., 2007; Jahnke et al., 2007b; Piekarz et al., 2007; Primbs et al., 2008; Shoeib et al., 2006; Stock et al., 2007; Stock et al., 2004). Degradation of polyfluorinated volatile compounds to PFCA and PFSA during or after the transport reveal their contribution to the ubiquitous distribution of the persistent acids (D'Eon et al., 2006; Ellis et al., 2004; Martin et al., 2006; Sulbaek Andersen et al., 2005; Young et al., 2007). Studies describing the worldwide occurrence and distribution of (semi-)volatile polyfluorinated compounds in ambient air only display a snap-shot of PFC air concentrations - emission events, seasonality, or fluctuations in the highly dynamic atmospheric system are not accounted for. However, knowledge about concentration variations in dependence of distinct atmospheric conditions is of utmost importance in order to compare the results of different studies.

Studies investigating temporal trends have been focused mainly on long term variations of PFCA and PFSA concentrations in biota (Bossi et al., 2005; Butt et al., 2007; Smithwick et al., 2006). In contrast, studies investigating temporal concentration changes of volatile polyfluorinated compounds, especially on an annual basis are rare. For the period from 1998 to 2005 FTOH concentrations in air were calculated to increase by at least one order of magnitude (Schenker et al., 2008). For the same period, PFOS-based volatile compounds were expected to decrease (Schenker et al., 2008). However, whereas field data support the FTOH estimates, decreasing concentrations of PFOS-based substances were not observed in field measurements. Stock et al. (2005) presented a poster showing gas and particle-phase concentrations of FTOH, FASA, and FASE collected every two weeks throughout 2002 and 2003 in Toronto, Canada. They measured air concentrations of individual substances ranging from not detected to 650 pg m^{-3}. On average, concentrations were higher in summer than in winter. Barber et al. (2008) investigated the seasonal variability of atmospheric PFC concentrations at an urban and a rural site in the UK in 2006. They found concentrations to be higher at the urban (ΣPFC 377 pg m^{-3}) than at the rural (ΣPFC 183 pg m^{-3}) site. Variability was higher at the rural site. Especially the more volatile compounds such as 6:2 FTOH occurred in higher concentrations in winter than in summer, possibly due to decreased atmospheric breakdown in winter. The same authors also observed that concentrations were highest when air masses were originating from Central Europe.

The objective of this study was to elucidate temporal concentration changes of polyfluorinated compounds in ambient air at two sites close but at different distances to Hamburg. Therefore samples were taken continuously in intervals of three to four days within a period of 14 months from April 2007 to June 2008. FTOH, FTA, FASA, and FASE were determined in the gas and particle phase. PFCA, PFSA, and perfluorinated sulfinates were determined in the particle fraction only. Meteorological parameters, NO_x and O_3 were determined as well. These data as well as trajectory and statistical analyses were used to interpret the observed concentration variations. Specifically, the addressed questions were: 1. Which amounts of polyfluorinated compounds can be observed in air samples of northern Germany? 2. How do concentrations of various polyfluorinated analytes vary over time and are there seasonal changes in concentrations? 3. How do meteorological conditions or atmospheric transport influence the observed concentration pattern? 4. Do both sites differ from each other in terms of PFC concentrations and pattern and what are reasons for potential differences?

2. Experimental

2.1. Sampling & Sample Analysis

To elucidate the site specific intra-annual concentration variations of PFC, sampling was conducted at two sites located in the vicinity of Hamburg, Germany from 2nd April 2007 to 1st June 2008 (figure 2-1). These sites were located in different distances and directions to the city of Hamburg and were also chosen to look for small-scale spatial variations close to a big city in a temperate region. The site Barsbüttel (BAR) is a monitoring site of the Environmental Agency (Staatliches Umweltamt Itzehoe) and is situated approximately 20 km east of Hamburg (1 770 000 inhabitants) at 53°34'14'' N and 10°12'55'' E. The GKSS site is located approximately 40 km southeast of the city centre of Hamburg close to the city of Geesthacht (30 000 inhabitants) at 53°24'26'' N, 10°25'20'' E. The sites have a semi-rural character and are characterized by winds coming predominantly from westerly directions.

Generally, samples were taken continuously for three (Monday to Thursday) and four (Thursday to Monday) days using high volume air samplers. Exceptions were periods when the sites were not accessible and sampling times had to be extended up to 5 days and once to 14 days (Christmas). For about one week in early November 2007 samples were taken daily at the GKSS site to cover the same intervals as a sampling campaign in the German Bight (Dreyer and Ebinghaus, 2009). In total 117 samples were taken at the BAR and 121 at the GKSS site with sampling volumes of 1200 to 1800 m^3 for each sample and a flow rate of 500 $m^3\ d^{-1}$. In addition to the PFC sampling, meteorological parameters (air temperature, wind speed, wind direction, humidity, air pressure, and precipitation) were recorded at both sites. At Barsbüttel, NO, NO_2, and O_3 were measured as well.

A sandwich of polyurethane foam (PUF) and Amberlite XAD-2 (Orbo PUF/XAD-2/PUF cartridges 2500) as well as glass fibre filters (GFF) were used to collect gaseous and particle-bound polyfluorinated compounds separately. Prior to the sampling, 50 µL of a standard solution containing eight mass labelled volatile PFC (200 pg μL^{-1}) were spiked directly onto the upper PUF disk of column to account for analyte losses during sampling and sample preparation. Filters were not spiked until the extraction, to assure that internal standards are not transferred to the column during sampling. After the sampling, samples were sealed air tight and stored at -20 °C. Gas-phase samples were analyzed within five months, particle samples within ten months after the sampling.

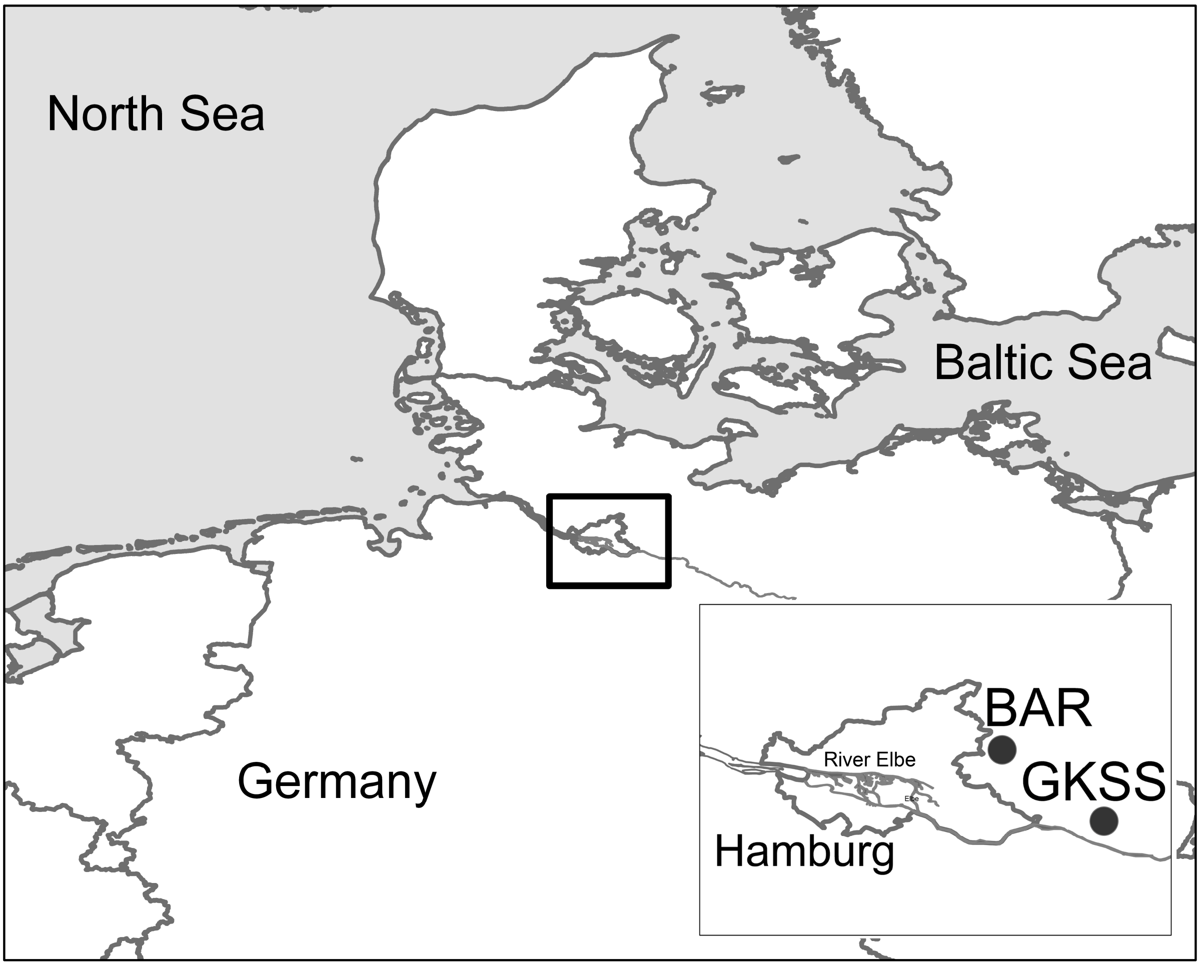


Figure 2-1: Location of the sampling sites. BAR: site at Barsbüttel, GKSS: site at the GKSS Research Center.

Cartridges were extracted thrice with methyl-tert-butyl ether (MTBE):acetone 1:1. It seemed that neutral volatile particle-bound compounds were lost during long storage times since analytes were not detected in first extracts of these samples. Therefore only the most recent filters from April and May 2008 were extracted with MTBE:acetone 1:1 using fluidized bed extraction to determine neutral volatile PFC. The remaining filters from April 2007 until March 2008 were extracted for perfluorinated acids using fluidized bed extraction and methanol as extraction solvent. Detection of neutral polyfluorinated analytes in the gas and particle phase was performed by gas chromatography-mass spectrometry with positive chemical ionization (PCI) using the selected ion monitoring (SIM) mode. To confirm the detection of FASA, samples were also run in the negative chemical ionization (NCI) mode. Methanol-extracted polyfluorinated compounds were determined by high performance liquid chromatography - mass spectrometry (HPLC- MS/MS) using the electro spray ionization

(ESI) mode. Detailed descriptions of chemicals, sample preparations, and instrumental analyses are given elsewhere (Dreyer and Ebinghaus, 2009; Dreyer et al., 2008) and in the supporting information.

Average recovery rates for analytes in the gas phase were between 25+/-17 % (^{13}C 4:2 FTOH) and 60+/-19 % (EtFOSE D_9). Since internal standards were spiked to the cartridges prior to the sampling process, losses during sampling are included in these recovery rates. Average recovery rates for particle-bound analytes were between 46+/-29 % (^{13}C PFOA) and 95+/-64 % (^{13}C PFUnDA). Analytical performance of particle extraction strongly depended on the particle load and type of particles. For instance poor recoveries occurred for filters that were heavily loaded with pollen. Four GKSS and 1 Barsbüttel particle samples as well as 3 Barsbüttel and 4 GKSS gas-phase samples were discarded due to high water or matrix content. The average uncertainty based on 1 day paired measurements (n=7) of gas-phase analytes was 45 % +/- 30 % (Dreyer and Ebinghaus, 2009) . Due to low recovery rates and/or elevated uncertainty of 4:2 FTOH and PFOSA, concentrations of these analytes should be treated qualitatively rather than quantitatively. The uncertainty of particle concentrations was not calculated due to the lack of a sufficient number of paired measurements. However, due to analytical problems described above and low PFC concentrations the uncertainty is expected to be larger.

2.2. Blanks

Laboratory blanks (solvent blanks for gaseous samples, filter blanks for particulate samples) were taken with each set of samples that was extracted. Almost all compounds were detected in solvent and filter blanks in very low concentrations (on average 0.2 pg m^{-3} and 0.7 pg m^{-3}, respectively). Therefore, all concentrations reported were laboratory blank-corrected. To determine contamination of sampling, sampling transport, and storage field blanks were taken at both sites about once a month. Field blanks were treated the same way as samples and were usually in the range of solvent and filter blanks showing that contamination was not due to sampling or sample handling. Blank concentrations are reported in the supporting information.

2.3. Trajectory Analysis

Seven days air mass backward trajectories were calculated with the model Hysplit 4.8 using NCEP's Global Data Assimilation System (GDAS) data with 1 degree latitude/longitude resolution provided by NOAA-Air Resources Laboratory (Draxler and Rolph, 2003). Trajectories were calculated for intervals of six hours and an arrival height of 2 m (sampling height). The trajectories' uncertainty is expected to be approximately 20 % of the travel distance. To obtain main air mass pathways, back trajectories were clustered. Cluster analysis of trajectories was performed with Hysplit 4.8. The final number of clusters was based on a 20 % separation criterion of 96 hours back trajectories calculated for twelve hours intervals. Since samples were taken for three or more days, they were assigned to that cluster representing the most frequent trajectories. If one sample had exactly the same number of two clusters, it was assigned to both. Due to the resolution of GDAS data, GKSS and BAR cluster did not differ and only clusters for the Barsbüttel site are being discussed here to elucidate the air mass origin.

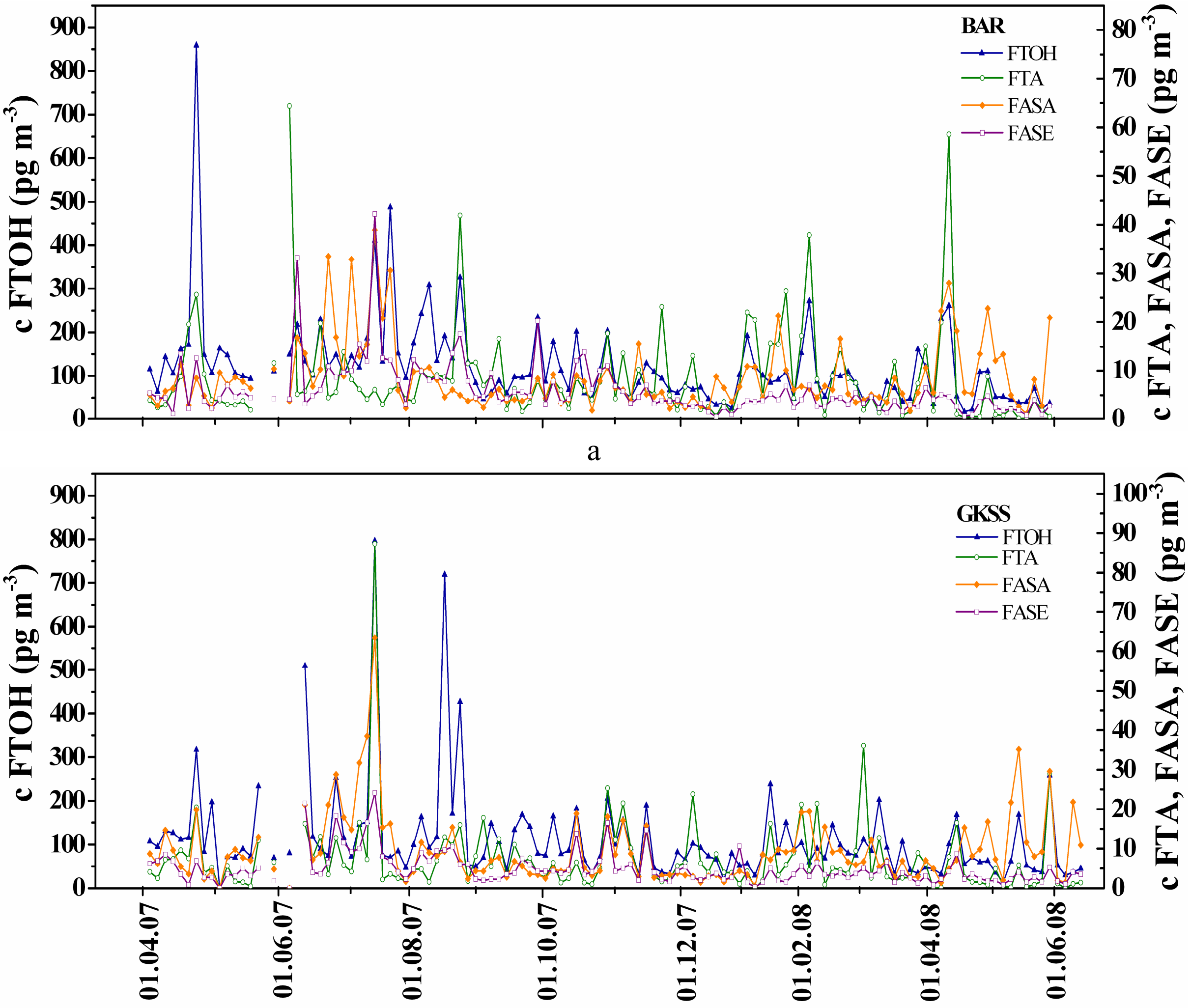
2.4. Statistical Analysis

Since particle-phase concentrations were close to the detection limit and therefore more uncertain, only the time series of gas-phase data are statistically evaluated. Gas-phase concentrations at both sites were tested for (log-)normal distribution using the Kolmogorov-Smirnov test. Peak events were eliminated for seasonality considerations. Elimination was based on the interquartile range method (Sachs, 2002). Analyte concentrations grouped by sites or trajectory clusters were averaged and log-normal-distributed concentrations were compared using analysis of variance (ANOVA). PFC concentrations were correlated to each other and to meteorological parameters using Pearson correlation.

3. Results & Discussion

3.1. PFC Concentrations & Proportions

Figure 2-2 gives an overview of the time series of gas-phase concentrations for four classes of polyfluorinated compounds analysed in this study. PFC were found predominantly in the gas phase. Total gas-phase concentrations ranged from 17 to 972 pg m^{-3}. These gas-phase concentrations are comparable to those observed at similar (Jahnke et al., 2007a) or other urban sites such as Manchester (Barber et al., 2007) or Toronto (Martin et al., 2002; Shoeib et al., 2006; Stock et al., 2004; Stock et al., 2005) and are at least one order of magnitude higher than marine background concentrations in the northern hemisphere observed by Shoeib et al. (2006). Concentrations varied strongly. Due to the peak events, the compounds standard deviations and inner-quartile ranges over the entire period sampled were usually 100 % or higher without a tendency concerning sites or substances. In general, concentrations were uni-modal and right-skewed distributed. Except for 4:2 FTOH, Me_2FOSA, and PFOSA which were detected only occasionally in air samples, substances detected in the gas phase were log-normal distributed. This was statistically verified ($p < 0.05$) for 20 of 26 time series. With only 8 exceptions in the particulate fraction, per- and polyfluorinated compounds were detected in the gas and particle phase of all analysed air samples at both sites.



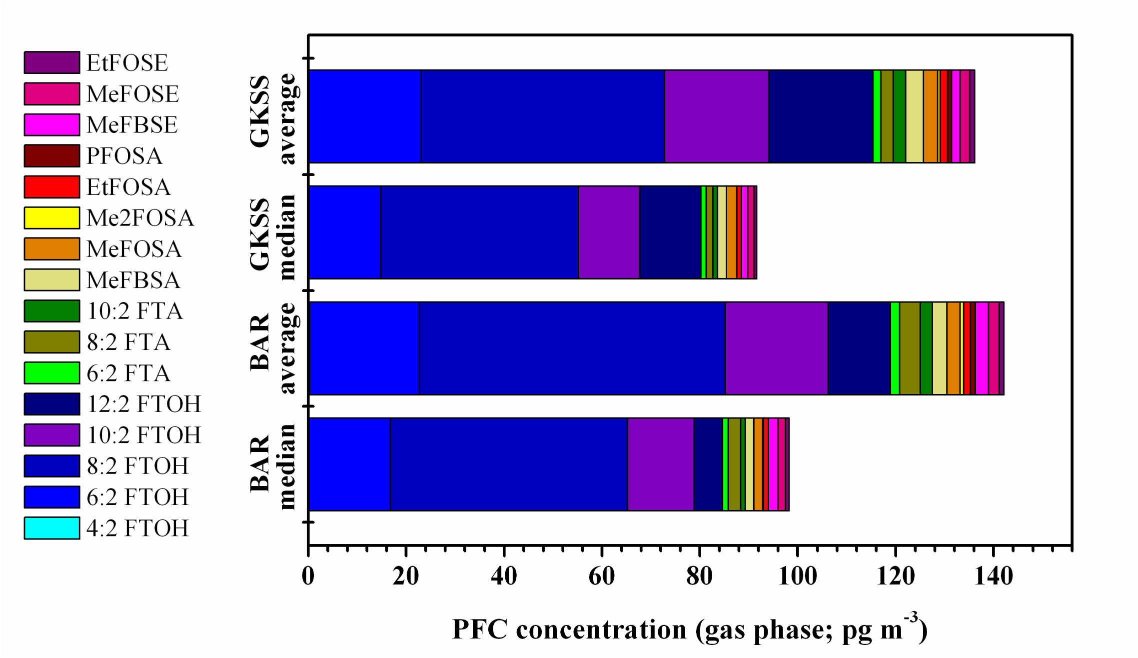
a

b

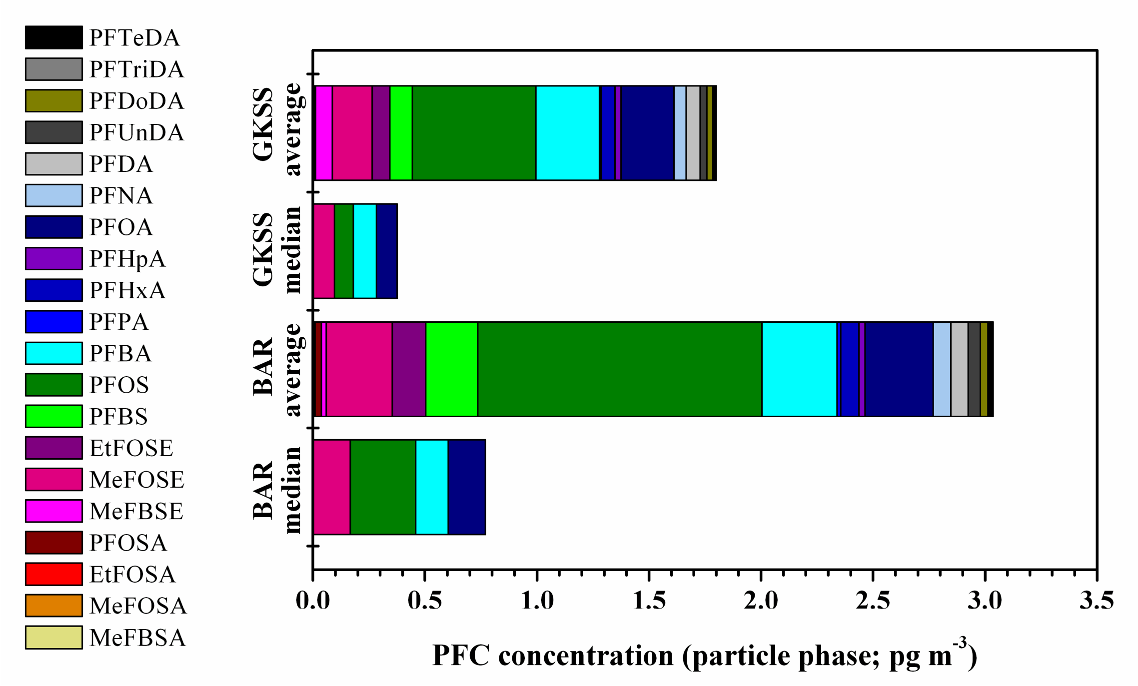
Figure 2-2: Gas-phase concentrations of Σ FTOH, Σ FTA, Σ FASA, Σ FASE at the (a): Barsbüttel and (b): GKSS site. Note that if sample losses occurred symbols were not connected.

For the majority of analytes, concentrations, arithmetic concentration means, and medians were slightly higher at the Barsbüttel site than at the GKSS site (figure 2-3a). These differences were most pronounced for 8:2 FTOH. An exception was 12:2 FTOH that was present in higher concentrations at the GKSS site. Concentration differences may not be significant in light of method uncertainties. With proportions of more than 80 %, FTOH were the dominant class of compounds, followed by FASE, FTA and FASA. Among the FTOH, 8:2 FTOH was observed in maximum proportions followed by 6:2 FTOH, 10:2 FTOH, and 12:2 FTOH. This composition is typical for European air masses (Barber et al., 2007; Dreyer and Ebinghaus, 2009; Jahnke et al., 2007a). Average PFC compositions were similar between both locations. At Barsbüttel, the proportion of 8:2 FTOH was elevated whereas the proportion of 12:2 FTOH was reduced.

Of neutral analytes in the particulate phase, MeFOSE and EtFOSE were often determined in low concentrations (figure 2-3 b). MeFOSA, MeFBSE, MeFBSA, EtFOSA, and PFOSA were only sporadically found. FTOH and FTA, even the most volatile ones, were occasionally detected in low concentrations. However, the detection of these compounds in field blank samples suggests that this was probably due to contamination. In contrast to these findings, other authors described gas to particle partitioning of (long-chain) FTOH, especially at colder temperatures (Jahnke et al., 2007a; Piekarz et al., 2007; Shoeib et al., 2006). Average PFC particle concentrations varied between not detected and 1.3 pg m^{-3} at Barsbüttel and between not detected and 0.6 pg m^{-3} at GKSS and appear to be higher at Barsbüttel. Although concentration differences between GKSS and Barsbüttel seem to be more pronounced in the particle phase than in the gas phase, the higher uncertainty of particle-phase concentrations should be considered carefully. Furthermore, sorption of gaseous PFCA to the glass fiber filters as demonstrated by Arp and Goss (2008) may have biased the particle-phase concentrations. PFHxS, PFDS, PFSi, PFHxDA, and PFOcDA were not detected in any particle sample, whereas PFOS, PFBA, PFHxA, PFOA, and PFNA were frequently and PFBS, PFPA, PFHpA, PFDA, PFUnDA, PFDoDA, PFTriDA, and PFTeDA less often detected in the particle phase. With 13.5 pg m^{-3} PFOS was the analyte detected in maximum concentrations in the particle phase. This study's particle-phase concentrations are comparable to those observed by Kim and Kannan (2007) for an urban area in the US or by Harada et al. (2005) for rural regions of Japan. Particle-phase PFOS and/or PFOA concentrations determined at urban regions in the UK and Japan were up to two orders of magnitude higher which was attributed to traffic based emissions or emissions from production facilities (Barber et al., 2007; Harada et al., 2005; Sasaki et al., 2003). Unlike the findings of Barber et al. (2007) and Harada et al.(2005) who reported PFOA in maximum proportions in the particle fraction, in this study PFOS was the dominant compound, usually followed by PFBA, PFOA, and MeFOSE. Barsbüttel samples contained higher proportions of PFOS than the GKSS ones.



a

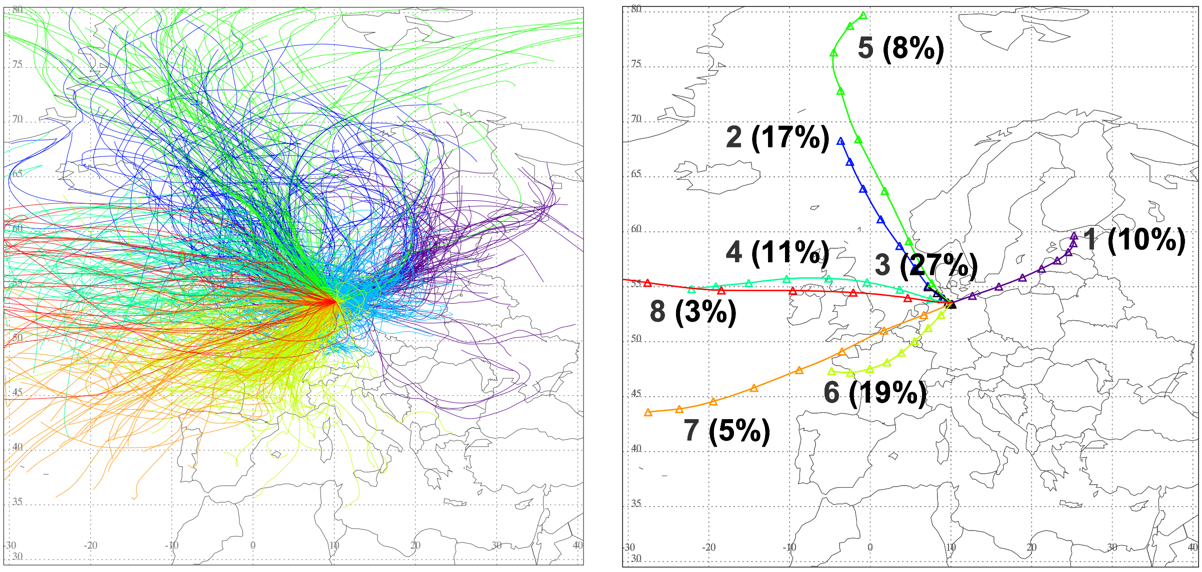


b

Figure 2-3: Average and median concentrations (pg m^{-3}) of poly- and perfluorinated compounds in (a) the gas phase and (b) the particle phase. Note that FTOH detected in the particle phase are not included in the figure since data suggested contamination.

3.2. Air Mass Origin

Figure 2-4 illustrates the results of air mass back trajectories cluster analyses for the Barsbüttel site. Clustering trajectories revealed eight main air mass origins (figure 4a) that are represented by eight average trajectories (figure 4b). The majority of trajectories were assigned to clusters 3 (27 %) and 6 (19 %). These clusters were characterized by short trajectories i.e. slow air masses that travelled close to ground and originated from surrounding and western directions. Clusters 5, 7, and 8 (below 10 % each) contained few but long, i.e. fast trajectories from northern and western directions. Clusters 1, 2, and 4 consisted of intermediately long trajectories from eastern, northern and western directions, respectively.



a b

Figure 2-4: Cluster analysis on trajectories calculated for the BAR site. (a) Ninety-six hours air mass back trajectories grouped into 8 clusters. Cluster specific trajectories are colour coded. (b) Mean cluster trajectories. Note: Only Barsbüttel trajectories were used since the GDAS data did not resolve small scale spatial differences between GKSS and BAR. Cluster numbers were assigned by Hysplit.

Average PFC concentrations observed in this study were quite different among the clusters revealing that the air mass origin, i.e. the source region was a driving parameter for the air concentrations of polyfluorinated compounds. Peak event-corrected (see below) average gas-phase concentrations of polyfluorinated analytes (table 2-1) were usually highest in samples assigned to clusters 3 and 6 suggesting source regions west of the sites. PFC concentrations in clusters 3 and 6, particularly those of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, were strongly elevated compared to PFC levels observed in the remaining clusters. The lower the PFC concentrations the more uniformly they were distributed among the clusters. Air masses of clusters 1, 2, 4, and 7 contained medium levels of PFC in the gas phase. Analyte concentrations were lowest in clusters 5 and 8. Concentrations of 10:2 FTOH and 12:2 FTOH in cluster 2 were in the same order than those of clusters 3 and 6. Since sampling was performed continuously for several days some of the samples grouped into cluster 2 also got a small quantity of air parcels arriving from more polluted regions (usually cluster 3). It was observed that in terms of air mass origin pure cluster 2 samples had much lower PFC concentrations than such mixed samples. Thus, although northern marine air masses are generally less polluted, elevated average concentrations were observed in cluster 2. Further information on this issue is presented in the Supporting Information Section.

Table 2-1: Trajectory cluster averages of gas-phase concentrations (pg m^{-3}) of poly- and perfluorinated compounds at Barsbüttel. Peak concentrations were not accounted for in the calculations. v.fast: very fast.

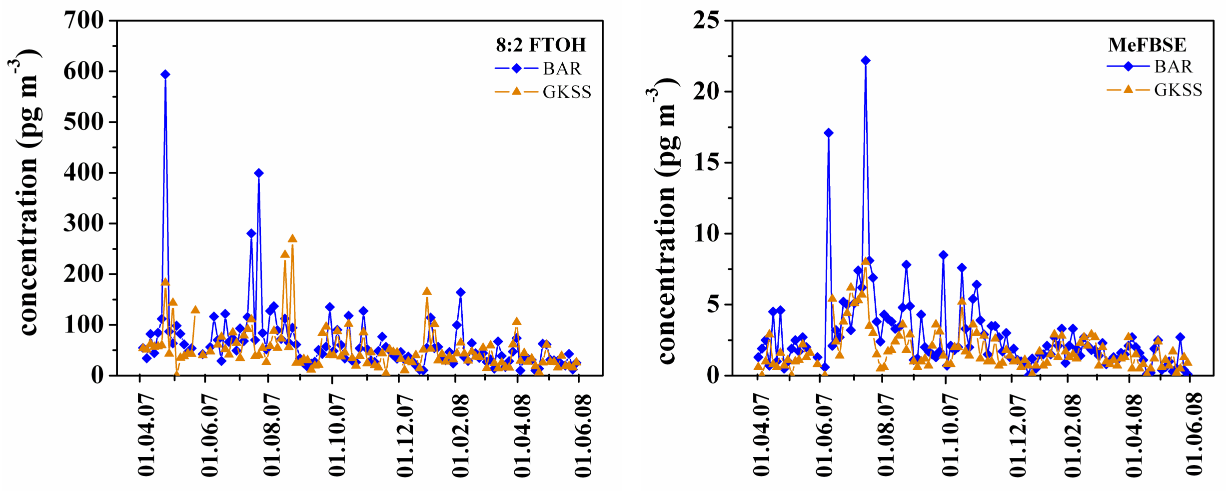
	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5	Cluster 6	Cluster 7	Cluster 8
trajectory character	**E, slow**	**NW, fast**	**stationary**	**W, fast**	**NW, v. fast**	**SW, slow**	**SW, v. fast**	**W, v. fast**
trajectory number	n=12	n=20	n=25	n=13	n=10	n=30	n=5	n=5
4:2 FTOH	0.3	0.0	0.4	0.5	0.3	0.2	0.0	0.3
6:2 FTOH	17	17	22	20	13	21	16	9.5
8:2 FTOH	42	56	63	48	31	62	46	39
10:2 FTOH	13	19	23	16	10	20	15	6.8
12:2 FTOH	3.6	5.3	5.6	6.4	3.8	7.5	8.9	8.3
ΣFTOH	**76**	**98**	**114**	**91**	**58**	**111**	**87**	**64**
6:2 FTA	0.6	1.1	1.4	1.9	0.9	2.0	1.3	0.8
8:2 FTA	2.5	2.3	2.8	3.2	2.2	2.8	2.9	1.3
10:2 FTA	0.9	0.9	0.9	1.2	0.8	1.1	1.0	2.1
ΣFTA	**4.0**	**4.2**	**5**	**6.2**	**3.9**	**5.9**	**5.2**	**4.2**
MeFBSA	1.4	1.4	2.5	1.8	1.0	2.9	2.4	1.4
MeFOSA	1.8	1.8	2.1	1.5	1.2	2.2	2.0	0.8
Me2FOSA	0.1	0.1	0.2	0.3	0.2	0.2	0.1	0.1
EtFOSA	0.5	1.0	1.3	1.3	0.8	1.4	1.4	0.7
PFOSA	0.2	0.1	0.1	0.2	0.5	0.3	0.0	0.4
ΣFASA	**4.0**	**4**	**6.3**	**5.1**	**3.7**	**7**	**5.9**	**3.5**
MeFBSE	1.6	2.1	2.0	2.9	1.7	2.3	1.6	1.5
MeFOSE	1.1	1.5	1.7	2.0	1.1	1.9	1.3	1.3
EtFOSE	0.7	0.7	1.1	0.8	0.8	0.8	0.8	0.7
ΣFASE	**3.4**	**4.3**	**4.8**	**5.7**	**3.6**	**5.1**	**3.7**	**3.6**
total	**87**	**111**	**130**	**108**	**69**	**129**	**101**	**75**

Elevated PFC air concentrations in air masses arriving from central Europe were also observed by Barber et al. (2008). That concentrations of polyfluorinated compounds increased with air masses arriving from densely populated and industrialized areas was also shown by Primbs et al. (2008). They observed that gas-phase FTOH concentrations increased significantly with the time that the air mass parcel spent over California's urban areas and that high concentrations were associated with frontal activity over urban areas of the US west coast. Dreyer and Ebinghaus (2009) did not observe concentrations differences between the port of Hamburg located in the city centre and Barsbüttel and GKSS in a set of samples taken at the same time. Taking the results of both studies into account the origins of airborne PFC appear to be located rather in highly populated and industrialized areas southwest and west of Hamburg than in the city itself. However, the exact role of Hamburg as PFC source cannot be satisfactorily resolved.

3.3. Intra-Annual Variations

Concentrations of polyfluorinated compounds in the gas phase strongly varied over time. The course is characterized by a fluctuating baseline that is interrupted by short singular events of high PFC concentrations. This is exemplarily shown for 8:2 FTOH, the analyte found in highest concentrations, and for MeFBSE, a polyfluorinated sulfonamido ethanol that is used as substitute for long-chain polyfluorinated compounds (figure 2-5). During peak events, concentrations of all analytes were abruptly changing for at least one order of magnitude, e.g. from 54 pg m^{-3} (average concentration without peak events) to 594 pg m^{-3} (maximum concentration) for 8:2 FTOH at Barsbüttel. High concentration events were unevenly distributed. Overall, they occurred when air masses were arriving from directions represented by cluster 3 and 6. Relationships of these high concentrations to locally observed parameters such as temperature, locally different wind direction, precipitation or concentrations of O_3, NO, and NO_2 were not observed. High concentrations were found more often in summer than in winter and did not necessarily occur at the same time at both sampling sites. These distinct, irregular, and highly elevated gas-phase concentrations without a compound-specific fingerprint may give evidence for different nearby point sources of (semi-)volatile polyfluorinated compounds with pulsing emission patterns.

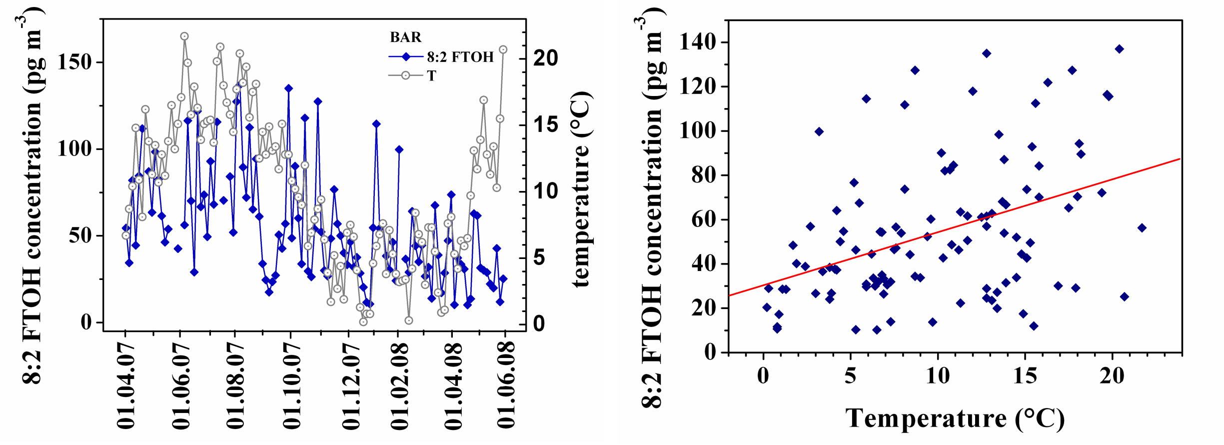
Reliable statements for particle-bound compounds are difficult since results were close to the detection limit. However, for a few particle-bound analytes such as PFBA, concentrations appear to increase towards the winter time.



a b

Figure 2-5: Gas-phase concentrations (pg m^{-3}) of 8:2 FTOH (a) and MeFBSE (b) at Barsbüttel (blue) and GKSS (orange) over the entire sampling period.

To determine if gas-phase PFC concentrations depended on seasonal variations, data representing events of high concentrations were excluded for further analysis. 8:2 FTOH and 10:2 FTOH belonged to the analytes that were least affected by the exclusion of high concentration events at the Barsbüttel site (only 4 eliminated events), 10:2 FTA (19 events) and 12:2 FTOH (18 events) belonged to the most affected ones. At the GKSS site, 12:2 FTOH (5 events) was the least affected analyte, 10:2 FTA (18 events) and PFOSA (20 events) were the most affected ones. Exclusion of these events resulted in a less interrupted concentration course over the year that, except for two main periods (27.08.2007-24.09.2007 and 28.04.2007-02.06.2007), roughly followed the temperature course (figure 2-6, figure S2-8). Overall, the majority of polyfluorinated analytes were correlated significantly to temperature ($p < 0.05$). Correlation coefficients were below 0.5 revealing that concentrations of polyfluorinated analytes in air were not well described by temperature variation. The two periods of divergent PFC concentration and temperature courses are probably due to air masses arriving from less polluted areas, for the first period from northern and north-western marine regions (cluster 2, 4, 5), for the second period from eastern regions (cluster 1). Correlation analysis of temperature and PFC concentrations without these divergent data resulted in increased correlation coefficients. Density-corrected PFOS profiles in ice core samples (Young et al., 2007) suggest that the production of perfluorinated acids from atmospheric precursor oxidation and subsequent deposition, is seasonally dependent. This indicates that precursor air concentrations may vary over the seasons in remote locations as well. Furthermore, seasonal concentration variations are rather anticipated for FASA, FASE, or particle-bound PFC than for gas-phase compounds.



a b

Figure 2-6: Local temperature (°C) and gas-phase concentrations (pg m^{-3}) of 8:2 FTOH at Barsbüttel. a: Temperature and concentration course over the entire sampling period. b: Correlation of 8:2 FTOH and temperature. R=0.4. Note that high concentration events were excluded for these considerations.

In this study, average individual PFC concentration decreased in the order of summer > spring, fall > winter and were most pronounced for the substances found in high concentrations. The lower planetary boundary layer height as well as reduced degradation by OH radicals in winter should lead to increased PFC concentrations during the winter season as it was observed by Barber et al. (2008). Since the majority of air masses were arriving from westerly located source regions in summer and in winter, the observed concentration differences may be explained by temperature dependent emissions of (semi-)volatile PFC from diffuse sources, for instance residual PFC present in products that are currently in use (Dinglasan-Panlilio and Mabury, 2006; Kaiser et al., 2004). Enhanced deposition due to increased PFC partitioning to particles may additionally explain the observed concentration differences for FASA or FASE but not for FTOH since these were not observed on particles. An influence of temperature (season) on recovery rates (e.g. increased losses of internal standards during spiking in the field at elevated temperatures) and thus PFC concentrations was not observed.

3.4. Correlation Analyses

Except for the coherence with temperature (see above), gas-phase concentrations of volatile and semi-volatile polyfluorinated compounds were not controlled by local meteorology or chemistry. Since a correlation to NO_x was not observed it can be concluded that, as expected, gas-phase PFC did not originate from nearby combustion related sources. Correlation of FTOH to combustion related PAH as observed by Primbs et al. (2008) should therefore be interpreted rather as spatially similar source regions than as qualitatively related sources for these groups of substances. Of those PFC detected frequently in the gas phase, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were usually significantly correlated ($p < 0.05$, $r \leq 0.75$). Significant correlations ($r \leq 0.6$) were also observed for 8:2 FTOH and 10:2 FTOH to EtFOSA, MeFOSA, MeFBSE, EtFOSE, and MeFOSE. The majority of individual FASA and FASE were correlated to each other as well ($r \leq 0.7$). These results reveal similar source pattern for the majority of volatile PFC. Correlation analysis of those samples that were contained in trajectory cluster 3 or 6 yielded an increased number of analytes that were correlated significantly at partly higher correlation coefficients ($r \leq 0.85$). This is another indication for diffuse sources west of Hamburg. Fingerprint ratios of 6:2 FTOH to 8:2 FTOH and 10:2 FTOH to 8:2 FTOH for impregnating agents (0.02, 0.6, respectively) and lubricants (> 0.9, 0.7-0.8, respectively) were suggested by Fiedler et al. (submitted). Ratios of 6:2 FTOH to 8:2 FTOH and 10:2 FTOH to 8:2 FTOH determined for average and cluster average PFC concentrations of this study were between 0.3 and 0.4 revealing contributions of more than only these sources. Permanent emissions from application, volatilisation, or distant manufacturing of volatile and semi-volatile polyfluorinated compounds which have been found in commercial and industrial fluoropolymers and surfactants (Dinglasan-Panlilio and Mabury, 2006; Fiedler et al., submitted; Jensen et al., 2008) contribute to the diffuse air contamination that have been detected in this study.

This study demonstrates that measurements covering long periods are valuable tools to assess concentration variations although short time series may yield representative concentration estimates. Furthermore, these results raise new questions about distinct local sources or unknown driving forces.

Acknowledgements

Annekatrin Dreyer was funded by the scholarship program of the German Federal Environmental Foundation (Deutsche Bundesstiftung Umwelt, DBU). We wish to thank Uwe Eckermann from the Environmental Agency (Staatliches Umweltamt Itzehoe) for his support concerning the Barsbüttel site. We thank Vera Langer, Sabine Struwe, and Ingo Weinberg for their helping hands during 14 months of sampling and Michael Radke for his valuable comments on the manuscript. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the Hysplit transport and dispersion model.

Supporting Information

Supporting information is available giving analytical details, sample concentrations, and information on the trajectory analyses.

References

Arp, H. P. H.; Goss, K. U. 2008. Irreversible sorption of trace concentrations of perfluorocarboxylic acids to fiber filters used for air sampling. *Atmospheric Environment*, *42*, 6869-6872.

Barber, J. L.; Berger, M. L.; Chaemfa, C.; Huber, S.; Jahnke, A.; Temme, C.; Jones, K. C. 2007. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *Journal of Environmental Monitoring*, *9*, 530-541.

Barber, J. L.; Chaemfa, C.; Jones, K. C.; Huber, S. 2008. Seasonal variability in atmospheric concentrations of polyfluorinated chemicals (PFCs) at 2 sites in the UK. *1st International Workshop Fuorinated Surfactants - New Developments, http://pft.fh-fresenius.de/, Idstein, Germany*.

Beach, S. A.; Newsted, K. C.; Giesy, J. P. 2006. Ecotoxicological evaluation of Perfluorooctanesulfonate (PFOS). *Review of Environmental Contaminations and Toxicology*, *186*, 133-174.

Bossi, R.; Riget, F. F.; Dietz, R. 2005. Temporal and spatial trends of perfluorinated compounds in ringed seal (Phoca hispida) from Greenland. *Environmental Science & Technology*, *39*, 7416-7422.

Butt, C. M.; Muir, D. C. G.; Stirling, I.; Kwan, M.; Mabury, S. A. 2007. Rapid response of arctic ringed seals to changes in perfluoroalkyl production. *Environmental Science & Technology*, *41*, 42-49.

Caliebe, C.; Gerwinski, W.; Hühnerfuss, H.; Theobald, N. 2004. Occurrence of perfluorinated organic acids in the water of the North Sea. *Organohalogen Compounds*, *66*, 4024-4028.

D'Eon, J. C.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. 2006. Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, C4F9SO2N(CH3)CH2CH2OH: Kinetics and mechanism of reaction with OH. *Environmental Science & Technology*, *40*, 1862-1868.

Dinglasan-Panlilio, M. J. A.; Mabury, S. A. 2006. Significant residual fluorinated alcohols present in various fluorinated materials. *Environmental Science & Technology*, *40*, 1447-1453.

Draxler, R. R.; Rolph, G. D. 2003. HYSPLIT (HYbrid Single-Particle Langerian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). *NOAA Air Resources Laboratory, Silver Spring, MD.*

Dreyer, A.; Ebinghaus, R. 2009. Polyfluorinated Compounds in Ambient Air from ship- and land-based measurements in northern Germany. *Atmospheric Environment*, *43*, 1527-1535.

Dreyer, A.; Temme, C.; Sturm, R.; Ebinghaus, R. 2008. Optimized method avoiding solvent-induced response enhancement in the analysis of volatile and semi-volatile polyfluorinated alkylated compounds using gas chromatography-mass spectrometry. *Journal of Chromatography A*, *1178*, 199-205.

Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. 2004. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environmental Science & Technology*, *38*, 3316-3321.

European Community 2006. Directive 2006/122/EC of the European Parliament and of the Council. *Official Journal of the European Union*, *L 372*, 32-34.

Fiedler, S.; Pfister, G.; Schramm, K.-W. submitted. Poly- and perfluorinated compounds in household consumer products. *Environmental Science & Technology*, *es-2008-03109g*.

Giesy, J. P.; Kannan, K. 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environmental Science & Technology*, *35*, 1339-1342.

Giesy, J. P.; Kannan, K. 2002. Perfluorochemical surfactants in the environment. *Environmental Science & Technology*, *36*, 146A-152A.

Harada, K.; Nakanishi, S.; Saito, N.; Tsutsui, T.; Koizumi, A. 2005. Airborne perfluorooctanoate may be a substantial source contamination in Kyoto area, Japan. *Bulletin of Environmental Contamination and Toxicology*, *74*, 64-69.

Haukas, M.; Berger, U.; Hop, H.; Gulliksen, B.; Gabrielsen, G. W. 2007. Bioaccumulation of per- and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web. *Environmental Pollution*, *148*, 360-371.

Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. G. 2006. Biological monitoring of polyfluoroalkyl substances: A review. *Environmental Science & Technology*, *40*, 3463-3473.

Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. 2004. Atmospheric chemistry of perfluorinated carboxylic acids: Reaction with OH radicals and atmospheric lifetimes. *Journal of Physical Chemistry A*, *108*, 615-620.

Jahnke, A.; Ahrens, L.; Ebinghaus, R.; Temme, C. 2007a. Urban versus remote air concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany. *Environmental Science & Technology*, *41*, 745-752.

Jahnke, A.; Berger, U.; Ebinghaus, R.; Temme, C. 2007b. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53 degrees N-33 degrees S). *Environmental Science & Technology*, *41*, 3055-3061.

Jensen, A. A.; Poulsen, P. B.; Bossi, R. 2008. Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. *Survey of Chemical Substances in Consumer Products, Danish Ministry of the Environment*, *No. 99*.

Kaiser, M. A.; Cobranchi, D. P.; Kao, C. P. C.; Krusic, P. J.; Marchione, A. A.; Buck, R. C. 2004. Physicochemical properties of 8-2 fluorinated Telomer B alcohol. *Journal of Chemical and Engineering Data*, *49*, 912-916.

Kim, S. K.; Kannan, K. 2007. Perfluorinated acids in air, rain, snow, surface runoff, and lakes: Relative importance of pathways to contamination of urban lakes. *Environmental Science & Technology*, *41*, 8328-8334.

Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. 2006. Atmospheric chemistry of perfluoroalkanesulfonamides: Kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. *Environmental Science & Technology*, *40*, 864-872.

Martin, J. W.; Muir, D. C. G.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. 2002. Collection of airborne fluorinated organics and analysis by gas chromatography/chemical ionization mass spectrometry. *Analytical Chemistry*, *74*, 584-590.

McLachlan, M. S.; Holmstrom, K. E.; Reth, M.; Berger, U. 2007. Riverine discharge of perfluorinated carboxylates from the European continent. *Environmental Science & Technology*, *41*, 7260-7265.

Piekarz, A. M.; Primbs, T.; Field, J. A.; Barofsky, D. F.; Simonich, S. 2007. Semivolatile fluorinated organic compounds in Asian and western U.S air masses. *Environmental Science & Technology*, *41*, 8248-8255.

Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. 2006. Sources, fate and transport of perfluorocarboxylates. *Environmental Science & Technology*, *40*, 32-44.

Primbs, T.; Piekarz, A.; Wilson, G.; Schmedding, D.; Higginbotham, C.; Field, J.; Simonich, S. M. 2008. Influence of Asian and Western United States urban areas and fires on the atmospheric transport of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and fluorotelomer alcohols in the Western United States. *Environmental Science & Technology*, *42*, 6385-6391.

Sachs, L. Angewandte Statistik. In; Sringer Verlag: Berlin Heidelberg New York, 2002; Vol. 10. Auflage.

Sasaki, K.; Harada, K.; Saito, N.; Tsutsui, T.; Nakanishi, S.; Tsuzuki, H.; Koizumi, A. 2003. Impact of airborne perfluorooctane sulfonate on the human body burden and the ecological system. *Bulletin of Environmental Contamination and Toxicology*, *71*, 408-413.

Schenker, U.; Scheringer, M.; Macleod, M.; Martin, J. W.; Cousins, I. T.; Hungerbuhlert, K. 2008. Contribution of volatile precursor substances to the flux of perfluorooctanoate to the arctic. *Environmental Science & Technology*, *42*, 3710-3716.

Shoeib, M.; Harner, T.; Vlahos, P. 2006. Perfluorinated chemicals in the Arctic atmosphere. *Environmental Science & Technology*, *40*, 7577-7583.

Smithwick, M.; Norstrom, R. J.; Mabury, S. A.; Solomon, K.; Evans, T. J.; Stirling, I.; Taylor, M. K.; Muir, D. C. G. 2006. Temporal trends of perfluoroalkyl contaminants in polar bears (Ursus maritimus) from two locations in the North American Arctic, 1972-2002. *Environmental Science & Technology*, *40*, 1139-1143.

Stock, N. L.; Furdui, V. I.; Muir, D. C. G.; Mabury, S. A. 2007. Perfluoroalkyl contaminants in the canadian arctic: Evidence of atmospheric transport and local contamination. *Environmental Science & Technology*, *41*, 3529-3536.

Stock, N. L.; Lau, F. K.; Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. 2004. Polyfluorinated telomer alcohols and sulfonamides in the north American troposphere. *Environmental Science & Technology*, *38*, 991-996.

Stock, N. L.; Muir, D.; Mabury, S. A. 2005. Airborne perfluorinated sulfonamides and telomer alcohols in Toronto: a long-term study. *Fluoros, Toronto*, *Poster*.

Sulbaek Andersen, M. P.; Nielsen, O. J.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. 2005. Atmospheric chemistry of 4 : 2 fluorotelomer alcohol (n-C4F9CH2CH2OH): Products and mechanism of Cl atom initiated oxidation in the presence of NOx. *Journal of Physical Chemistry A*, *109*, 1849-1856.

Tao, L.; Kannan, K.; Kajiwara, N.; Costa, M. M.; Fillmann, G.; Takahashi, S.; Tanabe, S. 2006. Perfluorooctanesulfonate and related fluorochemicals in albatrosses, elephant seals, penguins, and Polar Skuas from the Southern Ocean. *Environmental Science & Technology*, *40*, 7642-7648.

US-EPA 2002. Perfluoroalkyl Sulfonates; Significant New Use Rule; Final Rule and Supplemental Proposed Rule. *Federal Register*, *67*.

Wei, S.; Chen, L. Q.; Taniyasu, S.; So, M. K.; Murphy, M. B.; Yamashita, N.; Yeung, L. W. Y.; Lam, P. K. S. 2007. Distribution of perfluorinated compounds in surface seawaters between Asia and Antarctica. *Marine Pollution Bulletin*, *54*, 1813-1818.

Yamashita, N.; Taniyasu, S.; Petrick, G.; Wei, S.; Gamo, T.; Lam, P. K. S.; Kannan, K. 2008. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. *Chemosphere*, *70*, 1247-1255

Young, C. J.; Furdui, V. I.; Franklin, J.; Koerner, R. M.; Muir, D. C. G.; Mabury, S. A. 2007. Perfluorinated acids in arctic snow: New evidence for atmospheric formation. *Environmental Science & Technology*, *41*, 3455-3461.

Supporting Information

The supporting information covers the following topics:

18 pages, 11 tables, 8 figures

Chemicals

Table S2-1: Solvents and gases used for the analysis of PFC in air samples.

substances	abbreviation	purity	producer
ethyl acetate	-	Picograde	Promochem, Wesel, Germany
acetone	-	Picograde	Promochem, Wesel, Germany
methyl-tert-butylether	MTBE	Picograde	Promochem, Wesel, Germany
methanol	MeOH	Residue Analysis	J.T. Baker, Griesheim, Germany
nitrogen	-	6.0	Air Liquide, Germany

Table S2-2: Mass-labeled standard compounds used for the analysis of PFC in air samples.

substances	abbreviation	purity (%)	producer
2-Perfluorohexyl-($^{13}C_2$)-ethanol	^{13}C 6:2 FTOH	> 98	Wellington Laboratories, Guelph, Canada
2-Perfluorooctyl-($^{13}C_2$)-ethanol	^{13}C 8:2 FTOH	> 98	Wellington Laboratories, Guelph, Canada
2-Perfluorodecyl-($^{13}C_2$)-ethanol	^{13}C 10:2 FTOH	> 98	Wellington Laboratories, Guelph, Canada
methyl-D_3-perfluorooctane sulfonamide	D_3 MeFOSA	> 98	Wellington Laboratories, Guelph, Canada
ethyl-D_5-perfluorooctane sulfonamide	D_5 EtFOSA	> 98	Wellington Laboratories, Guelph, Canada
methyl-D_7-perfluorooctane sulfonamido ethanol	D_7 MeFOSE	> 98	Wellington Laboratories, Guelph, Canada
ethyl-D_9-perfluorooctane sulfonamido ethanol	D_9 MeFOSE	> 98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-butanoic acid	^{13}C PFBA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-hexanoic acid	^{13}C PFHxA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-octanoic acid	^{13}C PFOA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-nonanoic acid	^{13}C PFNA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-decanoic acid	^{13}C PFDA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-undecanoic acid	^{13}C PFUnDA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-dodecanoic acid	^{13}C PFDoA	>98	Wellington Laboratories, Guelph, Canada
sodium perfluoro-(^{18}O2)-hexane sulfonate	$^{18}O_2$-PFHxS	>99	Wellington Laboratories, Guelph, Canada
sodium perfluoro-(^{13}C4)-octane sulfonate	^{13}C-PFOS	>98	Wellington Laboratories, Guelph, Canada
sodium perfluoro-(^{13}C4)-octane sulfinate	^{13}C-PFOSi	~90	Wellington Laboratories, Guelph, Canada
hexachlorobenzene ^{13}C6	^{13}C HCB	97	Dr. Ehrenstorfer, Augsburg, Germany
1,3,5-trichlorobenzene D_3	TCB D_3	98	Aldrich, Munich, Germany
2,4-dichlorophenol ^{13}C6	^{13}C DCP	>99	Dr. Ehrenstorfer, Augsburg, Germany
perfluorooctane sulfonamido-D_5-acetic acid	D_5 EtFOSAA	>98	Wellington Laboratories, Guelph, Canada

Table S2-3: Analyte standards used for the analysis of PFC in air samples.

substances	abbreviation	purity (%)	producer
perfluorobutyl ethanol	4:2 FTOH	97	Aldrich, Munich, Germany
perfluorohexyl ethanol	6:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
perfluorooctyl ethanol	8:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
perfluorodecyl ethanol	10:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
perfluorododecyl ethanol	12:2 FTOH	-	donated by Jones group, Lancaster University, UK
perfluorohexyl ethylacylate	6:2 FTA	97	Aldrich, Munich, Germany
perfluorooctyl ethylacylate	8:2 FTA	97	Fluorochem, Old Glossop, UK
perfluorodecyl ethylacylate	10:2 FTA	97	Fluorochem, Old Glossop, UK
n-methyl perfluorobutane sulfonamide	MeFBSA	-	donated by 3M, Germany
n-methyl perfluorooctane sulfonamide	MeFOSA	-	donated by 3M, Germany
n-ethyl perfluorooctane sulfonamide	EtFOSA	95	ABCR, Karlsruhe, Germany
perfluorooctane sulfonamide	PFOSA	-	donated by 3M, USA
dimethylperfluoroocatane sulfonamide	Me2FOSA	98	Wellington Laboratories, Guelph, Canada
n-methyl perfluorobutane sulfonamido ethanol	MeFBSE	-	donated by 3M, USA
n-methyl perfluorooctane sulfonamidoethanol	MeFOSE	-	donated by 3M, USA
n-ethyl perfluorooctane sulfonamido ethanol	EtFOSE	-	donated the Mabury group, Toronto University, Canada
potassium perfluorobutane sulfonate	PFBS-K	98	ABCR, Karlsruhe, Germany
potassium perfluorohexane sulfonate	PFHxS-K	98	Fluka, Buchs, Switzerland
potassium perfluorooctane sulfonate	PFOS-K	98	Fluka, Buchs, Switzerland
potassium perfluorodecane sulfonate	PFDS-K	>98	Wellington Laboratories, Guelph, Canada
perfluorobutanoic acid	PFBA	99	ABCR, Karlsruhe, Germany
perfluoropentanoic acid	PFPA	98	Alfa Aesar, Karlsruhe, Germany
perfluorohexanoic acid	PFHxA	98	ABCR, Karlsruhe, Germany
perfluoroheptanoic acid	PFHpA	98	Lancaster Synthesis, Frankfurt, Germany
perfluorooctanoic acid	PFOA	95	Lancaster Synthesis, Frankfurt, Germany
perfluorononanoic acid	PFNA	98	Alfa Aesar, Karlsruhe, Germany
perfluorodecanoic acid	PFDA	98	ABCR, Karlsruhe, Germany
perfluoroundecanoic acid	PFUnDA	96	ABCR, Karlsruhe, Germany
perfluorododecanoic acid	PFDoDA	96	Alfa Aesar, Karlsruhe, Germany
perfluorotridecanoic acid	PFTrDA	>98	Wellington Laboratories, Guelph, Canada
perfluorotetradecanoic acid	PFTeDA	96	Alfa Aesar, Karlsruhe, Germany
perfluorohexadecanoic acid	PFHxDA	95	Alfa Aesar, Karlsruhe, Germany
perfluorooctadecanoic acid	PFOcDA	97	Alfa Aesar, Karlsruhe, Germany
sodium perfluorohexane sulfinate	PFHxSi	98	Wellington Laboratories, Guelph, Canada
sodium perfluorooctane sulfinate	PFOSi	98	Wellington Laboratories, Guelph, Canada
sodium perfluorodecane sulfinate	PFDSi	98	Wellington Laboratories, Guelph, Canada

Recovery Rates

Table S2-4: Minimum (min), maximum (max), and average recovery rates (R, %), absolute and relative standard deviation (S.D., %) of mass- labeled internal standards in the gas phase by GC-MS. Losses during the sampling process are included in these recovery rates since mass-labeled standards were added prior to the sampling.

	R (average, %)	S.D. (abs., %)	S.D. (rel., %)	R (min, %)	R (max %)
4:2 FTOH ^{13}C	25	17	66	1	111
6:2 FTOH ^{13}C	42	22	53	0	148
8:2 FTOH ^{13}C	51	26	50	1	195
10:2 FTOH ^{13}C	46	33	71	0	191
EtFOSA D_5	46	19	42	0	99
MeFOSA D_3	39	19	47	8	135
MeFOSE D_7	60	24	40	18	196
EtFOSE D_9	60	19	31	13	134

Table S2-5: Minimum (min), maximum (max), and average recovery rates (R, %), absolute and relative standard deviation (S.D., %) of mass-labeled internal standards in the particle phase by GC-MS. Losses during the sampling process are not included in these recovery rates.

	R (average, %)	S.D. (abs., %)	S.D. (rel., %)	R (min, %)	R (max %)
4:2 FTOH ^{13}C	22	15	70	1	87
6:2 FTOH ^{13}C	26	15	59	1	70
8:2 FTOH ^{13}C	27	15	58	1	62
10:2 FTOH ^{13}C	31	19	59	1	94
EtFOSA D_5	42	21	51	2	124
MeFOSA D_3	35	18	50	2	92
MeFOSE D_7	60	32	54	5	161
EtFOSE D_9	50	22	44	7	117

Table S2-6: Minimum (min), maximum (max), and average recovery rates (R, %), absolute and relative standard deviation (S.D., %) of mass-labeled internal standards in the particle phase detected by HPLC-MS/MS. MS. Losses during the sampling process are not included in these recovery rates.

	R (average, %)	S.D. (abs., %)	S.D. (rel., %)	R (min, %)	R (max %)
^{18}O2-PFHxS	63	38	61	2	164
^{13}C-PFOS	67	41	60	2	232
^{13}C-PFOSi	66	43	66	2	214
^{13}C-PFBA	95	77	81	4	346
^{13}C-PFHxA	48	33	69	1	165
^{13}C-PFOA	46	29	63	1	120
^{13}C-PFNA	55	30	55	1	148
^{13}C-PFDA	74	44	60	2	257
^{13}C-PFUDA	94	64	68	4	285
^{13}C-PFDoA	95	64	67	2	287
D_3-MeFOSA	47	36	76	1	202
D_5-EtFOSA	55	39	72	1	209
D_7-MeFOSE	79	62	78	1	305
D_9-EtFOSE	69	50	73	1	259

Blanks

Table S2-7: Concentrations (c) of solvent (gas phase, n = 51) and filter (particle phase, n=15) blanks observed during the analysis of PFC in air samples using GC-MS (pg m^{-3}). Field concentrations reported in this study were corrected by blank values.

	C (solvent blank, pg m^{-3})		C (filter blank, pg m^{-3})	
	average	**max**	**average**	**max**
6:2 FTA	0.3	0.8	n.d.	n.d.
4:2 FTOH	0.2	0.6	n.d.	n.d.
6:2 FTOH	0.2	1.0	0.2	0.5
8:2 FTA	0.2	0.5	n.d.	n.d.
8:2 FTOH	0.2	0.9	1.1	3.7
Me$_2$FOSA	n.d.	n.d.	n.d.	n.d.
10:2 FTA	0.2	0.5	n.d.	n.d.
10:2 FTOH	0.1	0.7	0.6	2.7
12:2 FTOH	0.1	0.8	0.6	2.5
EtFOSA	0.1	0.3	0.8	2.6
MeFBSA	n.d.	n.d.	n.d.	n.d.
MeFOSA	0.2	0.4	0.1	0.3
MeFOSE	0.1	0.7	0.3	1.1
MeFBSE	0.2	0.3	2.3	2.4
EtFOSE	0.1	0.8	0.3	1.2
PFOSA	n.d.	n.d.	n.d.	n.d.

Table S2-8: PFC concentrations (pg m^{-3}) observed in field blanks during the analysis of PFC in gas (n=18)- and particle-phase (n=9) samples using GC-MS. Field blanks were taken about once a month at both sites and were treated the same way as samples, i.e. sampling media were placed into the high volume samplers, samplers were run for 5 minutes, sampling media were removed and stored until analysis.

	C (field blank, gas phase, pg m^{-3})		C (field blank, particle phase, pg m^{-3})	
	average	**max**	**average**	**max**
6:2 FTA	1.0	2.2	n.d.	n.d.
4:2 FTOH	1.4	2.1	n.d.	n.d.
6:2 FTOH	1.3	2.8	n.d.	n.d.
8:2 FTA	0.7	1.6	n.d.	n.d.
8:2 FTOH	0.8	1.8	n.d.	n.d.
Me$_2$FOSA	n.d.	n.d.	n.d.	n.d.
10:2 FTA	0.9	0.9	n.d.	n.d.
10:2 FTOH	1.0	3.0	0.4	0.5
12:2 FTOH	1.0	2.3	0.3	0.3
EtFOSA	0.2	0.4	n.d.	n.d.
MeFBSA	0.7	1.2	n.d.	n.d.
MeFOSA	0.6	1.1	0.0	0.1
MeFOSE	0.7	1.5	0.1	0.3
MeFBSE	0.9	0.9	n.d.	n.d.
EtFOSE	0.8	1.6	n.d.	n.d.
PFOSA	n.d.	n.d.	n.d.	n.d.

Table S2-9: PFC concentrations (pg m^{-3}) observed in filter blanks (n=28) during the analysis of PFC in air samples using HPLC-MS/MS. Field concentrations reported in this study were corrected by blank values.

	C (average) pg m^{-3}	C (max) pg m^{-3}
PFBS	0.3	1.5
PFHxS	0.3	0.8
PFHpS	0.0	0.1
PFOS	1.2	3.5
PFDS	0.0	0.0
PFHxSi	0.0	0.7
PFOSi	0.2	0.8
PFDSi	n.d.	n.d.
PFBA	0.6	3.3
PFPA	0.2	2.8
PFHxA	0.2	0.5
PFHpA	0.1	0.8
PFOA	1.1	2.8
PFNA	0.2	1.1
PFDA	0.2	0.8
PFUnDA	0.3	0.9
PFDoDA	0.2	0.8
PFTriDA	0.1	1.0
PFTeDA	0.1	0.7
PFHxDA	0.1	1.5
PFOcDA	0.1	2.3
FOSA	0.2	1.1
NMeFOSA	n.d.	n.d.
NEtFOSA	0.0	0.0
NMeFOSE	1.8	3.4
NEtFOSE	1.0	2.2
MeFBSA	n.d.	n.d.
MeFBSE	n.d.	n.d.

Analyte Concentrations

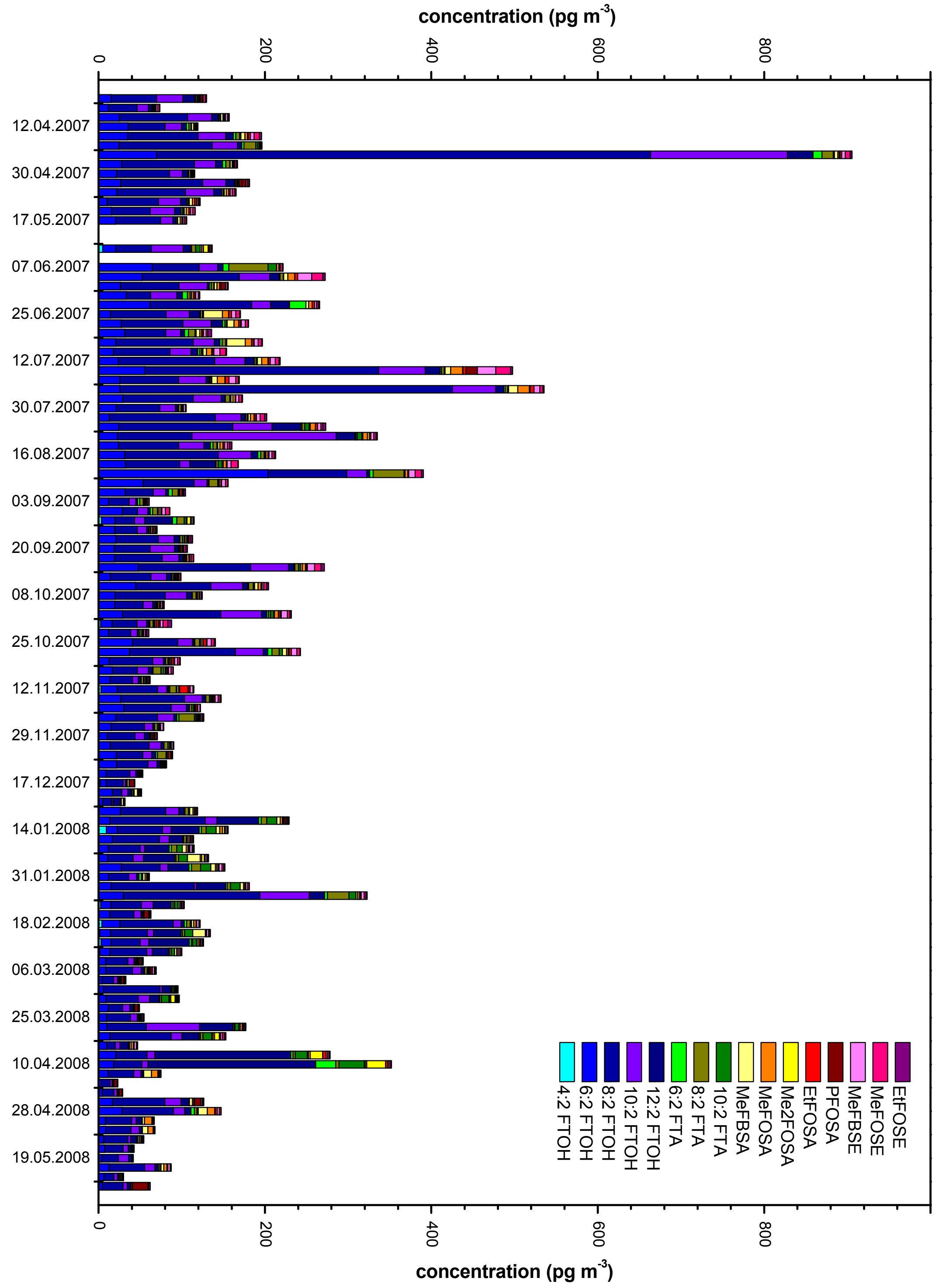


Figure S2-1: Gas-phase concentrations (pg m^{-3}) of volatile and semi-volatile polyfluorinated compounds at the Barsbüttel site.

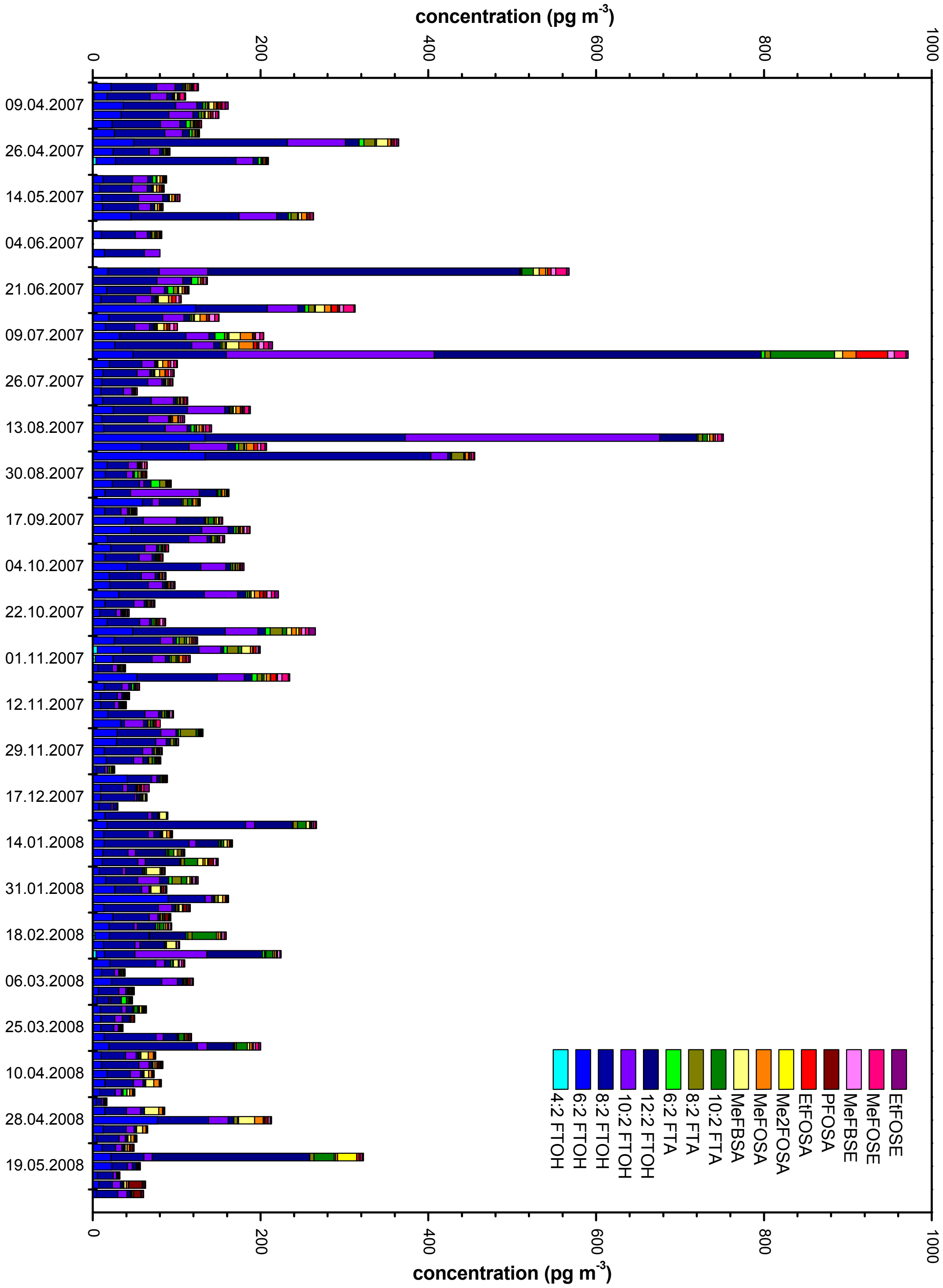


Figure S2-2: Gas-phase concentrations (pg m^{-3}) of volatile and semi-volatile polyfluorinated compounds at the GKSS site.

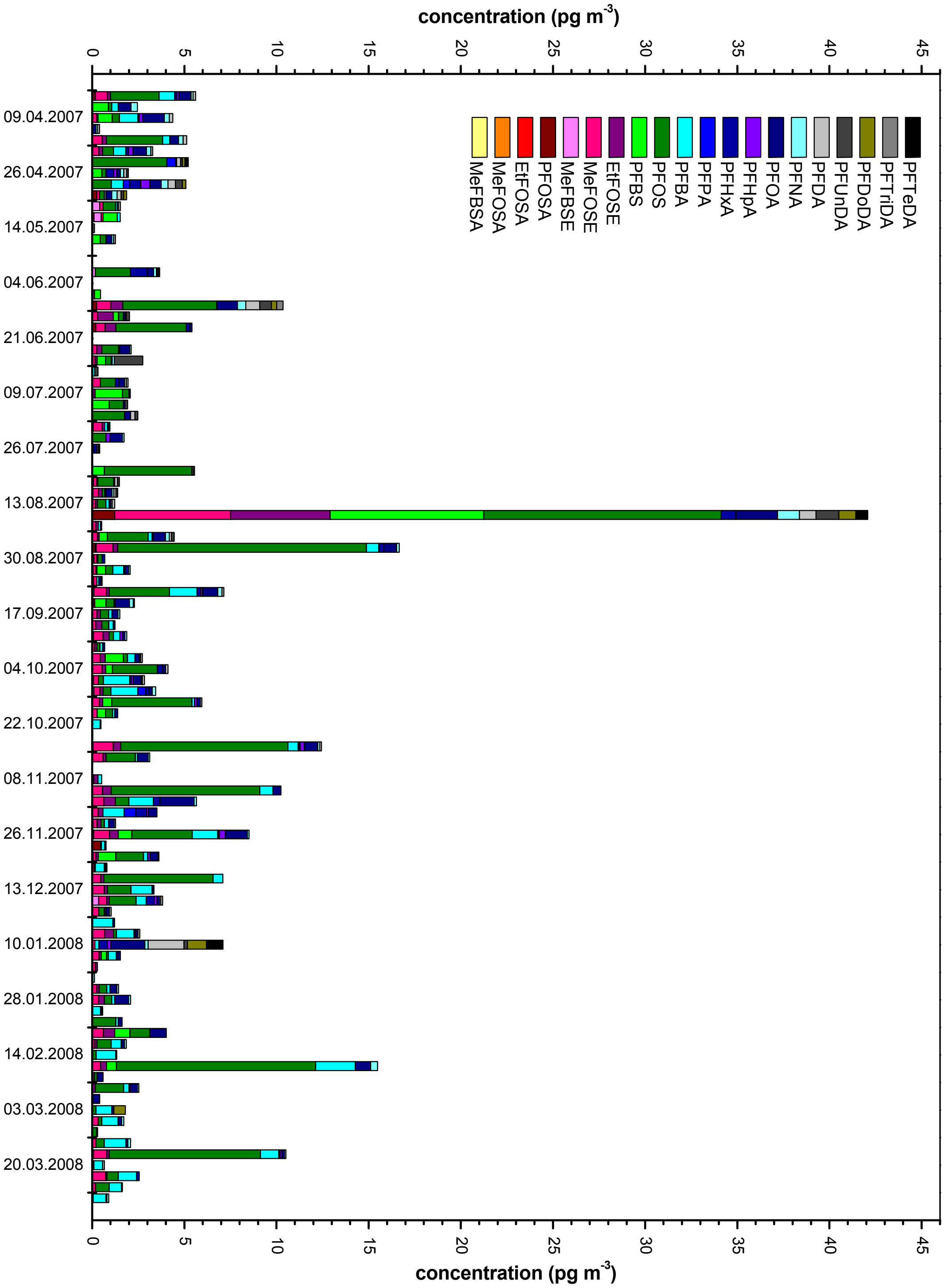


Figure S2-3: Particle-phase concentrations (pg m^{-3}) of detected per- and polyfluorinated compounds at the Barsbüttel site.

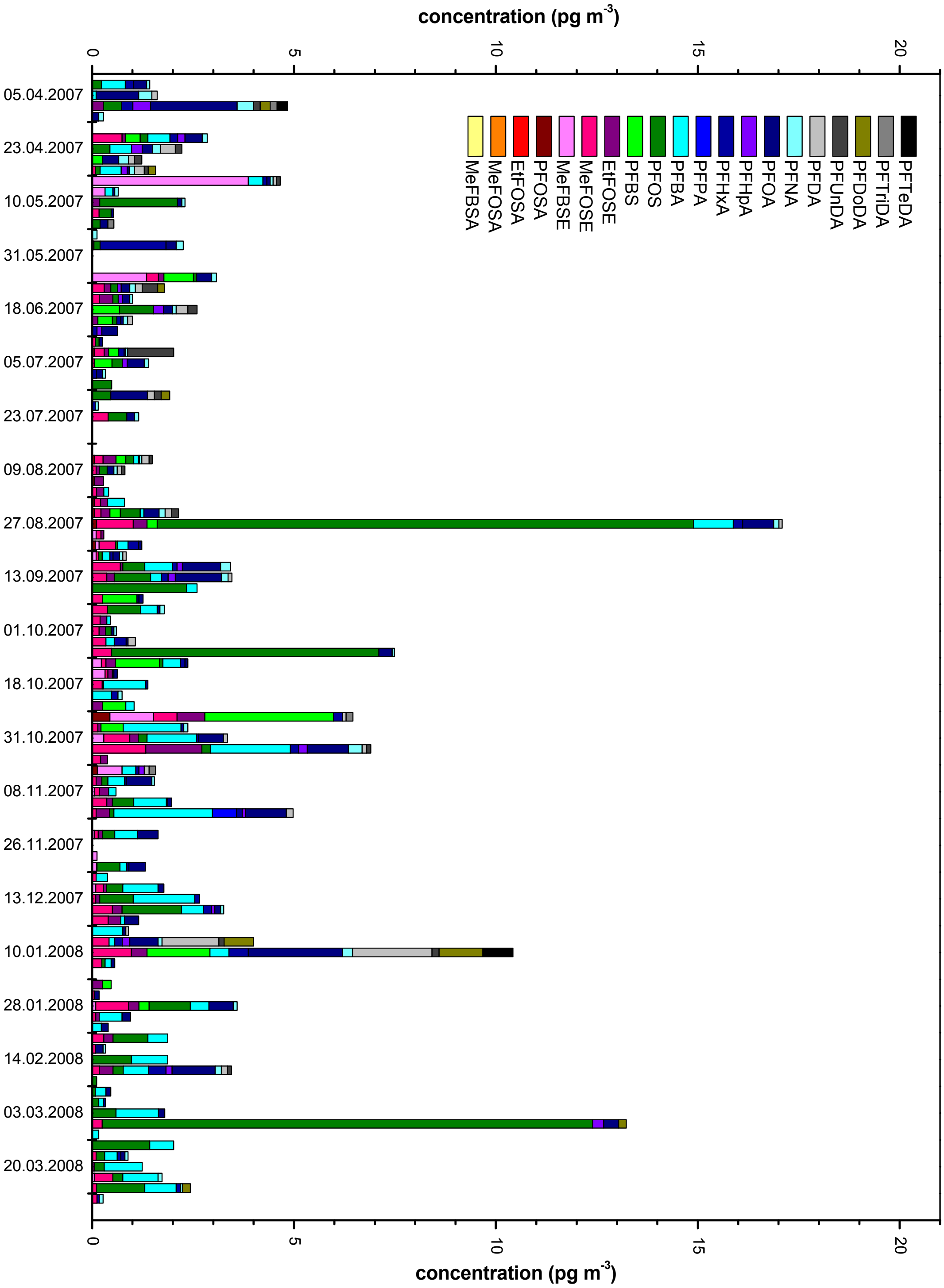


Figure S2-4: Particle-phase concentrations (pg m^{-3}) of detected per- and polyfluorinated compounds at the GKSS site.

Average and Median PFC Concentrations in the Gas Phase

Table S2-10: Average and median gas-phase concentrations (pg m^{-3}) of poly- and perfluorinated compounds, standard deviations (S.D.), and skewness at the Barsbüttel and GKSS site. Individual concentrations were weighted according to the sampling duration, i.e. to each day one value per substance was assigned.

	GKSS samples				BAR samples			
	median	**average**	**S.D.**	**scewness**	**median**	**average**	**S.D.**	**scewness**
4:2 FTOH	0.0	0.1	0.6	5.6	0.0	0.3	1.2	4.9
6:2 FTOH	15	23	24	3.0	17	22	22	5.7
8:2 FTOH	40	50	41	2.9	48	62	66	5.1
10:2 FTOH	13	21	37	6.0	14	21	23	4.4
12:2 FTOH	5	16	52	6.3	5.8	13	25	5.8
Σ FTOH	80	110	113	3.9	101	119	98	3.9
6:2 FTA	1.0	1.6	1.9	2.4	1.2	1.9	3.3	4.8
8:2 FTA	1.4	2.5	3.1	2.8	2.5	4.2	6.5	4.5
10:2 FTA	0.9	2.6	7.5	7.6	1.0	2.5	4.2	3.7
Σ FTA	4.3	6.7	9.3	5.3	5.9	8.6	10	3.2
MeFBSA	1.8	3.6	4.2	1.9	1.7	3.0	3.8	3.1
MeFOSA	2.1	2.9	3.0	2.6	1.9	2.6	2.5	2.2
Me2FOSA	0.0	0.5	2.0	10.0	0.1	0.8	2.6	6.5
EtFOSA	0.9	1.5	3.3	9.4	1.0	1.3	1.3	3.3
PFOSA	0.0	0.8	2.0	4.6	0.0	1.0	2.5	4.5
Σ FASA	7.0	9.3	9.0	2.7	6.5	9.2	8.2	2.8
MeFBSE	1.3	1.7	1.4	1.7	2.0	2.7	2.8	3.9
MeFOSE	1.3	2.0	2.2	3.2	1.6	2.2	2.3	3.5
EtFOSE	0.6	1.0	1.1	2.9	0.7	1.0	0.9	1.8
Σ FASE	3.6	4.7	4.0	2.4	4.3	5.9	5.4	3.5
total	96	131	127	3.9	121	143	109	3.3

Average and median PFC concentrations in the Particle Phase

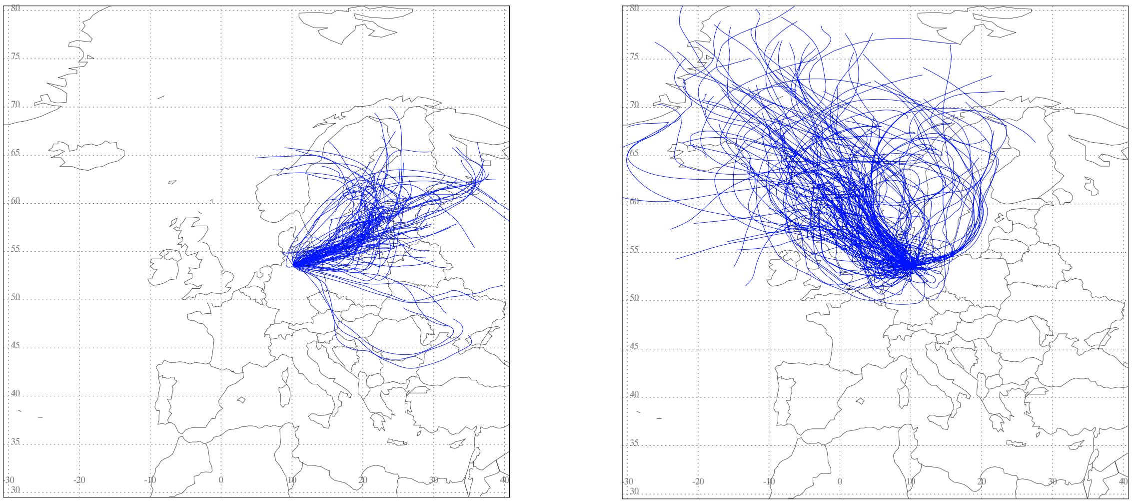
Table S2-11: Average and median particle-phase concentrations of poly- and perfluorinated compounds (pg m^{-3}), standard deviation (S.D.), and skewness at the Barsbüttel and GKSS site. Individual concentrations were weighted according to the sampling duration, i.e. to each day one value per substance was assigned.

	BAR				GKSS			
	median	average	S.D.	skewness	median	average	S.D.	skewness
4:2 FTOH	----	----	----	----	----	----	----	----
6:2 FTOH	0.0	0.0	0.1	4.2	----	----	----	----
8:2 FTOH	----	----	----	----	----	----	----	----
10:2 FTOH	0.0	0.1	0.3	1.9	0.0	0.1	0.3	2.1
12:2 FTOH	0.0	0.1	0.2	1.9	0.0	0.1	0.3	2.0
Σ FTOH	0.0	0.3	0.5	1.7	0.0	0.3	0.6	2.0
6:2 FTA	----	----	----	----	----	----	----	----
8:2 FTA	0.0	0.0	0.1	3.8	----	----	----	----
10:2 FTA	0.0	0.0	0.1	4.1	----	----	----	----
Σ FTA	0.0	0.1	0.2	3.9	----	----	----	----
MeFBSA	----	----	----	----	----	----	----	----
NMeFOSA	0.0	0.0	0.0	8.4	0.0	0.0	0.0	4.8
Me2FOSA	----	----	----	----	----	----	----	----
NEtFOSA	0.0	0.0	0.0	11	0.0	0.0	0.0	6.5
PFOSA	0.0	0.0	0.1	7.6	0.0	0.0	0.0	11
Σ FASA	0.0	0.0	0.1	6.6	0.0	0.0	0.0	5.4
MeFBSE	0.0	0.0	0.1	5.7	0.0	0.1	0.4	8.2
NMeFOSE	0.2	0.3	0.6	7.9	0.1	0.2	0.2	2.1
NEtFOSE	0.0	0.1	0.5	8.9	0.0	0.1	0.1	3.3
Σ FASE	0.3	0.5	1.2	8.6	0.2	0.3	0.5	4.2
PFBS	0.0	0.2	0.9	8.0	0.0	0.1	0.3	5.1
PFHxS	----	----	----	----	----	----	----	----
PFHpS	----	----	----	----	----	----	----	----
PFOS	0.3	1.3	2.5	3.2	0.1	0.6	1.9	5.7
PFDS	----	----	----	----	----	----	----	----
Σ PFSA	0.4	1.5	3.1	4.1	0.2	0.7	1.9	5.6

Table S2-11: cont.

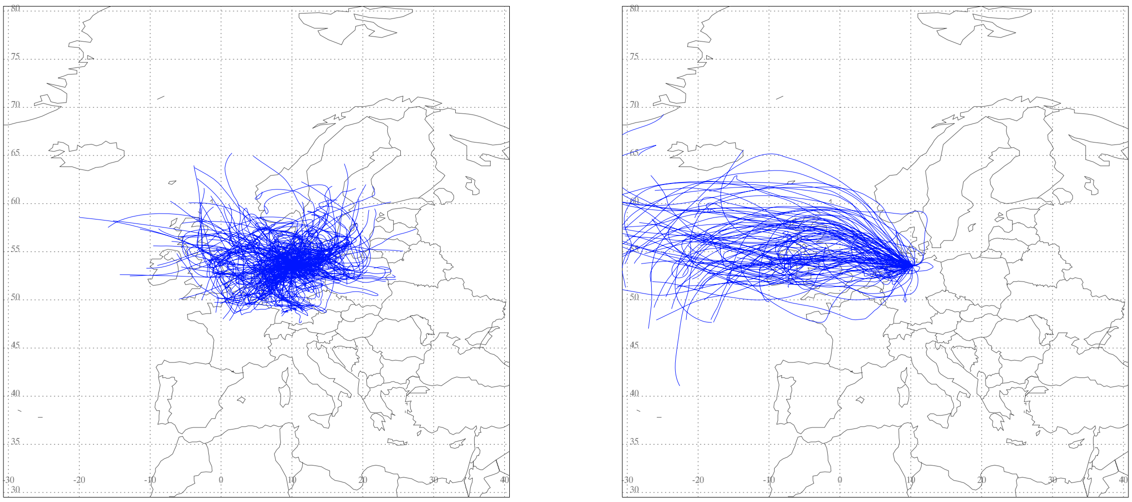
	BAR				GKSS			
	median	**average**	**S.D.**	**skewness**	**median**	**average**	**S.D.**	**skewness**
PFHxSi	----	----	----	----	----	----	----	----
PFOSi	----	----	----	----	----	----	----	----
PFDSi	----	----	----	----	----	----	----	----
Σ PFSi	----	----	----	----	----	----	----	----
PFBA	0.1	0.3	0.4	1.5	0.1	0.3	0.4	2.4
PFPA	0.0	0.0	0.1	5.4	0.0	0.0	0.1	9.2
PFHxA	0.0	0.1	0.2	3.1	0.0	0.1	0.2	6.8
PFHpA	0.0	0.0	0.1	3.5	0.0	0.0	0.1	3.1
PFOA	0.2	0.3	0.4	2.5	0.1	0.2	0.4	3.1
PFNA	0.0	0.1	0.2	4.7	0.0	0.1	0.1	1.9
PFDA	0.0	0.1	0.2	6.1	0.0	0.1	0.2	6.8
PFUnDA	0.0	0.1	0.2	5.6	0.0	0.0	0.1	7.4
PFDoDA	0.0	0.0	0.2	5.4	0.0	0.0	0.1	6.6
PFTriDA	0.0	0.0	0.0	11	0.0	0.0	0.0	6.1
PFTeDA	0.0	0.0	0.1	6.4	0.0	0.0	0.1	8.3
PFHxDA	----	----	----	----	----	----	----	----
PFOcDA	----	----	----	----	----	----	----	----
Σ PFCA	0.6	1.0	1.3	3.1	0.5	0.8	1.1	3.6
total	1.3	3.1	5.7	22.3	0.9	1.8	3.5	18.7

Trajectory Analysis



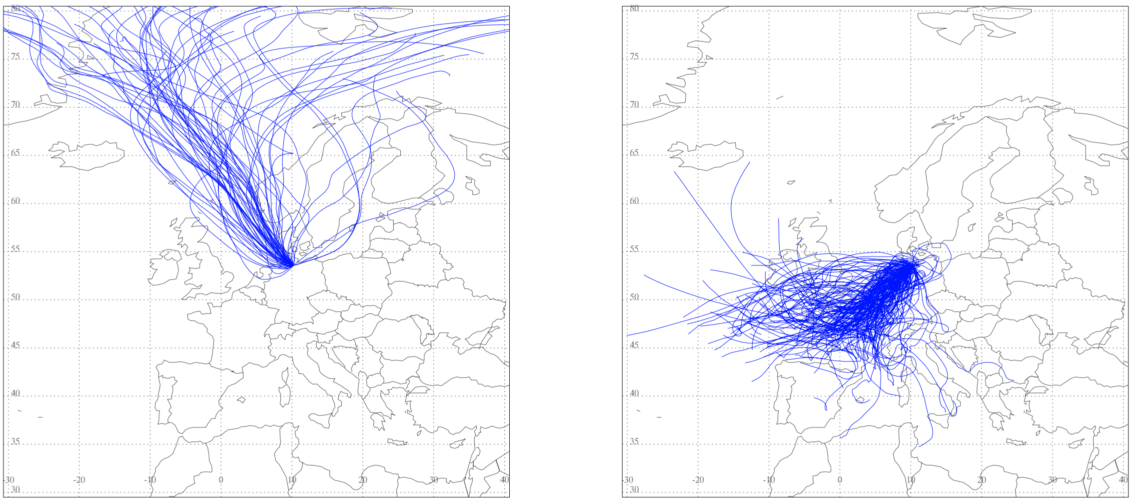
Cluster 1 (n=12)

Cluster 2 (n=20)



Cluster 3 (n=25)

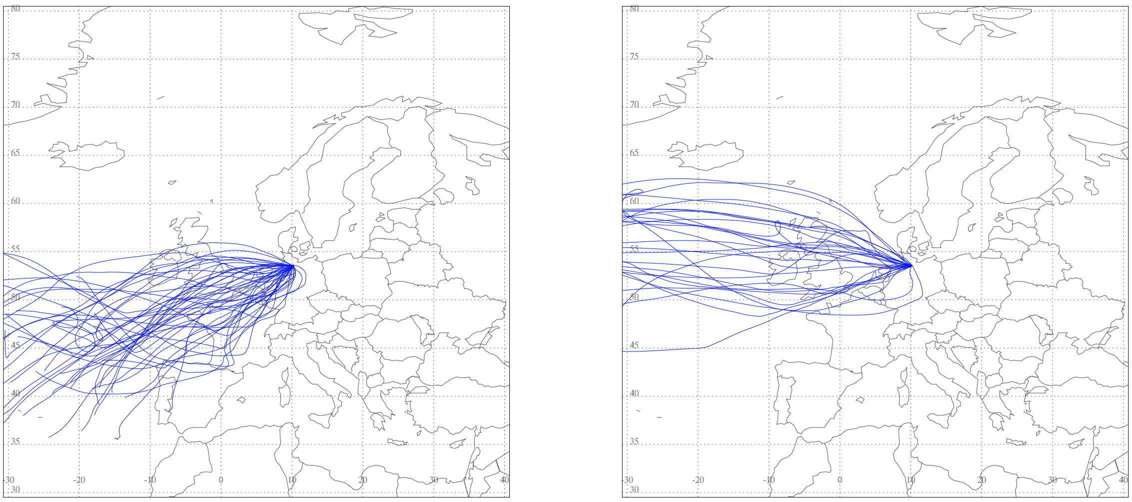
Cluster 4 (n=13)



Cluster 5 (n=10)

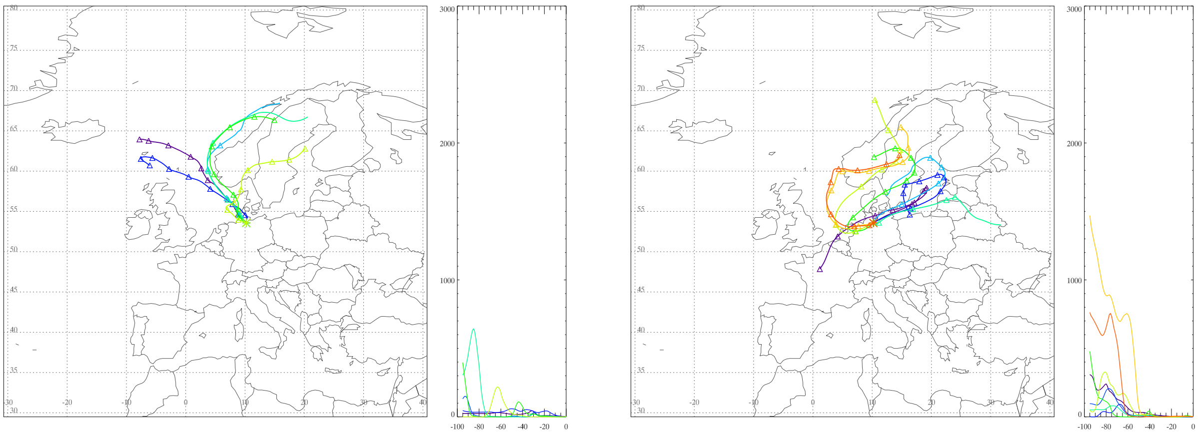
Cluster 6 (n=30)

Figure S2-5: Results of the cluster analysis of twelve hours back trajectories using Hysplit 4.8.



Cluster 7 (n=5) Cluster 8 (n=5)

Figure S2-5: cont.



low concentrations high concentrations

a b

Figure S2-6: Twelve hours air mass back trajectories and altitudinal profiles of the air mass parcels for two Barsbüttel samples. If air masses from low concentration regions such as northern marine air masses (cluster 2) were sampled PFC concentrations were lower in pure samples i.e. air masses were arriving from regions of only one cluster (a) such as BAR 113 (16.05.2008) than of mixed samples i.e. air masses were partly arriving from regions of another cluster (b) such as BAR 51 (27.09.2007). The air parcel travelled within the planetary boundary layer in both cases.

Intra-Annual Concentration Variations

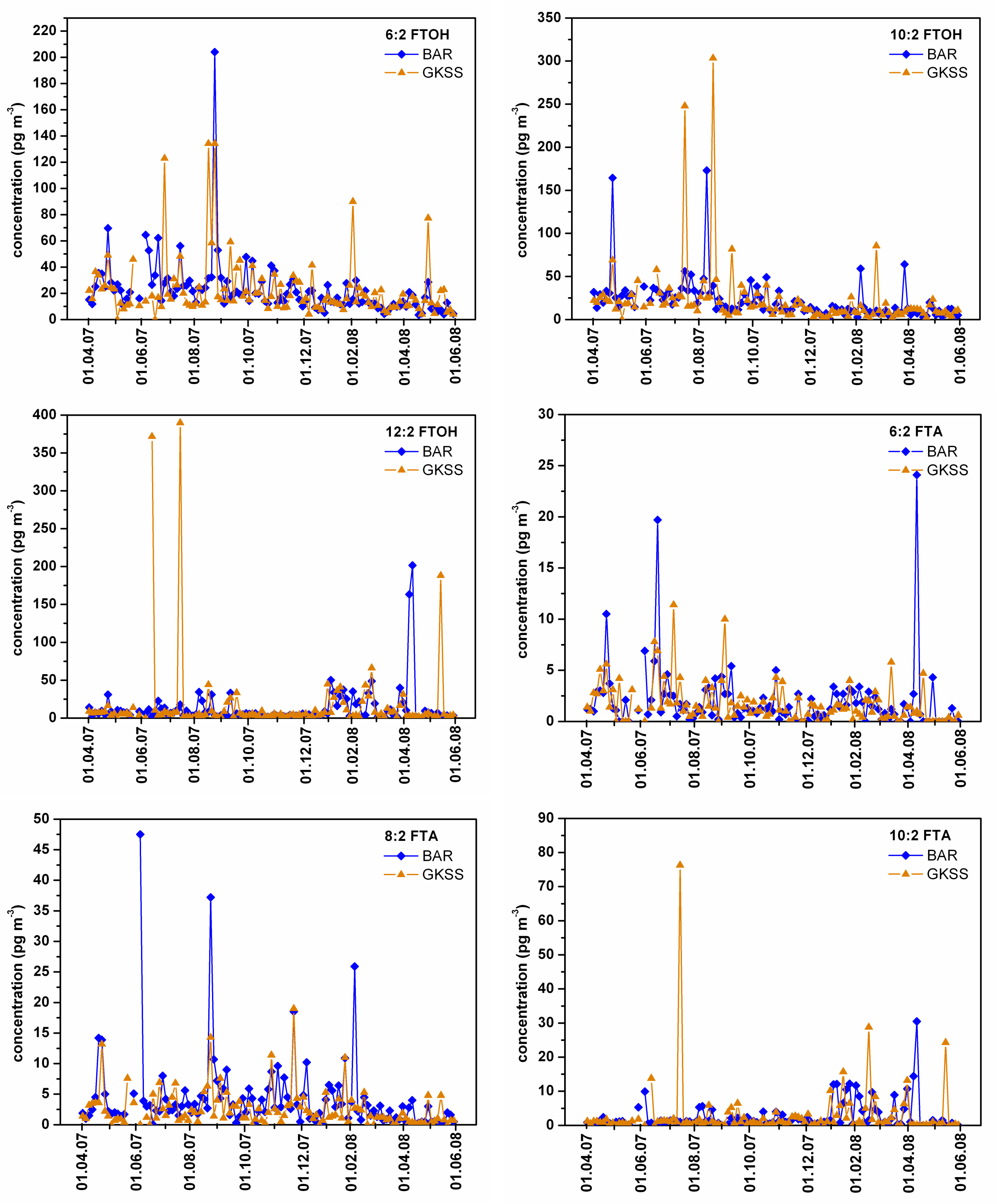


Figure S2-7: Intra-annual concentration variations of several volatile and semi-volatile polyfluorinated substances in the gas phase.

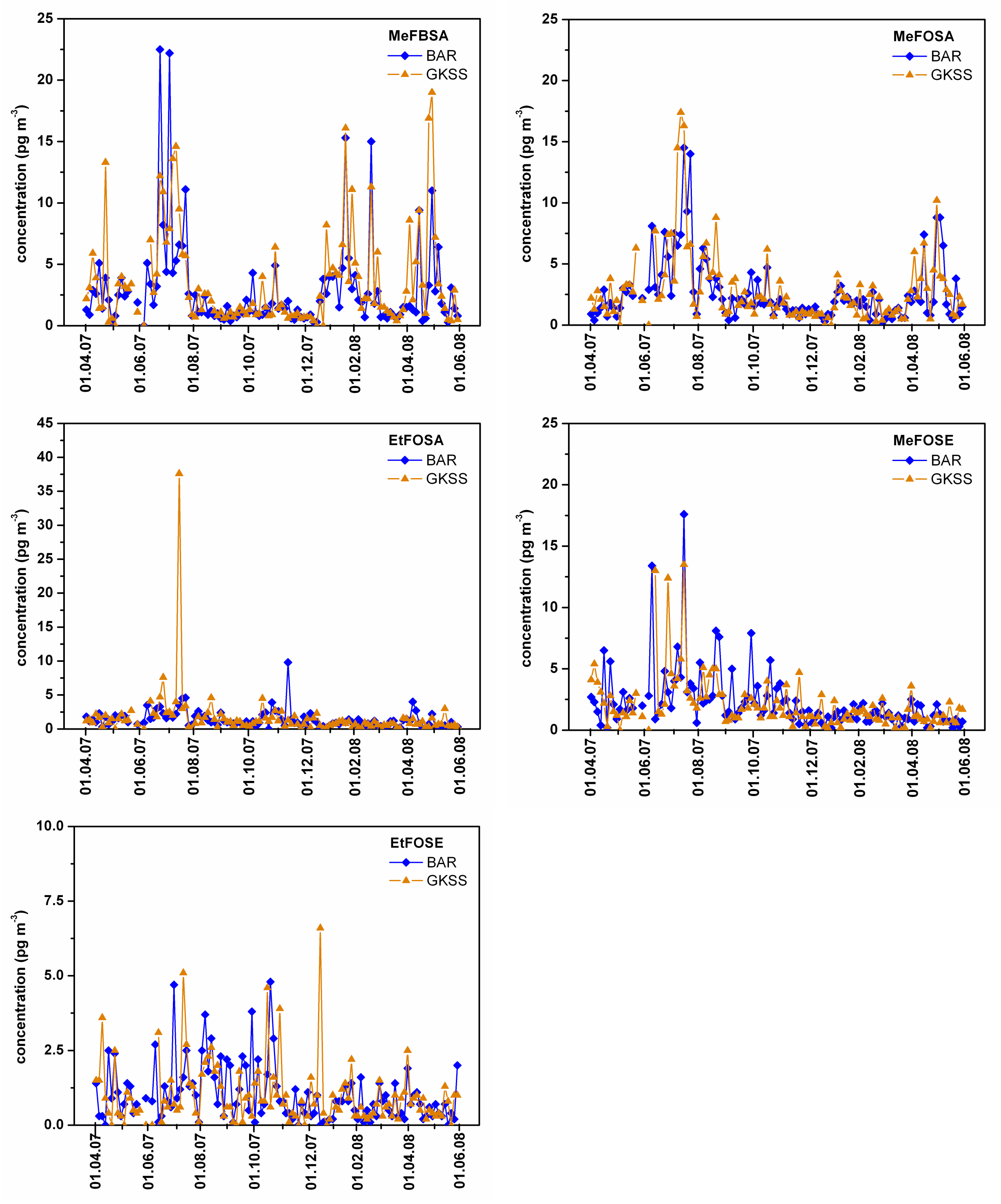
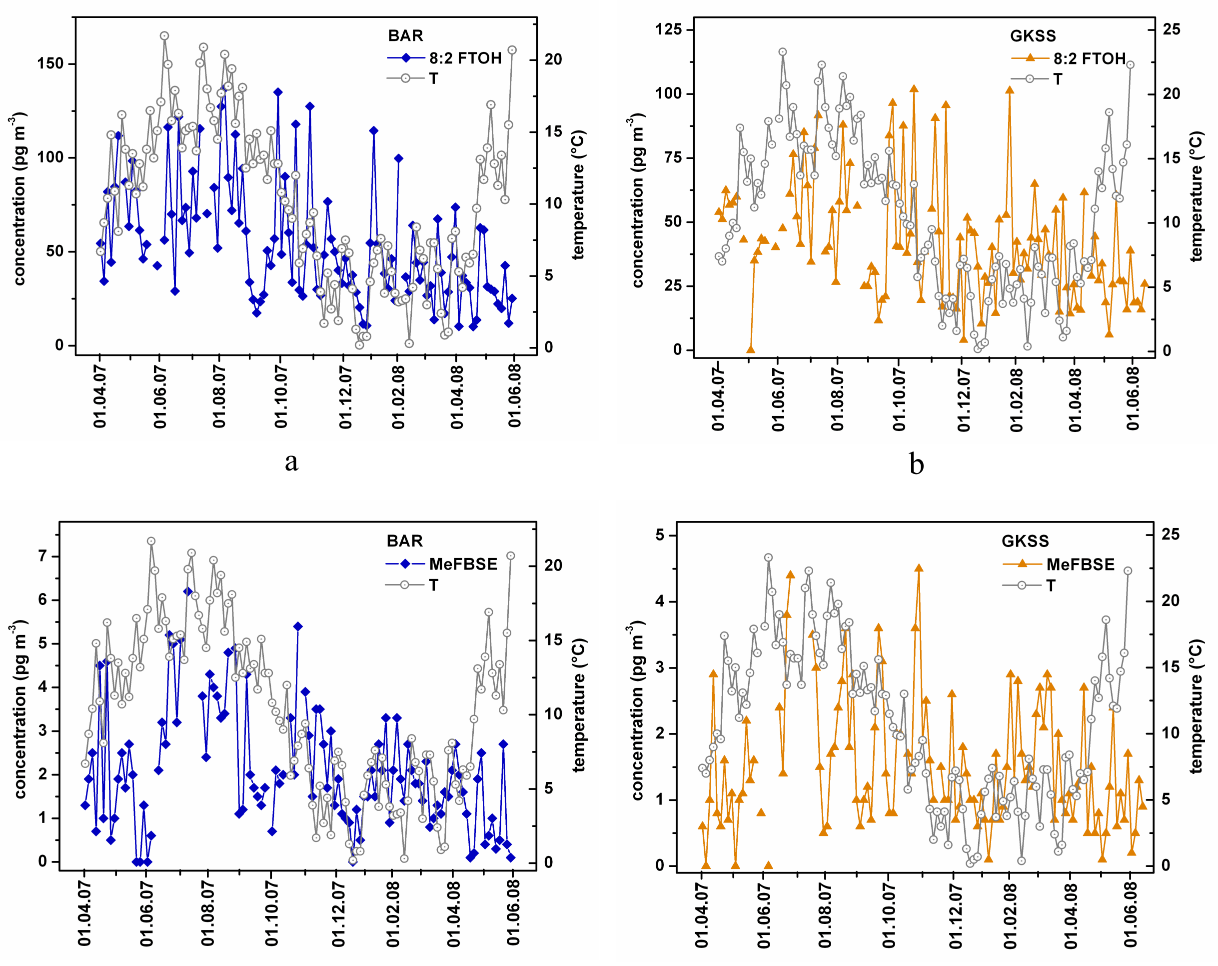


Figure S2-7: cont.

PFC Concentrations & Temperature

Figure S2-8 presents the local temperature and concentration course exemplarily for two analytes: 8:2 FTOH that was detected in gas-phase samples only and MeFBSE that was detected in gas and particle phase. Except for two main periods (27.08.2007-24.09.2007 and 28.04.2007-02.06.2007), PFC concentrations roughly followed the temperature course. Although correlations between the analytes and temperature were significant ($p < 0.05$), correlation coefficients were below 0.5 revealing that concentrations of polyfluorinated analytes in air are not well described by temperature variation.



a b

c d

Figure S2-8: **Local temperature (°C) and gas-phase concentrations (pg m-3) of 8:2 FTOH (a, b) and MeFBSE (c, d) at Barsbüttel and GKSS over the entire sampling period. High concentration events were excluded for these considerations.**

Study 3

Polyfluorinated Compounds in Ambient Air from Ship- and Land-Based Measurements in Northern Germany

Annekatrin Dreyer, Ralf Ebinghaus

Atmospheric Environment (2009) 43 1527-1535

Polyfluorinated Compounds in Ambient Air from Ship- and Land-Based Measurements in Northern Germany

Annekatrin Dreyer and Ralf Ebinghaus

GKSS Research Centre Geesthacht, Max Planck Str. 1, 21502 Geesthacht, Germany

Abstract

Neutral volatile and semi-volatile polyfluorinated organic compounds (PFC) and ionic perfluorinated compounds were determined in air samples collected at two sites in the vicinity of Hamburg, Germany, and onboard the German research vessel Atair during a cruise in the German Bight, North Sea, in early November 2007. PUF/XAD-2/PUF cartridges and glass fiber filters as sampling media were applied to collect several fluorotelomer alcohols (FTOH), fluorotelomer acrylates (FTA), perfluoroalkyl sulfonamides (FASA), and perfluoroalkyl sulfonamido ethanols (FASE) in the gas and particle phase as well as a set of perfluorinated carboxylic acids (PFCA) and sulfonic acids (PFSA) in the particle phase. This study presents the distribution of PFC in ambient air of the German North Sea and in the vicinity of Hamburg for the first time. Average total PFC concentrations in and around Hamburg (180 pgm^{-3}) were higher than those observed in the German Bight (80 pg m^{-3}). In the German Bight, minimum-maximum gas-phase concentrations of 17 - 82 pg m^{-3} (ΣFTOH), 2.6 - 10 pg m^{-3} (ΣFTA), 10 - 15 pg m^{-3} (ΣFASA), and 2 - 4.4 pg m^{-3} (ΣFASE) were determined. In the vicinity of Hamburg, minimum-maximum gas-phase concentrations of 32 - 204 pg m^{-3} for ΣFTOH, 3 -26 pg m^{-3} for ΣFTA, 3 - 18 pg m^{-3} for ΣFASA, and 2 - 15 pg m^{-3} for ΣFASE were detected. Concentrations of perfluorinated acids were in the range of 1 to 11 pg m^{-3}. FTOH clearly dominated the substance spectrum; 8:2 FTOH occurred in maximum proportions. Air mass back trajectories, cluster, and correlation analyses revealed that the air mass origin and thus medium to long-range atmospheric transport was the governing parameter for the amount of PFC in ambient air. Southwesterly located source regions seemed to be responsible for elevated PFC concentrations, local sources appeared to be of minor importance.

Keywords

PFC; atmospheric transport; North Sea; Hamburg; fluorotelomer alcohols; FTOH; perfluoroalkyl sulfonamides, PFCA

1. Introduction

In recent years, long-chain perfluorinated carboxylates (PFCA) and -sulfonic acids (PFSA) such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) have been found to be persistent, bioaccumulative, and entailing toxic properties (Beach et al., 2006; Giesy and Kannan, 2002; Haukas et al., 2007; Houde et al., 2006; Prevedouros et al., 2006). Furthermore, global distribution to remote regions caused by extensive industrial application and consumer use has been demonstrated for these classes of compounds (Bossi et al., 2005; Giesy and Kannan, 2001; Prevedouros et al., 2006; Smithwick et al., 2005; Taniyasu et al., 2003; Tao et al., 2006; Young et al., 2007).

The awareness of producers as well as political stakeholders for appropriate action concerning these compounds is reflected by voluntary commitments of the fluorochemical industry and regulation efforts of political institutions. Examples are the voluntary phase out of PFOS-based compounds by its main producer 3M in 2002 or the commitment to reduce PFOA emissions by 95 % until 2010 as well as several restrictions concerning manufacturing, marketing, and use of PFOS by the United States Environmental Protection Agency or the European Community. There are still many unknowns concerning environmental fate, distribution, and sources, especially in the perspective various polyfluorinated compounds which are also being used as PFOS and PFOA substitutes. Therefore, there is an ongoing need of decision makers for further information to evaluate polyfluorinated compounds properly.

The ubiquitous distribution of PFCA and PFSA pointed at two main transport pathways. Transport in the water phase, partly in relation to the global oceanic circulation system, has been demonstrated in various studies (Caliebe et al., 2004; McLachlan et al., 2007; So et al., 2007; Yamashita et al., 2008). However, this transport pathway does not explain the entire PFC burden of pristine ecosystems, especially of those that are not effected by marine influences. Due to their low volatility and efficient scavenging by wet and dry deposition, PFCA and PFSA are unlikely to travel long distances in the atmosphere (Hurley et al., 2004). However, an atmospheric transport with subsequent degradation of volatile and semi-volatile precursor compounds like fluorotelomer alcohols (FTOH), perfluorinated sulfonamides (FASA) and perfluorinated sulfonamido ethanols (FASE) to persistent PFCA and PFSA, was hypothesized to be a main transport mechanism (D'Eon et al., 2006; Ellis et al., 2004; Martin et al., 2006; Sulbaek Andersen et al., 2005). Because of their slow reaction with hydroxyl radicals, estimates of atmospheric lifetimes of more than 10-20 days for FTOH and more than 20-50 days for FASA in smog chamber studies (Ellis et al., 2003; Martin et al., 2006) and atmospheric residence times of more than 50 days for FTOH in field studies (Piekarz et al., 2007) indicate the possibility of regional and long-range atmospheric transport. PFCA and PFSA were also determined in snow samples of the high Arctic which experienced contamination solely from atmospheric sources confirming the indirect precursor-based atmospheric transport and deposition of these compounds (Young et al., 2007).

Only few studies examined the spatial distribution of polyfluorinated compounds in air (Barber et al., 2007; Jahnke et al., 2007b; Shoeib et al., 2006). Barber et al. (2007) found that PFC concentrations in air samples from northwest Europe were declining up to two orders of magnitude with decreasing degree of urbanisation. Shoeib et al. (2006) determined FTOH and FASE in air masses of northern Canada and the North Atlantic and observed a widespread distribution and increasing concentrations of volatile PFC in air towards coastal areas of Europe and North America. Jahnke et al. (2007b) found decreasing concentrations of FTOH, FASA, and FASE towards the southern hemisphere along a north-south transect from Bremerhaven, Germany to Cape Town, South Africa. The same authors analysed volatile polyfluorinated compounds in urban and remote air in Germany and observed no significant differences of PFC concentrations between those locations (Jahnke et al., 2007a). Concentrations of (semi-)volatile polyfluorinated substances covering four orders of magnitude have been determined at some selected locations in North America and Japan (Martin et al., 2002; Oono et al., 2008; Piekarz et al., 2007; Stock et al., 2004).

In this study, we present the spatial distribution of polyfluorinated compounds in air samples collected during a cruise in the German Bight (North Sea) on the research vessel Atair and at two permanent land-based sites in the vicinity of Hamburg, Germany. Samples were taken using high volume air samplers and analyzed for volatile and persistent PFC such as FTOH, FASA, FASE, PFCA, and PFSA. PFC concentrations were elucidated and the origin of PFC contamination was traced using air mass back trajectories, correlation-, and cluster analysis. Data presented in this study yield new information on the spatial atmospheric distribution of polyfluorinated compounds on a regional scale as well as the identification of source regions in the North Sea area.

2. Experimental

2.1. Chemicals

All chemicals, standard compounds, and gases were of high quality and purity. Details on chemicals concerning supplier and purity can be found in the supporting information.

2.2. Sampling

Daily air samples were taken onboard the German research vessel Atair during a cruise from Hamburg to the German Bight, North Sea from October 30th to November 06th 2007 (Atair 155, figure 1). Samples were taken in parallel using two high volume air samplers (A and B) which were installed at the observation deck of the ship approximately 16 m above sea level. To ensure that ship exhaust were not sampled, samplers were controlled by a computer connected to the ship's meteorological system avoiding that sampling and thus ship-borne contamination was occurring with relative winds arriving from the rear of the ship.

Land-based sampling was conducted at two permanent sampling sites located in the vicinity of Hamburg with sampling durations varying between 1 and 4 days (figure 1). The site Barsbüttel (BAR) is situated approximately 20 km east of Hamburg (1 770 000 inhabitants) at 53°34'14'' N and 10°12'55'' E. The GKSS site is located approximately 40 km southeast of the city centre of Hamburg close to the city Geesthacht (30000 inhabitants) at 53°24'26'' N, 10°25'20'' E. Both sites have a semi-rural character. Local meteorological parameters such as temperature or wind direction were recorded at the ship as well as at the land-based sampling sites.

In general, 350 m^3 of air per day were sampled. Cartridges filled with a sandwich of polyurethane foam (PUF) and Amberlite XAD-2 (Orbo PUF/XAD-2/PUF cartridges 2500, Supelco, Munich, Germany) and glass fibre filters (GFF, Macherey & Nagel, Düren, Germany) were used to collect gaseous and particle-bound polyfluorinated compounds. Prior to the sampling, 50 µL of a standard solution containing ^{13}C 4:2 FTOH, ^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH, D_3 MeFOSA, D_5 EtFOSA, D_7 MeFOSE, and D_9 MeFOSE (200 pg μL^{-1}) were added to the cartridge to account for analyte losses during sampling and sample preparation. Samples were sealed air tight and stored at -20 °C until analysis in the laboratory. Gas-phase samples were analyzed within one month, particle samples within three months after the sampling.

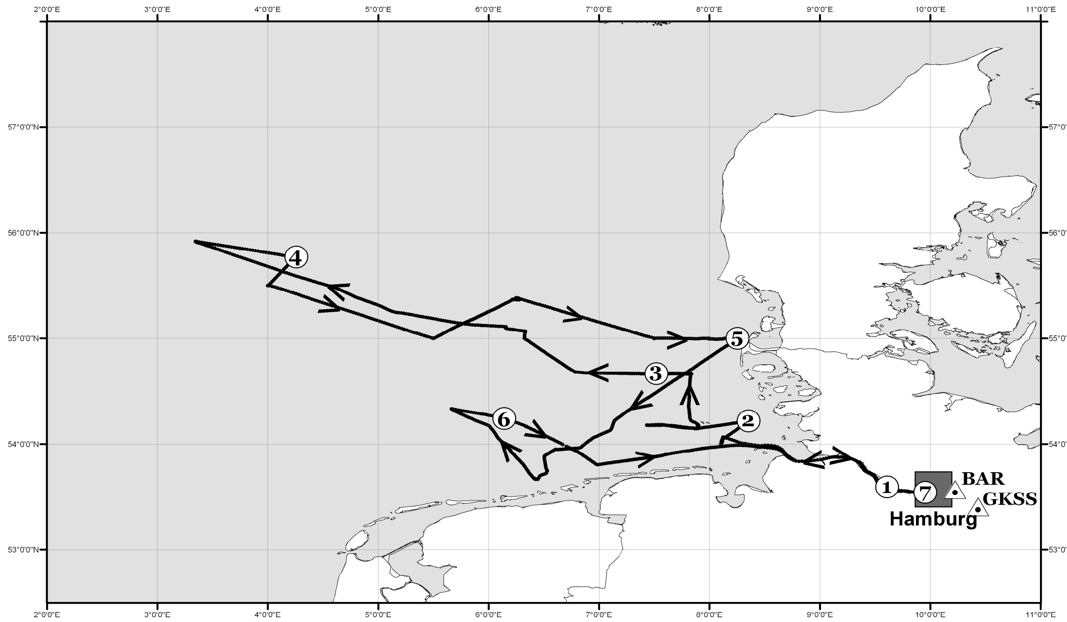


Figure 3-1: Location of the two permanent sites Barsbüttel and GKSS and track of RV Atair during the cruise in the German Bight. Numbered dots mark the start point of each sample during the cruise. Samples were taken in between this and the following location. Sample 7 was taken while the ship was staying in the port of Hamburg situated in the city centre.

2.3. Sample Preparation

Gas-phase samples: All cartridges were extracted thrice with acetone:MTBE 1:1 (v:v). Solvent was filled into the cartridges until the entire sandwich was covered. For the extraction, the solvent was allowed to soak into the adsorption material for 1hour (extraction step 1 and 2) and ½ hour (extraction step 3). After each extraction step, the solvent was emptied into a flask using a glass stop cock, the remaining solvent in the cartridge was blown out with nitrogen. The combined solvent (approximately 500 mL) was evaporated with ethyl acetate as keeper to 150 µL using rotary evaporators (Buechi R200, Flawil, Switzerland, 440 mbar, 30 °C) and a gentle stream of preheated (30°C) nitrogen (Optocontrol, Barkey, Leopoldshoehe, Germany). Fifty µL of the injection standard containing mass-labeled trichlorobenzene (D_3 TCB) and hexachlorobenzene (^{13}C HCB) (400 pg µL^{-1}) were added prior to the measurement to correct for volume differences.

Particle-phase samples: Prior to the extraction of particle-bound compounds filters were cut into two pieces. ¼ of each filter was used to determine the particle load of the filter and the aerosols' content of particulate organic carbon (POC), ¾ were used for the PFC extraction. All filters were extracted by fluidized bed extraction (fexIKA vario control, IKA, Staufen, Germany). Filters taken with sampler A during the Atair cruise were extracted with 150 mL acetone:MTBE 1:1 (v:v) to determine the particle concentrations of neutral volatile polyfluorinated compounds. Prior to the extraction, 50 µL of a standard solution containing ^{13}C 4:2 FTOH, ^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH, D_3 MeFOSA, D_5 EtFOSA, D_7 MeFOSE, and D_9 MeFOSE (200 pg μL^{-1}) were added to each filter. Three extraction cycles of 30 minutes with a maximum temperature of 70 °C hold for 30 min were used. Between the cycles, the solvent was allowed to cool down to 30 °C. The extract volume was reduced to 150 µL as described above. Fifty µL of the injection standard containing D_3 TCB and ^{13}C HCB (400 pg μL^{-1}) were added prior to the measurement. Filters taken at Barsbüttel and GKSS and those taken with sampler B during the Atair cruise were extracted with 150 mL methanol to determine the concentrations of ionic perfluorinated carboxylic and sulfonic acids bound to atmospheric particles. Prior to the extraction, 100 µL of a standard solution containing $^{18}O_2$ PFHxS, ^{13}C PFOS, ^{13}C PFOSi, ^{13}C PFBA, ^{13}C PFHxA, ^{13}C PFOA, ^{13}C PFNA, ^{13}C PFDA, ^{13}C PFUnDA and ^{13}C PFDoA (100 pg μL^{-1}) were added to each filter. Three extraction cycles of 25 min and a maximum temperature of 100 °C hold for 35 min were used. The extract volume was reduced to 150 µL using rotary evaporators (160 mbar, 30 °C) and nitrogen. Fifty µL of the injection standard containing mass-labeled dichlorophenol (^{13}C DCP) and n-ethyl perfluorooctanesulfonamidoacetate (D_5 EtFOSAA) (400 pg μL^{-1}) were added prior to the measurement.

2.4. Instrumental Analysis & Quantification

Detection of neutral polyfluorinated compounds extracted by MTBE:acetone (5 FTOH, 3 fluorotelomer acrylates (FTA), 5 FASA, 4 FASE) was performed by gas chromatography-mass spectrometry (6890 GC/5975 MS, Agilent Technologies, Waldbronn, Germany) with positive chemical ionization (PCI) using the selected ion monitoring (SIM) mode. To confirm the detection of FASA, samples were also run in the negative chemical ionization (NCI) mode. For analytes separation, a 60 m Supelcowax10 capillary column (Supelco, Munich, Germany) was used. Methanol-extracted polyfluorinated compounds (13 PFCA, 5 PFSA, 3 perfluoro sulfinates (PFSI)) were determined by HPLC-ESI-MS/MS. Analytes were separated on a Synergi Hydro RP 80A column (Phenomenex, Torrence, Ca, USA; 150 x 2 mm, 4 micron). Details on the instrumental specifications concerning GC-MS and HPLC-MS/MS measurements can be found in Dreyer et al. (2008) and Ahrens et al. (2007).

Quantification was based on peak areas. Analyte concentrations were calculated with the internal standards method using a seven point calibration. Internal standards were used to correct for analyte losses. Compounds were classified as not detected (n.d.) with signal to noise ratio (S/N) below 3 and not quantified (n.q.) with S/N below 10. Method quantification (MQL) and detection limits (MDL) as well as instrumental detection limits are shown in the supporting information. Based on the signal to noise ratio, MDLs were typically below 1 pg m^{-3}. A high MQL of 23 pg m^{-3} was found for PFOSA as a result of highly variable GC-MS performance for this compound.

2.5. Quality Assurance & Quality Control

Sample preparation was performed in a clean lab (class 10.000). Perfluorinated materials or fluorinated polymers were avoided during sampling and sample preparation. Prior to the sampling, PUF/XAD-2/PUF cartridges were cleaned with MTBE:acetone and acetone for 24 hours using Soxhlet extraction. Filters were heated at 300°C for at least 24 hours and equilibrated prior to the weighting according to US EPA guidelines (EPA, 2005). Silicon-Teflon septa were used for GC/MS measurements (vials), however, pre-tests showed no contamination with (semi-)volatile polyfluorinated compounds. The glassware was machine-washed, heated at 250 °C for twelve hours, and washed with the applied solvent before use. Mass-labeled injection standards and internal standards were used to correct for losses and irregularities during analysis and measurement. Average recoveries were between 22 +/- 7 % (^{13}C 4:2 FTOH) and 73 % +/- 16 % (EtFOSE D_9) in gas-phase samples and between 31+/- 2 % (^{13}C 8:2 FTOH) and 123 +/- 23% (PFUnDA) in particle samples. Concerning GC-MS measurements, one target ion (PCI) and one qualifier ion (PCI and/or NCI) were measured to identify compounds correctly. A seven point calibration was run with each set of samples measured. Calibration linearity was checked with each set of samples quantified.

To determine possible contamination field blanks were taken during the sampling campaigns. Additionally, solvent blanks (for gaseous samples) and filter blanks (for particle samples) were taken with each set of samples that was extracted. Some compounds were detected in blank samples occasionally. These were 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, MeFBSE, EtFOSE, MeFOSE in solvent blanks for gas-phase samples and EtFOSE, MeFOSE, MeFOSA, 6:2 FTA and 6:2 FTOH in filter blanks for particle samples. Various PFSA and PFCA were frequently determined in filter blanks, probably due to contamination of the filters themselves although they have been baked at high temperatures. Therefore, all concentrations reported are blank-corrected. PFCA and PFSA concentrations of particle samples associated with one high filter blank were not accounted for in statistical analyses. Field blanks were usually in the range of solvent and filter blanks showing that contamination was not due to sampling or sample handling. Blanks are reported in the supplemental information.

The uncertainty of the entire method (sampling, sample preparation, detection) was calculated according to ISO 20988 (2007). Based on paired measurements of volatile polyfluorinated compounds during the Atair campaign the standard uncertainty for the determination of gaseous compounds was within the range of 18 % (EtFOSA) to 160 % (PFOSA). Given the high standard uncertainty of PFOSA, analyses for this substance are rather qualitative than quantitative. For a complete report of uncertainties refer to the supplemental information. Since particle samples were analysed for different compound classes and thus with different methods, the uncertainty of the entire method for particle-bound compounds could not be calculated.

2.6. Air Mass Trajectories

Seven days air mass backward trajectories were calculated with the model Hysplit 4.8 using NCEP's Global Data Assimilation System (GDAS) data with 1 degree latitude/longitude resolution provided by NOAA-Air Resources Laboratory (Draxler and Rolph, 2003). Trajectories were calculated for intervals of three and six hours and an arrival height of 16 m (sampling height). In order to verify the origin of air masses obtained by these computations, back trajectories were also calculated exemplarily for arrival heights of 100 and 500 m using GDAS data as well as for the sampling height using NCEP's reanalysis data. The observed differences were in the range of the trajectories' uncertainty of approximately 20 % of the travel distance.

2.7. Statistical Analysis

Statistical analyses were performed using Winstat (version 2007). Concentrations of poly- and perfluorinated compounds in the gas and particle phase were tested for normal distribution. Normal-distributed analytes concentrations in the gas phase and in the particle phase were tested for correlation using Pearson Correlation. Proportions of all analytes were calculated and used for cluster analysis applying the Ward agglomeration method.

3. Results

3.1. PFC Concentrations

Gas and particle-phase concentrations of volatile PFC determined during ship and land-based sampling campaigns are presented in table 1 and 2. Except for 4:2 FTOH, 6:2 FTA, Me_2FOSA, PFOSA, and EtFOSE all analytes were detected in the gas phase of all samples. In the particle fraction, only MeFOSA, EtFOSA, MeFOSE, and EtFOSE were detected, their concentrations were slightly higher than those of corresponding analytes in the gaseous phase. Generally, gaseous concentrations of volatile PFC were higher in and around Hamburg than at sea. Highest gas-phase total concentrations of volatile PFC were observed for samples Atair 7 (224 pg m^{-3}) and GKSS 62a (240 pg m^{-3}). Lowest PFC total concentrations were found in samples Atair 3 (39 pg m^{-3}) and Atair 5 (35 pg m^{-3}). In this study, low concentrations of particle-bound ionic compounds were observed (table 3). Of 21 analytes, only PFBS, PFOS, PFBA, PFPA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, and PFDoDA were determined in some samples. Generally, maximum concentrations in Atair samples were reached for PFOA (6.1 pg m^{-3}) followed by PFOS (2.3 pg m^{-3}) and/or PFBA (1.6 pg m^{-3}). PFOS (9.1 pg m^{-3}) and PFBA (2.0 pg m^{-3}) were determined in maximum concentrations in land-based samples. However, high concentrations of some PFCA and PFSA detected in a filter blank for one set of samples may have biased these findings. Total concentrations of PFCA and PFSA were in the range of 1-11 pg m^{-3}. Slightly elevated concentrations were determined for sample Atair 2 (11 pg m^{-3}), Atair 7 (6.4 pg m^{-3}) and BAR 60 (11 pg m^{-3}).

3.2. PFC Composition

The contribution of single PFC to the total amount of PFC in the gas phase is presented in figure 2. In all gas-phase samples, FTOH were the dominating class of compounds accounting for 50 to 80 % followed by FASA (6-36 %), FASE (3-9 %), and FTA (6-11 %) in marine air samples and by FTA (5-15 %), FASA (4-9 %), and FASE (2-7 %) in land-based samples. In Atair particle samples, MeFOSA and EtFOSA were the dominating neutral compounds. For ionic compounds, PFCA were dominating the substance profile (up to 80 %), usually with main contributions of PFOA (40 %) and PFBA (35 %). Details on the proportions of ionic compounds can be found in the supporting information.

Table 3-1: Gas- and particle-phase concentrations (pg m^{-3}) of volatile PFC in ambient air of the German Bight and Hamburg (Atair 7) determined during the sampling campaign on RV Atair. c(g): gas-phase concentration. c(p): particle-phase concentration. n.d.: not detected. n.q.: not quantified. [a] Due to the high water content of this sample analytes could not be detected. [b] The elevated particle-phase concentrations are probably due to a single contamination event that occurred during analysis in the lab.

	Atair 1		**Atair 2**		**Atair 3**		**Atair 4**		**Atair 5**		**Atair 6**		**Atair 7**	
	10/30-10/31/2007		**10/31-11/01/2007**		**11/01-11/02/2007**		**11/02-11/03/2007**		**11/03-11/04/2007**		**11/04-11/05/2007**		**11/05-11/06/2007**	
	c(g)	**c(p)**	**c(g)**	**c(p)**	**c(g)**	**c(p)**	**c(g)**	**c(p)[a]**	**c(g)**	**c(p)[b]**	**c(g)**	**c(p)**	**c(g)**	**c(p)**
4:2 FTOH	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	2.3	n.d.	1.8	n.d.	1.4	n.d.	n.d.	n.d.
6:2 FTOH	5.0	n.q.	8.6	n.q.	5.8	n.q.	5.7	n.d.	3.3	n.q.	15	n.q.	13	n.q.
8:2 FTOH	11	n.d.	56	n.d.	13	n.d.	16	n.d.	8.2	n.d.	28	n.q.	130	n.d.
10:2 FTOH	2.8	n.d.	15	n.d.	3.5	n.d.	5.7	n.d.	2.1	n.d.	6.7	n.d.	29	n.d.
12:2 FTOH	1.7	n.d.	3.1	n.d.	1.3	n.d.	1.3	n.d.	1.5	n.d.	2.3	n.d.	8.0	n.d.
Σ FTOH	**21**	**0.0**	**82**	**0.0**	**24**	**0.0**	**31**	**0.0**	**17**	**0.0**	**53**	**0.0**	**180**	**0.0**
6:2 FTA	n.d.	n.d.	5.7	n.d.	n.d.	n.q.	n.d.	n.d.	n.q.	n.d.	n.d.	n.d.	4.2	n.q.
8:2 FTA	2.2	n.d.	3.2	n.d.	1.9	n.d.	1.7	n.d.	1.8	n.d.	3.6	n.q.	15	n.q.
10:2 FTA	0.9	n.d.	1.3	n.d.	0.8	n.d.	1.2	n.d.	0.8	n.d.	1.2	n.d.	6.6	n.q.
Σ FTA	**3.1**	**0.0**	**10**	**0.0**	**2.8**	**0.0**	**2.9**	**0.0**	**2.6**	**0.0**	**4.8**	**0.0**	**26**	**0.0**
MeFBSA	7.1	n.d.	5.8	n.d.	3.1	n.d.	3.4	n.d.	6.0	n.d.	4.7	n.d.	3.4	n.d.
MeFOSA	3.7	4.2	1.5	3.3	2.5	n.d.	3.3	n.d.	3.9	9.2	3.1	5.6	2.4	3.4
Me$_2$FOSA	n.d.	n.d.	0.5	n.d.	n.d.	n.d.	1.4	n.d.	0.5	n.d.	0.7	n.d.	0.5	n.d.
EtFOSA	1.7	3.1	0.8	2.1	0.4	n.d.	1.4	n.d.	1.5	7.9	1.1	3.1	0.5	2.4
PFOSA	2.5	n.d.	1.9	n.d.	3.4	n.d.	2.8	n.d.	n.q.	n.d.	n.d.	n.d.	7.3	n.d.
Σ FASA	**15**	**7.3**	**11**	**5.4**	**9.5**	**0.0**	**12**	**0.0**	**12**	**17**	**9.7**	**8.7**	**14**	**5.7**
MeFBSE	0.6	n.d.	1.4	n.d.	1.0	n.d.	1.3	n.d.	0.6	n.d.	1.0	n.d.	2.5	n.d.
MeFOSE	1.3	n.d.	0.9	7.0	2.0	n.d.	2.5	n.d.	2.2	13	1.2	n.d.	1.4	9.0
EtFOSE	n.d.	n.d.	0.1	5.5	n.d.	4.4	0.3	n.d.	0.3	15	n.d.	8.0	n.d.	6.9
Σ FASE	**1.9**	**0.0**	**2.4**	**12**	**3.0**	**4.4**	**4.2**	**0.0**	**3.2**	**28**	**2.2**	**8.0**	**3.9**	**16**
Total	**41**	**7**	**105**	**18**	**39**	**4.4**	**50**	**0.0**	**35**	**45**	**70**	**17**	**224**	**22**

Table 3-2: Gas-phase concentrations (pg m^{-3}) of volatile PFC in ambient air determined at the land-based sites Barsbüttel (BAR) and GKSS. c(g): gas-phase concentration. n.d.: not detected. n.q.: not quantified.

	BAR 60	BAR 61	BAR 62	GKSS 60b	GKSS 60c	GKSS 61a	GKSS 61b	GKSS 62a
	10/29-11/01/2007	11/01-11/05/2007	11/05-11/08/2007	10/30-10/31/2007	10/31-11/01/2007	11/01-11/02/2007	11/02-11/05/2007	11/05-11/06/2007
c in pg/m³	**c(g)**	**c(g)**	**c(g)**	**c(g)**	**c(g)**	**c(g)**	**c(g)**	**c(g)**
4:2 FTOH	n.d.	n.d.	n.d.	n.d.	5.8	3.5	n.d.	n.d.
6:2 FTOH	38	13	17	26	31	22	7	54
8:2 FTOH	127	52	30	56	91	47	17	96
10:2 FTOH	34	13	14	15	26	16	6	32
12:2 FTOH	5.5	2.5	4.7	4.8	4.2	5.5	1.8	10
Σ FTOH	**204**	**81**	**65**	**102**	**159**	**94**	**32**	**192**
6:2 FTA	5.4	0.4	1.2	4.0	5.1	2.8	1.0	7.2
8:2 FTA	8.9	2.9	9.8	6.9	14	6.6	1.7	6.5
10:2 FTA	4.2	1.4	3.4	2.9	4.6	2.5	0.7	2.9
Σ FTA	**18**	**5**	**14**	**14**	**23**	**12**	**3**	**17**
MeFBSA	4.9	1.4	1.7	2.9	10	1.6	1.3	2.6
MeFOSA	2.1	1.8	1.3	2.6	2.6	4.2	1.0	4.8
Me$_2$FOSA	1.0	0.2	n.d.	1.7	1.4	n.d.	n.d.	0.6
EtFOSA	2.7	2.6	1.4	1.8	3.2	3.1	0.7	7.1
PFOSA	n.d.	0.6	1.6	n.d.	n.d.	n.d.	n.d.	1.4
Σ FASA	**11**	**6.5**	**6.1**	**9.0**	**18**	**8.9**	**2.9**	**17**
MeFBSE	6.4	3.9	2.9	1.9	2.5	1.6	1.0	5.5
MeFOSE	3.8	2.3	2.5	0.6	0.9	2.6	0.7	7.4
EtFOSE	0.8	0.8	0.4	1.8	1.7	1.8	0.3	1.9
Σ FASE	**11**	**6.9**	**5.8**	**4.3**	**5.1**	**6.0**	**2.0**	**15**
Total	**244**	**99**	**91**	**129**	**205**	**121**	**40**	**240**

Table 3-3: Particle-phase concentrations (pg m^{-3}) of ionic PFC determined in ambient air of the German Bight, Barsbüttel (BAR), and GKSS. n.d.: not detected. n.q.: not quantified. [a] Filter blank problems occurred in these samples leading the not quantified status for some analytes of the samples.

	Atair 1	Atair 2	Atair 3	Atair 4	Atair 5	Atair 6	Atair 7	BAR 60	BAR 61 [a]	BAR 62 [a]	GKSS 60b	GKSS 60c [a]	GKSS 61a [a]	GKSS 61b	GKSS 62a
	10/30- 10/31/2007	10/31- 11/01/2007	11/01- 11/02/2007	11/02- 11/03/2007	11/03- 11/04/2007	11/04- 11/05/2007	11/05- 11/06/2007	10/29- 11/01/2007	11/01- 11/05/2007	11/05- 11/08/2007	10/30- 10/31/2007	10/31- 11/01/2007	11/01- 11/02/2007	11/02- 11/05/2007	11/05- 11/06/2007
c (pg/m³)	**c(p)**	**c(p)**	**c(p)**	**c(p)**	**c(p)**	**c(p)**	**c(p)**	**c(g)**	**c(g)**	**c(g)**	**c(g)**	**c(g)**	**c(g)**	**c(g)**	**c(g)**
PFBS	0.8	0.8	n.d.	n.q.	n.q.	n.q.	0.7	2.3	1.2	0.4	0.7	5.1	1.5	n.q.	n.d.
PFHxS	n.d.	0.2	n.d.	0.3	n.d.	n.d.	n.q.	n.q.	n.d.	n.q.	n.d.	n.q.	n.q.	n.q.	n.q.
PFHpS	n.d.	n.d.	n.d.	n.d.	0.3	n.d.	0.4	n.d.	n.d.	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0.8	2.3	0.1	0.8	0.6	1.2	1.7	n.q.	n.q.	n.q.	0.6	n.q.	n.q.	n.q.	0.1
PFDS	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.q.	n.d.	n.d.
Σ PFSA	**1.5**	**3.2**	**0.1**	**1.1**	**0.9**	**1.2**	**2.8**	**2.3**	**1.2**	**0.4**	**1.3**	**5.1**	**1.5**	**0.0**	**0.1**
PFHxSi	n.d.	n.d.	n.d.	n.d.	n.d.	n.q.	n.q.	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOSi	n.q.	n.q.	n.d.	n.q.	n.q.	n.d.	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1
PFDSi	n.q.	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.
Σ PFSi	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.1**
PFBA	1.6	0.3	1.0	0.3	0.7	0.9	n.q.	3.5	n.q.	n.q.	1.4	n.q.	n.q.	n.q.	0.5
PFPA	0.1	0.3	n.d.	0.1	0.1	n.d.	0.2	0.3	0.2	n.q.	0.0	n.d.	n.d.	0.9	0.3
PFHxA	0.1	0.2	0.2	0.0	0.2	0.2	0.2	0.7	0.1	n.q.	0.1	0.9	1.9	n.q.	0.2
PFHpA	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	2.1	0.4	n.q.	n.d.	n.d.	2.3	n.q.	0.2
PFOA	2.3	6.1	1.9	2.1	2.3	2.1	2.9	n.q.	n.q.	n.q.	0.2	2.4	6.1	n.q.	0.4
PFNA	0.2	0.6	0.0	0.4	0.2	0.2	0.0	n.q.	n.q.	n.q.	0.2	n.q.	3.2	n.q.	0.1
PFDA	n.q.	0.2	n.q.	n.q.	n.q.	n.q.	n.q.	0.9	0.2	n.q.	n.q.	1.5	1.6	0.1	0.2
PFUnDA	n.q.	0.1	n.q.	n.q.	n.q.	n.d.	0.1	0.3	0.1	n.q.	n.q.	1.9	2.2	n.q.	0.1
PFDoDA	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	0.2	0.3	n.q.	n.q.	n.q.	1.0	1.2	n.q.	n.q.
PFTriDA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.9	n.d.	0.4	n.q.	0.8	0.1	0.3	n.q.
PFTeDA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.q.	n.d.	0.5	n.d.	0.2	n.d.
PFHxDA	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.
PFOcDA	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.
Σ PFCA	**4.3**	**7.9**	**3.1**	**3.0**	**3.5**	**3.4**	**3.6**	**9.0**	**0.9**	**0.4**	**2.0**	**9.1**	**18.6**	**1.5**	**2.0**
Total	**5.9**	**11**	**3.2**	**4.1**	**4.5**	**4.6**	**6.4**	**11**	**2**	**0.8**	**3.2**	**14**	**20**	**1.5**	**2.2**

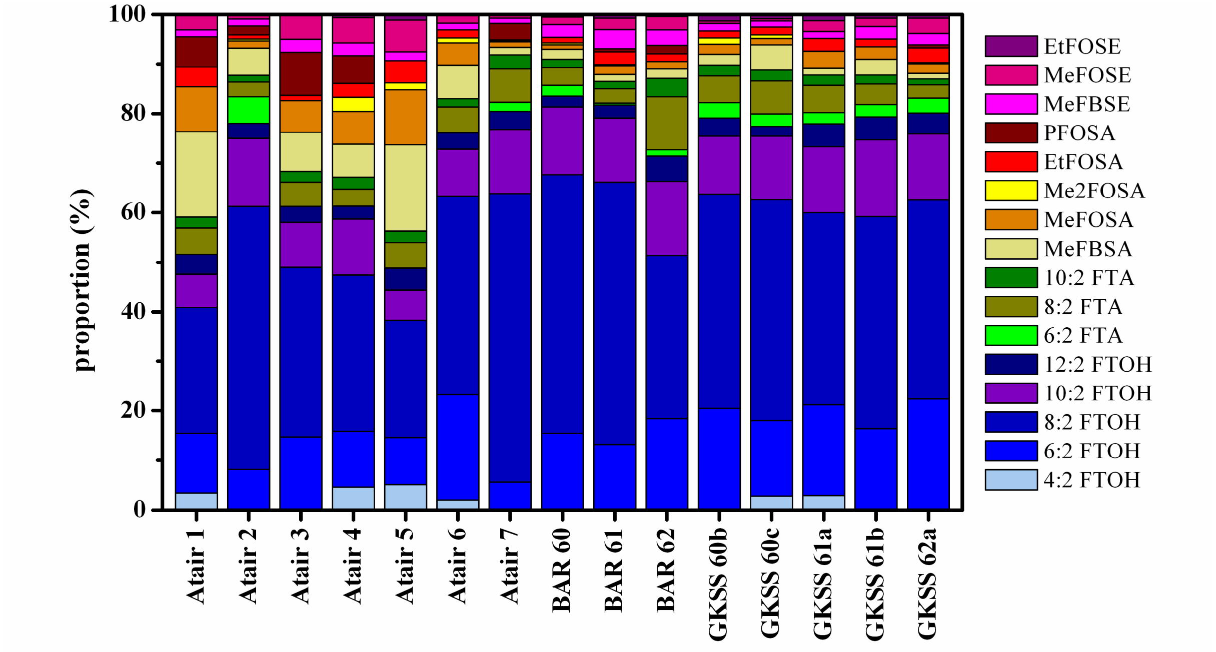


Figure 3-2: Proportions (%) of volatile PFC in gas-phase samples.

Cluster analysis performed with the proportions of gas-phase analytes yielded two main clusters (figure 3). Cluster 1 consisted of samples Atair 1, 3, 4, and 5. The remaining samples were assigned to cluster 2.

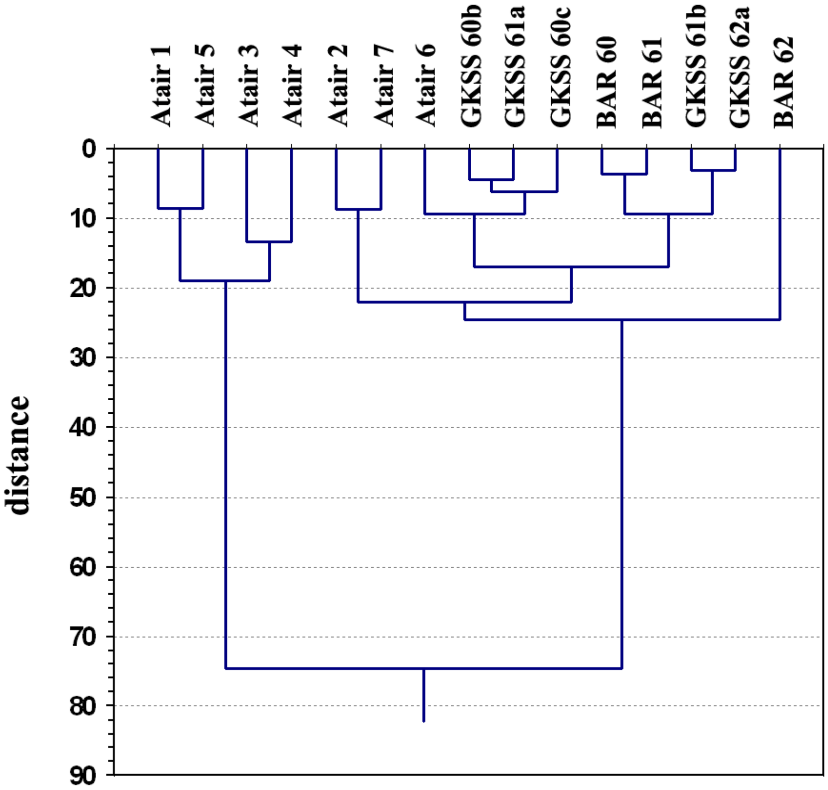


Figure 3-3: Result of cluster analysis of the PFC composition of air samples from the German Bight and the vicinity of Hamburg.

3.3. Correlation Analysis

Concerning substance classes in Atair gas-phase samples, only ΣFTA and ΣFTOH were highly significantly ($p < 0.05$) positively correlated. No correlation to ΣFASA and ΣFASE was observed. In land-based samples, sum concentrations of all substance classes were significantly positively correlated except for the combination of ΣFTA and ΣFASE. All individual FTOH and FTA as well as MeFOSA and EtFOSA were highly positively correlated in most of the gas-phase samples. Significantly positive correlations were also observed between MeFBSE and MeFOSE, all FASA and 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, and to some extent FTA in land-based samples. In Atair samples, significant correlations were found between MeFOSE and EtFOSE, MeFBSA and EtFOSA, as well as MeFBSE and 8:2 FTOH, 10:2 FTOH, 12:2 FTOH. Significantly negative (FTOH, FTA) or no (FASA, FASE) correlations existed between gas-phase analytes and ambient temperatures. Particle-bound PFOS, PFPA, PFHxA and PFOA were significantly positively correlated. Significant correlations were also observed between PFNA and PFBS and between PFNA and PFOA. Detailed information about correlation analyses are presented in the supporting information. Particle-bound analytes did not correlate to the particle mass and the aerosols' content of particulate organic carbon.

4. Discussion

Concentrations of gas-phase FTOH, FASA, and FASE were in about the same range as in other studies for comparable locations. However, it should be noted that analysed substances in those studies differed to some extent (Barber et al., 2007; Jahnke et al., 2007a; Jahnke et al., 2007b; Martin et al., 2002; Shoeib et al., 2006). In general, high PFC concentrations in samples Atair 7 (Hamburg), BAR 60, GKSS 60c, and GKSS 62a were consistent with concentrations determined in German and other European and American urban regions (Barber et al., 2007; Jahnke et al., 2007a; Martin et al., 2002; Shoeib et al., 2006; Stock et al., 2004) but lower than those of urban and traffic-influenced areas in Japan (Oono et al., 2008). The low concentrations of volatile polyfluorinated compounds in this study were comparable to those determined for marine regions (Jahnke et al., 2007b; Shoeib et al., 2006).

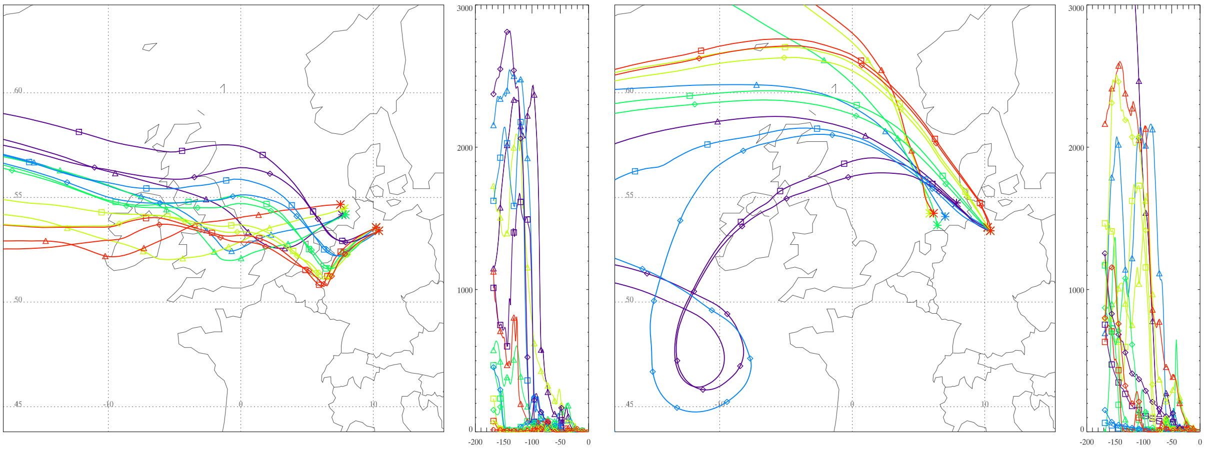
PFCA and PFSA concentrations in the particle phase determined in this study are in the same range as those observed by Kim and Kannan (2007) for an urban area in the US, by Harada et al. (2005) for rural regions of Japan, or by Jahnke et al. (2007b) for marine regions.

Concentrations of PFCA and PFSA were up to 2 orders of magnitude lower than those determined for British and Japanese urban regions (Barber et al., 2007; Harada et al., 2005; Sasaki et al., 2003). The fact that MeFOSA, EtFOSA, MeFOSE, and EtFOSE were the only neutral PFC detected in the particle phase is in contrast to some studies where, high molecular weight FTOH were rather constantly detected in the particulate phase in low concentrations (Jahnke et al., 2007a; Shoeib et al., 2006). However, revolatilisation of particle-bound substances and/or sorption of the compounds of interest to the glass fiber filter as it has been demonstrated for some PFCA by Arp and Goss (2008) may have biased the observed gas-particle partitioning.

As presented in other studies in Europe (Barber et al., 2007; Jahnke et al., 2007a; Jahnke et al., 2007b), FTOH were the dominating class of compounds in the gas phase with 8:2 FTOH in maximum concentrations. High concentrations and proportions of FASA and FASE as detected for some American sites (Martin et al., 2002; Piekarz et al., 2007; Shoeib et al., 2004; Shoeib et al., 2005; Stock et al., 2004) were not observed in this study. Besides the influence of different usage patterns and individual point sources, these observations are likely be explained by the phase-out of PFOS-based chemistry and thus changing PFC pattern since the year 2000. In our study, the increase of neutral PFC concentrations in the gas phase was mainly due to increasing concentrations of FTOH; proportions of FASA, FASE, and FTA decreased in respective samples. PFC proportions in high concentration Atair samples (Atair 2 and Atair 7) and those of the GKSS and Barsbüttel sites were quite similar suggesting a common origin of PFC contamination. This is also supported by the results of the cluster analysis which clearly separated the low gas-phase PFC concentration samples Atair 1, 3, 4, and 5 from the remaining high PFC concentrations samples of the Atair campaign, Barsbüttel, and the GKSS site which were characterized by higher FTOH proportions. Various significant correlations especially among FTOH, FTA, and to a lesser extent FASA, FASE, and ionic PFC seem to confirm common emission sources.

Regional-scale spatial variations of the concentrations of volatile PFC in the gas phase were observed between the German Bight and adjacent coastal areas. PFC concentrations averaged for the same period of time were decreasing from the main land towards the open sea. However, changes in concentrations were rather due to the different regions sampled air was arriving from (and far away sources); point sources located close to the sites appear to be of rather minor importance (see below).

As the analysis of air mass backward trajectories reveals (figure 4), low PFC concentrations were observed when air masses of marine origin, i.e. northern and northwestern air masses, were sampled (samples Atair 1, 3-6, GKSS 61b). For these samples, differences in PFC air concentrations are probably due to the varying degree air masses have passed coastal and/or terrestrial areas. Lowest concentrations of volatile PFC were observed in sample Atair 5, where air masses originated completely from marine regions (figure 4b). Elevated concentrations in sample Atair 6 might be explained by local winds from southwesterly located coastal regions which were observed by onboard measurements and are not shown by the trajectories. Highest PFC concentrations in the German Bight region were observed in sample Atair 2. This coincided with strongly elevated PFC concentrations at the land-based stations at GKSS and Barsbüttel (GKSS 60c, BAR 60). As the back trajectories for these samples reveal (figure 4a), sampled air masses passed Southern UK, the Netherlands, and highly industrialized areas of Germany, regions that are known to be point sources for other inorganic and organic pollutants such as NO_x, SO_x, hydrofluorocarbons, non methane volatile organic compounds, or polycyclic aromatic hydrocarbons (PAH) (EEA, 2008).



a b

Figure 3-4: Details of seven days air mass back trajectories calculated for six hours intervals and an arrival height of 16 m as generated by Hysplit 4.8 using GDAS data for (a) samples Atair 2, GKSS 60c, BAR 60 and (b) samples Atair 5, GKSS 61b, BAR 61. Asterisks mark the location of the sampling site or the ship's positions, respectively. Trajectory colors code six hours time intervals of arrival times. Triangles, squares, and rhombs of individual trajectories show the position of the air parcel in twelve hours intervals for Atair, Barsbüttel, and GKSS samples, respectively. Additionally, a plot is provided showing the trajectory heights.

Since concentrations of volatile PFC in air differed only slightly between the port of Hamburg (Atair 7) and the GKSS site (GKSS 62a) it can be assumed that airborne PFC samples at these sites during the period of this study originated rather from diffusive sources and/or medium to long-distance atmospheric transport than from local sources. Industrial areas in the western and southwestern parts of Germany and eastern parts of the Netherlands may act as potential source regions for air masses in Hamburg and its surroundings. These results confirm findings of Jahnke et al. (2007a) who determined concentrations of airborne PFC in the city of Hamburg and at the remote sampling site at Waldhof located approximately 100 km southeast of Hamburg. Although samples in Hamburg and Waldhof were taken at different times and thus different air masses were sampled, significant concentration differences for the majority of PFC at both sites were generally not observed. However, this comparison should be considered carefully as PFC concentrations are fluctuating in dependence of air mass origin which may have differed between these studies.

That pollution in the North Sea area is rather caused by long-distance transport than by local sources was also observed by other authors. Varying concentrations of organic micropollutants in dependence of air mass origin were determined by some authors for two sites close to the North Sea (Bjorseth et al., 1979; Lunde and Bjorseth, 1977). There, concentrations of benzo(a)pyrene and other PAH in high volume air samples were much higher in air from continental western Europe and Great Britain (southwestern and southeastern air) than in air from northern and northwestern directions. Preston and Merrett (1991) found that hydrocarbon contamination in air was highest when air masses originated from continental Europe and the UK. Air that arrived over the open sea showed lowest hydrocarbon concentrations.

This study demonstrated the widespread distribution of particle-bound perfluorinated acids and their volatile precursors in ambient air of the German Bight and around Hamburg reflecting a continuous emission of these compounds to the atmosphere. The comparably high resolution of sampling of one day enabled the observation of fluctuating PFC concentrations in air and allowed the application of statistical and trajectory analysis to identify PFC source regions. This study demonstrated that the air mass origin is an important parameter governing the concentrations of PFC in ambient air of the German Bight and northern Germany. The city of Hamburg with its industrialized areas around the port appeared to be a rather minor source for airborne PFC during our study. However, in order to elucidate the impact of a city such as Hamburg on the PFC air concentration, examinations of longer time series, e.g. one year are necessary. Our results give further support to the hypothesis that volatile polyfluorinated compounds are transported from source regions over long distances and thus representing a transportation pathway of perfluorinated compounds to pristine regions.

Acknowledgements

Annekatrin Dreyer was funded by the scholarship program of the German Federal Environmental Foundation (Deutsche Bundesstiftung Umwelt, DBU). We thank Norbert Theobald and Wolfgang Gerwinski from the Federal Maritime and Hydrographic Agency of Germany (BSH) for the organization of this cruise. We wish to thank the PI, captain, and crew of the Atair 155 campaign who made this data set available. Thanks to Volker Matthias for the valuable help with the trajectories analyses and Christian Temme and Michael Radke for helpful comments on the manuscript. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the Hysplit transport and dispersion model.

Appendix

Supplemental information is available covering several methodological aspects as well as details on trajectories and correlation analyses.

References

Ahrens, L.; Plaßmann, M.; Temme, C.; Ebinghaus, R. 2007. Determination of per- and polyfluorinated alkyl compounds using liquid chromatography tandem mass spectrometry in water samples. *Organohalogen Compounds*, *69*, 2804-2807.

Arp, H. P. H.; Goss, K. U. 2008. Irreversible sorption of trace concentrations of perfluorocarboxylic acids to fiber filters used for air sampling. *Atmospheric Environment*, *42*, 6869-6872.

Barber, J. L.; Berger, U.; Chaemfa, C.; Huber, S.; Jahnke, A.; Temme, C.; Jones, K. C. 2007. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *Journal of Environmental Monitoring*, *9*, 530-541.

Beach, S. A.; Newsted, K. C.; Giesy, J. P. 2006. Ecotoxicological evaluation of Perfluorooctanesulfonate (PFOS). *Review of Environmental Contaminations and Toxicology*, *186*, 133-174.

Bjorseth, A.; Lunde, G.; Lindskog, A. 1979. Long-Range Transport of Polycyclic Aromatic-Hydrocarbons. *Atmospheric Environment*, *13*, 45-53.

Bossi, R.; Riget, F. F.; Dietz, R. 2005. Temporal and spatial trends of perfluorinated compounds in ringed seal (Phoca hispida) from Greenland. *Environmental Science & Technology*, *39*, 7416-7422.

Caliebe, C.; Gerwinski, W.; Hühnerfuss, H.; Theobald, N. 2004. Occurrence of perfluorinated organic acids in the water of the North Sea. *Organohalogen Compounds*, *66*, 4024-4028.

D'Eon, J. C.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. 2006. Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, C4F9SO2N(CH3)CH2CH2OH: Kinetics and mechanism of reaction with OH. *Environmental Science & Technology*, *40*, 1862-1868.

Draxler, R. R.; Rolph, G. D. 2003. HYSPLIT (HYbrid Single-Particle Langerian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). *NOAA Air Resources Laboratory, Silver Spring, MD.*

Dreyer, A.; Temme, C.; Sturm, R.; Ebinghaus, R. 2008. Optimized method avoiding solvent-induced response enhancement in the analysis of volatile and semi-volatile polyfluorinated alkylated compounds using gas chromatography-mass spectrometry. *Journal of Chromatography A*, *1178*, 199-205.

EEA 2008. The European Pollutant Emission Register (EPER). *http://www.eper.ec.europe.eu.*

Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. 2004. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environmental Science & Technology*, *38*, 3316-3321.

Ellis, D. A.; Martin, J. W.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. 2003. Atmospheric lifetime of fluorotelomer alcohols. *Environmental Science & Technology*, *37*, 3816-3820.

EPA 2005. Reference method for the determination of particulate matter as PM10 in the atmosphere - Appendix j to Part 50. *U.S. EPA's 40 CFR, Part 50.*

Giesy, J. P.; Kannan, K. 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environmental Science & Technology*, *35*, 1339-1342.

Giesy, J. P.; Kannan, K. 2002. Perfluorochemical surfactants in the environment. *Environmental Science & Technology*, *36*, 146A-152A.

Harada, K.; Nakanishi, S.; Saito, N.; Tsutsui, T.; Koizumi, A. 2005. Airborne perfluorooctanoate may be a substantial source contamination in Kyoto area, Japan. *Bulletin of Environmental Contamination and Toxicology*, *74*, 64-69.

Haukas, M.; Berger, U.; Hop, H.; Gulliksen, B.; Gabrielsen, G. W. 2007. Bioaccumulation of per- and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web. *Environmental Pollution*, *148*, 360-371.

Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. G. 2006. Biological monitoring of polyfluoroalkyl substances: A review. *Environmental Science & Technology*, *40*, 3463-3473.

Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. 2004. Atmospheric chemistry of perfluorinated carboxylic acids: Reaction with OH radicals and atmospheric lifetimes. *Journal of Physical Chemistry A*, *108*, 615-620.

ISO-20988 2007. Air quality - Guidelines for estimating measurement uncertainty.

Jahnke, A.; Ahrens, L.; Ebinghaus, R.; Temme, C. 2007a. Urban versus remote air concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany. *Environmental Science & Technology*, *41*, 745-752.

Jahnke, A.; Berger, U.; Ebinghaus, R.; Temme, C. 2007b. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53 degrees N-33 degrees S). *Environmental Science & Technology*, *41*, 3055-3061.

Kim, S. K.; Kannan, K. 2007. Perfluorinated acids in air, rain, snow, surface runoff, and lakes: Relative importance of pathways to contamination of urban lakes. *Environmental Science & Technology*, *41*, 8328-8334.

Lunde, G.; Bjorseth, A. 1977. Polycyclic Aromatic-Hydrocarbons in Long-Range Transported Aerosols. *Nature*, *268*, 518-519.

Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. 2006. Atmospheric chemistry of perfluoroalkanesulfonamides: Kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. *Environmental Science & Technology*, *40*, 864-872.

Martin, J. W.; Muir, D. C. G.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. 2002. Collection of airborne fluorinated organics and analysis by gas chromatography/chemical ionization mass spectrometry. *Analytical Chemistry*, *74*, 584-590.

McLachlan, M. S.; Holmstrom, K. E.; Reth, M.; Berger, U. 2007. Riverine discharge of perfluorinated carboxylates from the European continent. *Environmental Science & Technology*, *41*, 7260-7265.

Oono, S.; Matsubara, E.; Harada, K. H.; Takagi, S.; Hamada, S.; Asakawa, A.; Inoue, K.; Watanabe, I.; Koizumi, A. 2008. Survey of airborne polyfluorinated telomers in Keihan area, Japan. *Bulletin of Environmental Contamination and Toxicology*, *80*, 102-106.

Piekarz, A. M.; Primbs, T.; Field, J. A.; Barofsky, D. F.; Simonich, S. 2007. Semivolatile fluorinated organic compounds in Asian and western U.S air masses. *Environmental Science & Technology*, *41*, 8248-8255.

Preston, M. R.; Merrett, J. 1991. The Distribution and origins of the hydrocarbon fraction of particulate material in the North-Sea atmosphere. *Marine Pollution Bulletin*, *22*, 516-522.

Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. 2006. Sources, fate and transport of perfluorocarboxylates. *Environmental Science & Technology*, *40*, 32-44.

Sasaki, K.; Harada, K.; Saito, N.; Tsutsui, T.; Nakanishi, S.; Tsuzuki, H.; Koizumi, A. 2003. Impact of airborne perfluorooctane sulfonate on the human body burden and the ecological system. *Bulletin of Environmental Contamination and Toxicology*, *71*, 408-413.

Shoeib, M.; Harner, T.; Ikonomou, M.; Kannan, K. 2004. Indoor and outdoor air concentrations and phase partitioning of perfluoroalkyl sulfonamides and polybrominated diphenyl ethers. *Environmental Science & Technology*, *38*, 1313-1320.

Shoeib, M.; Harner, T.; Vlahos, P. 2006. Perfluorinated chemicals in the Arctic atmosphere. *Environmental Science & Technology*, *40*, 7577-7583.

Shoeib, M.; Harner, T.; Wilford, B. H.; Jones, K. C.; Zhu, J. P. 2005. Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: Occurrence, partitioning, and human exposure. *Environmental Science & Technology*, *39*, 6599-6606.

Smithwick, M.; Mabury, S. A.; Solomon, K. R.; Sonne, C.; Martin, J. W.; Born, E. W.; Dietz, R.; Derocher, A. E.; Letcher, R. J.; Evans, T. J.; Gabrielsen, G. W.; Nagy, J.; Stirling, I.; Taylor, M. K.; Muir, D. C. G. 2005. Circumpolar study of perfluoroalkyl contaminants in polar bears (Ursus maritimus). *Environmental Science & Technology*, *39*, 5517-5523.

So, M. K.; Miyake, Y.; Yeung, W. Y.; Ho, Y. M.; Taniyasu, S.; Rostkowski, P.; Yamashita, N.; Zhou, B. S.; Shi, X. J.; Wang, J. X.; Giesy, J. P.; Yu, H.; Lam, P. K. S. 2007. Perfluorinated compounds in the Pearl River and Yangtze River of China. *Chemosphere*, *68*, 2085-2095.

Stock, N. L.; Lau, F. K.; Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. 2004. Polyfluorinated telomer alcohols and sulfonamides in the north American troposphere. *Environmental Science & Technology*, *38*, 991-996.

Sulbaek Andersen, M. P.; Nielsen, O. J.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. 2005. Atmospheric chemistry of 4 : 2 fluorotelomer alcohol (n-C4F9CH2CH2OH): Products and mechanism of Cl atom initiated oxidation in the presence of NOx. *Journal of Physical Chemistry A*, *109*, 1849-1856.

Taniyasu, S.; Kannan, K.; Horii, Y.; Hanari, N.; Yamashita, N. 2003. A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan. *Environmental Science & Technology*, *37*, 2634-2639.

Tao, L.; Kannan, K.; Kajiwara, N.; Costa, M. M.; Fillmann, G.; Takahashi, S.; Tanabe, S. 2006. Perfluorooctanesulfonate and related fluorochemicals in albatrosses, elephant seals, penguins, and Polar Skuas from the Southern Ocean. *Environmental Science & Technology*, *40*, 7642-7648.

Yamashita, N.; Taniyasu, S.; Petrick, G.; Wei, S.; Gamo, T.; Lam, P. K. S.; Kannan, K. 2008. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. *Chemosphere*, *70*, 1247-1255

Young, C. J.; Furdui, V. I.; Franklin, J.; Koerner, R. M.; Muir, D. C. G.; Mabury, S. A. 2007. Perfluorinated acids in arctic snow: New evidence for atmospheric formation. *Environmental Science & Technology*, *41*, 3455-3461.

Supporting Information

The supporting information covers the following topics:

12 pages, 14 tables, 3 figures

Chemicals

Table S3-1: Solvents and gases used for the analysis of PFC in air samples.

substances	abbreviation	purity	producer
ethyl acetate	-	Picograde	Promochem, Wesel, Germany
acetone	-	Picograde	Promochem, Wesel, Germany
methyl-tert-butylether	MTBE	Picograde	Promochem, Wesel, Germany
methanol	MeOH	Residue Analysis	J.T. Baker, Griesheim, Germany
nitrogen	-	6.0	Air Liquide, Germany

Table S3-2: Mass-labeled standard compounds used for the analysis of PFC in air samples.

substances	abbreviation	purity (%)	producer
2-Perfluorohexyl-($^{13}C_2$)-ethanol	^{13}C 6:2 FTOH	> 98	Wellington Laboratories, Guelph, Canada
2-Perfluorooctyl-($^{13}C_2$)-ethanol	^{13}C 8:2 FTOH	> 98	Wellington Laboratories, Guelph, Canada
2-Perfluorodecyl-($^{13}C_2$)-ethanol	^{13}C 10:2 FTOH	> 98	Wellington Laboratories, Guelph, Canada
methyl-D_3-perfluorooctane sulfonamide	D_3 MeFOSA	> 98	Wellington Laboratories, Guelph, Canada
ethyl-D_5-perfluorooctane sulfonamide	D_5 EtFOSA	> 98	Wellington Laboratories, Guelph, Canada
methyl-D_7-perfluorooctane sulfonamido ethanol	D_7 MeFOSE	> 98	Wellington Laboratories, Guelph, Canada
ethyl-D_9-perfluorooctane sulfonamido ethanol	D_9 MeFOSE	> 98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-butanoic acid	^{13}C PFBA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-hexanoic acid	^{13}C PFHxA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-octanoic acid	^{13}C PFOA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-nonanoic acid	^{13}C PFNA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-decanoic acid	^{13}C PFDA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-undecanoic acid	^{13}C PFUnDA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-dodecanoic acid	^{13}C PFDoA	>98	Wellington Laboratories, Guelph, Canada
sodium perfluoro-(^{18}O2)-hexane sulfonate	$^{18}O_2$-PFHxS	>99	Wellington Laboratories, Guelph, Canada
sodium perfluoro-(^{13}C4)-octane sulfonate	^{13}C-PFOS	>98	Wellington Laboratories, Guelph, Canada
sodium perfluoro-(^{13}C4)-octane sulfinate	^{13}C-PFOSi	~90	Wellington Laboratories, Guelph, Canada
hexachlorobenzene ^{13}C6	^{13}C HCB	97	Dr. Ehrenstorfer, Augsburg, Germany
1,3,5-trichlorobenzene D_3	TCB D_3	98	Aldrich, Munich, Germany
2,4-dichlorophenol ^{13}C6	^{13}C DCP	>99	Dr. Ehrenstorfer, Augsburg, Germany
perfluorooctane sulfonamido-D_5-acetic acid	D_5 EtFOSAA	>98	Wellington Laboratories, Guelph, Canada

Table S3-3: Analyte standards used for the analysis of PFC in air samples.

substances	abbreviation	purity (%)	producer
perfluorobutyl ethanol	4:2 FTOH	97	Aldrich, Munich, Germany
perfluorohexyl ethanol	6:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
perfluorooctyl ethanol	8:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
perfluorodecyl ethanol	10:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
perfluorododecyl ethanol	12:2 FTOH	-	donated by Jones group, Lancaster University, UK
perfluorohexyl ethylacylate	6:2 FTA	97	Aldrich, Munich, Germany
perfluorooctyl ethylacylate	8:2 FTA	97	Fluorochem, Old Glossop, UK
perfluorodecyl ethylacylate	10:2 FTA	97	Fluorochem, Old Glossop, UK
n-methyl perfluorobutane sulfonamide	MeFBSA	-	donated by 3M, Germany
n-methyl perfluorooctane sulfonamide	MeFOSA	-	donated by 3M, Germany
n-ethyl perfluorooctane sulfonamide	EtFOSA	95	ABCR, Karlsruhe, Germany
perfluorooctane sulfonamide	PFOSA	-	donated by 3M, USA
dimethylperfluoroocatane sulfonamide	Me2FOSA	98	Wellington Laboratories, Guelph, Canada
n-methyl perfluorobutane sulfonamido ethanol	MeFBSE	-	donated by 3M, USA
n-methyl perfluorooctane sulfonamidoethanol	MeFOSE	-	donated by 3M, USA
n-ethyl perfluorooctane sulfonamido ethanol	EtFOSE	-	donated the Mabury group, Toronto University, Canada
potassium perfluorobutane sulfonate	PFBS-K	98	ABCR, Karlsruhe, Germany
potassium perfluorohexane sulfonate	PFHxS-K	98	Fluka, Buchs, Switzerland
potassium perfluorooctane sulfonate	PFOS-K	98	Fluka, Buchs, Switzerland
potassium perfluorodecane sulfonate	PFDS-K	>98	Wellington Laboratories, Guelph, Canada
perfluorobutanoic acid	PFBA	99	ABCR, Karlsruhe, Germany
perfluoropentanoic acid	PFPA	98	Alfa Aesar, Karlsruhe, Germany
perfluorohexanoic acid	PFHxA	98	ABCR, Karlsruhe, Germany
perfluoroheptanoic acid	PFHpA	98	Lancaster Synthesis, Frankfurt, Germany
perfluorooctanoic acid	PFOA	95	Lancaster Synthesis, Frankfurt, Germany
perfluorononanoic acid	PFNA	98	Alfa Aesar, Karlsruhe, Germany
perfluorodecanoic acid	PFDA	98	ABCR, Karlsruhe, Germany
perfluoroundecanoic acid	PFUnDA	96	ABCR, Karlsruhe, Germany
perfluorododecanoic acid	PFDoDA	96	Alfa Aesar, Karlsruhe, Germany
perfluorotridecanoic acid	PFTrDA	>98	Wellington Laboratories, Guelph, Canada
perfluorotetradecanoic acid	PFTeDA	96	Alfa Aesar, Karlsruhe, Germany
perfluorohexadecanoic acid	PFHxDA	95	Alfa Aesar, Karlsruhe, Germany
perfluorooctadecanoic acid	PFOcDA	97	Alfa Aesar, Karlsruhe, Germany
sodium perfluorohexane sulfinate	PFHxSi	98	Wellington Laboratories, Guelph, Canada
sodium perfluorooctane sulfinate	PFOSi	98	Wellington Laboratories, Guelph, Canada
sodium perfluorodecane sulfinate	PFDSi	98	Wellington Laboratories, Guelph, Canada

Detection & Quantification Limits

Table S3-4: Instrumental detection limits (LOD), instrumental quantification limits (LOQ), method quantification limits (MQL), and method detection limits (MDL) for neutral volatile and semi-volatile polyfluorinated compounds determined in the gas phase (g) and particle phase (p) based on signal to noise ratios.

	MQL(g) pg m^{-3}	MDL(g) pg m^{-3}	MQL(p) pg m^{-3}	MDL(p) pg m^{-3}	LOQ pg μL^{-1}	LOD pg μL^{-1}	LOQ pg abs.	LOD pg abs.
4:2 FTOH	<1.2	0.5	n.d.	n.d.	1.1	0.8	2.1	1.7
6:2 FTOH	<0.9	<0.9	n.q.	n.q.	1.1	0.9	2.2	1.8
8:2 FTOH	<1.8	<1.8	n.q.	n.q.	1.0	0.8	2.0	1.6
10:2 FTOH	<0.7	<0.7	n.q.	n.q.	1.0	0.8	2.0	1.6
12:2 FTOH	0.4	0.4	n.q.	n.q.	1.0	0.8	2.0	1.6
6:2 FTA	0.5	0.5	n.d.	n.d.	0.2	0.1	0.4	0.2
8:2 FTA	0.1	0.1	n.d.	n.d.	0.2	0.1	0.4	0.2
10:2 FTA	<0.1	<0.1	n.d.	n.d.	0.2	0.1	0.4	0.2
MeFBSA	<0.3	<0.3	n.d.	n.d.	0.2	0.1	0.4	0.2
MeFOSA	<0.4	<0.4	0.1	<0.1	0.2	0.1	0.4	0.2
Me2FOSA	0.5	<0.1	n.d.	n.d.	0.1	0.0	0.2	0.0
EtFOSA	0.1	<0.1	0.2	<0.2	0.2	0.1	0.4	0.2
PFOSA	0.5	<0.5	<23	<23	8.2	4.1	16.4	8.2
MeFBSE	0.1	<0.1	1.6	<1.5	0.2	0.1	0.4	0.2
MeFOSE	0.4	0.2	0.1	<0.1	0.2	0.1	0.4	0.2
EtFOSE	0.1	<0.1	0.3	<0.3	0.4	0.2	0.9	0.4

Table S3-5: Instrumental detection limits (LOD), instrumental quantification limits (LOQ), method quantification limits (MQL), and method detection limits (MDL) for ionic polyfluorinated compounds determined in the particle phase (p) based on signal to noise ratios.

	MQL(p) pg m^{-3}	MDL(p) pg m^{-3}	LOQ pg µL^{-1}	LOD pg µL^{-1}	LOQ pg abs.	LOD pg abs.
PFBS	0.3	0.1	0.05	0.02	0.5	0.2
PFHxS	0.2	0.1	0.05	0.02	0.5	0.2
PFHpS	0.3	<0.3	0.05	0.02	0.5	0.2
PFOS	0.1	<0.05	0.1	0.05	1.0	0.5
PFDS	0.4	n.d.	0.05	0.02	0.5	0.2
PFHxSi	0.5	n.d.	0.1	0.05	1.0	0.5
PFOSi	n.q.	n.q.	0.05	0.02	0.5	0.2
PFDSi	0.5	n.d.	0.1	0.05	1.0	0.5
PFBA	0.1	<0.1	0.2	0.2	2.0	2.0
PFPA	0.4	<0.05	0.1	0.05	1.0	0.5
PFHxA	<0.05	<0.05	0.1	0.05	1.0	0.5
PFHpA	0.1	<0.1	0.1	0.05	1.0	0.5
PFOA	<<1.8	<<1.8	0.1	0.05	1.0	0.5
PFNA	<0.05	<0.05	0.1	0.05	1.0	0.5
PFDA	0.1	0.05	0.1	0.05	1.0	0.5
PFUnDA	<0.1	<0.1	0.2	0.1	2.0	1.0
PFDoDA	<0.2	<0.2	0.1	0.05	1.0	0.5
PFTriDA	0.2	<0.2	0.1	0.05	1.0	0.5
PFTeDA	0.2	<0.2	0.2	0.10	2.0	1.0
PFHxDA	n.d.	n.d.	0.2	0.10	2.0	1.0
PFOcDA	n.d.	n.d.	0.2	0.10	2.0	1.0

Blanks

Table S3-6: Solvent blank (SB) and field blank (FldB) concentrations for gas-phase analytes (pg m^{-3}).

	Atair SB 1	Atair SB 2	Atair SB 3	Atair FldB1	Atair FldB2	GKSS-BAR SB25	GKSS-BAR SB26	GKSS-BAR SB27	GKSS FldB Nov	BAR FldB Nov
6:2 FTA	0.1	1.8	1.2	0.2	1.8	n.d.	n.d.	n.d.	0.5	1.6
4:2 FTOH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2
6:2 FTOH	1.2	1.9	1.3	1.4	2.0	0.2	n.d.	n.d.	1.0	1.2
8:2 FTA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	1.0
8:2 FTOH	1.3	1.7	1.3	n.d.	2.0	0.3	0.2	n.d.	0.7	0.5
Me2FOSA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2 FTA	n.d.	n.d.	n.d.	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10:2 FTOH	0.7	1.5	1.0	1.9	1.7	0.2	0.1	n.d.	0.7	0.1
12:2 FTOH	n.d.	n.d.	n.d.	n.d.	1.9	0.4	n.d.	n.d.	1.3	n.d.
EtFOSA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	n.d.
MeFBSA	n.d.	n.d.	n.d.	1.3	2.2	n.d.	n.d.	n.d.	n.d.	n.d.
MeFOSA	n.d.	n.d.	n.d.	1.6	2.9	n.d.	n.d.	n.d.	n.d.	n.d.
MeFOSE	0.4	2.5	0.9	23.1	2.8	n.d.	n.d.	n.d.	0.5	n.d.
MeFBSE	1.0	1.8	1.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
EtFOSE	n.d.	2.5	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOSA	n.d.	n.d.	n.d.	n.d.	7.2	n.d.	n.d.	n.d.	n.d.	n.d.

Table S3-7: Filter blank (FB) and field blank concentration (FldB) for particle-phase analytes (pg m^{-3}).

	Atair SB 1	Atair SB 2	Atair FB2	GKSS-BAR FB17	GKSS-BAR FB18	GKSS-BAR FB19	GKSS FldB Nov	BAR FldB Nov
PFBS	n.d.	0.5	1.3	0.0	0.4	0.0	n.q.	n.q.
PFHxS	0.2	0.5	0.3	0.0	1.9	0.0	n.q.	n.q.
PFHpS	n.d.	n.d.	n.d.	0.0	0.5	0.0	n.d.	n.d.
PFOS	0.6	0.4	0.1	0.0	75.3	0.0	n.q.	n.q.
PFDS	n.d.	n.d.	n.d.	0.0	0.0	0.0	n.d.	n.d.
PFHxSi	n.d.	n.d.	n.d.	0.0	0.0	0.0	n.d.	n.d.
PFOSi	n.d.	0.3	n.d.	0.1	0.0	0.0	n.q.	n.d.
PFDSi	n.d.	n.d.	n.d.	0.0	0.0	0.0	n.d.	n.d.
PFBA	1.6	2.3	1.7	0.1	6.4	0.0	n.q.	n.q.
PFPA	n.d.	n.d.	0.0	0.0	0.1	0.0	n.q.	n.q.
PFHxA	0.3	0.1	0.3	0.0	0.2	0.0	0.1	0.1
PFHpA	0.4	n.d.	0.2	0.0	0.4	0.0	n.q.	n.q.
PFOA	1.3	0.6	1.1	0.1	9.5	0.1	n.q.	0.1
PFNA	n.d.	0.4	0.2	0.0	1.7	0.0	n.q.	n.q.
PFDA	n.d.	0.6	0.3	0.1	0.2	0.0	n.q.	n.q.
PFUnDA	0.2	0.1	0.1	0.1	0.8	0.0	n.q.	n.q.
PFDoDA	0.2	0.4	0.2	0.1	0.8	0.0	n.d.	n.q.
PFTriDA	0.0	0.1	n.d.	0.1	0.2	0.0	n.d.	n.d.
PFTeDA	n.d.	n.d.	n.d.	0.1	0.0	0.0	n.d.	n.d.
PFHxDA	0.2	n.d.	n.d.	0.3	0.0	0.0	n.d.	n.d.
PFOcDA	n.d.	n.d.	n.d.	0.4	0.0	0.0	n.d.	n.d.

Recovery Rates

Table S3-8: Minimum (min), maximum (max) and average recovery rates (R) for gas-phase extractions (%). SD: standard deviation. RSD: relative standard deviation.

	R(min) (%)	R(max) (%)	R(average) (%)	SD (%)	RSD (%)
4:2 FTOH ^{13}C	13	41	22	7	34
6:2 FTOH ^{13}C	29	86	49	14	28
8:2 FTOH ^{13}C	31	94	53	15	28
10:2 FTOH ^{13}C	33	79	58	13	23
EtFOSA D_5	18	88	49	21	42
MeFOSA D_3	16	85	49	22	45
MeFOSE D_7	52	96	73	14	19
EtFOSE D_9	51	98	73	16	21

Table S3-9: Minimum (min), maximum (max) and average recovery rates (R) for particle-phase extractions (%). SD: standard deviation. RSD: relative standard deviation.

	R(min) (%)	R(max) (%)	R(average) (%)	SD (%)	RSD (%)
4:2 FTOH ^{13}C	27	36	32	3	10
6:2 FTOH ^{13}C	30	40	35	3	9
8:2 FTOH ^{13}C	29	34	31	2	6
10:2 FTOH ^{13}C	36	50	45	5	11
EtFOSA D_5	63	79	72	6	9
MeFOSA D_3	45	64	52	6	12
MeFOSE D_7	49	73	64	9	14
EtFOSE D_9	42	78	61	15	25
$^{18}O2$-PFHxS	48	90	66	15	23
^{13}C-PFOS	62	81	70	7	10
^{13}C-PFOSi	55	74	67	7	10
^{13}C-PFBA	43	98	62	20	31
^{13}C-PFHxA	41	74	60	12	20
^{13}C-PFOA	27	48	39	8	20
^{13}C-PFNA	36	57	49	9	18
^{13}C-PFDA	47	96	72	16	22
^{13}C-PFUDA	91	159	123	23	18
^{13}C-PFDoA	71	134	96	23	23

Uncertainty of the Method

Table S3-10: Relative standard and expanded uncertainties for gas-phase samples (%) calculated according to ISO 20988 based on paired measurements of volatile polyfluorinated compounds during the Atair campaign. Uncertainties were being referred to average concentration levels.

	standard uncertainty	**expanded uncertainty**
6:2 FTA	66	153
4:2 FTOH	36	83
6:2 FTOH	38	88
8:2 FTA	140	323
8:2 FTOH	27	62
Me2FOSA	55	128
10:2 FTA	19	45
10:2 FTOH	31	71
12:2 FTOH	42	97
EtFOSA	18	41
MeFBSA	46	107
MeFOSA	58	134
MeFOSE	60	139
MeFBSE	27	61
EtFOSE	21	49
PFOSA	159	368

Particle-Phase PFCA Composition

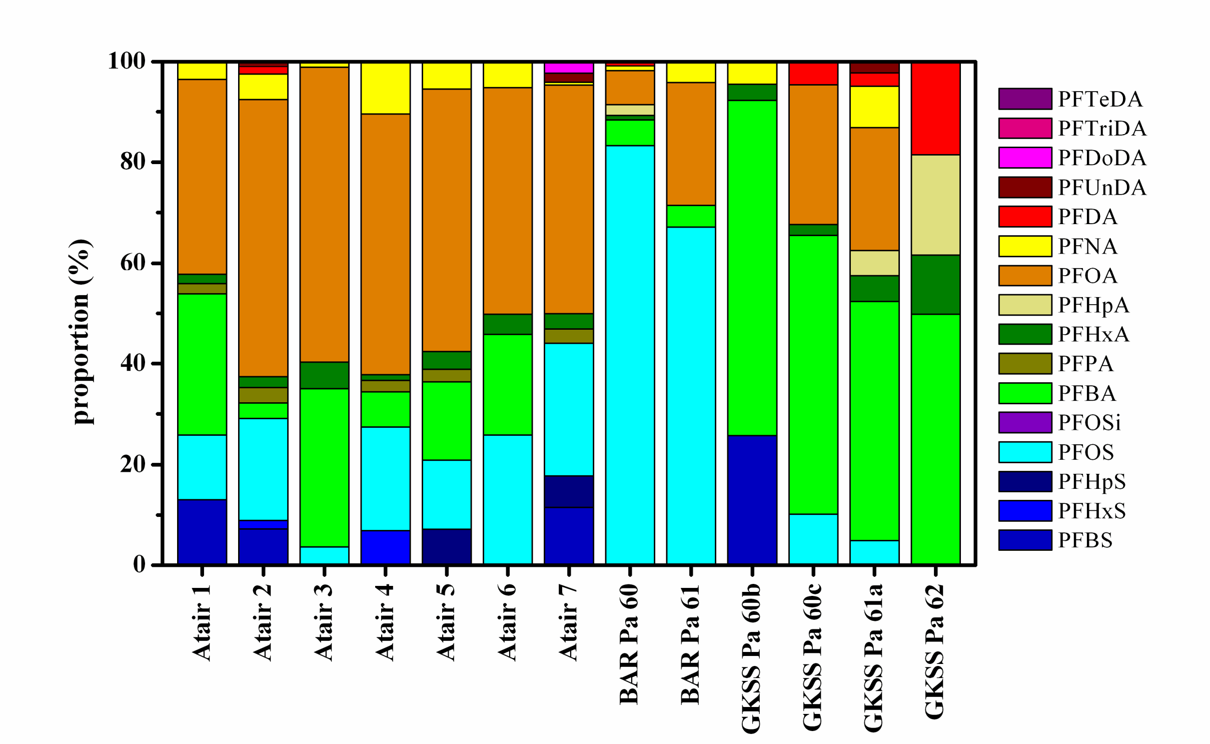


Figure S3-1: Composition of ionic PFC in the particle phase. Note that filter blank problems occurred in some BAR and GKSS samples resulting in the absence of samples BAR Pa62 and GKSS Pa 61b and some analytes such as PFOS and PFOA.

Correlation Coefficients

Table S3-11: Correlation coefficients for the correlation of neutral volatile analytes in the gas phase of Atair samples. [a] significant at 0.05 level. [b] significant at 0.1 level.

	4:2 FTOH	**6:2 FTOH**	**8:2 FTOH**	**10:2 FTOH**	**12:2 FTOH**	**6:2 FTA**	**8:2 FTA**	**10:2 FTA**	**Me FBSA**	**Me FOSA**	**Me2 FOSA**	**Et FOSA**	**P FOSA**	**Me FBSE**	**MeFOSE**	**EtFOSE**	**Σ FTOH**	**Σ FTA**	**Σ FASA**	**Σ FASE**
6:2 FTOH	-0.4																			
8:2 FTOH	-0.2	0.6[b]																		
10:2 FTOH	0.2	0.6[b]	1[a]																	
12:2 FTOH	-0.8	0.6[b]	1[a]	1[a]																
6:2 FTA	0	-1[a]	-1[a]	-1[a]	-1[a]															
8:2 FTA	-0.7	0.6[b]	1[a]	0.9[a]	1[a]	-1[a]														
10:2 FTA	0.3	0.5	1[a]	0.9[a]	1[a]	-1[a]	1[a]													
MeFBSA	-0.7	-0.3	-0.3	-0.3	-0.3	1[a]	-0.3	-0.4												
MeFOSA	-0.2	-0.4	-0.6	-0.6	-0.5	-1[a]	-0.4	-0.3	0.3											
Me$_2$FOSA	0.8	-0.2	-0.4	-0.4	-0.4	-1[a]	-0.3	-0.3	-0.6	0.4										
EtFOSA	0.1	-0.5	-0.6	-0.6	-0.5	1[a]	-0.5	-0.5	0.6[b]	0.8[a]	0.5									
PFOSA	1[a]	0.8	0.8[a]	0.8	0.9[a]	-1[a]	0.9[a]	1[a]	-0.5	-0.1	-0.3	-0.5								
MeFBSE	0.7	0.6	0.9[a]	1[a]	0.9[a]	-1[a]	0.9[a]	0.9[a]	-0.6	-0.6	-0.1	-0.7	0.8[a]							
MeFOSE	0.9[a]	-0.6	-0.4	-0.4	-0.4	-1[a]	-0.3	-0.2	-0.4	0.5	0.7	0.3	0.0	-0.2						
EtFOSE	1[a]	-0.9	-1	-1.0	-1[a]	0	-1[a]	-0.6	-0.5	1.0	0.5	1.0	1[a]	-0.6	1					
Σ FTOH	-0.2	0.7	1[a]	1[a]	1[a]	-1[a]	1[a]	0.9[a]	-0.3	-0.6	-0.4	-0.6	0.8[a]	0.9[a]	-0.4	-1				
Σ FTA	-0.5	0.6	1[a]	1[a]	1[a]	-1[a]	1[a]	1[a]	-0.3	-0.5	-0.4	-0.6	0.9[a]	0.9[a]	-0.4	-1[a]	1[a]			
Σ FASA	0.0	-0.2	0.3	0.3	0.4	-1[a]	0.4	0.4	0.3	0.4	0.1	0.4	0.4	0.2	0.0	1	0.3	0.4		
Σ FASE	1[a]	-0.1	0.3	0.4	0.3	-1[a]	0.4	0.5	-0.7[a]	0.0	0.5	-0.2	0.5	0.6	0.7[a]	0.8	0.3	0.4	0.1	
T (°C)	0.8	-0.5	-0.9[a]	-0.8[a]	-0.9[a]	1[a]	-0.9[a]	-0.9[a]	0	0.1	0.3	0.1	-0.8	-0.7[a]	0.4	1[a]	-0.9[a]	-0.9[a]	-0.6	-0.3

Table S3-12: Correlation coefficients for the correlation of neutral volatile analytes in the gas phase of Barsbüttel and GKSS samples. [a] significant at 0.05 level. [b] significant at 0.1 level.

	4:2 FTOH	**6:2 FTOH**	**8:2 FTOH**	**10:2 FTOH**	**12:2 FTOH**	**6:2 FTA**	**8:2 FTA**	**10:2 FTA**	**Me FBSA**	**Me FOSA**	**Me2 FOSA**	**Et FOSA**	**P FOSA**	**Me FBSE**	**MeFOSE**	**EtFOSE**	**Σ FTOH**	**Σ FTA**	**Σ FASA**	**Σ FASE**
6:2 FTOH	1[a]																			
8:2 FTOH	1[a]	0.8[a]																		
10:2 FTOH	1[a]	0.9[a]	1[a]																	
12:2 FTOH	-1[a]	0.9[a]	0.5	0.7[a]																
6:2 FTA	1[a]	1[a]	0.8[a]	0.9[a]	0.8[a]															
8:2 FTA	1[a]	0.4	0.5	0.6	0.3	0.5														
10:2 FTA	1[a]	0.6	0.7[a]	0.7[a]	0.4	0.6[a]	0.9[a]													
MeFBSA	1[a]	0.4	0.6[b]	0.5[b]	0.0	0.5[b]	0.8[a]	0.8[a]												
MeFOSA	-1[a]	0.7[a]	0.4	0.5[b]	0.8[a]	0.7[a]	0.2	0.2	0.1											
Me_2FOSA	0	0.1	0.1	0.0	-0.1	0.3	0.6	0.6	0.5	-0.1										
EtFOSA	1[a]	0.9[a]	0.6[b]	0.7[a]	0.9[a]	0.8[a]	0.2	0.3	0.2	0.9[a]	-0.4									
PFOSA	0	0.4	0.0	0.4	0.6	0.4	0.9	1[a]	0.6	0.2	1[a]	0.2								
MeFBSE	1[a]	0.7[a]	0.8[a]	0.8[a]	0.6[b]	0.6[b]	0.2	0.4	0.1	0.2	-0.5	0.6[b]	0.0							
MeFOSE	-1[a]	0.8[a]	0.5	0.7[a]	0.9[a]	0.6[b]	0.0	0.2	-0.2	0.6[a]	-0.6	0.9[a]	0.4	0.8[a]						
EtFOSE	-1[a]	0.6	0.4	0.4	0.6[b]	0.7[a]	0.3	0.3	0.3	0.9[a]	0.5	0.6[a]	0.1	0	0.2					
Σ FTOH	1[a]	0.9[a]	1[a]	1[a]	0.7[a]	0.9[a]	0.5	0.7[a]	0.6	0.5	0.1	0.7[a]	0.2	0.8[a]	0.6[b]	0.5				
Σ FTA	1[a]	0.7[a]	0.7[a]	0.8[a]	0.5[b]	0.8[a]	0.9[a]	1[a]	0.8[a]	0.4	0.6	0.4	0.9	0.4	0.2	0.5	0.8[a]			
Σ FASA	1[a]	0.8[a]	0.8[a]	0.8[a]	0.7[a]	0.9[a]	0.7[a]	0.7[a]	0.7[a]	0.7[a]	0.2	0.8[a]	0.3	0.4	0.5	0.7[a]	0.8[a]	0.8[a]		
Σ FASE	-1[a]	0.9[a]	0.7[a]	0.8[a]	0.8[a]	0.7[a]	0.1	0.4	0.0	0.6	-0.5	0.9[a]	0.2	0.9[a]	1[a]	0.3	0.8[a]	0.4	0.6[b]	
T (°C)	-1[a]	-0.2	0.0	-0.1	-0.3	-0.2	0.0	-0.1	0.2	0.2	-0.2	-0.1	-1[a]	-0.2	-0.2	0.1	0.0	-0.1	0.0	-0.2

Table S3-13: Correlation coefficients for the correlation of neutral volatile analytes in the gas phase of Barsbüttel and GKSS samples. [a] significant at 0.05 level. [b] significant at 0.1 level.

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTA	8:2 FTA	10:2 FTA	Me FBSA	Me FOSA	Me2 FOSA	Et FOSA	P FOSA	Me FBSE	MeFOSE	EtFOSE	Σ FTOH	Σ FTA	Σ FASA	Σ FASE
6:2 FTOH	0.9[a]																			
8:2 FTOH	0.9[a]	0.7[a]																		
10:2 FTOH	1[a]	0.8[a]	1[a]																	
12:2 FTOH	0.7[b]	0.8[a]	0.8[a]	0.9[a]																
6:2 FTA	1[a]	0.7[a]	0.7[a]	0.8[a]	0.6[a]															
8:2 FTA	1[a]	0.5[a]	0.8[a]	0.8[a]	0.7[a]	0.3														
10:2 FTA	1[a]	0.5[a]	0.9[a]	0.8[a]	0.7[a]	0.4	1.0[a]													
MeFBSA	0.4	0	0.1	0.1	-0.2	0.6[a]	0.2	0.1												
MeFOSA	-0.5	0.3	0	0	0.3	0.5[b]	-0.1	-0.1	0.2											
Me_2FOSA	0.6	0.2	0	0	-0.1	0.2	0.2	0.2	0.2	0.1										
EtFOSA	0.9[a]	0.9[a]	0.4	0.6[a]	0.7[a]	0.5[b]	0.2	0.2	0	0.6[a]	0.0									
PFOSA	1[a]	-0.3	0.5	0.3	0.2	0.2	0.6[b]	0.7[a]	0.2	0.0	0.1	-0.5								
MeFBSE	1[a]	0.8[a]	0.8[a]	0.8[a]	0.7[a]	0.4	0.4	0.5[a]	-0.1	0.0	-0.1	0.7[a]	-0.3							
MeFOSE	-0.2	0.7[a]	0.3	0.5[a]	0.6[a]	0.4	0	0.1	-0.3	0.5[a]	-0.2	0.8[a]	-0.3	0.7[a]						
EtFOSE	0.8[b]	0.7[a]	0.5[b]	0.6[a]	0.7[a]	0.4	0.6[a]	0.6[a]	0.1	0.6[a]	0.4	0.7[a]	-0.4	0.3	0.3					
Σ FTOH	0.9[a]	0.8[a]	1.0[a]	1[a]	0.9[a]	0.8[a]	0.8[a]	0.8[a]	0.1	0.1	0	0.6[a]	0.3	0.8[a]	0.5[a]	0.6[a]				
Σ FTA	1[a]	0.6[a]	0.9[a]	0.9[a]	0.8[a]	0.6[a]	1[a]	1[a]	0.2	-0.1	0.2	0.3	0.5	0.6[a]	0.2	0.6[a]	0.9[a]			
Σ FASA	0.5	0.4	0.4	0.4	0.4	0.8[a]	0.4	0.4	0.7[a]	0.6[a]	0.2	0.5[a]	0.4	0.2	0.3	0.5[b]	0.4[b]	0.4[b]		
Σ FASE	0.8[a]	0.9[a]	0.6[a]	0.7[a]	0.7[a]	0.5[b]	0.3	0.4	-0.2	0.3	-0.1	0.9[a]	-0.4	0.9[a]	0.9[a]	0.5[b]	0.7[a]	0.5[a]	0.3	
T (°C)	-0.5	-0.5[a]	-0.5[a]	-0.6[a]	-0.7[a]	0	-0.6[a]	-0.6[a]	0.3	0.2	-0.1	-0.3	-0.1	-0.5[a]	-0.2	-0.3	-0.6[a]	-0.6[a]	0	-0.4

Table S3-14: Correlation coefficients for the correlation of ionic analytes in the particle phase of Atair samples. [a] significant at 0.05 level. [b] significant at 0.1 level.

	PFBS	PFOS	PFBA	PFPA	PFHxA	PFOA
PFOS	0.5					
PFBA	-1	-0.5				
PFPA	0.8	0.9[a]	-0.3			
PFHxA	0.4	0.6[b]	-0.1	0.8[a]		
PFOA	0.8	0.8[a]	-0.4	1.0[a]	0.6[b]	
PFNA	1[a]	0.5	-0.7[b]	0.5	-0.1	0.6[b]

Back Trajectories

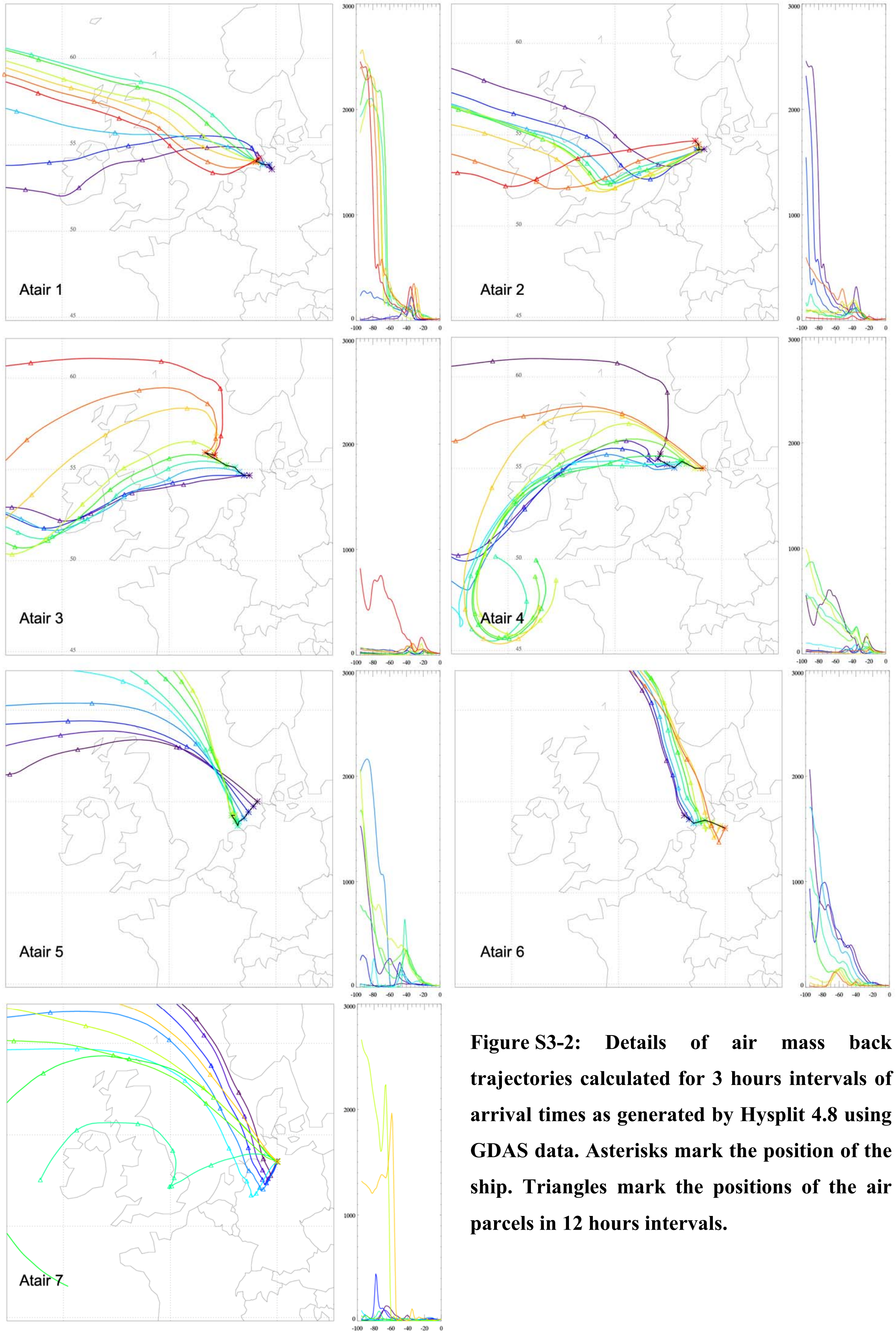


Figure S3-2: Details of air mass back trajectories calculated for 3 hours intervals of arrival times as generated by Hysplit 4.8 using GDAS data. Asterisks mark the position of the ship. Triangles mark the positions of the air parcels in 12 hours intervals.

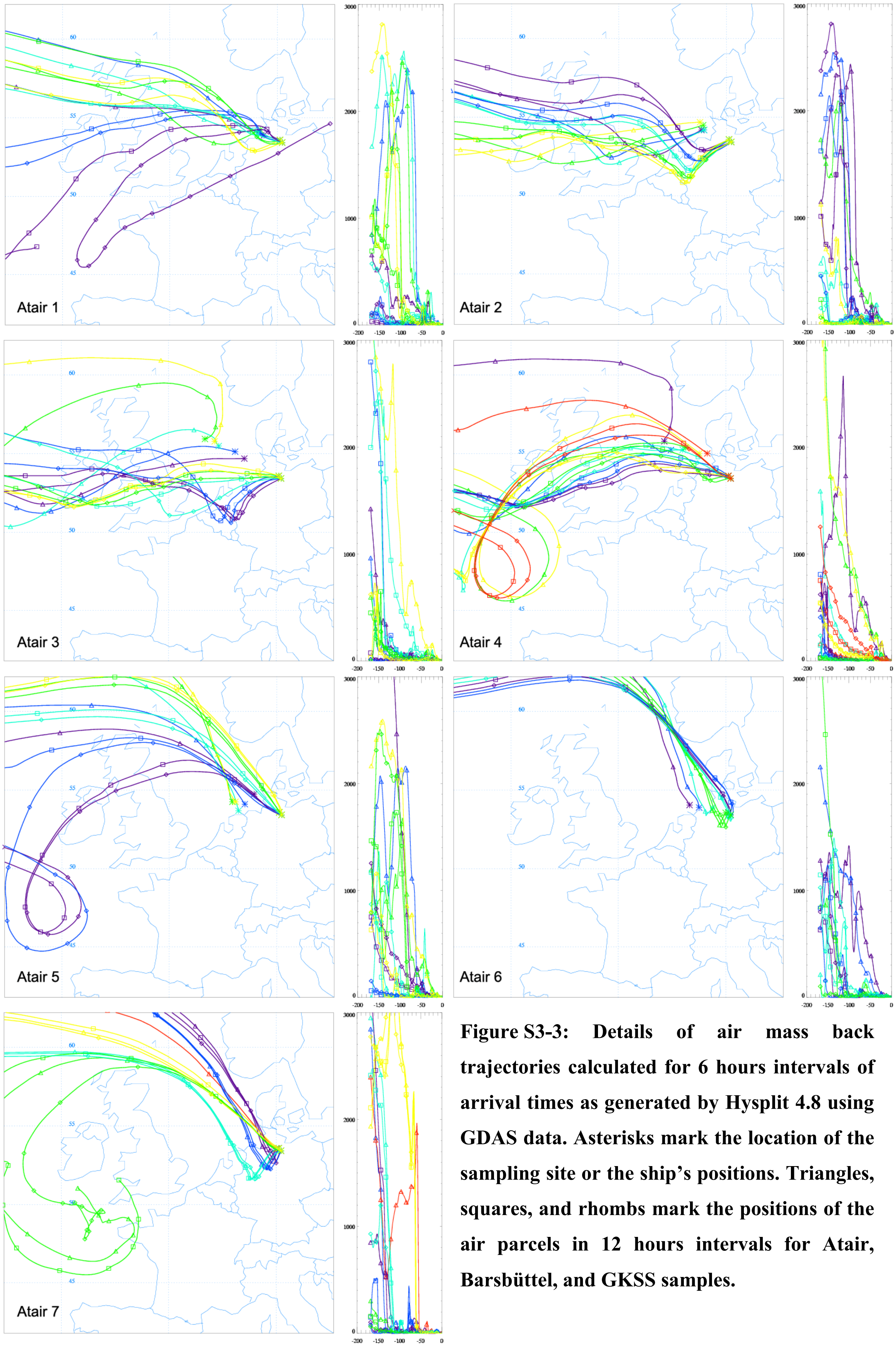


Figure S3-3: Details of air mass back trajectories calculated for 6 hours intervals of arrival times as generated by Hysplit 4.8 using GDAS data. Asterisks mark the location of the sampling site or the ship's positions. Triangles, squares, and rhombs mark the positions of the air parcels in 12 hours intervals for Atair, Barsbüttel, and GKSS samples.

Study 4

Polyfluorinated Compounds in the Atmosphere of the Atlantic and Southern Ocean: Evidence for a Global Distribution

Annekatrin Dreyer, Ingo Weinberg, Christian Temme, and Ralf Ebinghaus

Environmental Science & Technology (submitted)

Polyfluorinated Compounds in the Atmosphere of the Atlantic and Southern Ocean: Evidence for a Global Distribution

Annekatrin Dreyer[1], Ingo Weinberg[1,2], Christian Temme[1], and Ralf Ebinghaus[1]

[1] GKSS Research Centre, Institute for Coastal Research, Max Planck Str. 1, 21502 Geesthacht, Germany

[2] Leuphana University Lüneburg, Institute for Ecology and Environmental Chemistry, Scharnhorststr. 1, 21335 Lüneburg, Germany

Abstract

Air samples taken onboard several research vessels in the Atlantic Ocean, the Southern Ocean, and the Baltic Sea as well as at one land-based site close to Hamburg, Germany in 2007 and 2008 were analysed for per- and polyfluorinated organic compounds (PFC). A set of neutral, volatile PFC such as fluorotelomer alcohols (FTOH) or perfluoroalkyl sulfonamides and ionic non-volatile PFC like perfluorinated carboxylates (PFCA) and sulfonates (PFSA) were collected on PUF/XAD-2/PUF cartridges and glass fiber filters and determined using GC-MS and HPLC-MS/MS. PFC were detected in all air samples, even in Antarctic regions and occurred predominantly in the gas phase. Total gas-phase concentrations of ship-based samples ranged from 4.5 pg m^{-3} in the Southern Ocean to 335 pg m^{-3} in European source regions. Concentrations of 8:2 FTOH, the analyte that was usually observed in highest concentrations, were between 1.8 and 130 pg m^{-3}. PFC concentrations decreased from continental towards marine regions and from Central Europe towards the Arctic and Antarctica. Southern hemispheric concentrations of individual PFC were significantly lower than those of the northern hemisphere. Based on this data set, marine background PFC concentrations and atmospheric residence times were calculated. This study gives further evidence that volatile PFC undergo atmospheric long-range transport to remote regions and may contribute to their contamination of persistent PFCA and PFSA.

1. Introduction

Since persistent, bioaccumulative, and toxicologically relevant polyfluorinated compounds (PFC) such as perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) (Conder et al., 2008; Lau et al., 2007) have been detected in humans (Calafat et al., 2007) as well as in polar fauna (Smithwick et al., 2006; Tao et al., 2006), there is an ongoing interest concerning their environmental fate and transport. One key question to resolve is, how and to which extent these perfluorinated carboxylates (PFCA) and sulfonates (PFSA), starting from their point of emission, reach remote locations where they are being accumulated.

PFCA and PFSA, especially those of chain lengths less than ten carbon atoms, have been detected globally in rivers and oceans and are considered to be transported significantly via that pathway (McLachlan et al., 2007; Wei et al., 2007; Yamashita et al., 2008). It is estimated that the majority of these compounds is emitted directly to the water phase during manufacturing and use (Paul et al., 2009; Prevedouros et al., 2006). Perfluorooctanoate that reaches the Arctic via oceanic transport is calculated to be between 2 and 23 t a^{-1} (Armitage et al., 2006; Prevedouros et al., 2006; Wania, 2007). Being dissolved in the water phase or enriched at the water surface these ionic PFC may also be transported into the air as marine aerosols (Prevedouros et al., 2006). However, atmospheric removal by wet and dry deposition is expected to occur in the order of a few days (Hurley et al., 2004). Atmospheric transport and degradation of PFCA and PFSA precursors is considered as another main transport mechanism but, its importance is discussed controversially. Basically, PFCA and PFSA precursors like fluorotelomer alcohols (FTOH) and acrylates (FTA) or perfluoroalkyl sulfonamides (FASA) and sulfonamido ethanols (FASE) are thought to be emitted to the atmosphere during their manufacturing or the production of fluoropolymers (Paul et al., 2009; Prevedouros et al., 2006) and more important by diffuse sources during use and disposal (Barber et al., 2007; Dinglasan-Panlilio and Mabury, 2006; Paul et al., 2009; Sinclair et al., 2007). Precursors are more volatile than PFCA and PFSA and therefore are more likely to undergo atmospheric long-range transport. Being in the atmosphere, these volatile compounds are degraded to PFCA and PFSA by OH radical initiated oxidation (D'Eon et al., 2006; Ellis et al., 2004; Ellis et al., 2003; Martin et al., 2006). Precursors were determined in a number of field studies in North America, Europe, Asia, and the Atlantic Ocean (Barber et al., 2007; Dreyer et al., 2009; Jahnke et al., 2007b; Oono et al., 2008; Shoeib et al., 2006; Stock et al., 2004) and modelling results reveal the ubiquitous atmospheric distribution of FTOH and its degradation products (Wallington et al., 2006). The actual extent to which the atmospheric transport and degradation of precursors contribute to the PFCA and PFSA contamination of remote regions is still unclear. Some studies estimated that this pathway is less important than oceanic transport, mainly due to the low PFCA and PFSA yield of the degradation reactions and too low historic precursor emissions (Prevedouros et al., 2006; Wania, 2007). Several recent studies estimated the Arctic deposition of perfluorooctanoate from FTOH oxidation to be between 50 and 500 kg a^{-1} (Schenker et al., 2008; Wallington et al., 2006; Wania, 2007; Yarwood et al., 2007) whereas an earlier estimate by Ellis et al. (2004) assumed an approximate flux of 0.1-10 t a^{-1} of PFCA to the Arctic. Nevertheless, the presence of PFCA and PFSA in glacial ice caps that received their contamination solely from the atmosphere (Young et al., 2007), their existence in air and lake water of remote mountains (Loewen et al., 2008), or the occurrence of precursor degradation intermediates in precipitation (Loewen et al., 2005; Scott et al., 2006), Arctic sediments and air particles (Stock et al., 2007) reveal that the atmospheric transport and degradation is an important contamination mechanism in remote locations.

The objective of this study was to determine concentrations of a variety of airborne PFC on a global scale with one method and short sampling intervals. Specifically, spatial gradients of PFC concentrations should be evaluated. The PFC contamination of Arctic and for the first time of Antarctic Air should be assessed and hemispheric (background) levels be defined. Therefore, air samples with one to three days resolution were taken onboard research vessels during several sampling campaigns along north-south transects in the Atlantic Ocean covering regions from Svalbard, Norway (78°N) to Antarctica (70°S) as well two east-west transects from the Canary Islands, Spain (28°N, 16°W) to Newfoundland, Canada (47°N, 53°W) and from Recife, Brazil (8°S, 35°W) to Dakar, Senegal (15°N, 17°W). Data obtained in this study are also valuable to validate and improve existing models.

2. Experimental

Chemicals

All chemicals, standard compounds, and gases were of high quality and purity. Details on chemicals concerning chemicals' abbreviations, supplier and purity can be found in the supplemental information.

Sampling

High volume air samples were taken at the observation deck of different research vessels (RV Polarstern, RV Maria S. Merian, RV L'Atalante, RV Atair) during several sampling campaigns along north-south and east-west transects as well as in coastal areas in the Baltic Sea, the Atlantic and Southern Ocean (Atair 155, German Bight, North Sea, 09/2007; MSM05/1, Las Palmas, Spain - St. John's, Canada, 04/2007; MSM05/6, Longyearbyen, Norway - Kiel, Germany, 08/2007; MSM08/3, Rostock, Germany - Tallinn, Estonia - Kiel, Germany, 06/2008; AntXXIV-1 and AntXXV-1, Bremerhaven, Germany - Cape Town, South Africa, 11/2007, 11/2008; AntXXV-2, Cape Town, South Africa - Neumayer Station, Antarctica - Cape Town, South Africa, 12/2008; L'Atalante leg 2 MARSÜD, Recife, Brazil - Dakar, Senegal, 01/2008; figure 4-1). Sampling height varied between 16 and 20 m. Samples were taken continuously for one to three days. Parallel one day samples were taken during the Atair 155 campaign since spatially highly resolved samples were needed in the area covered by the sampling and PFC concentrations were expected to be high (Dreyer and Ebinghaus, 2009). To reach a compromise between a high spatial resolution and a sensitive analysis of airborne PFC in northern hemispheric remote regions one and three day samples were taken in parallel during the campaigns MSM05/1, MSM05/6, MSM08/3, and AntXXIV-1. Two day samples were taken at the campaigns in the equatorial and southern Atlantic. Since PFC concentrations were expected to be close to the limit of detection, samples were taken in parallel during the cruise AntXXV-1. To minimize ship-borne contamination air samplers were controlled by a computer connected to the ship's meteorological system assuring that the sampling was interrupted when relative winds were arriving from the rear of the ship. For the determination of continental PFC air concentrations, a permanent land-based sampling site was established at Barsbüttel (BAR; 53°34'14'' N and 10°12'55'' E) in the vicinity of Hamburg (1 770 000 inhabitants)(Dreyer et al., 2009). In general, sampling durations varied between 1 and 4 days at that site. The average sampling rate for land- and ship-based samples was about 450 m^3 d^{-1}.

Airborne PFC were enriched on glass fiber filters and cartridges filled with a sandwich of polyurethane foam (PUF) and Amberlite XAD-2. Prior to the sampling, 50 µL of an internal standard solution containing mass-labeled PFC were added to the cartridge to account for analyte losses in the gas phase during sampling and sample preparation. Samples were sealed air tight and stored at -20 °C until analysis in the laboratory.

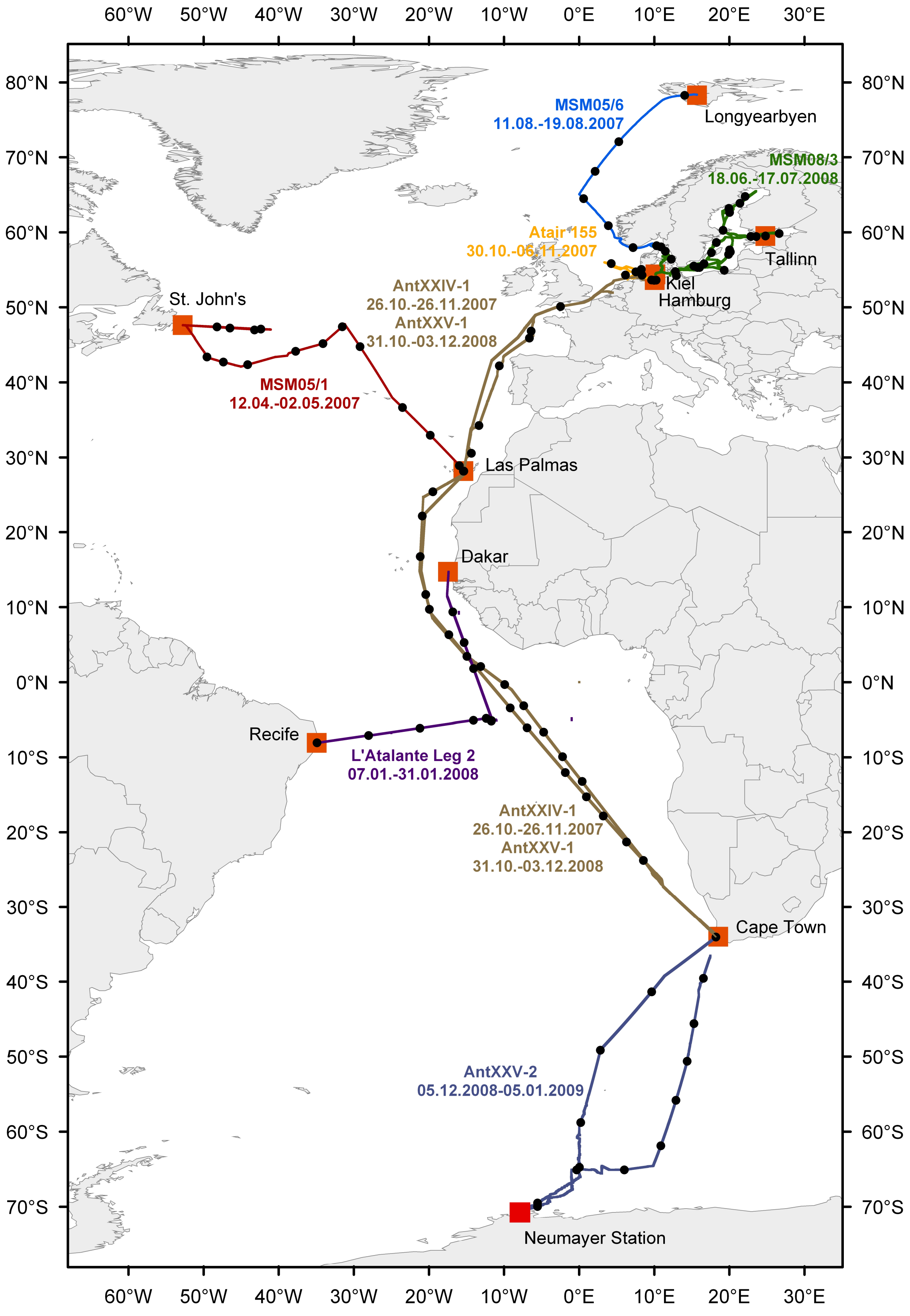


Figure 4-1: **Overview about the cruise tracks. Black dots mark the start point of each sample during the cruises. Samples were taken in between this and the following location.**

Sample Preparation & Instrumental Analysis

Detailed descriptions of sample preparations, and instrumental analyses are given elsewhere (Dreyer and Ebinghaus, 2009; Dreyer et al., 2008). Briefly, gas-phase samples were extracted three times using methyl-tert-butyl ether (MTBE):acetone 1:1. Particle-phase samples were extracted with MTBE:acetone 1:1 or methanol to determine neutral volatile PFC or ionic PFC, respectively. Mass-labeled internal and injection standards were applied. Detection of MTBE:acetone extracted PFC was performed by GC-MS using positive chemical ionization. Methanol-extracted PFC were determined by HPLC-MS/MS. Quantification was based on peak areas. Compounds were classified as not detected (n.d.) with signal to noise ratio (S/N) below 3 and not quantified (n.q.) with S/N below 10. Analyte concentrations were calculated with the internal standards method using a seven point calibration. Internal standards were used to correct for analyte losses. Average recovery rates of gas-phase analytes ranged from 21+/-27 % (^{13}C 4:2 FTOH, n=127) to 68+/-32 % (MeFOSE D_7, n=173) for ship-based samples and between 21+/-13 % (^{13}C 4:2 FTOH, n=45) and 60+/-27 % (EtFOSE D_9, n=118) for land-based samples. Average recovery rates for particle-bound analytes were between 41+/-15 % (^{13}C 4:2 FTOH, n=117) and 123+/-76 % (^{13}C PFUnDA, n=43) for ship-based samples and between 24+/-31 % (^{13}C 4:2 FTOH, n=47) and 106 +/-48 % (^{13}C PFDoDA, n=103) for BAR samples. Analytical performance of particle extraction strongly depended on the particle load and kind of particles and was worst with much pollen (land-based samples) or sea salt (ship-based samples) on filters. See SI for further information.

The uncertainty of the analysis of gas-phase analytes including sampling based on paired measurements (ISO-20988, 2007) (n=30) was 0.2 (Me_2FOSA) and 2.7 pg m^{-3} (8:2 FTOH). The combined uncertainty ranged between 0.3 and 5.3 pg m^{-3}. The uncertainty of the measurement relative to average ship-based concentrations ranged between 13 % (8:2 FTOH) and 163 % (PFOSA). Given the high uncertainty, results for analytes such as PFOSA are rather qualitative than quantitative. The measurement uncertainties for analytes determined in the particle phase were not calculated due to the lack of a sufficient number of paired measurements. However, because of low concentrations and low particle loads it was expected to be larger. Additional details are presented in the supporting information.

Blanks

Solvent blanks (for gaseous samples) and filter blanks (for particle samples) were taken with each set of samples that was extracted. Most of the compounds were detected in solvent and filter blanks at very low concentrations (on average 0.2 pg m^{-3} and 0.7 pg m^{-3}, respectively). Therefore, all concentrations reported were blank-corrected. Except for FTOH in the particle phase, field blanks were usually in the range of solvent and filter blanks revealing that contamination was most likely not due to sampling or sample handling.

Trajectory Analysis

Seven days air mass backward trajectories were calculated with the model Hysplit 4.8 using NCEP's Global Data Assimilation System data with 1 degree latitude/longitude resolution provided by NOAA-Air Resources Laboratory (Draxler and Rolph, 2003). Trajectories were calculated for intervals of three and six hours with the sampling height as arrival height.

Statistical Analysis

Because particle-phase concentrations were often close to the detection limit only gas-phase data were statistically evaluated. Concentrations of poly- and perfluorinated compounds were tested for normal distribution. The differences between hemispheric average concentrations were evaluated using the t-test. Normal-distributed analytes concentrations in the gas phase were tested for correlation using Pearson Correlation.

Atmospheric Residence Times

An important parameter that influences the transport of a substance in the atmosphere is the substance's atmospheric life or residence time. Using the spatial and temporal variability of mixing ratios of atmospheric trace gases, Junge (1974) developed the empirical relation $\tau \times \sigma = 0.14$ years to estimate the atmospheric residence time of a compound (τ) with σ being the relative standard deviation of the mixing ratio. It was already applied to obtain atmospheric residence times of several compounds such as methyl bromide (Colman et al., 1998), mercury (Slemr et al., 1981), PCB (Anderson and Hites, 1996; Manchester-Neesvig and Andren, 1989; Panshin and Hites, 1994), or recently FTOH (Piekarz et al., 2007). The Junge relation assumes one uniformly distributed sink. The compounds of interest are supposed to be measured at several locations for at least 1 year and the error of measurement should be smaller than the mixing ratio variance in space and time. FTOH, FTA, FASA, and FASE are primarily removed by OH radicals. Partitioning to the ocean or the particle phase is negligible for FTOH and FTA, however, it might play a minor role for FASA and FASE. In this study, the data base consists of one data set covering a large area with single (ship-based) measurements and another that comprises a 14 months time series at one (land-based) location. We calculated the atmospheric residence time for both data sets separately, i.e. using a temporal and a spatial approach. Since Colman et al. (1998) suggested to use only samples remote from sources to decouple the empirical variability from individual source strengths, we excluded ship-based samples that were taken close to or directly influenced by air masses arriving from potential source regions. For both data sets, the measurement uncertainty was lower than the standard deviations of the data sets used.

An alternative method estimating of the residence time of gases that partition to the particle phase was suggested by Manchester-Neesvig and Andren (1989). Given a residence time of particles in the northern hemisphere of 6 days (Manchester-Neesvig and Andren, 1989), the residence time of the gas would be $6/\phi$ with ϕ being the fraction of the gas in a given volume that is associated with particles. Residence times of MeFOSA, EtFOSA, MeFBSE, MeFOSE and EtFOSE were calculated with this method. For the remaining analytes, partition to the particle was not relevant or the data base was not sufficient enough.

3. Results & Discussion

PFC Concentrations

Neutral volatile and semi volatile PFC were detected almost exclusively in the gas phase. Only MeFBSA, MeFOSA, EtFOSA, MeFBSE, MeFOSE, and EtFOSE were observed on particles. On average, the particle-phase contribution of these compounds did not exceed 20 %. PFC gas-phase concentrations are presented in table S4-21. PFC, although to a different degree, were detected in all, even in Antarctic air samples in concentrations above laboratory and/or field blanks demonstrating the atmospheric long-range transport of these compounds as well as their global distribution. Total gas-phase concentrations of ship-based samples ranged from 4.5 pg m^{-3} in the Southern Ocean to 335 pg m^{-3} in source regions. Concentrations of 8:2 FTOH, the analyte that was usually observed in highest concentrations, were between 1.8 and 130 pg m^{-3}. Overall, gas-phase PFC concentrations of this study are in the same range as in studies covering similar locations (Barber et al., 2007; Jahnke et al., 2007b; Shoeib et al., 2006). Concentrations of individual particle-bound precursors were usually below 1 pg m^{-3}. Maximum particle-phase concentrations were reached for MeFOSE in the port of Hamburg (9 pg m^{-3}). MeFOSA and MeFOSE were the compounds that were most frequently observed. FASE were observed in higher concentrations than FASA.

Of ionic PFC, only PFBS, PFHxS, PFOS, PFBA, PFPA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTriDA were detected in the particle fraction (table 4-S22). Most frequently, PFOS, PFBA, PFHxA, PFOA, PFNA, and PFDA were quantified. The average concentrations of individual PFSA (< 0.3 pg m^{-3}) were lower than those of PFCA (<1 pg m^{-3}). Maximum concentrations were observed for PFOS (2 pg m^{-3}) and PFOA (6 pg m^{-3}) in samples taken in the German Bight. Concentrations of ionic PFC in the particle phase were quite similar to those observed by Jahnke et al. (2007b) during a campaign from Bremerhaven to Cape Town. The average PFOS concentration of ship-based samples was lower than that of land-based samples whereas the concentration averages of PFOA and other PFCA were higher in samples taken onboard the ships. Since PFCA are ubiquitously distributed in ocean waters (Wei et al., 2007; Yamashita et al., 2008) this may indicate that sea spray contains and transports PFCA. However, sorption of gaseous PFCA to the glass fiber filters was described by Arp and Goss (2008) and particle-phase concentrations may therefore be biased.

PFC Composition

The mean PFC gas-phase composition of the entire set of ship-based samples was quite similar to the annual average PFC composition at the land-based site in Germany (table 4-1). In all of the gas-phase samples, FTOH were the dominant class of compounds, followed by FASA, FASE, and FTA. With a contribution of more than 40 % on average, 8:2 FTOH was the main individual gas-phase PFC in all but four 1-day samples and the parallel 3-day sample (sample ID 2-6, 114). In these samples 6:2 FTOH was occurring in highest proportions. The gas-phase PFC compositions corroborate results of other studies in Europe and the Atlantic Ocean (Barber et al., 2007; Jahnke et al., 2007b; Shoeib et al., 2006). PFC compositions changed to some extend in specific source regions (see below). For example, samples close to the Canadian Coast (sample ID 95, 98) contained elevated proportions of ΣFASA and ΣFASE (18 % and 11 %, respectively). A sample taken in the shipyard of Las Palmas (ID 84) was characterized by strongly elevated EtFOSA proportions (20 %). In a sample taken close to Cape Town (ID 36) an increased proportion of MeFOSA (7 %) was observed. Neutral particle-phase analytes were on average dominated by the class of FASE with MeFOSE in highest proportions. This was more pronounced at the land-based site. PFCA occurred in higher proportions in ship-based than in land-based samples where similar proportions of PFSA and PFCA were observed.

Table 4-1: Gas- and particle-phase PFC composition (%) of ship-based and land-based air samples. Particle-phase neutral and ionic PFC were evaluated separately.

	gas-phase proportion (%)		particle-phase proportion (neutral and ionic analytes; %)				
compound	ship average	BAR average	ship average	BAR average	compound	ship average	BAR average
4:2 FTOH	0	0	0	0	**PFBS**	1	0
6:2 FTOH	13	14	0	0	**PFHxS**	2	0
8:2 FTOH	42	40	0	0	**PFHpS**	0	1
10:2 FTOH	14	11	0	0	**PFOS**	5	54
12:2 FTOH	6	5	0	0	**PFDS**	0	0
Σ FTOH	**76**	**84**	**0**	**0**	**Σ PFSA**	**8**	**56**
6:2 FTA	3	1	0	0	**PFBA**	29	14
8:2 FTA	2	2	0	0	**PFPA**	1	1
10:2 FTA	0	1	0	0	**PFHxA**	7	3
Σ FTA	**5**	**5**	**0**	**0**	**PFHpA**	6	1
MeFBSA	3	1	0	0	**PFOA**	14	13
MeFOSA	4	2	27	1	**PFNA**	7	3
Me$_2$FOSA	0	0	0	0	**PFDA**	22	3
EtFOSA	2	1	9	1	**PFUnDA**	2	2
PFOSA	1	0	0	6	**PFDoDA**	3	1
Σ FASA	**11**	**5**	**37**	**7**	**PFTriDA**	1	0
MeFBSE	2	2	8	4	**PFTeDA**	0	1
MeFOSE	6	1	37	58	**PFHxDA**	0	0
EtFOSE	1	1	18	30	**PFOcDA**	0	0
Σ FASE	**9**	**4**	**63**	**93**	**Σ PFCA**	**92**	**44**

Composition of FTOH was also expressed as concentration ratios of 6:2 FTOH to 8:2 FTOH to 10:2 FTOH relative to the FTOH of lowest concentration as suggested by Piekarz et al (2007). The average FTOH ratio of ship-based samples was the same as that of the 14 months average land-based samples (1.1 to 3.0 to1.0). Average FTOH ratios varied between the North Atlantic >60°N (9.7 to 4.8 to 1.0), temperate Atlantic (1.2 to 3.2 to 1.0), tropical Atlantic (1.0 to 3.2 to 1.7), and Southern Ocean (1.0 to 11.7 to 5.0). Based on these regional average ratios, there was an overall decrease of 6:2 FTOH contributions and an increase of 10:2 FTOH from the north towards the south; 8:2 FTOH contribution increased from its potential source region in temperate regions towards the north and the south. As observed by Piekarz et al. (2007) there was an overall enrichment of 8:2 FTOH relative to indoor air studies (Barber et al., 2007; Shoeib et al., 2008) assuming far more (diffuse) sources, as indicated by several studies

(Dinglasan-Panlilio and Mabury, 2006; Fiedler et al., submitted; Jensen et al., 2008; Paul et al., 2009; Sinclair et al., 2007).

Correlation Analyses

Correlation analyses revealed that almost all volatile PFC were significantly correlated, although to different degrees (table S4-23). Correlations were particularly high between 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 8:2 FTA, and 10:2 FTA. Fluorotelomer alcohols are used as precursors to produce FTA for fluorotelomer-based polymers (Prevedouros et al., 2006). Overall, results of the correlation analysis indicate that volatile PFC in the lower troposphere of the Atlantic Ocean have similar sources and are principally transported by the same process. Partitioning of FASA and FASE to the particles may have resulted in lower correlation coefficients to FTOH and FTA.

Spatial Distribution

In figure 4-2, the geographical distribution of PFC gas-phase concentrations is exemplarily presented for 8:2 FTOH. Spatial distribution as well as the order of magnitude appear to be well represented by modeling results of Wallington et al. (2006). The spatial trend observed for 8:2 FTOH is, independently of the actual contamination level, similar for all gas-phase analytes. Gas-phase PFC concentrations between continental (land-based site) and marine air masses differed up to two orders of magnitude. The 14 months average ΣPFC gas-phase concentration at the land-based site was about 140 pg m^{-3}. The maximum concentration at this site was above 900 pg m^{-3} (Dreyer et al., 2009). The 14 months average concentration of 8:2 FTOH was 60 pg m^{-3}. At maximum, almost 600 pg m^{-3} were reached. These concentrations are comparable to those observed at similar (Jahnke et al., 2007a) or other urban sites such as Manchester (Barber et al., 2007) or Toronto (Martin et al., 2002; Shoeib et al., 2006; Stock et al., 2004) and are being discussed in detail by Dreyer et al. (2009). PFC concentrations decreased from coastal areas towards the open sea. However, the actual concentrations strongly depended on the air mass history: whenever air masses recently arrived from populated and/or industrial areas, PFC concentrations in coastal areas increased up to one order of magnitude. This is exemplarily presented for selected samples in figure 4-3 and is discussed in detail for the German Bight region in Dreyer and Ebinghaus (2009).

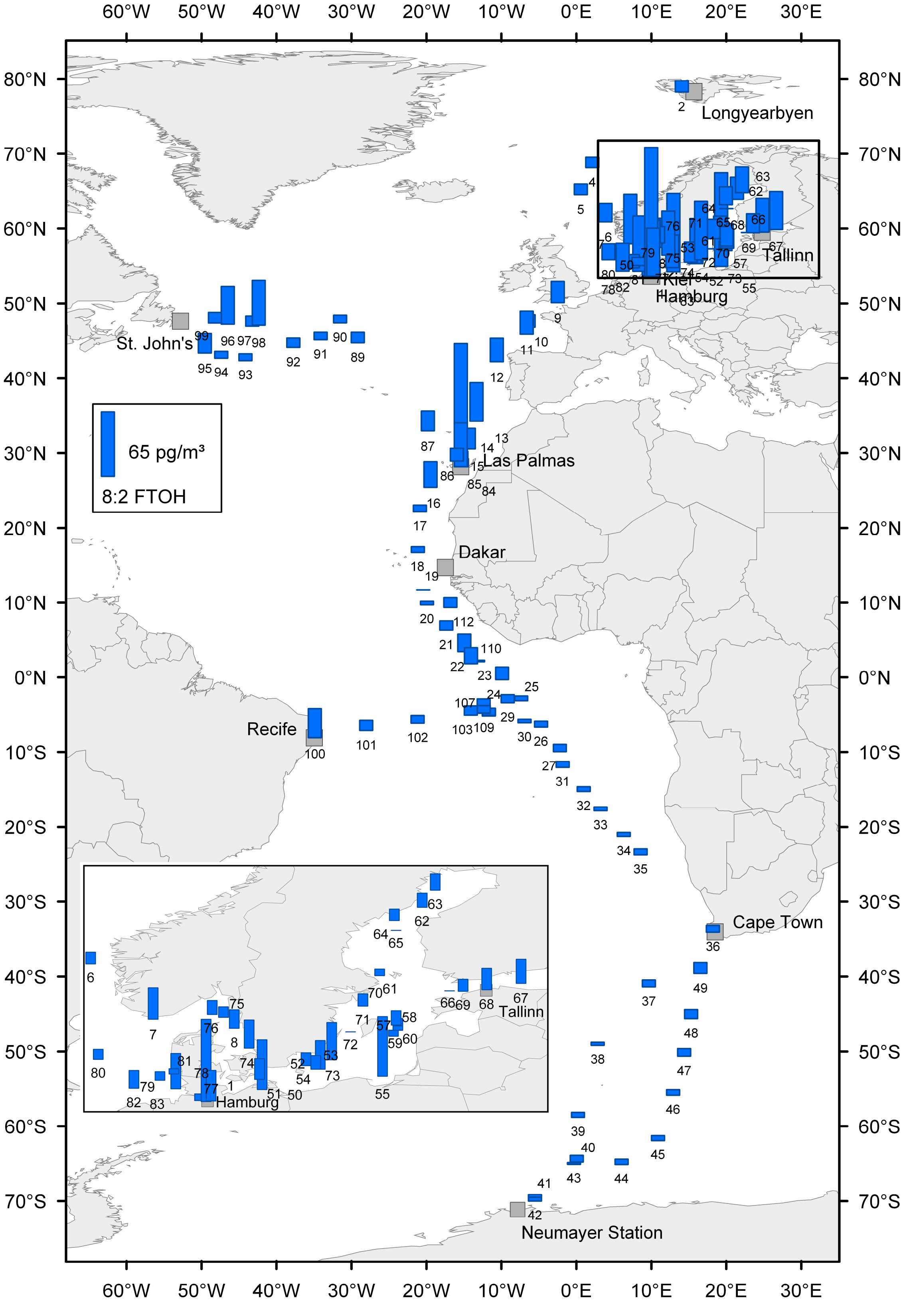
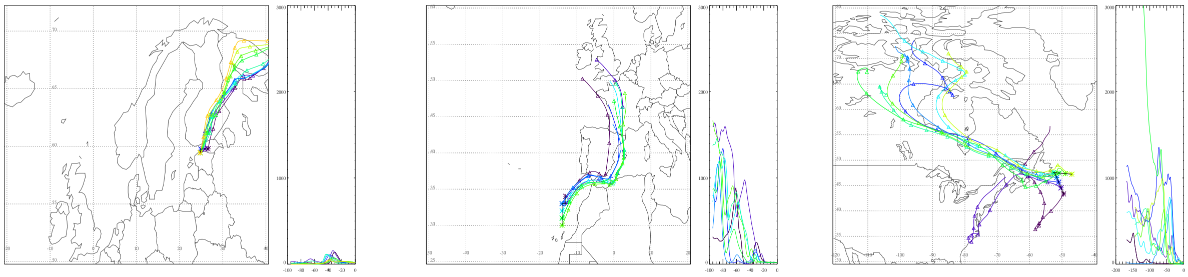
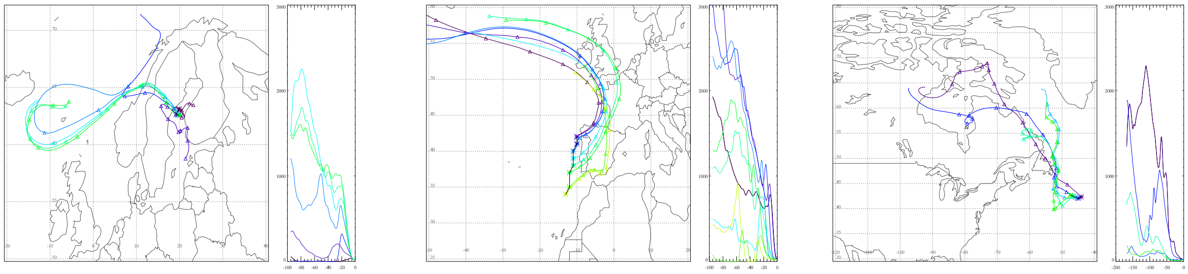


Figure 4-2: Spatial distribution of 8:2 FTOH gas-phase concentrations determined during several cruises in the Baltic Sea, the Atlantic and Southern Ocean. Note that the close-up of the Baltic Sea region is not to scale.



Sample ID 67: ΣPFC 80 pg m^{-3} Sample ID 13: ΣPFC 125 pg m^{-3} Sample ID 95: ΣPFC 62 pg m^{-3}



Sample ID 64: ΣPFC 34 pg m^{-3} Sample ID 12: ΣPFC 62 pg m^{-3} Sample ID 93: ΣPFC 15 pg m^{-3}

Figure 4-3: Total gas-phase PFC concentrations as a function of air mass history that is expressed as back trajectories of selected samples for three different regions (Baltic Sea, Northwest Africa, Northeast America). Upper graphs reveal the high-concentration conditions, lower graphs the low-concentration conditions of respective regions. Asterisks mark the ship's positions, respectively. Triangles show the position of the air parcel in twelve hours intervals for. Additionally, plots are provided presenting the trajectory heights.

Lowest PFC concentrations in the northern hemisphere were determined in marine air masses that were sampled in the middle of the North Atlantic Ocean. There, ΣFTOH concentrations were around 15 pg m^{-3}. ΣFASA+FASE concentrations were below 5 pg m^{-3}, and ΣFTA concentrations were below 1 pg m^{-3}. Shoeib et al. (2006) analyzed three FTOH, MeFOSE, and EtFOSE in the North Atlantic (at about 60 °N) and the Canadian Archipelago in 2005 and observed average concentrations of 16.3, 8.3, and 1.9 pg m^{-3}, respectively. The average concentrations of Atlantic samples only were 11, 6, and 1 pg m^{-3}. In contrast to our findings, Shoeib et al (2006) observed significant amounts of FTOH attached to particles. Compared to the marine air masses discussed above, arctic air sampled close to Svalbard, Norway, was characterized by around twice as high PFC concentrations. These elevated concentrations may reveal the more concentrated human activity in that region compared to the open ocean.

Concentrations of PFC sampled in air of the tropical Atlantic Ocean were generally comparable to those of the North Atlantic. Elevated concentrations of MeFBSE were probably due to contamination that may have occurred by painting works on a deck below the samplers. Lowest concentrations in the southern hemisphere were observed in the Southern

Ocean. There, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were detected in concentrations up to 4 pg m^{-3}. These concentrations were in the same order of magnitude as those of individual PCBs and organochlorine pesticides determined in similar latitudes by passive and active air sampling (Choi et al., 2008; Montone et al., 2005). Concentrations of FASA and FASE determined for that region were close to the field blanks and are therefore not further discussed.

Gas-phase PFC concentrations as function of latitude are presented exemplarily for 8:2 FTOH in figure 4-4 because concentration gradients were most obvious for analytes of highest concentration. Roughly, PFC concentrations decreased from the northern hemispheric mid latitudes (Central Europe) towards the north and the south. Strongly elevated 8:2 FTOH concentrations at about 30°N are from source region related samples at or close to the Canary Islands before being sampled. This is consistent with findings for persistent organic pollutants such as PCB, PBDE or organochlorine pesticides (Jaward et al., 2004a; Jaward et al., 2004b; Luek et al., 2008) and for some FTOH and FASA during a cruise from Bremerhaven to Cape Town (Jahnke et al., 2007b). Except for samples taken in subtropical regions of the northern hemisphere, actual concentration values of volatile PFC sampled in 2007/8 (this study) and 2005 (Jahnke et al., 2007b) were quite similar. In northern hemispheric subtropical regions, this study's samples were characterized by higher precursor concentration than those of 2005, which is most likely a result of air mass origin.

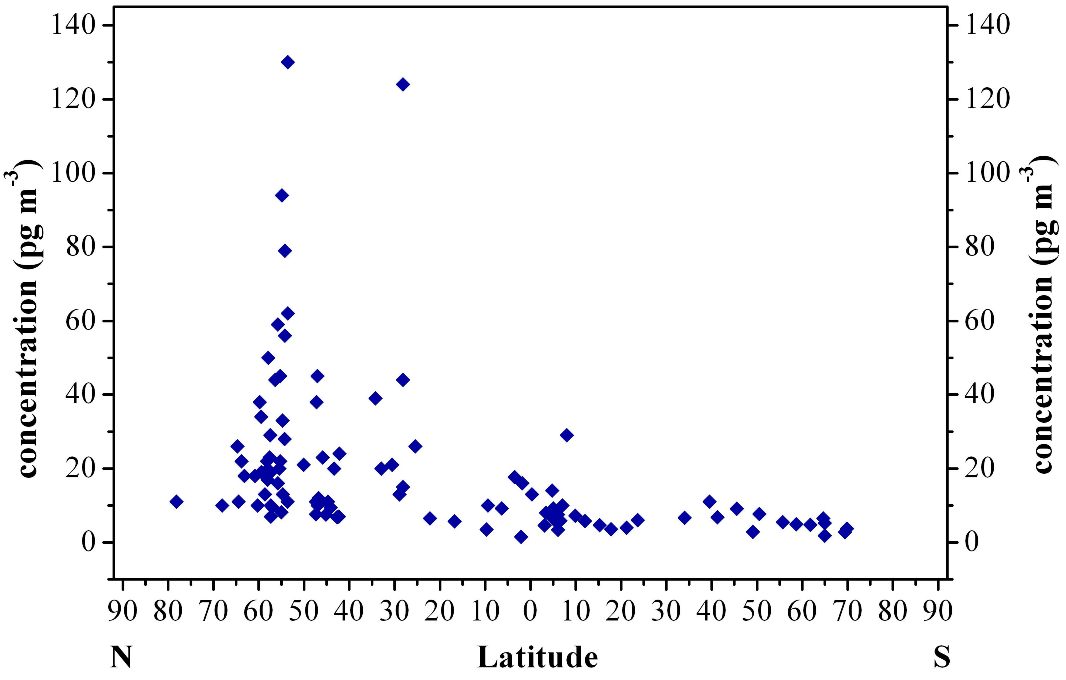


Figure 4-4: 8:2 FTOH gas-phase concentrations (pg m^{-3}) as function of latitude. The very high concentration observed at about 30°N is most properly due to the urban influence of the Canary Islands.

On average, southern hemispheric overall and marine background concentrations of precursors in the gas and particle-phase were lower than those of the northern hemisphere (table 4-2). Hemispheric concentrations were significantly different for most of the gas phase FTOH and selected FASA and FASE.

Table 4- 2: Average gas and particle-phase concentrations (c_g; c_p) of volatile PFC in the northern (NH) and southern (SH) hemisphere and average marine background concentrations in the northern (BG-NH) and southern (BG-SH) hemisphere (pg m^{-3}). [a] Average concentrations are significantly different at the $p<0.05$ level. [b] concentrations are significantly different at the $p<0.1$ level. Note, that the assignment of samples to the north or south hemisphere was dependent on the position of the Intertropical Convergence Zone (ITCZ). For calculation of the marine background concentrations only those samples were chosen that were not influenced by land-derived air masses. Background average concentrations for the particle phase were not calculated.

	c_g (NH) (all samples) pg m^{-3}, n=66	c_g (SH) (all samples) pg m^{-3}, n=39	c_g (BG – NH) (BG samples) pg m^{-3}, n=16	c_g (BG – SH) (BG samples) pg m^{-3}, n=28	c_p (NH) (all samples) pg m^{-3}, n=63	c_p (SH) (all samples) pg m^{-3}, n=34
4:2FTOH	0.1	0.0	0.1	0.0	0.0	0.0
6:2FTOH	9.0	1.7	5.2[a]	1.2[a]	0.2	0.0
8:2FTOH	27[a]	7.8[a]	9.1[a]	6.0[a]	0.5	0.1
10:2FTOH	8.1[a]	3.6[a]	2.7	2.7	0.1	0.1
12:2FTOH	4.1[a]	1.5[a]	2.0[a]	1.0[a]	0.5	0.0
Σ FTOH	**47[a]**	**16[a]**	**19[a]**	**11[a]**	**1.3**	**0.3**
6:2FTA	1.6	1.3	0.9	1.0	0.0	0.0
8:2 FTA	1.5[a]	0.4[a]	0.4	0.2	0.0	0.0
10:2FTA	0.6[a]	0.1[a]	0.1	0.0	0.0	0.0
Σ FTA	**3.6[a]**	**1.8[a]**	**1.4[a]**	**1.2[a]**	**0.0**	**0.0**
MeFBSA	2.0[a]	0.3[a]	1.0[a]	0.2[a]	0.0	0.0
MeFOSA	2.3[a]	0.8[a]	1.0[b]	0.6[b]	0.5	0.0
Me$_2$FOSA	0.3	0.0	0.1	0.0	0.0	0.0
EtFOSA	2.2[b]	0.4[b]	0.4	0.3	0.3	0.0
PFOSA	0.8	0.0	0.2[a]	0.0[a]	0.0	0.0
Σ FASA	**7.6[a]**	**1.5[a]**	**2.8[a]**	**1.1[a]**	**0.7**	**0.0**
MeFBSE	1.2[a]	0.3[a]	0.6	0.3	0.1	0.1
MeFOSE	2.0	2.2	1.4	1.6	0.5	0.2
EtFOSE	0.7	0.6	0.4	0.5	0.5	0.3
□Σ FASE	**3.8**	**3.0**	**2.2**	**2.2**	**1.1**	**0.6**
Total	**62[a]**	**21[a]**	**26[a]**	**16[a]**	**4.3**	**0.8**

Atmospheric Residence Times

Atmospheric residence times calculated by the Junge method (1974) and the partitioning ratio (Manchester-Neesvig and Andren, 1989) are presented in table 4-3.

Table 4-3: Atmospheric residence times (τ) in days based on the Junge relation and the partitioning ratio of a gaseous substance to particles. n.c.: not calculated, due to lack of data.

	τ (Junge relation; d)		τ (partition ratio; d)	
	ship samples	**BAR samples**	**ship samples**	**BAR samples**
4:2 FTOH	n.c.	n.c.	n.c.	n.c.
6:2 FTOH	39	52	n.c.	n.c.
8:2 FTOH	56	48	n.c.	n.c.
10:2 FTOH	66	46	n.c.	n.c.
12:2 FTOH	48	26	n.c.	n.c.
6:2 FTA	33	30	n.c.	n.c.
8:2 FTA	33	33	n.c.	n.c.
10:2 FTA	23	30	n.c.	n.c.
MeFBSA	39	40	n.c.	n.c.
MeFOSA	46	53	36	n.c.
Me$_2$FOSA	n.c.	n.c.	n.c.	n.c.
EtFOSA	27	55	57	n.c.
PFOSA	n.c.	n.c.	n.c.	n.c.
MeFBSE	42	50	66	n.c.
MeFOSE	46	49	30	35
EtFOSE	38	53	15	n.c.

Residence times varied between the different approaches up to a factor of 2, in case of EtFOSE by a factor of 3.5. Residence times calculated for FTOH were between those estimated by Piekarz (2007) using the Junge method (50 d, 80 d, and 70d, for 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively) and atmospheric lifetimes of 20 days determined in smog chamber studies (Ellis et al., 2003). Except for MeFBSE, atmospheric residence times of FASA and FASE were in the same range as lifetimes determined in smog chamber studies (D'Eon et al., 2006; Martin et al., 2006). The study of D'eon et al. (2006) revealed a MeFBSE lifetime of 2 days, which is one order of magnitude below the atmospheric residence time estimated here. Similar differences of atmospheric residence times determined here and those observed in the lab were observed for FTA (Butt et al., 2009). However, limitations of the indirect methods to estimate the atmospheric residence times should be taken into account.

Samples that were collected at different locations do not reflect potential seasonal changes. In ship-based samples FASA and FASE were often observed in concentrations close to the detection limit. Furthermore, the analytical method of trace amounts of PFC might not be as precise as required to get accurate residence times. Considering these limitations, atmospheric residence times determined here are in good agreement to those observed in other studies. These results give further evidence that volatile polyfluorinated precursor compounds are subject to atmospheric long-range transport and therefore may contribute signficantly to the contamination of remote regions with persistent PFCA and PFSA.

Acknowledgements

The authors thank the PIs, captains, and crews of the sampling campaigns who made this data set available. We wish to thank Jon Barber, Petra Günnewig, and Gesine Witt for their valuable help in air sampling as well as Armando Caba and Jan Bödewadt for the technical support. We thank Volker Matthias and Torben Kirchgeorg for the valuable help concerning the trajectory analysis. The authors gratefully acknowledge the NOAA Air Resource Laboratory (ARL) for the provision of the Hysplit transport and dispersion model. We are grateful to the German Federal Environmental Foundation (Deutsche Bundesstiftung Umwelt, DBU) for financial support.

Supporting Information

Supporting information is available covering chemicals, additional methodological aspects, PFC concentrations of the gas and particle phase as well as details of results' analyses.

References

Anderson, P. N.; Hites, R. A. 1996. OH Radical Reactions: The Major Removal Pathway for Polychlorinated Biphenyls from the Atmosphere. *Environmental Science & Technology*, *30*, 1756-1763.

Armitage, J.; Cousins, I. T.; Buck, R. C.; Prevedouros, K.; Russell, M. H.; MacLeod, M.; Korzeniowski, S. H. 2006. Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. *Environmental Science & Technology*, *40*, 6969-6975.

Arp, H. P. H.; Goss, K. U. 2008. Irreversible sorption of trace concentrations of perfluorocarboxylic acids to fiber filters used for air sampling. *Atmospheric Environment*, *42*, 6869-6872.

Barber, J. L.; Berger, U.; Chaemfa, C.; Huber, S.; Jahnke, A.; Temme, C.; Jones, K. C. 2007. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *Journal of Environmental Monitoring*, *9*, 530-541.

Butt, C. M.; Young, C. J.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. 2009. Atmospheric Chemistry of 4:2 Fluorotelomer Acrylate [C4F9CH2CH2OC(O)CH=CH2]: Kinetics, Mechanisms, and Products of Chlorine-Atom- and OH-Radical-Initiated Oxidation. *Journal of Physical Chemistry A*, *113*, 3155-3161.

Calafat, A. M.; Kuklenyik, Z.; Reidy, J. A.; Caudill, S. P.; Tully, J. S.; Needham, L. L. 2007. Serum concentrations of 11 polyfluoroalkyl compounds in the US population: Data from the National Health and Nutrition Examination Survey (NHANES) 1999-2000. *Environmental Science & Technology*, *41*, 2237-2242.

Choi, S.-D.; Baek, S.-Y.; Chang, Y.-S.; Wania, F.; Ikonomou, M. G.; Yoon, Y.-J.; Park, B.-K.; Hong, S. 2008. Passive Air Sampling of Polychlorinated Biphenyls and Organochlorine Pesticides at the Korean Arctic and Antarctic Research Stations: Implications for Long-Range Transport and Local Pollution. *Environmental Science & Technology*, *42*, 7125-7131.

Colman, J. J.; Blake, D. R.; Rowland, F. S. 1998. Atmospheric residence time of CH3Br estimated from the Junge spatial variability relation. *Science (Washington, D. C.)*, *281*, 392-396.

Conder, J. M.; Hoke, R. A.; De Wolf, W.; Russell, M. H.; Buck, R. C. 2008. Are PFCAs bioaccumulative? A critical review and comparison with regulatory lipophilic compounds. *Environmental Science & Technology*, *42*, 995-1003.

D'Eon, J. C.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. 2006. Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, C4F9SO2N(CH3)CH2CH2OH: Kinetics and mechanism of reaction with OH. *Environmental Science & Technology*, *40*, 1862-1868.

Dinglasan-Panlilio, M. J. A.; Mabury, S. A. 2006. Significant residual fluorinated alcohols present in various fluorinated materials. *Environmental Science & Technology*, *40*, 1447-1453.

Draxler, R. R.; Rolph, G. D. 2003. HYSPLIT (HYbrid Single-Particle Langerian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). *NOAA Air Resources Laboratory, Silver Spring, MD.*

Dreyer, A.; Ebinghaus, R. 2009. Polyfluorinated Compounds in Ambient Air from ship- and land-based measurements in northern Germany. *Atmospheric Environment*, *43*, 1527-1535.

Dreyer, A.; Matthias, V.; Temme, C.; Ebinghaus, R. 2009. Annual Time-Series of Air Concentrations of polyfluorinated Compounds. *Environmental Science & Technology, 43,* 4029-4036.

Dreyer, A.; Temme, C.; Sturm, R.; Ebinghaus, R. 2008. Optimized method avoiding solvent-induced response enhancement in the analysis of volatile and semi-volatile polyfluorinated alkylated compounds using gas chromatography-mass spectrometry. *Journal of Chromatography A*, *1178*, 199-205.

Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. 2004. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environmental Science & Technology*, *38*, 3316-3321.

Ellis, D. A.; Martin, J. W.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. 2003. Atmospheric lifetime of fluorotelomer alcohols. *Environmental Science & Technology*, *37*, 3816-3820.

Fiedler, S.; Pfister, G.; Schramm, K.-W. submitted. Poly- and perfluorinated compounds in household consumer products. *Environmental Science & Technology*, *es-2008-03109g*.

Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. 2004. Atmospheric chemistry of perfluorinated carboxylic acids: Reaction with OH radicals and atmospheric lifetimes. *Journal of Physical Chemistry A*, *108*, 615-620.

ISO-20988. 2007. Air quality - Guidelines for estimating measurement uncertainty.

Jahnke, A.; Ahrens, L.; Ebinghaus, R.; Temme, C. 2007a. Urban versus remote air concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany. *Environmental Science & Technology*, *41*, 745-752.

Jahnke, A.; Berger, U.; Ebinghaus, R.; Temme, C. 2007b. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53 degrees N-33 degrees S). *Environmental Science & Technology*, *41*, 3055-3061.

Jaward, F. M.; Barber, J. L.; Booij, K.; Dachs, J.; Lohmann, R.; Jones, K. C. 2004a. Evidence for dynamic air-water coupling and cycling of persistent organic pollutants over the open Atlantic Ocean. *Environmental Science & Technology*, *38*, 2617-2625.

Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. 2004b. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environmental Science & Technology*, *38*, 34-41.

Jensen, A. A.; Poulsen, P. B.; Bossi, R. 2008. Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. *Survey of Chemical Substances in Consumer Products, Danish Ministry of the Environment*, *No. 99*.

Junge, C. E. 1974. Residence time and variability of tropospheric trace gases. *Tellus*, *26*, 477-488.

Lau, C.; Anitole, K.; Hodes, C.; Lai, D.; Pfahles-Hutchens, A.; Seed, J. 2007. Perfluoroalkyl acids: A review of monitoring and toxicological findings. *Toxicological Sciences*, *99*, 366-394.

Loewen, M.; Halldorson, T.; Wang, F. Y.; Tomy, G. 2005. Fluorotelomer carboxylic acids and PFOS in rainwater from an urban center in Canada. *Environmental Science & Technology*, *39*, 2944-2951.

Loewen, M.; Wania, F.; Wang, F. Y.; Tomy, G. 2008. Altitudinal transect of atmospheric and aqueous fluorinated organic compounds in western Canada. *Environmental Science & Technology*, *42*, 2374-2379.

Luek, J.; Dickhut, R. M.; Cochran, M.; Geisz, H. N. 2008. Persistent Organic Pollutants in Air over the Atlantic and Southern Oceans. *SETAC North America 29th Meeting, Tampa, USA, Poster*.

Manchester-Neesvig, J. B.; Andren, A. W. 1989. Seasonal variation in the atmospheric concentration of polychlorinated biphenyl congeners. *Environmental Science &Technology*, *23*, 1138-1148.

Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. 2006. Atmospheric chemistry of perfluoroalkanesulfonamides: Kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. *Environmental Science & Technology*, *40*, 864-872.

Martin, J. W.; Muir, D. C. G.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. 2002. Collection of airborne fluorinated organics and analysis by gas chromatography/chemical ionization mass spectrometry. *Analytical Chemistry*, *74*, 584-590.

McLachlan, M. S.; Holmstrom, K. E.; Reth, M.; Berger, U. 2007. Riverine discharge of perfluorinated carboxylates from the European continent. *Environmental Science & Technology*, *41*, 7260-7265.

Montone, R. C.; Taniguchi, S.; Boian, C.; Weber, R. R. 2005. PCBs and chlorinated pesticides (DDTs, HCHs, and HCB) in the atmosphere of the southwest Atlantic and Antarctic oceans. *Marine Pollution Bulletin*, *50*, 778-782.

Oono, S.; Harada, K. H.; Mahmoud, M. A. M.; Inoue, K.; Koizumi, A. 2008. Current levels of airborne polyfluorinated telomers in Japan. *Chemosphere*, *73*, 932-937.

Panshin, S. Y.; Hites, R. A. 1994. Atmospheric Concentrations of Polychlorinated Biphenyls in Bermuda. *Environmental Science & Technology*, *28*, 2001-2007.

Paul, A. G.; Jones, K. C.; Sweetman, A. J. 2009. A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate. *Environmental Science & Technology*, *43*, 386-392.

Piekarz, A. M.; Primbs, T.; Field, J. A.; Barofsky, D. F.; Simonich, S. 2007. Semivolatile fluorinated organic compounds in Asian and western U.S air masses. *Environmental Science & Technology*, *41*, 8248-8255.

Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. 2006. Sources, fate and transport of perfluorocarboxylates. *Environmental Science & Technology*, *40*, 32-44.

Schenker, U.; Scheringer, M.; Macleod, M.; Martin, J. W.; Cousins, I. T.; Hungerbuhlert, K. 2008. Contribution of volatile precursor substances to the flux of perfluorooctanoate to the arctic. *Environmental Science & Technology*, *42*, 3710-3716.
Scott, B. F.; Spencer, C.; Mabury, S. A.; Muir, D. C. G. 2006. Poly- and perfluorinated carboxylates in north American precipitation. *Environmental Science & Technology*, *40*, 7167-7174.

Shoeib, M.; Harner, T.; Lee, S. C.; Lane, D.; Zhu, J. P. 2008. Sorbent-impregnated polyurethane foam disk for passive air sampling of volatile fluorinated chemicals. *Analytical Chemistry*, *80*, 675-682.

Shoeib, M.; Harner, T.; Vlahos, P. 2006. Perfluorinated chemicals in the Arctic atmosphere. *Environmental Science & Technology*, *40*, 7577-7583.

Sinclair, E.; Kim, S. K.; Akinleye, H. B.; Kannan, K. 2007. Quantitation of gas-phase perfluoroalkyl surfactants and fluorotelomer alcohols released from nonstick cookware and microwave popcorn bags. *Environmental Science & Technology*, *41*, 1180-1185.

Slemr, F.; Seiler, W.; Schuster, G. 1981. Latitudinal distribution of mercury over the Atlantic Ocean. *Journal of Geophysical Research, Sect. C: Oceans and Atmospheres*, *86*, 1159-1166.

Smithwick, M.; Norstrom, R. J.; Mabury, S. A.; Solomon, K.; Evans, T. J.; Stirling, I.; Taylor, M. K.; Muir, D. C. G. 2006. Temporal trends of perfluoroalkyl contaminants in polar bears (Ursus maritimus) from two locations in the North American Arctic, 1972-2002. *Environmental Science & Technology*, *40*, 1139-1143.

Stock, N. L.; Furdui, V. I.; Muir, D. C. G.; Mabury, S. A. 2007. Perfluoroalkyl contaminants in the canadian arctic: Evidence of atmospheric transport and local contamination. *Environmental Science & Technology*, *41*, 3529-3536.

Stock, N. L.; Lau, F. K.; Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. 2004. Polyfluorinated telomer alcohols and sulfonamides in the north American troposphere. *Environmental Science & Technology*, *38*, 991-996.

Tao, L.; Kannan, K.; Kajiwara, N.; Costa, M. M.; Fillmann, G.; Takahashi, S.; Tanabe, S. 2006. Perfluorooctanesulfonate and related fluorochemicals in albatrosses, elephant seals, penguins, and Polar Skuas from the Southern Ocean. *Environmental Science & Technology*, *40*, 7642-7648.

Wallington, T. J.; Hurley, M. D.; Xia, J.; Wuebbles, D. J.; Sillman, S.; Ito, A.; Penner, J. E.; Ellis, D. A.; Martin, J.; Mabury, S. A.; Nielsen, O. J.; Andersen, M. P. S. 2006. Formation of C7F15COOH (PFOA) and other perfluorocarboxylic acids during the atmospheric oxidation of 8 : 2 fluorotelomer alcohol. *Environmental Science & Technology*, *40*, 924-930.

Wania, F. 2007. A global mass balance analysis of the source of perfluorocarboxylic acids in the Arctic ocean. *Environmental Science & Technology*, *41*, 4529-4535.

Wei, S.; Chen, L. Q.; Taniyasu, S.; So, M. K.; Murphy, M. B.; Yamashita, N.; Yeung, L. W. Y.; Lam, P. K. S. 2007. Distribution of perfluorinated compounds in surface seawaters between Asia and Antarctica. *Marine Pollution Bulletin*, *54*, 1813-1818.

Yamashita, N.; Taniyasu, S.; Petrick, G.; Wei, S.; Gamo, T.; Lam, P. K. S.; Kannan, K. 2008. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. *Chemosphere*, *70*, 1247-1255

Yarwood, G.; Kemball-Cook, S.; Keinath, M.; Waterland, R. L.; Korzeniowski, S. H.; Buck, R. C.; Russell, M. H.; Washburn, S. T. 2007. High-resolution atmospheric modeling of fluorotelomer alcohols and perfluorocarboxylic acids in the north American troposphere. *Environmental Science & Technology*, *41*, 5756-5762.

Young, C. J.; Furdui, V. I.; Franklin, J.; Koerner, R. M.; Muir, D. C. G.; Mabury, S. A. 2007. Perfluorinated acids in arctic snow: New evidence for atmospheric formation. *Environmental Science & Technology*, *41*, 3455-3461.

Supporting Information

The supporting information covers the following topics:

30 pages, 23 tables, 9 figures

Chemicals

Table S4-1: Solvents and gases used for the analysis of PFC in air samples.

substances	abbreviation	purity	producer
ethyl acetate	-	Picograde	Promochem, Wesel, Germany
acetone	-	Picograde	Promochem, Wesel, Germany
methyl-tert-butylether	MTBE	Picograde	Promochem, Wesel, Germany
methanol	MeOH	Residue Analysis	J.T. Baker, Griesheim, Germany
nitrogen	-	6.0	Air Liquide, Germany

Table S4-2: Mass-labeled standard compounds used for the analysis of PFC in air samples.

substances	abbreviation	purity (%)	producer
2-Perfluorohexyl-($^{13}C_2$)-ethanol	^{13}C 6:2 FTOH	> 98	Wellington Laboratories, Guelph, Canada
2-Perfluorooctyl-($^{13}C_2$)-ethanol	^{13}C 8:2 FTOH	> 98	Wellington Laboratories, Guelph, Canada
2-Perfluorodecyl-($^{13}C_2$)-ethanol	^{13}C 10:2 FTOH	> 98	Wellington Laboratories, Guelph, Canada
methyl-D_3-perfluorooctane sulfonamide	D_3 MeFOSA	> 98	Wellington Laboratories, Guelph, Canada
ethyl-D_5-perfluorooctane sulfonamide	D_5 EtFOSA	> 98	Wellington Laboratories, Guelph, Canada
methyl-D_7-perfluorooctane sulfonamido ethanol	D_7 MeFOSE	> 98	Wellington Laboratories, Guelph, Canada
ethyl-D_9-perfluorooctane sulfonamido ethanol	D_9 MeFOSE	> 98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-butanoic acid	^{13}C PFBA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-hexanoic acid	^{13}C PFHxA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-octanoic acid	^{13}C PFOA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-nonanoic acid	^{13}C PFNA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-decanoic acid	^{13}C PFDA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-undecanoic acid	^{13}C PFUnDA	>98	Wellington Laboratories, Guelph, Canada
perfluoro-(^{13}C4)-dodecanoic acid	^{13}C PFDoA	>98	Wellington Laboratories, Guelph, Canada
sodium perfluoro-(^{18}O2)-hexane sulfonate	$^{18}O_2$-PFHxS	>99	Wellington Laboratories, Guelph, Canada
sodium perfluoro-(^{13}C4)-octane sulfonate	^{13}C-PFOS	>98	Wellington Laboratories, Guelph, Canada
sodium perfluoro-(^{13}C4)-octane sulfinate	^{13}C-PFOSi	~90	Wellington Laboratories, Guelph, Canada
hexachlorobenzene ^{13}C6	^{13}C HCB	97	Dr. Ehrenstorfer, Augsburg, Germany
1,3,5-trichlorobenzene D_3	TCB D_3	98	Aldrich, Munich, Germany
2,4-dichlorophenol ^{13}C6	^{13}C DCP	>99	Dr. Ehrenstorfer, Augsburg, Germany
perfluorooctane sulfonamido-D_5-acetic acid	D_5 EtFOSAA	>98	Wellington Laboratories, Guelph, Canada

Table S4-3: Analyte standards used for the analysis of PFC in air samples.

substances	abbreviation	purity (%)	producer
perfluorobutyl ethanol	4:2 FTOH	97	Aldrich, Munich, Germany
perfluorohexyl ethanol	6:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
perfluorooctyl ethanol	8:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
perfluorodecyl ethanol	10:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
perfluorododecyl ethanol	12:2 FTOH	-	donated by Jones group, Lancaster University, UK
perfluorohexyl ethylacylate	6:2 FTA	97	Aldrich, Munich, Germany
perfluorooctyl ethylacylate	8:2 FTA	97	Fluorochem, Old Glossop, UK
perfluorodecyl ethylacylate	10:2 FTA	97	Fluorochem, Old Glossop, UK
n-methyl perfluorobutane sulfonamide	MeFBSA	-	donated by 3M, Germany
n-methyl perfluorooctane sulfonamide	MeFOSA	-	donated by 3M, Germany
n-ethyl perfluorooctane sulfonamide	EtFOSA	95	ABCR, Karlsruhe, Germany
perfluorooctane sulfonamide	PFOSA	-	donated by 3M, USA
dimethylperfluoroocatane sulfonamide	Me2FOSA	98	Wellington Laboratories, Guelph, Canada
n-methyl perfluorobutane sulfonamido ethanol	MeFBSE	-	donated by 3M, USA
n-methyl perfluorooctane sulfonamidoethanol	MeFOSE	-	donated by 3M, USA
n-ethyl perfluorooctane sulfonamido ethanol	EtFOSE	-	donated the Mabury group, Toronto University, Canada
potassium perfluorobutane sulfonate	PFBS-K	98	ABCR, Karlsruhe, Germany
potassium perfluorohexane sulfonate	PFHxS-K	98	Fluka, Buchs, Switzerland
potassium perfluorooctane sulfonate	PFOS-K	98	Fluka, Buchs, Switzerland
potassium perfluorodecane sulfonate	PFDS-K	>98	Wellington Laboratories, Guelph, Canada
perfluorobutanoic acid	PFBA	99	ABCR, Karlsruhe, Germany
perfluoropentanoic acid	PFPA	98	Alfa Aesar, Karlsruhe, Germany
perfluorohexanoic acid	PFHxA	98	ABCR, Karlsruhe, Germany
perfluoroheptanoic acid	PFHpA	98	Lancaster Synthesis, Frankfurt, Germany
perfluorooctanoic acid	PFOA	95	Lancaster Synthesis, Frankfurt, Germany
perfluorononanoic acid	PFNA	98	Alfa Aesar, Karlsruhe, Germany
perfluorodecanoic acid	PFDA	98	ABCR, Karlsruhe, Germany
perfluoroundecanoic acid	PFUnDA	96	ABCR, Karlsruhe, Germany
perfluorododecanoic acid	PFDoDA	96	Alfa Aesar, Karlsruhe, Germany
perfluorotridecanoic acid	PFTrDA	>98	Wellington Laboratories, Guelph, Canada
perfluorotetradecanoic acid	PFTeDA	96	Alfa Aesar, Karlsruhe, Germany
perfluorohexadecanoic acid	PFHxDA	95	Alfa Aesar, Karlsruhe, Germany
perfluorooctadecanoic acid	PFOcDA	97	Alfa Aesar, Karlsruhe, Germany
sodium perfluorohexane sulfinate	PFHxSi	98	Wellington Laboratories, Guelph, Canada
sodium perfluorooctane sulfinate	PFOSi	98	Wellington Laboratories, Guelph, Canada
sodium perfluorodecane sulfinate	PFDSi	98	Wellington Laboratories, Guelph, Canada

Detection & Quantification Limits

Table S4-4: Instrumental detection limits (LOD), instrumental quantification limits (LOQ), method quantification limits (MQL), and method detection limits (MDL) for neutral volatile and semi-volatile polyfluorinated compounds determined in the gas phase (g) and particle phase (p) based on signal to noise ratios.

	MQL(g) pg m^{-3}	**MDL(g) pg m^{-3}**	**MQL(p) pg m^{-3}**	**MDL(p) pg m^{-3}**	**LOQ pg µL^{-1}**	**LOD pg µL^{-1}**	**LOQ pg abs.**	**LOD pg abs.**
4:2 FTOH	<1.2	0.5	n.d.	n.d.	1.1	0.8	2.1	1.7
6:2 FTOH	<0.9	<0.9	n.q.	n.q.	1.1	0.9	2.2	1.8
8:2 FTOH	<1.8	<1.8	n.q.	n.q.	1.0	0.8	2.0	1.6
10:2 FTOH	<0.7	<0.7	n.q.	n.q.	1.0	0.8	2.0	1.6
12:2 FTOH	0.4	0.4	n.q.	n.q.	1.0	0.8	2.0	1.6
6:2 FTA	0.5	0.5	n.d.	n.d.	0.2	0.1	0.4	0.2
8:2 FTA	0.1	0.1	n.d.	n.d.	0.2	0.1	0.4	0.2
10:2 FTA	<0.1	<0.1	n.d.	n.d.	0.2	0.1	0.4	0.2
MeFBSA	<0.3	<0.3	n.d.	n.d.	0.2	0.1	0.4	0.2
MeFOSA	<0.4	<0.4	0.1	<0.1	0.2	0.1	0.4	0.2
Me2FOSA	0.5	<0.1	n.d.	n.d.	0.1	0.0	0.2	0.0
EtFOSA	0.1	<0.1	0.2	<0.2	0.2	0.1	0.4	0.2
PFOSA	0.5	<0.5	<23	<23	8.2	4.1	16.4	8.2
MeFBSE	0.1	<0.1	1.6	<1.5	0.2	0.1	0.4	0.2
MeFOSE	0.4	0.2	0.1	<0.1	0.2	0.1	0.4	0.2
EtFOSE	0.1	<0.1	0.3	<0.3	0.4	0.2	0.9	0.4

Table S4-5: Instrumental detection limits (LOD), instrumental quantification limits (LOQ), method quantification limits (MQL), and method detection limits (MDL) for ionic polyfluorinated compounds determined in the particle phase based on signal to noise ratios.

	MQL pg m^{-3}	MDL pg m^{-3}	LOQ pg µL^{-1}	LOD pg µL^{-1}	LOQ pg abs.	LOD pg abs.
PFBS	0.3	0.1	0.05	0.02	0.5	0.2
PFHxS	0.2	0.1	0.05	0.02	0.5	0.2
PFHpS	0.3	<0.3	0.05	0.02	0.5	0.2
PFOS	0.1	<0.05	0.1	0.05	1.0	0.5
PFDS	0.4	n.d.	0.05	0.02	0.5	0.2
PFHxSi	0.5	n.d.	0.1	0.05	1.0	0.5
PFOSi	n.q.	n.q.	0.05	0.02	0.5	0.2
PFDSi	0.5	n.d.	0.1	0.05	1.0	0.5
PFBA	0.1	<0.1	0.2	0.2	2.0	2.0
PFPA	0.4	<0.05	0.1	0.05	1.0	0.5
PFHxA	<0.05	<0.05	0.1	0.05	1.0	0.5
PFHpA	0.1	<0.1	0.1	0.05	1.0	0.5
PFOA	<<1.8	<<1.8	0.1	0.05	1.0	0.5
PFNA	<0.05	<0.05	0.1	0.05	1.0	0.5
PFDA	0.1	0.05	0.1	0.05	1.0	0.5
PFUnDA	<0.1	<0.1	0.2	0.1	2.0	1.0
PFDoDA	<0.2	<0.2	0.1	0.05	1.0	0.5
PFTriDA	0.2	<0.2	0.1	0.05	1.0	0.5
PFTeDA	0.2	<0.2	0.2	0.10	2.0	1.0
PFHxDA	n.d.	n.d.	0.2	0.10	2.0	1.0
PFOcDA	n.d.	n.d.	0.2	0.10	2.0	1.0

Recovery Rates

Table S4-6: Recovery rates (R, %) of mass-labeled PFC in the gas phase of ship-based samples. S.D.: Standard deviation (%).

	n	$R_{average}$ (%)	R_{min} (%)	R_{max} (%)	S.D. (%)
4:2 FTOH ^{13}C	127	21	1	172	27
6:2 FTOH ^{13}C	173	46	2	201	29
8:2 FTOH ^{13}C	173	50	2	242	26
10:2 FTOH ^{13}C	171	58	2	200	37
EtFOSA D_5	173	61	11	298	33
MeFOSA D_3	173	49	10	200	22
MeFOSE D_7	173	68	19	351	32
EtFOSE D_9	166	66	14	161	27

Table S4-7: Recovery rates (%) of mass-labeled PFC in the particle phase of ship-based samples. S.D.: Standard deviation.

	n	$R_{average}$ (%)	R_{min} (%)	R_{max} (%)	S.D. (%)
4:2 FTOH ^{13}C	117	41	8	102	15
6:2 FTOH ^{13}C	118	46	1	108	18
8:2 FTOH ^{13}C	116	49	9	259	25
10:2 FTOH ^{13}C	119	73	5	492	67
EtFOSA D_5	119	53	17	118	16
MeFOSA D_3	119	49	18	119	14
MeFOSE D_7	119	58	13	122	17
EtFOSE D_9	119	61	16	130	20
$^{18}O_2$-PFHxS	43	71	27	172	36
^{13}C-PFOS	43	92	29	258	51
^{13}C-PFOSi	43	82	26	241	49
^{13}C-PFBA	43	64	9	177	36
^{13}C-PFHxA	43	61	26	162	29
^{13}C-PFOA	43	67	19	197	43
^{13}C-PFNA	43	74	22	276	48
^{13}C-PFDA	43	108	37	313	68
^{13}C-PFUDA	43	123	20	421	76
^{13}C-PFDoA	43	106	8	344	59

Table S4-8: Recovery rates (%) of mass-labeled PFC in the gas phase of land-based samples. S.D.: Standard deviation.

	n	$R_{average}$ (%)	R_{min} (%)	R_{max} (%)	S.D. (%)
4:2 FTOH ^{13}C	45	21	1	58	13
6:2 FTOH ^{13}C	109	39	0	128	20
8:2 FTOH ^{13}C	118	49	1	133	23
10:2 FTOH ^{13}C	118	45	0	170	32
EtFOSA D_5	118	45	9	99	19
MeFOSA D_3	118	41	8	135	19
MeFOSE D_7	118	60	20	196	27
EtFOSE D_9	115	59	15	134	21

Table S4-9: Recovery rates (%) of mass-labeled PFC in the particle phase of land-based samples. S.D.: Standard deviation.

	n	$R_{average}$ (%)	R_{min} (%)	R_{max} (%)	S.D. (%)
4:2 FTOH ^{13}C	47	25	1	87	31
6:2 FTOH ^{13}C	48	29	1	70	26
8:2 FTOH ^{13}C	48	27	1	62	15
10:2 FTOH ^{13}C	47	31	2	94	20
EtFOSA D_5	46	58	2	124	68
MeFOSA D_3	45	52	2	92	71
MeFOSE D_7	47	84	5	161	111
EtFOSE D_9	46	69	7	117	91
$^{18}O_2$-PFHxS	112	64	2	155	38
^{13}C-PFOS	112	72	2	232	42
^{13}C-PFOSi	112	70	2	199	45
^{13}C-PFBA	105	102	4	302	83
^{13}C-PFHxA	112	50	1	150	33
^{13}C-PFOA	112	46	1	120	29
^{13}C-PFNA	111	58	2	140	31
^{13}C-PFDA	112	81	3	243	48
^{13}C-PFUDA	103	104	5	326	76
^{13}C-PFDoA	102	106	3	303	75

Blanks

Table S4-10: Solvent (gas-phase) and filter (particle-phase) blank concentrations of neutral PFC (pg m^{-3}) observed during the analysis of ship-based air samples using GC-MS. Field concentrations reported in this study were corrected by blank values.

	Solvent Blanks (n=33, pg m^{-3})		Filter Blanks (n=19, pg m^{-3})	
	average	max	average	max
6:2 FTA	0.2	3.2	0.2	1.1
4:2 FTOH	0.0	0.1	n.d.	n.d.
6:2 FTOH	0.2	1.9	0.3	1.2
8:2 FTA	n.d.	n.d.	0.0	0.1
8:2 FTOH	0.2	1.7	1.1	2.9
Me_2FOSA	n.d.	n.d.	0.0	0.0
10:2 FTA	n.d.	n.d.	n.d.	n.d.
10:2 FTOH	0.1	1.5	1.1	2.1
12:2 FTOH	0.0	0.4	1.1	2.2
EtFOSA	0.0	1.4	0.1	1.4
MeFBSA	n.d.	n.d.	n.d.	n.d.
MeFOSA	0.0	0.9	0.1	1.7
MeFOSE	0.2	2.5	0.9	3.0
MeFBSE	0.2	1.8	0.0	0.7
EtFOSE	0.1	2.5	0.5	2.0
PFOSA	n.d.	n.d.	n.d.	n.d.

Table S4-11: Filter (particle-phase) blank concentrations of ionic PFC (pg m^{-3}) observed during the analysis of ship-based air samples using LC-MS/MS. Field concentrations reported in this study were corrected by blank values.

	Filter Blanks (n=6, pg m^{-3})	
	average	max
PFBS	0.3	1.1
PFHxS	0.1	0.2
PFHpS	0.0	0.0
PFOS	0.5	0.9
PFDS	0.0	0.0
PFHxSi	0.0	0.0
PFOSi	0.0	0.2
PFDSi	0.0	0.0
PFBA	0.2	0.6
PFPA	0.2	0.6
PFHxA	0.1	0.2

	Filter Blanks (n=6, pg m^{-3})	
	average	max
PFHpA	0.2	0.8
PFOA	0.7	1.3
PFNA	0.0	0.2
PFDA	0.1	0.4
PFUnDA	0.2	0.4
PFDoDA	0.2	0.4
PFTriDA	0.1	0.2
PFTeDA	0.0	0.2
PFHxDA	0.1	0.4
PFOcDA	0.0	0.0

Table S4-12: Gas- and particle-phase field blank concentrations (FldB) of neutral PFC (pg m^{-3}) observed during the analysis of ship-based air samples using GC-MS.

	FldB gas phase (n=14, pg m^{-3})		FldB particle phase (n=6, pg m^{-3})	
	average	max	average	max
6:2 FTA	0.6	3.3	0.0	0.0
4:2 FTOH	0.0	0.6	n.d.	n.d.
6:2 FTOH	0.2	4.0	0.8	4.4
8:2 FTA	0.0	0.3	0.0	0.0
8:2 FTOH	0.2	3.5	0.3	1.6
Me_2FOSA	n.d.	n.d.	n.d.	n.d.
10:2 FTA	0.0	0.9	n.d.	n.d.
10:2 FTOH	0.1	2.2	0.2	0.9
12:2 FTOH	0.0	7.2	0.3	1.4
EtFOSA	0.0	0.1	0.2	1.3
MeFBSA	0.0	2.2	n.d.	n.d.
MeFOSA	0.0	2.9	0.6	3.5
MeFOSE	0.2	23.1	0.0	0.0
MeFBSE	0.2	0.7	n.d.	n.d.
EtFOSE	0.1	0.5	n.d.	n.d.
PFOSA	0.0	7.2	n.d.	n.d.

Table S4-13: Particle-phase field blanks (FldB) of ionic PFC (pg m^{-3}) observed during the analysis of ship-based air samples using LC-MS/MS.

	FldB particle phase (n=7, pg m^{-3})	
	average	max
PFBS	0.0	0.1
PFHxS	n.d.	n.d.
PFHpS	n.d.	n.d.
PFOS	0.0	0.1
PFDS	n.d.	n.d.
PFHxSi	n.d.	n.d.
PFOSi	0.0	0.2
PFDSi	n.d.	n.d.
PFBA	0.6	1.4
PFPA	0.3	1.6
PFHxA	0.2	1.2

	FldB particle phase (n=7, pg m^{-3})	
	average	max
PFHpA	0.3	0.8
PFOA	0.3	1.4
PFNA	0.2	0.6
PFDA	0.1	0.5
PFUnDA	0.1	0.6
PFDoDA	0.1	0.5
PFTriDA	0.0	0.1
PFTeDA	n.d.	n.d.
PFHxDA	n.d.	n.d.
PFOcDA	0.1	0.4

Table S4-14: Solvent (gas-phase) and filter (particle-phase) blank concentrations of neutral PFC (pg m^{-3}) observed during the analysis of land-based air samples using GC-MS. Field concentrations reported in this study were corrected by blank values.

	Solvent Blanks (n=51, pg m^{-3})		Filter Blanks (n=15, pg m^{-3})	
	average	max	average	max
6:2 FTA	0.3	0.8	n.d.	n.d.
4:2 FTOH	0.2	0.6	n.d.	n.d.
6:2 FTOH	0.2	1	0.2	0.5
8:2 FTA	0.2	0.5	n.d.	n.d.
8:2 FTOH	0.2	0.9	1.1	3.7
Me_2FOSA	n.d.	n.d.	n.d.	n.d.
10:2 FTA	0.2	0.5	n.d.	n.d.
10:2 FTOH	0.1	0.7	0.6	2.7
12:2 FTOH	0.1	0.8	0.6	2.5
EtFOSA	0.1	0.3	0.8	2.6
MeFBSA	n.d.	n.d.	n.d.	n.d.
MeFOSA	0.2	0.4	0.1	0.3
MeFOSE	0.1	0.7	0.3	1.1
MeFBSE	0.2	0.3	2.3	2.4
EtFOSE	0.1	0.8	0.3	1.2
PFOSA	n.d.	n.d.	n.d.	n.d.

Table S4-15: Filter (particle-phase) blank concentrations of ionic PFC (pg m^{-3}) observed during the analysis of land-based air samples using LC-MS/MS. Field concentrations reported in this study were corrected by blank values.

	Filter Blanks (n=28, pg m^{-3})	
	average	max
PFBS	0.3	1.5
PFHxS	0.3	0.8
PFHpS	0	0.1
PFOS	1.2	3.5
PFDS	0	0
PFHxSi	0	0.7
PFOSi	0.2	0.8
PFDSi	n.d.	n.d.
PFBA	0.6	3.3
PFPA	0.2	2.8
PFHxA	0.2	0.5

	Filter Blanks (n=28, pg m^{-3})	
	average	max
PFHpA	0.1	0.8
PFOA	1.1	2.8
PFNA	0.2	1.1
PFDA	0.2	0.8
PFUnDA	0.3	0.9
PFDoDA	0.2	0.8
PFTriDA	0.1	1
PFTeDA	0.1	0.7
PFHxDA	0.1	1.5
PFOcDA	0.1	2.3

Table S4-16: Gas- and particle-phase field blank concentrations (FldB) of neutral PFC (pg m^{-3}) observed during the analysis of land-based air samples using GC-MS.

	FldB gas phase (n=18, pg m^{-3})		FldB particle phase (n=9, pg m^{-3})	
	average	max	average	max
6:2 FTA	1	2.2	n.d.	n.d.
4:2 FTOH	1.4	2.1	n.d.	n.d.
6:2 FTOH	1.3	2.8	n.d.	n.d.
8:2 FTA	0.7	1.6	n.d.	n.d.
8:2 FTOH	0.8	1.8	n.d.	n.d.
Me_2FOSA	n.d.	n.d.	n.d.	n.d.
10:2 FTA	0.9	0.9	n.d.	n.d.
10:2 FTOH	1	3	0.4	0.5
12:2 FTOH	1	2.3	0.3	0.3
EtFOSA	0.2	0.4	n.d.	n.d.
MeFBSA	0.7	1.2	n.d.	n.d.
MeFOSA	0.6	1.1	0	0.1
MeFOSE	0.7	1.5	0.1	0.3
MeFBSE	0.9	0.9	n.d.	n.d.
EtFOSE	0.8	1.6	n.d.	n.d.
PFOSA	n.d.	n.d.	n.d.	n.d.

Table S4-17: Particle-phase field blank concentrations (FldB) of ionic PFC (pg m^{-3}) observed during the analysis of land-based air samples using LC-MS/MS.

	FldB particle phase (n=12, pg m^{-3})	
	average	max
PFBS	0.0	0.0
PFHxS	0.0	0.0
PFHpS	n.d.	n.d.
PFOS	n.q.	0.0
PFDS	n.d.	0.0
PFHxSi	n.d.	0.0
PFOSi	0.0	0.0
PFDSi	n.d.	n.d.
PFBA	0.1	0.1
PFPA	0.0	0.0
PFHxA	0.0	0.1

	FldB particle phase (n=12, pg m^{-3})	
	average	max
PFHpA	0.0	0.1
PFOA	0.0	0.0
PFNA	0.0	0.0
PFDA	0.0	0.0
PFUnDA	0.0	0.0
PFDoDA	0.0	0.0
PFTriDA	0.0	0.0
PFTeDA	n.d.	n.d.
PFHxDA	n.d.	n.d.
PFOcDA	n.d.	n.d.

Uncertainty of the Method

Table S4-18: Standard uncertainty and combined uncertainty (pg m^{-3}) of the entire method (sampling, sample preparation, detection) based on paired measurements (n=30). The uncertainty was calculated according to ISO 20988. Parallel samples as well as 1-day samples averaged for three days and 3-day samples were used.

	standard uncertainty (pg m^{-3})	combined uncertainty (pg m^{-3})
4:2 FTOH	0.1	0.1
6:2 FTOH	1.7	3.3
8:2 FTOH	2.7	5.3
10:2 FTOH	1.5	2.9
12:2 FTOH	1.3	2.5
6:2 FTA	1.0	2.0
8:2 FTA	0.6	1.2
10:2 FTA	0.8	1.5
MeFBSA	0.8	1.6
MeFOSA	1.0	1.9
Me$_2$FOSA	0.2	0.3
EtFOSA	0.8	1.6
PFOSA	0.7	1.4
MeFBSE	0.5	0.9
MeFOSE	1.3	2.5
EtFOSE	0.4	0.9

Table S4-19: Standard uncertainty and combined uncertainty (%) of the method relative to average ship and land based samples.

	standard uncertainty (%)		combined uncertainty (%)	
	ship-based samples	land-based samples	ship-based samples	land-based samples
4:2 FTOH	156	22	305	42
6:2 FTOH	26	8	50	15
8:2 FTOH	13	4	26	8
10:2 FTOH	23	7	45	14
12:2 FTOH	35	10	68	20
6:2 FTA	99	53	193	105
8:2 FTA	66	14	129	28
10:2 FTA	147	30	289	60
MeFBSA	44	28	87	54
MeFOSA	46	36	91	71
Me$_2$FOSA	86	21	168	41
EtFOSA	52	60	103	118
PFOSA	163	70	320	137
MeFBSE	49	17	97	33
MeFOSE	81	57	158	111
EtFOSE	90	45	176	88

Sample Information

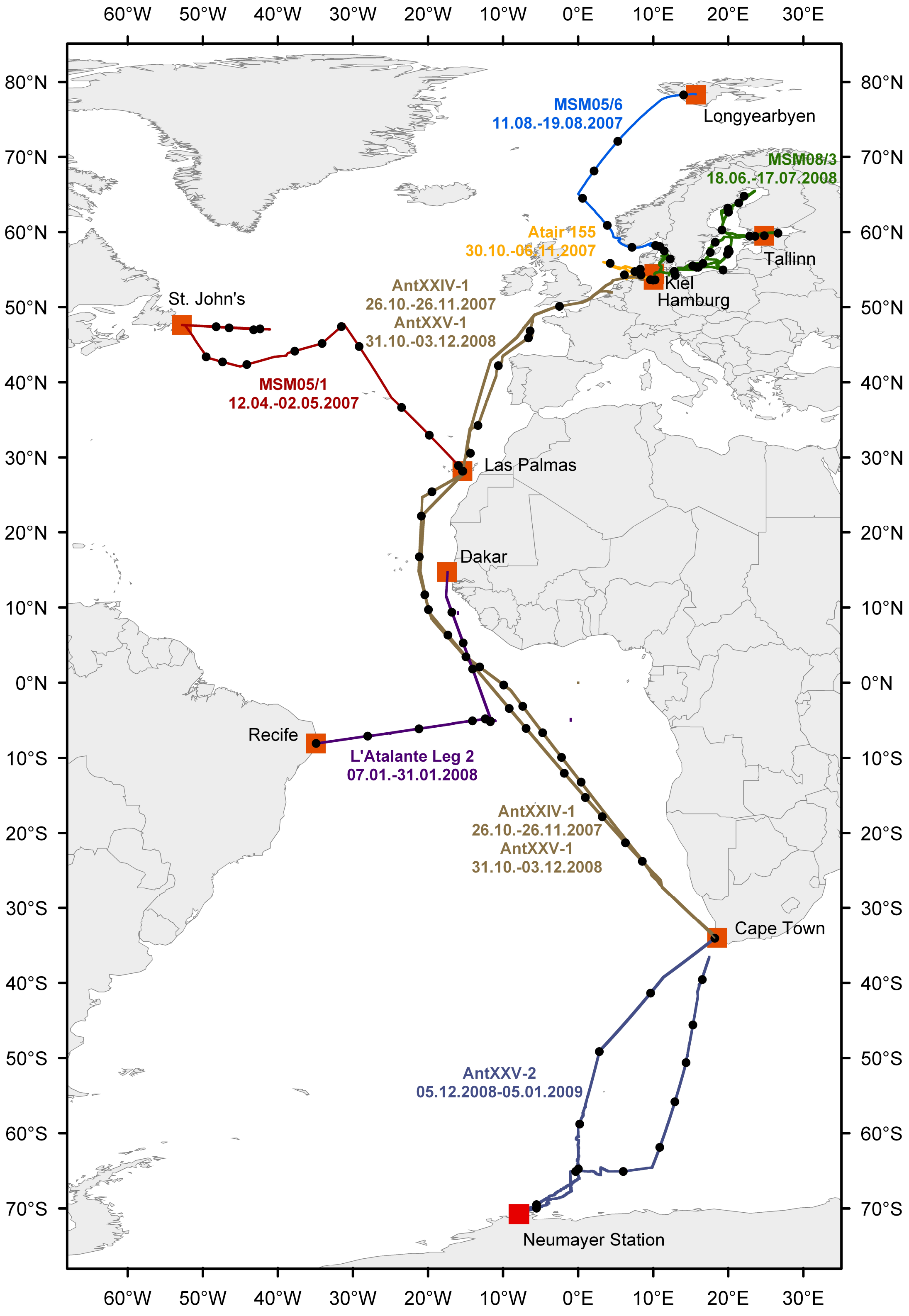


Figure S4-1: Overview about the cruise tracks. Black dots mark the start point of each sample during the cruises. Samples were taken in between this and the following location. Also see table S4-20.

Table S4-20: Sample information. LAT: latitude, LON: longitude, V: standardized air volume (m^3) (ISO-2533, 1975), T: temperature (°C). *: average volume/temperature.

ID	Sample name	DATE start	LAT start	LON start	DATE stop	LAT stop	LON stop	V (m^3)	T (°C)
1	**BAR**	02.04.2007	53.571	10.215	01.06.2008	53.571	10.215	1670*	10.0*
2	**MSM056-1**	11.08.2007	78.156	14.015	13.08.2007	71.991	5.251	432	5.8
3	**MSM056-3**	13.08.2007	71.991	5.251	14.08.2007	68.050	2.100	305	9.0
4	**MSM056-4**	14.08.2007	68.050	2.100	15.08.2007	64.423	0.565	374	11.7
5	**MSM056-6**	15.08.2007	64.423	0.565	16.08.2007	60.816	3.858	425	12.7
6	**MSM056-7**	16.08.2007	60.816	3.858	17.08.2007	57.890	7.156	369	13.1
7	**MSM056-9**	17.08.2007	57.890	7.156	18.08.2007	57.411	11.440	359	14.5
8	**MSM056-10**	18.08.2007	57.411	11.440	19.08.2007	54.317	10.136	450	16.6
9	**AntXXIV1-1**	28.10.2007	50.040	-2.503	29.10.2007	46.784	-6.388	337	14.1
10	**AntXXIV1-3**	29.10.2007	46.784	-6.388	30.10.2007	45.848	-6.638	649	14.8
11	**AntXXIV1-4**	30.10.2007	45.848	-6.638	31.10.2007	42.174	-10.629	421	15.3
12	**AntXXIV1-6**	31.10.2007	42.174	-10.629	02.11.2007	34.209	-13.335	362	17.6
13	**AntXXIV1-7**	02.11.2007	34.209	-13.335	03.11.2007	30.531	-14.353	426	20.1
14	**AntXXIV1-8**	03.11.2007	30.531	-14.353	04.11.2007	28.139	-15.348	325	20.9
15	**AntXXIV1-10**	04.11.2007	28.139	-15.348	05.11.2007	25.398	-19.459	438	21.1
16	**AntXXIV1-11**	05.11.2007	25.398	-19.459	06.11.2007	22.168	-20.870	408	22.1
17	**AntXXIV1-12**	06.11.2007	22.168	-20.870	07.11.2007	16.729	-21.146	212	24.2
18	**AntXXIV1-14**	07.11.2007	16.729	-21.146	08.11.2007	11.676	-20.417	548	27.7
19	**AntXXIV1-15**	08.11.2007	11.676	-20.417	09.11.2007	9.701	-19.929	429	28.2
20	**AntXXIV1-16**	09.11.2007	9.701	-19.929	10.11.2007	6.317	-17.346	396	27.8
21	**AntXXIV1-18**	10.11.2007	6.317	-17.346	11.11.2007	3.451	-14.954	408	27.0
22	**AntXXIV1-19**	11.11.2007	3.451	-14.954	12.11.2007	2.086	-13.114	403	26.4
23	**AntXXIV1-20**	12.11.2007	2.086	-13.114	13.11.2007	-0.311	-9.918	447	25.3
24	**AntXXIV1-22**	13.11.2007	-0.311	-9.918	14.11.2007	-3.143	-7.383	444	24.8
25	**AntXXIV1-23**	14.11.2007	-3.143	-7.383	15.11.2007	-6.642	-4.733	475	23.8
26	**AntXXIV1-24**	15.11.2007	-6.642	-4.733	16.11.2007	-9.906	-2.223	405	22.1
27	**AntXXIV1-26**	16.11.2007	-9.906	-2.223	17.11.2007	-13.197	0.393	415	20.5
28	**AntXXIV1-27**	17.11.2007	-13.197	0.393	18.11.2007	15.228	1.907	373	19.6
29	**AntXXV1-1**	22.11.2008	-3.416	-9.182	23.11.2008	-6.074	-6.937	454	24.5
30	**AntXXV1-2**	23.11.2008	-6.074	-6.937	25.11.2008	-12.021	-1.847	814	22.0
31	**AntXXV1-3**	25.11.2008	-12.021	-1.847	26.11.2008	-15.253	0.950	401	20.1
32	**AntXXV1-4**	26.11.2008	-15.253	0.950	27.11.2008	-17.799	3.190	509	19.3
33	**AntXXV1-5**	27.11.2008	-17.799	3.190	28.11.2008	-21.267	6.295	488	18.9
34	**AntXXV1-6**	28.11.2008	-21.267	6.295	29.11.2008	-23.713	8.525	419	18.5
35	**AntXXV1-7**	29.11.2008	-23.713	8.525	01.12.2008	-34.027	18.165	834	17.7
36	**AntXXV2-1**	06.12.2008	-34.027	18.165	08.12.2008	-41.302	9.635	894	17.6
37	**AntXXV2-2**	08.12.2008	-41.302	9.635	10.12.2008	-49.091	2.813	730	8.3
38	**AntXXV2-3**	10.12.2008	-49.091	2.813	12.12.2008	-58.708	0.193	846	-0.3
39	**AntXXV2-4**	12.12.2008	-58.708	0.193	14.12.2008	-64.673	0.022	891	-3.0
40	**AntXXV2-5**	14.12.2008	-64.673	0.022	16.12.2008	-69.406	-5.536	862	-3.2
41	**AntXXV2-6**	16.12.2008	-69.406	-5.536	20.12.2008	-69.894	-5.538	1776	-7.0
42	**AntXXV2-7**	20.12.2008	-69.894	-5.538	22.12.2008	-64.997	-0.344	1094	-3.6
43	**AntXXV2-8**	22.12.2008	-64.997	-0.344	24.12.2008	-65.000	6.000	946	-3.1
44	**AntXXV2-9**	24.12.2008	-65.000	6.000	26.12.2008	-61.812	10.846	946	-1.7
45	**AntXXV2-10**	26.12.2008	-61.812	10.846	28.12.2008	-55.747	12.864	722	0.2
46	**AntXXV2-11**	28.12.2008	-55.747	12.864	30.12.2008	-50.553	14.336	850	0.8
47	**AntXXV2-12**	30.12.2008	-50.553	14.336	01.01.2009	-45.540	15.262	858	3.6
48	**AntXXV2-13**	01.01.2009	-45.540	15.262	03.01.2009	-39.516	16.502	813	13.6
49	**AntXXV2-14**	03.01.2009	-39.516	16.502	04.01.2009	-37.188	17.215	378	18.2
50	**MSM083-A1**	17.06.2008	54.173	12.909	18.06.2008	54.711	12.775	448	17.9
51	**MSM083-A2**	18.06.2008	54.711	12.775	19.06.2008	55.251	15.983	410	16.8
52	**MSM083-A3**	19.06.2008	55.251	15.983	20.06.2008	55.253	15.743	387	15.6
53	**MSM083-A4**	20.06.2008	55.253	15.743	21.06.2008	55.439	15.229	326	15.0

Table S4-20 cont.

ID	Sample name	DATE start	LAT start	LON start	DATE stop	LAT stop	LON stop	V (m^3)	T (°C)
54	**MSM083-A5**	21.06.2008	55.439	15.229	22.06.2008	54.879	19.269	356	15.8
55	**MSM083-A6**	22.06.2008	54.879	19.269	23.06.2008	56.995	19.846	411	16.2
56	**MSM083-A7**	23.06.2008	56.995	19.846	24.06.2008	57.306	20.078	453	13.5
57	**MSM083-A8**	24.06.2008	57.306	20.078	25.06.2008	57.305	20.078	410	13.4
58	**MSM083-A9**	25.06.2008	57.305	20.078	26.06.2008	57.307	20.077	494	13.5
59	**MSM083-A10**	26.06.2008	57.307	20.077	27.06.2008	57.584	19.989	431	14.4
60	**MSM083-A11**	27.06.2008	57.584	19.989	28.06.2008	60.193	19.118	283	13.6
61	**MSM083-A12**	28.06.2008	60.193	19.118	29.06.2008	63.804	21.365	435	12.7
62	**MSM083-A13**	29.06.2008	63.804	21.365	30.06.2008	64.708	22.053	437	13.9
63	**MSM083-A14**	30.06.2008	64.708	22.053	01.07.2008	63.106	19.893	469	14.3
64	**MSM083-A15**	01.07.2008	63.106	19.893	02.07.2008	62.584	19.984	402	14.4
65	**MSM083-A16**	02.07.2008	62.584	19.984	03.07.2008	59.391	22.810	482	15.0
66	**MSM083-A17**	03.07.2008	59.391	22.810	04.07.2008	59.783	26.584	371	17.0
67	**MSM083-A18**	04.07.2008	59.783	26.584	06.07.2008	59.449	24.771	209	17.2
68	**MSM083-A19**	06.07.2008	59.449	24.771	07.07.2008	59.366	23.523	340	13.8
69	**MSM083-A20**	07.07.2008	59.366	23.523	08.07.2008	58.583	18.233	413	13.9
70	**MSM083-A21**	08.07.2008	58.583	18.233	09.07.2008	58.583	18.234	407	14.5
71	**MSM083-A22**	09.07.2008	58.583	18.234	10.07.2008	57.223	17.581	441	15.8
72	**MSM083-A23**	10.07.2008	57.223	17.581	11.07.2008	55.746	16.586	451	16.7
73	**MSM083-A24**	11.07.2008	55.746	16.586	12.07.2008	56.363	12.226	410	17.7
74	**MSM083-A25**	12.07.2008	56.363	12.226	13.07.2008	57.993	10.871	427	16.1
75	**MSM083-A26**	13.07.2008	57.993	10.871	14.07.2008	58.146	10.275	419	15.9
76	**MSM083-A27**	14.07.2008	58.146	10.275	15.07.2008	58.146	10.275	305	16.0
77	**Atair 1**	30.10.2007	53.594	9.606	31.10.2007	54.218	8.351	359	11.7
78	**Atair 2**	31.10.2007	54.218	8.351	01.11.2007	54.666	7.518	428	13.1
79	**Atair 3**	01.11.2007	54.666	7.518	02.11.2007	55.769	4.257	359	12.9
80	**Atair 4**	02.11.2007	55.769	4.257	03.11.2007	54.999	8.251	330	13.3
81	**Atair 5**	03.11.2007	54.999	8.251	04.11.2007	54.243	6.140	391	11.6
82	**Atair 6**	04.11.2007	54.243	6.140	05.11.2007	53.542	9.952	300	9.7
83	**Atair 7**	05.11.2007	53.542	9.952	06.11.2007	53.535	10.021	451	8.1
84	**MSM051-1**	12.04.2007	28.152	-15.411	13.04.2007	28.152	-15.411	451	18.1
85	**MSM051-3**	13.04.2007	28.152	-15.411	14.04.2007	28.894	-15.938	369	17.9
86	**MSM051-4**	14.04.2007	28.894	-15.938	15.04.2007	32.920	-19.809	356	18.0
87	**MSM051-6**	15.04.2007	32.920	-19.809	16.04.2007	36.609	-23.508	229	17.0
88	**MSM051-8**	16.04.2007	36.609	-23.508	18.04.2007	44.710	-29.147	42	15.4
89	**MSM051-9**	18.04.2007	44.710	-29.147	19.04.2007	47.368	-31.508	348	13.5
90	**MSM051-11**	19.04.2007	47.368	-31.508	20.04.2007	45.117	-34.083	364	14.4
91	**MSM051-12**	20.04.2007	45.117	-34.083	21.04.2007	44.092	-37.724	485	15.9
92	**MSM051-13**	21.04.2007	44.092	-37.724	23.04.2007	42.309	-44.103	449	11.3
93	**MSM051-15**	23.04.2007	42.309	-44.103	24.04.2007	42.655	-47.327	477	8.6
94	**MSM051-16**	24.04.2007	42.655	-47.327	25.04.2007	43.341	-49.513	476	9.8
95	**MSM051-18**	25.04.2007	43.341	-49.513	27.04.2007	47.192	-46.456	345	1.4
96	**MSM051-19**	27.04.2007	47.192	-46.456	28.04.2007	46.926	-43.190	461	1.8
97	**MSM051-21**	28.04.2007	46.926	-43.190	30.04.2007	47.047	-42.337	378	6.3
98	**MSM051-22**	30.04.2007	47.047	-42.337	01.05.2007	47.340	-48.167	391	6.3
99	**MSM051-24**	01.05.2007	47.340	-48.167	02.05.2007	47.549	-52.392	271	1.6
100	**Atalante 2**	07.01.2008	-8.057	-34.870	09.01.2008	-7.090	-28.014	260	28.2
101	**Atalante 3**	09.01.2008	-7.090	-28.014	11.01.2008	-6.121	-21.176	857	26.6
102	**Atalante 4**	11.01.2008	-6.121	-21.176	13.01.2008	-5.055	-14.081	874	26.2
103	**Atalante 5**	13.01.2008	-5.055	-14.081	15.01.2008	-4.810	-12.374	845	26.2
104	**Atalante 6**	15.01.2008	-4.810	-12.374	17.01.2008	-5.183	-11.692	919	26.0
105	**Atalante 7**	17.01.2008	-5.183	-11.692	19.01.2008	-5.097	-11.671	909	26.0
106	**Atalante 9**	19.01.2008	-5.097	-11.671	21.01.2008	-4.810	-12.373	806	25.9

Table S4-20 cont.

ID	**Sample name**	**DATE start**	**LAT start**	**LON start**	**DATE stop**	**LAT stop**	**LON stop**	**V (m^3)**	**T (°C)**
107	**Atalante 10**	21.01.2008	-4.810	-12.373	23.01.2008	-5.101	-11.685	435	26.2
108	**Atalante 11**	23.01.2008	-5.101	-11.685	25.01.2008	-4.800	-12.371	-	26.3
109	**Atalante 12**	25.01.2008	-4.800	-12.371	27.01.2008	1.820	-14.057	616	26.5
110	**Atalante 13**	27.01.2008	1.820	-14.057	28.01.2008	5.284	-15.312	400	28.8
111	**Atalante 15**	28.01.2008	5.284	-15.312	29.01.2008	9.350	-16.808	164	28.1
112	**Atalante 16**	29.01.2008	9.350	-16.808	30.01.2008	12.246	-17.534	308	25.9
113	**MSM056-2**	11.08.2007	78.156	14.015	14.08.2007	68.050	2.100	979	7.1
114	**MSM056-5**	14.08.2007	68.050	2.100	16.08.2007	60.816	3.858	753	12.2
115	**MSM056-8**	16.08.2007	60.816	3.858	18.08.2007	57.411	11.440	879	13.8
116	**MSM056-11**	18.08.2007	57.411	11.440	19.08.2007	54.317	10.136	426	16.6
117	**AntXXIV1-2**	28.10.2007	50.040	-2.503	30.10.2007	45.848	-6.638	806	14.6
118	**AntXXIV1-5**	30.10.2007	45.848	-6.638	03.11.2007	30.531	-14.353	1268	17.7
119	**AntXXIV1-9**	03.11.2007	30.531	-14.353	06.11.2007	22.168	-20.870	1217	21.3
120	**AntXXIV1-13**	06.11.2007	22.168	-20.870	09.11.2007	9.701	-19.929	1171	26.7
121	**AntXXIV1-17**	09.11.2007	9.701	-19.929	12.11.2007	2.086	-13.114	800	27.1
122	**AntXXIV1-21**	12.11.2007	2.086	-13.114	15.11.2007	-6.642	-4.733	1265	24.6
123	**AntXXIV1-25**	15.11.2007	-6.642	-4.733	18.11.2007	15.228	1.907	1167	22.2
124	**MSM083_GaB1**	17.06.2008	54.173	12.909	18.06.2008	54.711	12.775	398	17.9
125	**MSM083_GaB2**	18.06.2008	54.711	12.775	21.06.2008	55.439	15.229	1069	15.8
126	**MSM083_GaB3**	21.06.2008	55.439	15.229	24.06.2008	57.306	20.078	1000	15.0
127	**MSM083_GaB4**	24.06.2008	57.306	20.078	27.06.2008	57.584	19.989	727	13.8
128	**MSM083_GaB5**	27.06.2008	57.584	19.989	30.06.2008	64.708	22.053	936	13.4
129	**MSM083_GaB6**	30.06.2008	64.708	22.053	03.07.2008	59.391	22.810	931	14.4
130	**MSM083_GaB7**	03.07.2008	59.391	22.810	06.07.2008	59.449	24.771	785	16.5
131	**MSM083_GaB8**	06.07.2008	59.449	24.771	09.07.2008	58.583	18.234	1005	14.1
132	**MSM083_GaB9**	09.07.2008	58.583	18.234	12.07.2008	56.363	12.226	1323	16.8
133	**MSM083_GaB10**	12.07.2008	56.363	12.226	15.07.2008	58.146	10.275	1178	16.0
134	**MSM051-2**	12.04.2007	28.152	-15.411	14.04.2007	28.894	-15.938	882	18.0
135	**MSM051-5**	14.04.2007	28.894	-15.938	15.04.2007	32.946	-19.834	367	18.0
136	**MSM051-7**	15.04.2007	32.946	-19.834	18.04.2007	44.710	-29.147	288	16.3
137	**MSM051-10**	18.04.2007	44.710	-29.147	21.04.2007	44.092	-37.724	1131	14.6
138	**MSM051-14**	21.04.2007	44.092	-37.724	24.04.2007	42.655	-47.327	1475	10.5
139	**MSM051-17**	24.04.2007	42.655	-47.327	27.04.2007	47.192	-46.456	846	4.2
140	**MSM051-20**	27.04.2007	47.192	-46.456	30.04.2007	47.047	-42.337	643	5.0
141	**MSM051-23**	30.04.2007	47.047	-42.337	02.05.2007	47.549	-52.392	545	4.1

PFC Concentrations

Table S4- 21: Gas-phase concentrations of neutral polyfluorinated compounds of one and two day ship-based samples and the 14 months average of land-based samples. n.d.: not detected. n.q.: not quantified. n.a.: not analyzed due to the high water content of the samples. Values in brackets are instrumentally validated concentrations that appear to be erroneous: [a] singular contamination, probably during sampling or sample treatment. Value is usually not displayed by the three day parallel sample, [b] flow meter problems.

ID	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	Σ FTOH	6:2 FTA	8:2 FTA	10:2 FTA	Σ FTA	MeFBSA	MeFOSA	Me2FOSA	EtFOSA	PFOSA	Σ FASA	MeFBSE	MeFOSE	EtFOSE	ΣFASE	total
BAR 14 months average (02.04.2007 – 01.06.2008)																					
1	0.3	22	62	21	13	**119**	1.9	4.2	2.5	**8.6**	3.0	2.6	0.8	1.3	1.0	**9.2**	2.7	2.2	1.0	**5.9**	**143**
MSM05/6, Longyearbyen – Kiel (11.08.2007 – 19.08.2007)																					
2	n.d.	26	11	1.8	0.4	**40**	0.9	0.2	n.d.	**1.1**	0.3	0.4	n.d.	0.2	n.d.	**0.9**	n.q.	1.0	n.q.	**1.0**	**42**
3	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	**n.a.**
4	n.d.	15	10	2.2	0.8	**28**	1.0	0.3	0.1	**1.4**	0.3	0.6	n.d.	0.1	n.d.	**1.0**	0.1	0.6	0.5	**1.2**	**32**
5	n.d.	12	11	3.7	2.1	**28**	0.6	n.d.	n.d.	**0.6**	2.0	1.0	n.d.	0.2	n.d.	**3.3**	0.9	0.4	0.7	**1.9**	**34**
6	n.q.	51	18	3.0	1.6	**74**	8.9	5.2	0.1	**14**	6.0	7.7	n.d.	n.q.	n.q.	**14**	3.4	0.7	2.5	**6.7**	**108**
7	n.d.	13	50	11	6.2	**80**	n.d.	1.8	0.3	**2.1**	0.5	0.8	n.d.	n.q.	5.2	**6.5**	1.3	1.9	0.7	**3.9**	**92**
8	n.d.	16	29	7.2	4.4	**57**	2.4	2.1	0.2	**4.7**	4.8	4.3	n.d.	n.q.	2.4	**11**	n.q.	n.q.	n.q.	**0.0**	**73**
AntXXIV-1, Bremerhaven – Cape Town (26.10.2007-26.11.2007)																					
9	n.d.	7.5	21	4.5	8.7	**42**	4.9	2.0	n.d.	**6.9**	1.8	2.2	n.d.	1.3	n.d.	**5.3**	1.2	1.9	1.6	**4.7**	**59**
10	n.d.	8.2	12	1.9	1.4	**24**	n.q.	2.2	n.d.	**2.2**	1.6	1.6	0.1	0.5	n.d.	**3.8**	0.9	0.9	0.3	**2.1**	**32**
11	n.d.	11	23	4.6	11	**49**	6.7	n.d.	n.d.	**6.7**	2.6	2.5	n.d.	3.3	n.d.	**8.4**	n.d.	1.8	1.1	**2.8**	**67**
12	n.d.	9.6	24	5.6	8.4	**47**	2.7	1.3	n.d.	**4.0**	1.3	2.4	1.3	1.4	n.d.	**6.5**	1.1	1.4	1.5	**4.0**	**62**
13	n.d.	35	39	17	5.9	**97**	5.8	n.d.	n.d.	**5.8**	4.5	5.5	1.5	4.2	n.d.	**16**	2.1	2.5	2.0	**6.7**	**125**
14	n.d.	5.1	21	2.2	2.6	**31**	3.5	0.4	n.d.	**3.9**	0.6	1.1	0.4	0.7	n.d.	**2.8**	0.5	0.9	0.7	**2.1**	**39**
15	n.d.	9.3	15	3.1	8.2	**36**	3.9	0.9	n.d.	**4.8**	1.3	1.9	n.d.	1.8	n.d.	**5.0**	0.9	1.4	0.8	**3.2**	**49**
16	n.d.	9.5	26	4.1	8.2	**48**	7.4	3.5	n.d.	**11**	4.6	5.4	3.8	4.4	n.d.	**18**	1.6	1.2	2.1	**4.9**	**82**
17	n.d.	7.6	6.5	1.6	3.4	**19**	2.3	0.8	n.d.	**3.0**	0.8	0.9	0.9	0.5	n.d.	**3.1**	0.4	1.1	0.4	**1.9**	**27**
18	n.d.	1.6	5.7	1.3	3.2	**12**	3.0	n.d.	n.d.	**3.0**	n.d.	n.d.	n.d.	1.2	n.d.	**1.2**	0.7	1.0	0.8	**2.5**	**19**
19	n.d.	(13)[a]	(54)[a]	3.9	6.3	**10**	(16)[a]	2.5	1.2	**3.7**	1.7	2.1	n.d.	1.7	n.d.	**5.5**	2.4	2.7	1.9	**7.0**	**26**
20	n.d.	1.8	3.5	1.2	4.4	**11**	2.6	1.0	1.6	**5.2**	n.d.	0.7	n.d.	0.5	n.d.	**1.2**	0.3	0.8	0.3	**1.5**	**19**
21	n.d.	4.4	9.2	1.7	9.0	**24**	2.1	0.8	n.d.	**2.9**	n.d.	1.5	n.d.	0.7	n.d.	**2.2**	0.8	1.3	0.5	**2.6**	**32**
22	n.d.	6.5	17.7	7.1	5.2	**36**	4.0	n.d.	n.d.	**4.0**	1.3	1.1	n.d.	2.0	n.d.	**4.3**	1.9	3.6	0.4	**5.9**	**51**
23	n.d.	1.1	1.5	n.d.	(18)[a]	**2.6**	1.1	1.5	n.d.	**2.6**	n.d.	0.3	n.d.	0.5	n.d.	**0.8**	n.d.	1.1	0.2	**1.2**	**7.2**
24	n.d.	(40)[a]	13	3.0	(18)[a]	**34**	2.9	0.6	1.4	**5.0**	n.d.	1.4	n.d.	0.5	n.d.	**1.9**	n.d.	0.9	0.5	**1.4**	**42**
25	n.d.	2.4	4.6	0.8	1.5	**9.4**	7.3	1.9	n.d.	**9.1**	1.0	0.8	n.d.	1.5	n.d.	**3.3**	n.d.	2.8	0.3	**3.1**	**25**
26	n.d.	5.1	5.9	1.3	6.3	**19**	1.8	0.4	n.d.	**2.2**	n.d.	1.3	n.d.	0.5	n.d.	**1.8**	n.d.	1.1	0.4	**1.5**	**24**
27	n.d.	2.7	7.2	1.9	2.0	**14**	6.6	2.0	0.7	**9.3**	1.4	0.9	n.d.	1.8	n.d.	**4.1**	n.d.	3.7	0.8	**4.5**	**32**
28	n.d.	(19)[a]	(16)[a]	(90)[a]	(165)[a]	**34**	4.4	1.9	n.d.	**6.3**	n.d.	0.8	n.d.	1.9	n.d.	**2.7**	n.d.	3.7	0.4	**4.0**	**47**
AntXXV-1, Bremerhaven – Cape Town (31.10.2008 – 03.12.2008)																					
29	n.d.	1.2	8.0	2.2	n.d.	**11**	n.q.	n.d.	n.d.	**0.0**	n.d.	0.3	n.d.	n.d.	n.d.	**0.3**	0.9	1.3	0.2	**2.4**	**14**

Table S4-21: cont.

ID	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	Σ FTOH	6:2 FTA	8:2 FTA	10:2 FTA	Σ FTA	MeFBSA	MeFOSA	Me2FOSA	EtFOSA	PFOSA	Σ FASA	MeFBSE	MeFOSE	EtFOSE	ΣFASE	total
30	n.d.	0.6	3.4	0.7	n.d.	**4.7**	n.q.	n.d.	n.d.	**0.0**	n.d.	0.5	n.d.	n.d.	n.d.	**0.5**	0.2	0.6	0.2	**1.0**	**6.2**
31	n.d.	3.1	5.8	1.4	n.d.	**10**	n.q.	n.d.	n.d.	**0.0**	0.5	n.d.	n.d.	0.1	n.d.	**0.5**	0.9	0.6	0.3	**1.7**	**13**
32	n.d.	1.5	4.7	1.2	n.d.	**7.4**	n.q.	n.d.	n.d.	**0.0**	n.d.	0.2	n.d.	n.d.	n.d.	**0.2**	n.d.	1.1	n.d.	**1.1**	**8.7**
33	n.d.	n.d.	3.6	2.1	0.6	**6.3**	n.q.	n.d.	n.d.	**0.0**	1.6	1.5	n.d.	n.d.	n.d.	**3.1**	0.8	1.2	0.4	**2.4**	**12**
34	n.d.	1.0	4.0	2.1	n.d.	**7.1**	n.d.	n.d.	n.d.	**0.0**	n.d.	0.9	n.d.	n.d.	n.d.	**0.9**	n.d.	0.7	n.d.	**0.7**	**8.7**
35	n.d.	n.d.	6.0	1.6	n.d.	**7.6**	n.d.	n.d.	n.d.	**0.0**	n.d.	n.d.	n.d.	n.d.	n.d.	**0.0**	n.d.	0.3	0.2	**0.4**	**8.0**
AntXXV-2, Cape Town – Neumayer Station – Cape Town (05.12.2008 – 05.01.2009), average of parallel samples																					
36	n.d.	0.9	6.7	2.7	1.1	**11**	n.d.	n.d.	n.d.	**0.0**	0.3	1.0	0.0	n.d.	n.d.	**1.4**	0.4	0.9	0.3	**1.7**	**14**
37	n.d.	0.6	6.8	2.4	n.d.	**9.8**	0.9	n.d.	n.d.	**1.0**	0.4	0.3	n.d.	n.d.	n.d.	**0.7**	0.4	0.5	0.5	**1.1**	**13**
38	n.d.	0.7	2.9	1.1	n.d.	**4.8**	0.1	0.1	n.d.	**0.1**	0.4	0.1	n.d.	0.0	n.d.	**0.5**	0.5	0.6	n.d.	**1.1**	**6.4**
39	n.d.	n.d.	4.9	1.4	0.2	**7.0**	n.d.	n.d.	n.d.	**0.0**	n.d.	0.2	n.d.	n.d.	n.d.	**0.2**	0.7	0.9	0.3	**1.7**	**8.8**
40	n.d.	0.5	6.5	2.2	0.1	**9.3**	n.d.	n.d.	n.d.	**0.0**	n.d.	0.2	n.d.	0.1	n.d.	**0.2**	0.5	0.4	0.6	**1.0**	**11**
41	n.d.	n.d.	2.8	1.6	n.d.	**4.8**	n.d.	0.2	0.0	**0.1**	0.2	0.2	n.d.	n.d.	n.d.	**0.4**	0.1	0.3	0.6	**0.8**	**6.1**
42	n.d.	n.d.	3.7	1.7	n.d.	**5.6**	n.d.	n.d.	n.d.	**0.0**	n.d.	0.4	n.d.	n.d.	n.d.	**1.9**	0.3	4.5	0.2	**2.6**	**10**
43	n.d.	0.2	1.8	1.2	0.1	**3.2**	n.d.	n.d.	n.d.	**0.0**	0.3	0.6	n.d.	0.0	n.d.	**0.6**	0.3	0.4	0.2	**0.6**	**4.4**
44	n.d.	n.d.	5.2	1.8	n.d.	**7.0**	n.d.	n.d.	n.d.	**0.0**	n.d.	n.d.	n.d.	n.d.	n.d.	**0.0**	0.4	0.5	n.d.	**0.9**	**7.9**
45	n.d.	n.d.	4.8	2.5	0.6	**7.9**	n.d.	n.d.	n.d.	**0.0**	n.d.	1.2	n.d.	n.d.	n.d.	**1.2**	n.d.	2.2	n.d.	**2.2**	**11**
46	n.d.	n.q.	5.5	2.7	n.d.	**8.3**	n.d.	n.d.	n.d.	**0.0**	0.3	0.2	n.d.	n.d.	n.d.	**0.4**	0.5	1.2	0.1	**1.8**	**11**
47	n.d.	n.d.	7.7	2.6	n.d.	**10**	n.d.	n.d.	n.d.	**0.0**	n.d.	n.d.	n.d.	n.d.	n.d.	**0.0**	n.d.	n.d.	n.d.	**0.0**	**10**
48	n.d.	n.d.	9.1	3.0	n.d.	**15**	n.d.	n.d.	n.d.	**0.0**	0.3	0.6	n.d.	n.d.	n.d.	**0.9**	n.d.	n.d.	n.d.	**0.5**	**17**
49	n.d.	n.d.	11	4.2	n.d.	**16**	n.d.	n.d.	n.d.	**0.0**	1.3	2.3	n.d.	n.d.	n.d.	**3.6**	n.d.	n.d.	1.1	**2.1**	**21**
MSM08/3, Rostock – Tallinn – Kiel (18.06.2008 – 17.07.2008)																					
50	n.d.	16	79	33	12	**139**	0.6	3.7	2.7	**7.1**	4.4	5.4	n.q.	3.7	n.d.	**14**	2.5	1.2	0.6	**4.3**	**164**
51	n.d.	14	33	13	5.3	**64**	0.4	0.6	0.3	**1.3**	3.2	4.0	n.q.	2.0	n.d.	**9.3**	n.d.	0.8	n.d.	**0.8**	**76**
52	n.d.	8.1	45	9.6	3.6	**67**	0.1	0.3	n.d.	**0.4**	2.3	2.8	n.q.	1.7	n.d.	**6.8**	n.d.	0.9	n.d.	**0.9**	**75**
53	n.d.	6.9	22	9.5	6.6	**45**	0.1	0.2	n.d.	**0.3**	2.5	2.3	n.d.	1.6	n.d.	**6.3**	n.d.	0.4	n.d.	**0.4**	**52**
54	n.d.	4.4	20	7.1	3.4	**35**	0.1	0.1	n.d.	**0.2**	2.2	2.3	n.d.	1.9	n.d.	**6.5**	n.d.	0.1	n.d.	**0.1**	**42**
55	n.d.	6.9	94	18	0.1	**119**	0.7	0.4	0.3	**1.4**	1.2	1.3	n.d.	0.6	n.d.	**3.1**	1.0	1.3	0.7	**3.0**	**127**
56	n.d.	4.7	9.5	3.8	0.1	**18**	6.1	0.3	0.0	**6.4**	0.8	0.3	n.d.	0.3	n.d.	**1.4**	0.7	0.3	0.2	**1.2**	**27**
57	n.d.	2.7	19	4.2	1.3	**27**	0.7	0.2	0.1	**1.0**	1.0	1.0	n.d.	0.4	n.d.	**2.4**	n.d.	4.7	0.5	**5.2**	**35**
58	n.d.	1.6	10	2.2	0.9	**15**	n.d.	0.1	0.0	**0.1**	0.5	0.8	n.d.	0.2	n.d.	**1.5**	0.6	1.3	1.2	**3.1**	**20**
59	n.d.	3.1	7.0	8.0	2.5	**21**	0.7	0.2	0.1	**1.0**	1.2	0.9	n.d.	0.3	n.d.	**2.4**	0.9	4.7	0.2	**5.8**	**30**
60	n.d.	5.7	23	7.1	1.0	**36**	n.d.	0.3	0.2	**0.5**	0.6	1.2	0.1	0.6	n.d.	**2.5**	0.6	0.8	0.4	**1.8**	**41**
61	n.d.	3.3	10	5.0	1.8	**20**	0.1	n.d.	n.d.	**0.1**	0.8	0.9	n.q.	0.2	n.d.	**1.9**	0.2	0.5	n.d.	**0.6**	**23**
62	n.d.	9.4	22	8.5	2.1	**42**	0.4	0.5	0.1	**1.0**	0.6	0.7	0.1	1.3	n.d.	**2.7**	0.3	0.3	0.1	**0.8**	**47**
63	n.d.	4.8	26	9.2	2.3	**42**	0.9	0.4	0.1	**1.4**	1.1	1.5	0.2	0.5	n.d.	**3.3**	0.5	0.8	0.3	**1.7**	**48**
64	n.d.	11	18	1.3	1.6	**32**	n.d.	n.d.	n.d.	**0.0**	0.6	0.5	n.d.	n.d.	n.d.	**1.0**	n.d.	0.7	0.6	**1.2**	**34**
65	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	**n.a.**
66	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	**n.a.**
67	n.d.	8.8	38	8.5	5.6	**61**	n.d.	n.d.	1.3	**1.3**	1.7	(14)[a]	n.d.	n.d.	n.d.	**2**	n.d.	2.2	n.d.	**2**	**80**
68	n.d.	19	34	14	3.0	**69**	n.d.	1.3	0.5	**1.8**	1.2	1.7	0.3	n.d.	n.d.	**3.3**	4.1	2.3	n.d.	**6.4**	**81**
69	n.d.	7.1	19	9.9	4.2	**40**	n.d.	0.4	0.4	**0.8**	1.1	2.0	0.3	0.7	n.d.	**4.1**	0.9	1.1	n.d.	**2.0**	**47**

Table S4-21: cont.

ID	**4:2 FTOH**	**6:2 FTOH**	**8:2 FTOH**	**10:2 FTOH**	**12:2 FTOH**	**Σ FTOH**	**6:2 FTA**	**8:2 FTA**	**10:2 FTA**	**Σ FTA**	**MeFBSA**	**MeFOSA**	**Me2FOSA**	**EtFOSA**	**PFOSA**	**Σ FASA**	**MeFBSE**	**MeFOSE**	**EtFOSE**	**ΣFASE**	**total**
70	n.d.	1.8	13	5.2	6.6	**27**	n.d.	0.4	n.d.	**0.4**	n.d.	1.1	n.d.	0.6	n.d.	**1.7**	n.d.	11	n.d.	**11**	**39**
71	n.d.	3.6	19	7.5	0.6	**31**	0.5	0.2	n.d.	**0.7**	0.9	0.6	n.d.	0.3	n.d.	**1.9**	1.2	1.5	n.d.	**2.7**	**36**
72	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	**n.a.**
73	n.d.	15	59	16	n.d.	**90**	0.1	0.8	0.2	**1.1**	3.0	1.8	0.0	0.4	n.d.	**5.2**	1.9	2.5	n.d.	**4.5**	**101**
74	n.d.	(102)[a]	44	15	6.5	**66**	7.3	2.2	0.2	**9.6**	2.8	1.8	n.d.	n.d.	n.d.	**4.6**	2.3	2.7	n.d.	**5.0**	**85**
75	n.d.	4.7	17	4.8	0.5	**27**	n.d.	0.1	n.d.	**0.1**	1.2	0.8	n.d.	0.3	n.d.	**2.2**	0.1	0.7	0.2	**1.1**	**30**
76	n.d.	6.4	22	7.0	1.0	**36**	0.1	0.2	0.1	**0.3**	1.1	1.1	6.3	13	n.d.	**22**	0.2	1.2	n.d.	**1.4**	**60**
Atair 155, German Bight, North Sea (30.10.2007 – 06.11.2007), average of parallel samples																					
77	1.4	5.0	11	2.8	1.7	**21**	n.d.	2.2	0.9	**3.1**	7.1	3.7	n.d.	1.7	2.5	**15**	0.6	1.3	n.d.	**1.9**	**41**
78	n.d.	8.6	56	14	3.1	**82**	5.7	3.2	1.3	**10**	5.8	1.5	0.5	0.8	1.9	**11**	1.4	0.9	0.1	**2.4**	**105**
79	n.d.	5.8	13	3.5	1.3	**24**	n.d.	1.9	0.8	**2.8**	3.1	2.5	n.d.	0.4	3.4	**9.5**	1.0	2.0	n.d.	**3.0**	**39**
80	2.3	5.7	16	5.7	1.3	**31**	n.d.	1.7	1.2	**2.9**	3.4	3.3	1.4	1.4	2.8	**12**	1.3	2.5	0.3	**4.2**	**50**
81	1.8	3.3	8.2	2.1	1.5	**17**	n.q.	1.8	0.8	**2.6**	6.0	3.9	0.5	1.5	n.q.	**12**	0.6	2.2	0.3	**3.2**	**35**
82	1.4	15	28	6.7	2.3	**53**	n.d.	3.6	1.2	**4.8**	4.7	3.1	0.7	1.1	n.d.	**9.7**	1.0	1.2	n.d.	**2.2**	**70**
83	n.d.	13	130	29	8.0	**180**	4.2	15	6.6	**26**	3.4	2.4	0.5	0.5	7.3	**14**	2.5	1.4	n.d.	**3.9**	**224**
MSM05/1, Las Palmas – St. John's (12.04.2007-02.05.2007)																					
84	n.d.	7.6	124	53	35	**220**	n.d.	15	4.5	**19**	5.6	8.0	n.q.	67	n.q.	**81**	6.8	3.9	5.2	**16**	**335**
85	n.d.	7.3	44	19	10	**81**	n.d.	3.8	1.3	**5.1**	3.7	5.8	n.q.	3.0	11	**24**	9.3	9.6	5.0	**24**	**134**
86	n.d.	3.9	13	2.6	0.6	**20**	n.d.	0.3	0.1	**0.4**	1.0	1.0	n.q.	1.8	n.q.	**3.8**	0.4	0.9	0.2	**1.5**	**26**
87	n.d.	11	20	7.5	3.2	**42**	3.8	1.5	0.6	**5.9**	5.5	7.6	n.d.	6.1	7.4	**26**	2.7	7.2	3.9	**14**	**88**
88	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	**n.a.**
89	n.q.	4.6	11	3.8	2.3	**21**	n.d.	0.1	0.1	**0.2**	0.7	0.6	n.q.	0.2	n.d.	**1.6**	0.4	1.1	0.3	**1.8**	**25**
90	n.d.	3.9	7.6	2.4	1.3	**15**	0.5	0.2	<0.1	**0.7**	0.7	0.4	n.q.	0.1	n.d.	**1.2**	0.4	1.6	0.3	**2.3**	**19**
91	n.d.	5.7	7.5	1.9	1.3	**16**	0.5	0.2	<0.1	**0.7**	0.6	2.7	n.q.	0.2	2.6	**6.1**	0.3	3.1	0.2	**3.5**	**27**
92	n.d.	1.7	9.4	3.1	2.5	**17**	n.d.	0.1	<0.1	**0.1**	0.6	0.4	n.d.	n.q.	n.q.	**1.0**	0.2	1.2	0.2	**1.5**	**19**
93	n.q.	3.7	7.0	1.6	0.9	**13**	0.5	0.2	<0.1	**0.7**	0.4	0.4	n.q.	0.2	n.q.	**0.9**	0.2	0.5	0.2	**0.9**	**16**
94	n.q.	4.2	6.8	2.1	2.8	**16**	0.5	0.1	<0.1	**0.7**	0.5	0.4	n.d.	0.1	0.5	**1.5**	0.2	0.6	0.2	**1.0**	**19**
95	n.d.	5.9	20	5.3	2.2	**33**	2.1	1.3	0.5	**3.9**	2.1	6.7	n.d.	3.0	4.4	**16**	1.8	4.6	2.3	**8.7**	**62**
96	1.2	(165)[a]	38	12	2.9	**54**	0.7	0.5	0.1	**1.3**	0.7	0.8	n.d.	0.6	n.q.	**2.1**	0.9	0.8	n.q.	**1.7**	**59**
97	n.d.	4.8	10	3.8	2.4	**21**	1.3	0.3	0.1	**1.7**	0.5	0.8	n.d.	n.q.	n.q.	**1.3**	0.3	2.3	0.5	**3.0**	**27**
98	n.d.	9.0	45	14	4.9	**73**	4.1	1.8	0.6	**6.6**	2.1	3.1	n.d.	3.3	n.q.	**8.5**	3.7	2.6	1.3	**7.5**	**95**
99	n.d.	5.2	11	3.9	1.2	**21**	0.6	0.3	0.1	**1.0**	0.5	7.9	n.d.	0.5	n.q.	**8.9**	0.4	10	0.8	**11**	**42**
L'Atalante leg 2 MARSÜD IV, Recife – Dakar (07.01.2008 – 31.01.2008)																					
100	n.d.	6.4	29	24	6.5	**66**	5.5	3.6	n.d.	**9.1**	n.d.	n.d.	n.d.	1.5	n.d.	**1.5**	(42)[a]	20	n.d.	**20**	**97**
101	n.d.	2.2	10	4.8	0.4	**17**	1.0	n.d.	n.d.	**1.0**	0.7	1.6	n.d.	0.9	n.d.	**3.2**	(10)[a]	2.5	0.9	**3.4**	**25**
102	n.d.	3.7	7.5	5.0	2.6	**19**	n.d.	n.d.	n.d.	**0.0**	n.d.	0.5	n.d.	0.2	n.d.	**0.7**	(18)[a]	3.4	1.9	**5.3**	**25**
103	n.d.	2.8	9.2	4.3	1.8	**18**	0.8	0.4	n.d.	**1.2**	0.1	0.9	n.d.	0.6	n.d.	**1.6**	5.7)[a]	2.0	1.8	**3.8**	**25**
104	n.d.	6.3	14	7.6	2.1	**30**	0.6	n.d.	n.d.	**0.6**	0.2	1.7	n.d.	0.4	n.d.	**2.3**	(75)[a]	4.3	3.8	**8.1**	**41**
105	n.d.	n.d.	6.2	3.8	1.4	**11**	0.4	n.d.	n.d.	**0.4**	n.d.	0.3	n.d.	n.d.	n.d.	**0.3**	(1.0)[a]	n.d.	n.d.	**0.0**	**12**
106	n.d.	2.8	7.1	5.5	2.9	**18**	0.9	0.4	n.d.	**1.4**	n.d.	1.7	n.d.	0.1	n.d.	**1.8**	(12)[a]	4.1	1.9	**6.0**	**27**
107	n.d.	3.0	14	11	6.7	**35**	6.7	1.5	n.d.	**8.2**	n.d.	1.4	n.d.	n.d.	n.d.	**1.4**	(22)[a]	7.3	3.1	**10**	**55**
108[b]	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**0.0**	**0**

Table S4-21: cont

ID	**4:2 FTOH**	**6:2 FTOH**	**8:2 FTOH**	**10:2 FTOH**	**12:2 FTOH**	**Σ FTOH**	**6:2 FTA**	**8:2 FTA**	**10:2 FTA**	**Σ FTA**	**MeFBSA**	**MeFOSA**	**Me2FOSA**	**EtFOSA**	**PFOSA**	**Σ FASA**	**MeFBSE**	**MeFOSE**	**EtFOSE**	**ΣFASE**	**total**
109	n.d.	0.8	7.5	4.5	0.3	**13**	0.7	n.d.	n.d.	**0.7**	n.d.	n.d.	n.d.	1.2	n.d.	**1.2**	(1.6)[a]	0.4	0.5	**0.9**	**16**
110	n.d.	3.1	16	9.6	3.6	**33**	4.0	2.5	n.d.	**6.5**	n.d.	5.5	n.d.	1.9	n.d.	**7.4**	(18)[a]	6.9	2.3	**9.2**	**56**
111[b]	n.d.	(34)[a]	(77)	(45)	(20)	**(176)**	(1.2)	n.d.	n.d.	**(1.2)**	(5.6)	(1.9)	n.d.	(4.9)	n.d.	**(12)**	(209)	(15)	(7.9)	**(23)**	**(212)**
112	n.d.	1.4	10	6.9	4.8	**23**	4.3	n.d.	n.d.	**4.3**	n.d.	1.2	n.d.	n.d.	n.d.	**1.2**	2.9	4.3	n.d.	**4.3**	**33**
3 day parallel samples of all cruises																					
113	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	**n.a.**
114	n.d.	15	6.5	3.0	1.0	**25**	1.8	2.0	0.1	**3.8**	2.8	2.6	n.d.	2.5	1.0	**8.9**	n.q.	2.5	2.0	**4.6**	**42**
115	n.d.	13	32	8.1	2.4	**55**	2.2	2.8	0.1	**5.1**	3.5	4.1	n.d.	2.3	n.q.	**9.9**	2.2	0.6	1.4	**4.2**	**75**
116	n.d.	23	41	8.3	2.4	**75**	6.0	3.7	0.2	**9.9**	4.5	4.5	0.1	3.1	2.2	**14**	n.q.	1.3	2.3	**3.6**	**102**
117	n.d.	18	23	3.5	9.5	**54**	0.6	0.7	n.d.	**1.4**	1.1	1.1	0.3	0.5	n.d.	**3.1**	0.9	2.7	0.8	**4.4**	**63**
118	n.d.	11	18	7.6	3.4	**40**	n.d.	n.d.	n.d.	**0.0**	1.3	3.0	0.5	2.1	n.d.	**6.9**	2.1	2.4	0.2	**4.7**	**52**
119	n.d.	8.1	18	2.2	(14)	**28**	1.3	0.9	n.d.	**2.2**	1.8	1.5	1.7	1.9	n.d.	**6.9**	n.d.	0.9	n.d.	**0.9**	**38**
120	n.d.	4.6	8.4	4.2	2.8	**20**	1.0	1.3	n.d.	**2**	n.d.	2.8	n.d.	2.8	n.d.	**5.6**	1.6	4.9	0.6	**7.1**	**35**
121	n.d.	2.6	8.3	3.7	2.7	**17**	1.3	1.7	n.d.	**3.0**	2.6	2.4	n.d.	4.3	n.d.	**9.3**	n.d.	4.4	0.6	**5.0**	**35**
122	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	n.a.	n.a.	**n.a.**	n.a.	n.a.	n.a.	**n.a.**	**n.a.**
123	n.d.	6.2	8.6	14	12	**41**	2.8	4.1	2.6	**9.5**	n.d.	0.8	1.9	1.1	n.d.	**3.8**	0.6	2.5	0.4	**3.4**	**57**
124	n.d.	18	63	41	13	**134**	0.5	2.9	2.7	**6.2**	1.4	2.2	2.9	3.2	n.d.	**9.8**	2.8	1.4	0.7	**4.9**	**155**
125	n.d.	11	42	8.2	4.1	**66**	0.1	0.6	0.2	**0.9**	1.4	2.1	0.4	0.8	n.d.	**4.6**	0.3	0.6	0.2	**1.1**	**72**
126	n.d.	6.2	41	12	1.2	**60**	n.q.	1.0	0.9	**1.9**	1.8	1.8	n.d.	1.2	n.d.	**4.7**	0.9	1.5	0.4	**2.8**	**69**
127	n.d.	6.3	39	10	2.1	**58**	n.q.	2.5	2.1	**4.6**	4.2	3.9	2.1	2.3	n.d.	**12**	1.3	1.4	n.d.	**2.7**	**77**
128	n.d.	5.8	17	7.2	1.7	**31**	n.q.	2.0	1.3	**3.4**	1.6	1.8	6.0	n.d.	n.d.	**9.5**	1.3	1.4	n.d.	**2.7**	**47**
129	n.d.	5.1	13	8.2	2.1	**29**	n.q.	1.2	1.0	**2.2**	1.7	1.6	1.1	1.0	n.d.	**5.4**	1.1	0.8	0.3	**2.2**	**38**
130	n.d.	8.8	29	12	4.7	**55**	n.q.	2.2	1.5	**3.7**	1.5	1.8	1.5	1.4	n.d.	**6.2**	1.8	1.6	0.4	**3.8**	**69**
131	n.d.	4.1	19	5.1	13	**42**	n.d.	0.7	7.0	**7.8**	1.0	0.8	0.3	3.4	n.d.	**5.5**	2.4	1.4	n.d.	**3.7**	**59**
132	n.d.	9.4	41	52	13	**116**	0.3	0.3	0.6	**1.2**	2.6	1.3	0.0	0.4	n.d.	**4.4**	0.9	0.7	n.d.	**1.6**	**123**
133	n.d.	3.7	13	4.9	1.4	**23**	0.0	0.1	n.d.	**0.1**	1.1	0.6	0.0	0.1	n.d.	**1.8**	1.7	1.0	n.d.	**2.7**	**27**
134	n.d.	13	103	36	15	**167**	0.7	6.8	2.0	**9.5**	1.5	1.5	n.q.	14	n.d.	**17**	6.9	5.0	1.3	**13**	**207**
135	n.q.	7.9	11	3.1	1.8	**24**	1.7	0.3	0.1	**2.1**	0.7	1.0	n.d.	0.5	0.4	**2.6**	0.3	0.9	1.1	**2.3**	**31**
136	n.d.	11	33	12	5.8	**61**	0.6	0.7	0.3	**1.6**	1.4	1.3	n.d.	0.6	n.d.	**3.3**	1.7	2.0	0.4	**4.1**	**70**
137	n.d.	1.9	12	2.6	1.5	**18**	n.d.	n.d.	n.d.	**0**	0.3	2.7	n.d.	1.0	1.1	**5.1**	n.q.	1.1	n.d.	**1.1**	**24**
138	n.d.	4.5	12	3.5	1.7	**22**	0.2	0.2	<0.1	**0.4**	0.7	0.7	n.q.	0.1	0.2	**1.8**	0.4	1.0	0.1	**1.5**	**26**
139	0.1	4.1	14	2.7	0.9	**21**	0.3	0.2	0.1	**0.6**	0.5	0.8	n.d.	0.5	n.q.	**1.7**	0.2	0.5	0.2	**0.9**	**25**
140	n.q.	14	12	2.6	2.1	**31**	0.6	0.2	0.1	**0.9**	0.7	0.4	n.d.	0.1	n.d.	**1.2**	0.3	0.8	1.0	**2.0**	**35**
141	1.5	12	17	2.3	5.7	**39**	1.0	n.d.	0.1	**1.1**	n.q.	0.4	n.d.	0.1	n.q.	**0.4**	0.3	0.8	0.3	**1.4**	**42**

Table S4-22: Overview about particle-phase concentrations (c; pg m^{-3}) determined by GC-MS. C max: maximum concentration, NH: northern hemisphere, SH: southern hemisphere, BG-NH marine background concentration in the northern hemisphere, BG-SH: marine background concentration in the southern hemisphere.

		c_{max} (pg m^{-3})			$c_{average}$ (pg m^{-3})	
	all samples	**all samples**	**NH**	**SH**	**BG-NH**	**BG-SH**
	n=99	n=99	n=63	n=34	n=13	n=24
4:2 FTOH	0.1	0.0	0.0	0.0	0.0	0.0
6:2 FTOH	2.7	0.1	0.2	0.0	0.2	0.0
8:2 FTOH	3.1	0.4	0.5	0.1	0.8	0.1
10:2 FTOH	1.0	0.1	0.1	0.1	0.1	0.1
12:2 FTOH	5.4	0.4	0.5	0.0	1.0	0.0
ΣFTOH	8.1	0.9	1.3	0.3	2.0	0.2
6:2 FTA	0.3	0.0	0.0	0.0	0.0	0.0
8:2 FTA	0.0	0.0	0.0	0.0	0.0	0.0
10:2 FTA	0.0	0.0	0.0	0.0	0.0	0.0
ΣFTA	0.3	0.0	0.0	0.0	0.0	0.0
MeFBSA	0.1	0.0	0.0	0.0	0.0	0.0
MeFOSA	5.6	0.3	0.5	0.0	0.5	0.0
Me2FOSA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
EtFOSA	3.1	0.2	0.3	0.0	0.2	0.0
PFOSA	0.0	0.0	0.0	0.0	0.0	0.0
ΣFASA	8.7	0.5	0.7	0.0	0.7	0.0
MeFBSE	2.3	0.1	0.1	0.1	0.0	0.0
MeFOSE	9.0	0.4	0.5	0.2	0.2	0.2
EtFOSE	8.0	0.4	0.5	0.3	0.2	0.3
ΣFASE	15.9	0.9	1.1	0.6	0.4	0.5
total	43.3	3.0	4.3	0.8	3.1	0.7

Spatial Distribution of Selected PFC

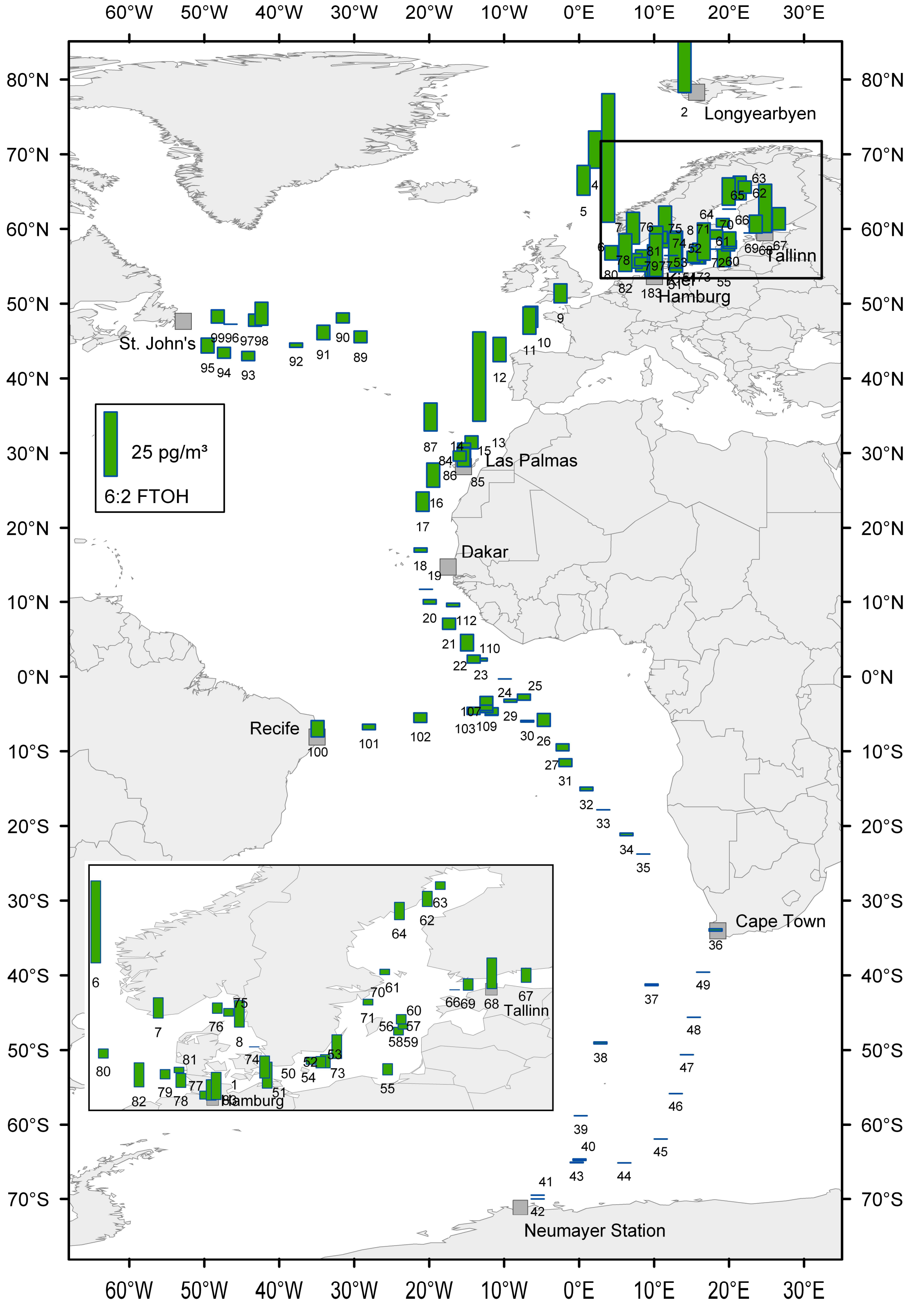


Figure S4-2: Spatial distribution of 6:2 FTOH gas-phase concentrations determined during several cruises in the Baltic Sea, the Atlantic and Southern Ocean. Note: Close-up of the Baltic Sea region is not to scale.

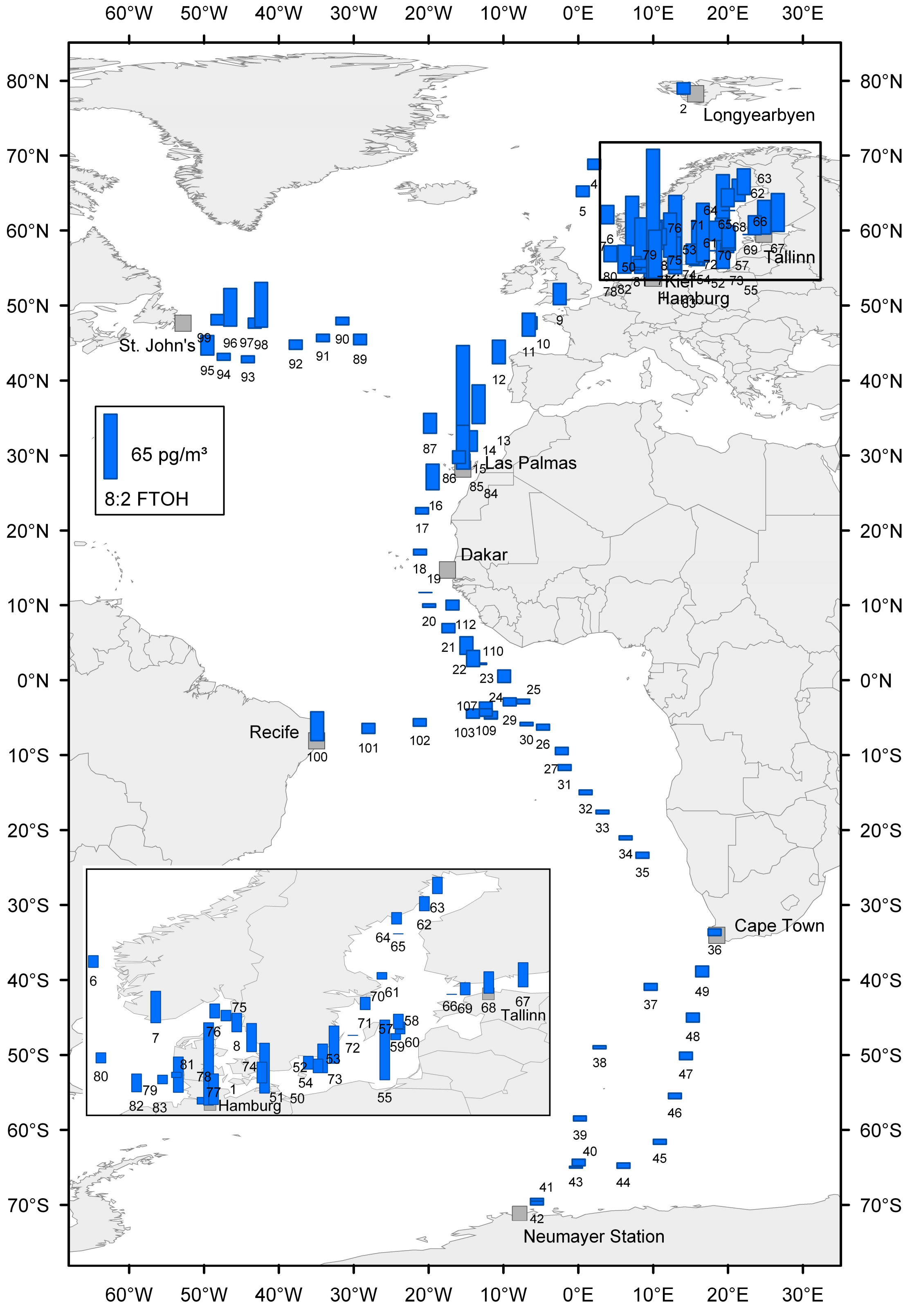


Figure S4-3: Spatial distribution of 8:2 FTOH gas-phase concentrations determined during several cruises in the Baltic Sea, the Atlantic and Southern Ocean. Note: Close-up of the Baltic Sea region is not to scale.

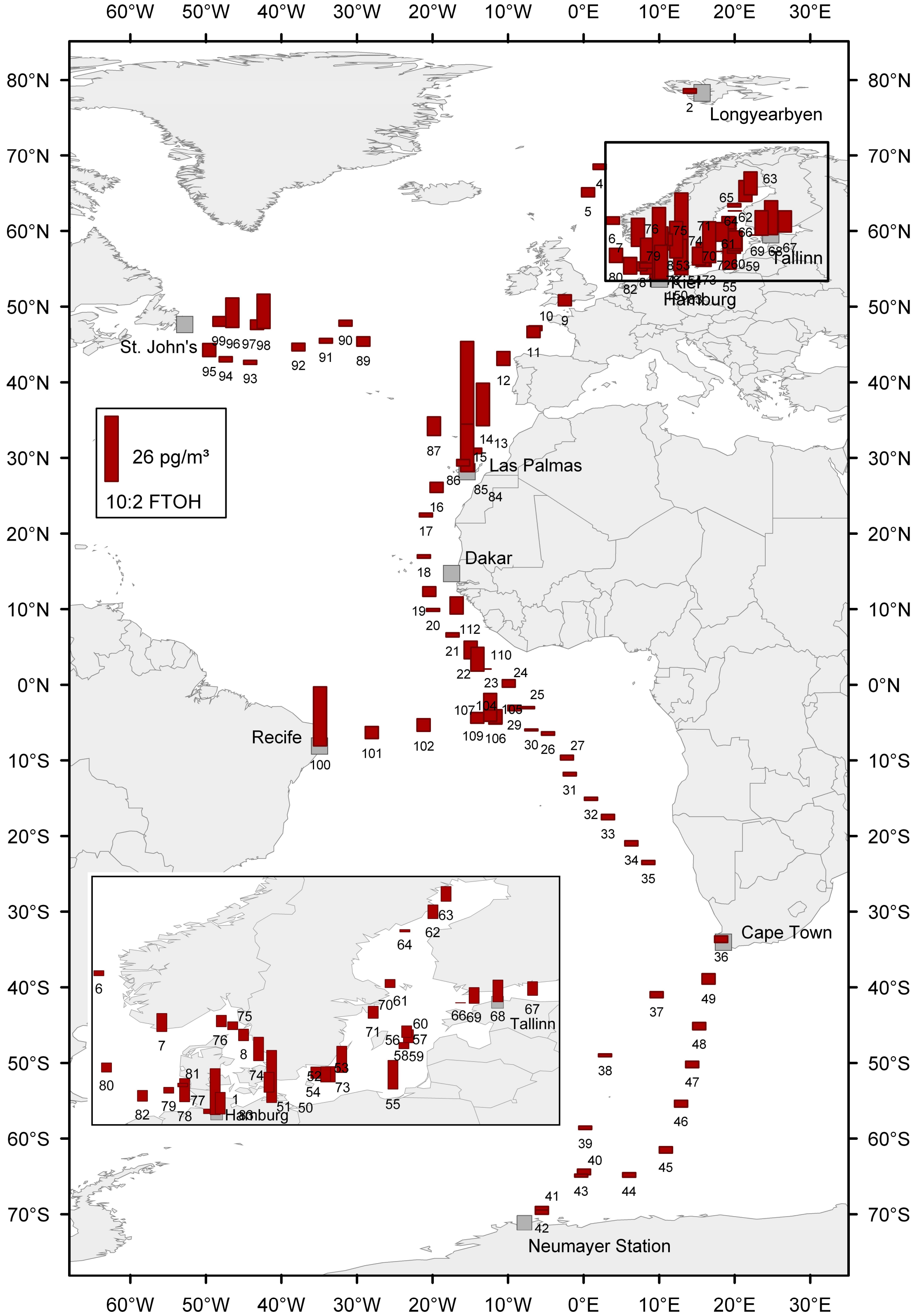


Figure S4-4: Spatial distribution of 10:2 FTOH gas-phase concentrations determined during several cruises in the Baltic Sea, the Atlantic and Southern Ocean. Note: Close-up of the Baltic Sea region is not to scale.

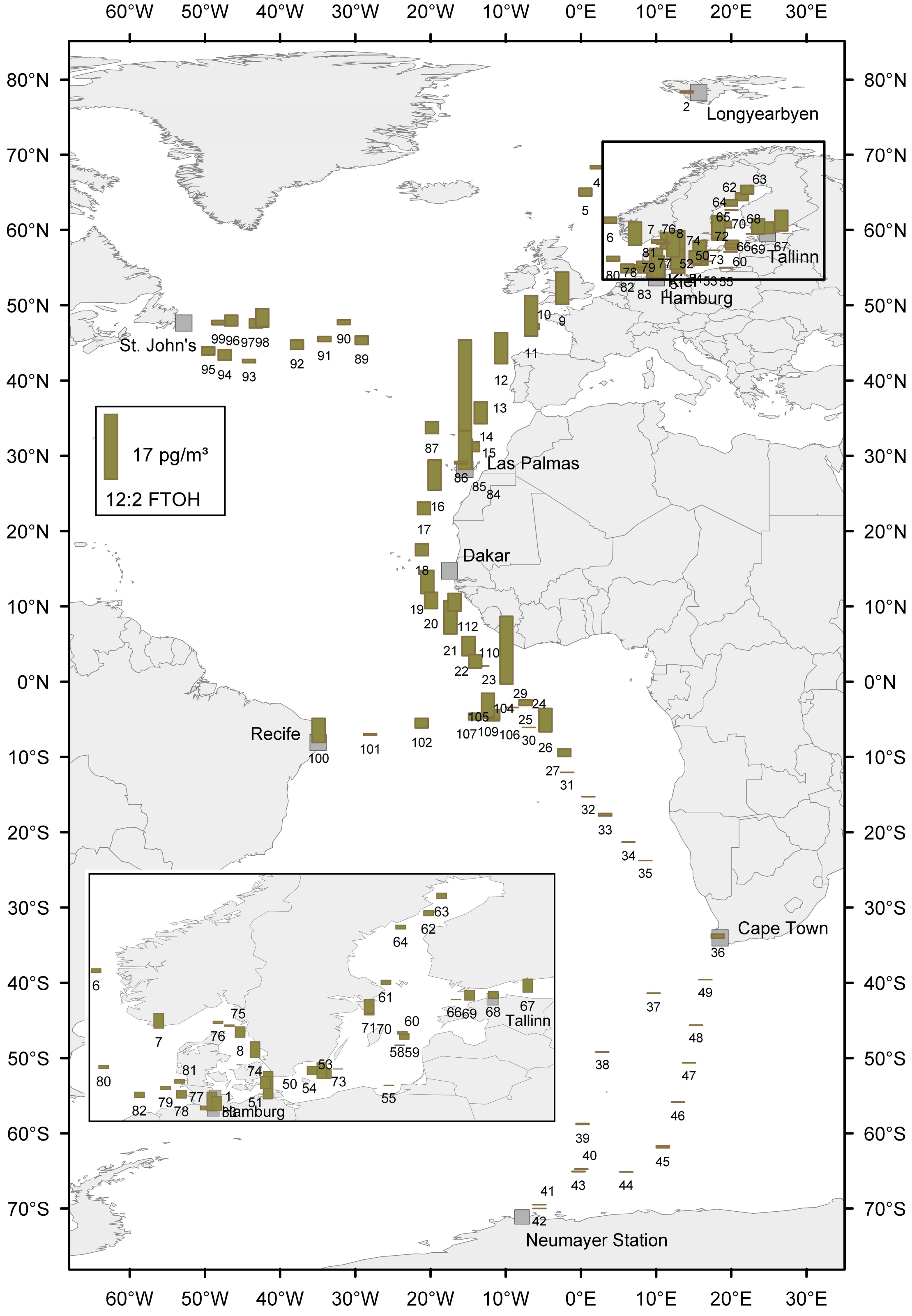


Figure S4-5: Spatial distribution of 12:2 FTOH gas-phase concentrations determined during several cruises in the Baltic Sea, the Atlantic and Southern Ocean. Note: Close-up of the Baltic Sea region is not to scale.

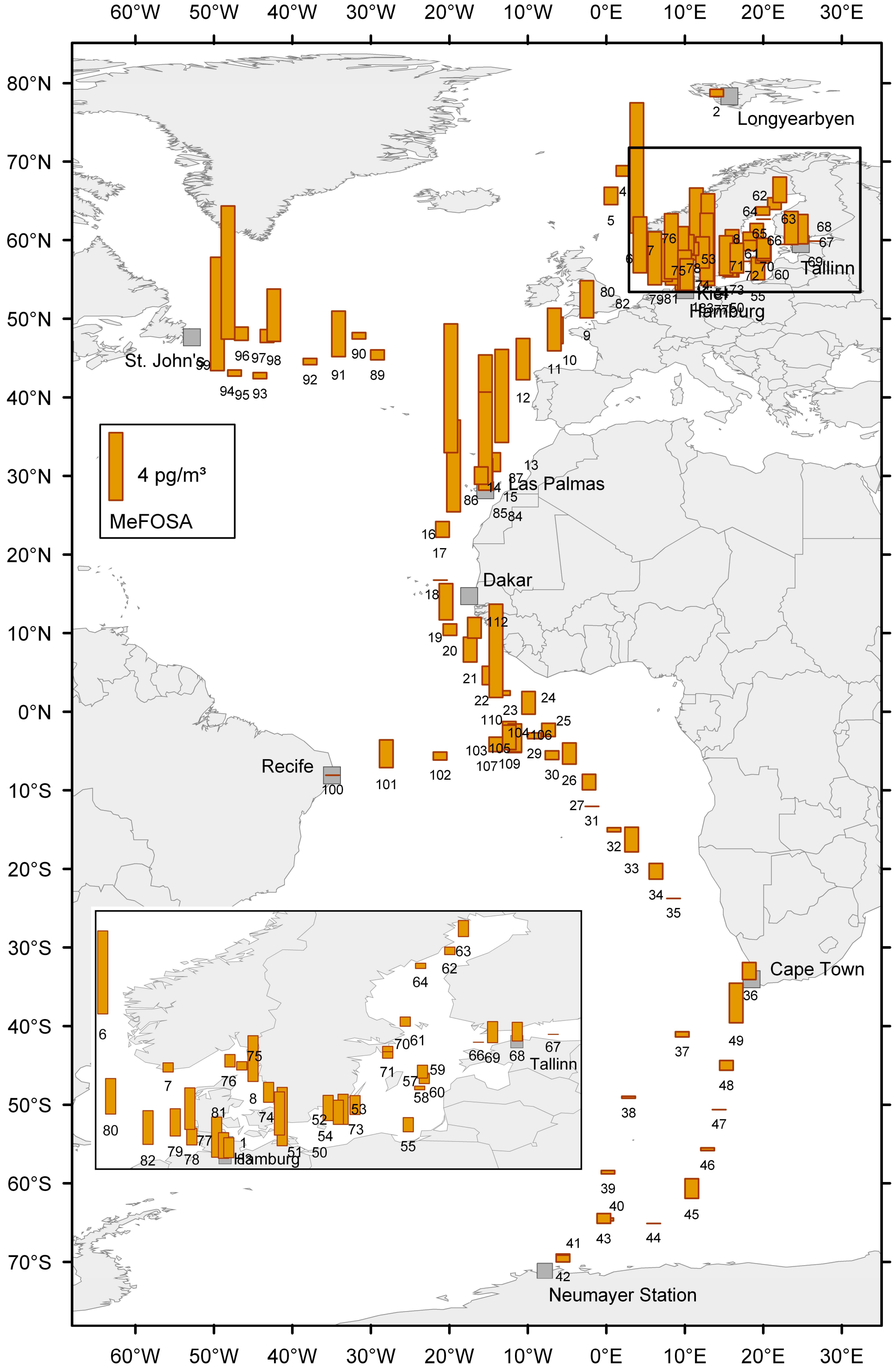


Figure S4-6: Spatial distribution of MeFOSA gas-phase concentrations determined during several cruises in the Baltic Sea, the Atlantic and Southern Ocean. Note: Close-up of the Baltic Sea region is not to scale.

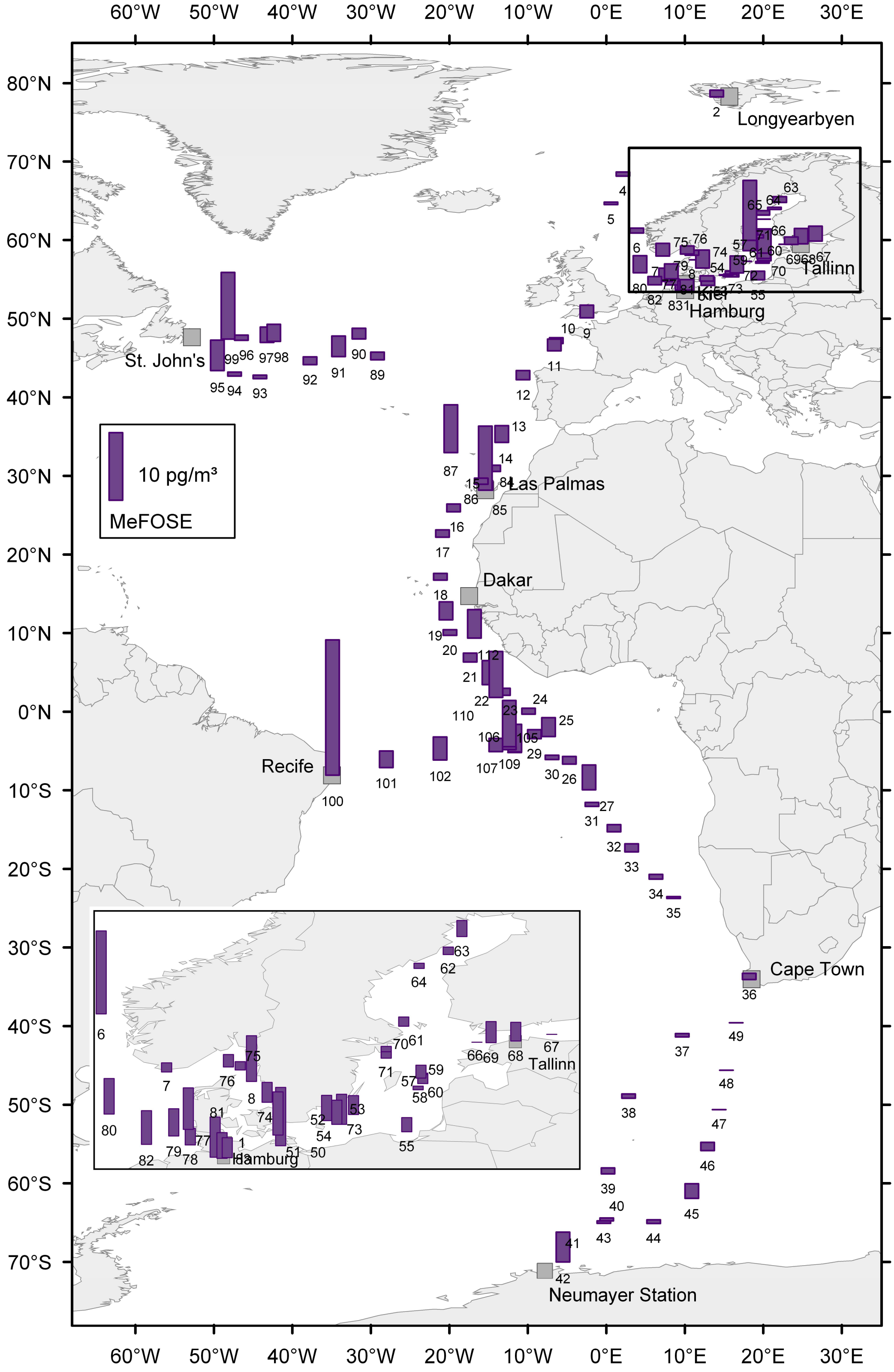
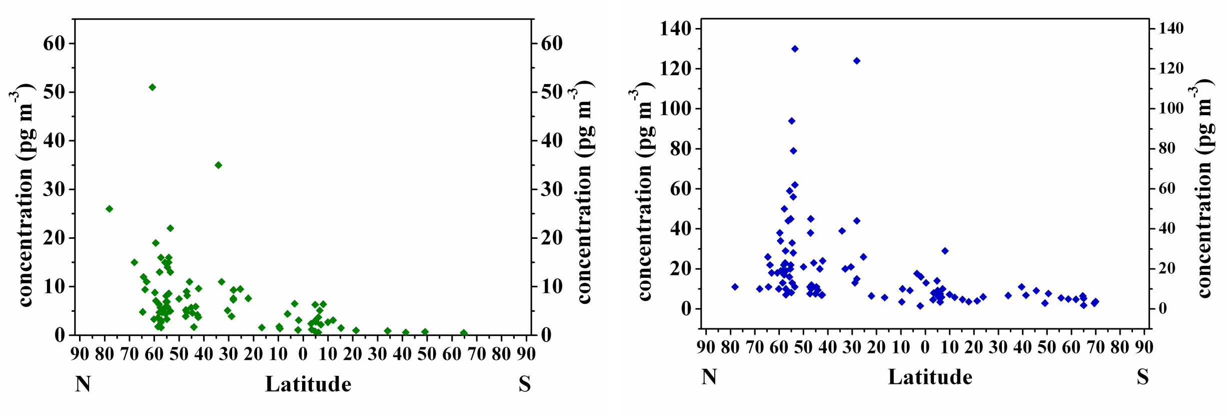
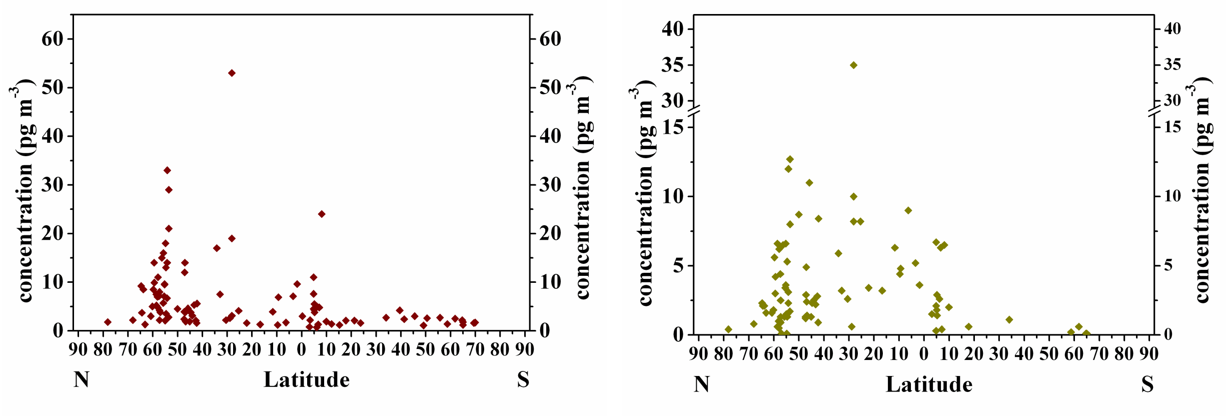


Figure S4-7: Spatial distribution of MeFOSE gas-phase concentrations determined during several cruises in the Baltic Sea, the Atlantic and Southern Ocean. Note: Close-up of the Baltic Sea region is not to scale.

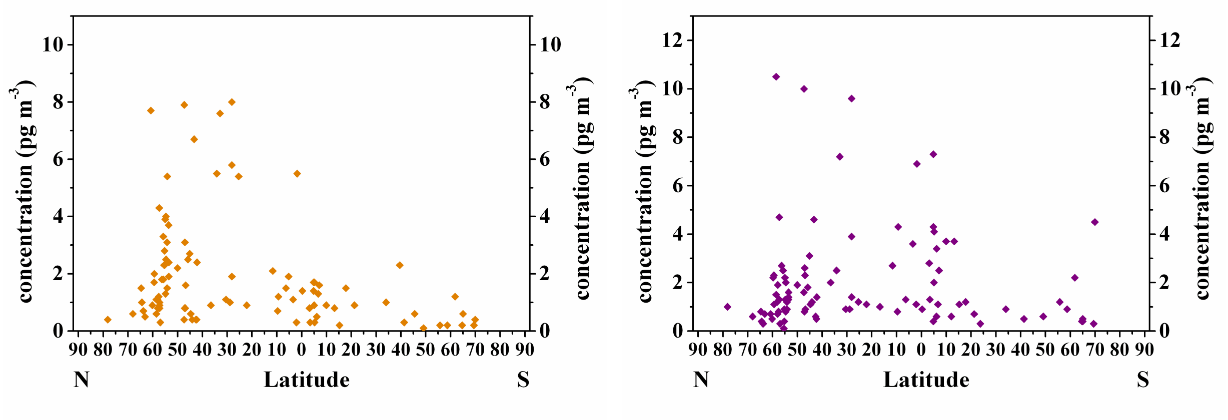
Latitudinal Distribution of Selected PFC



6:2 FTOH **8:2 FTOH**



10:2 FTOH **12:2 FTOH**



MeFOSA **MeFOSE**

Figure S4-8: Concentration of Selected PFC as function of latitude. Mind the different scale.

Gas-Phase PFC Composition

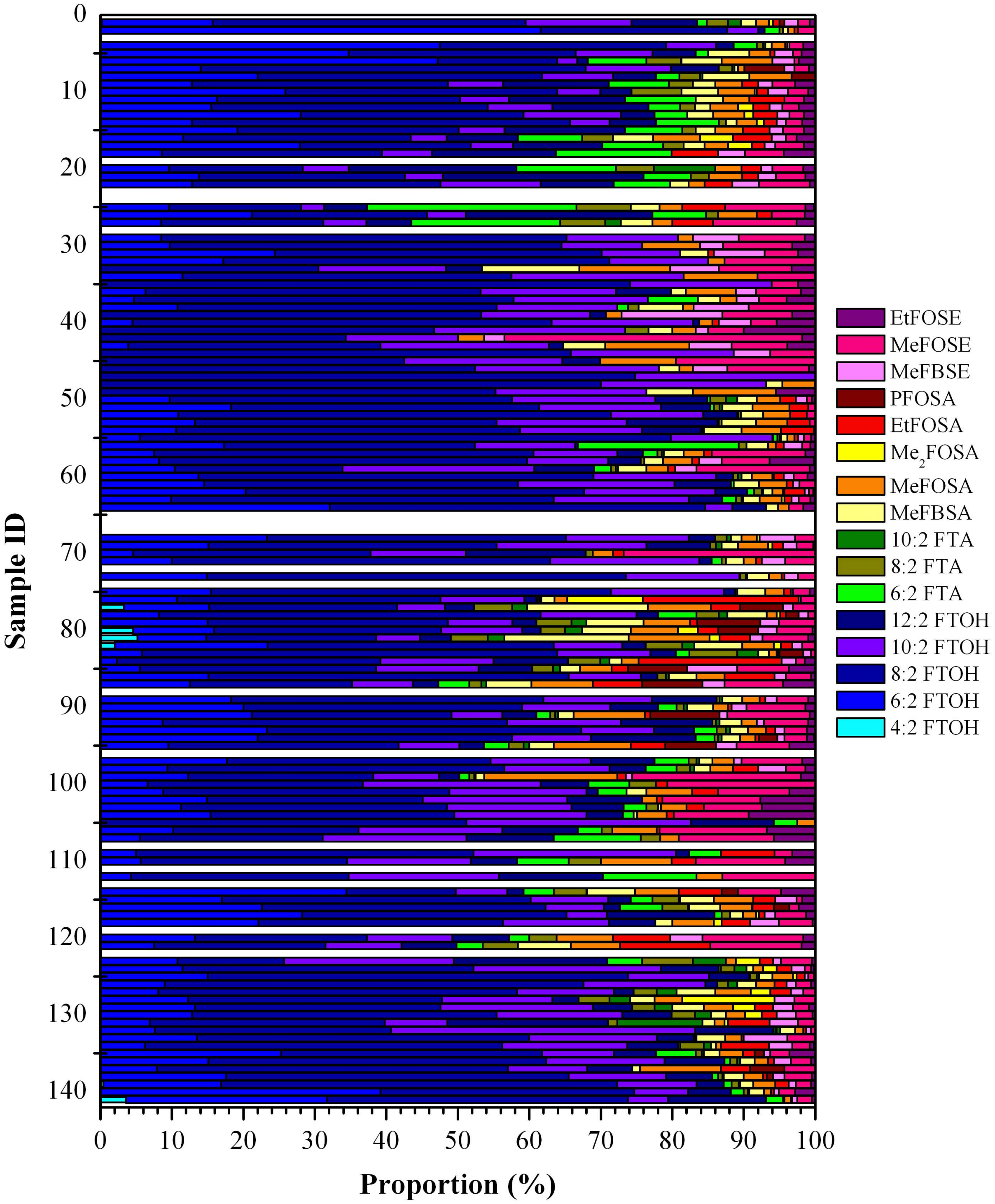


Figure S4-9: PFC Composition (proportions in %) of gas-phase samples. Empty Bars are samples that were not analyzed or not considered because of contamination with respect to certain individual analytes.

Correlation Analysis

Table S4-23: Correlation coefficients resulting from Pearson correlation of normal distributed PFC. [a] correlation is significant at the $p<0.05$ level.

	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTA	8:2 FTA	10:2 FTA	MeFBSA	MeFOSA	EtFOSA	MeFBSE	MeFOSE	EtFOSE
6:2 FTOH	0.31[a]	0.24[a]	0.11	0.33[a]	0.27[a]	0.04	0.44[a]	0.46[a]	0.08	0.36[a]	-0.06	0.27[a]
8:2 FTOH		0.89[a]	0.61[a]	0.09	0.75[a]	0.75[a]	0.43[a]	0.40[a]	0.52[a]	0.57[a]	0.08	0.44[a]
10:2 FTOH			0.74[a]	0.09	0.73[a]	0.71[a]	0.44[a]	0.48[a]	0.67[a]	0.69[a]	0.30[a]	0.56[a]
12:2 FTOH				0.38[a]	0.69[a]	0.64[a]	0.40[a]	0.45[a]	0.81[a]	0.64[a]	0.20[a]	0.57[a]
6:2 FTA					0.46	0.15	0.50	0.30	0.19	0.60	0.23	0.32
8:2 FTA						0.92[a]	0.54[a]	0.47[a]	0.63[a]	0.58[a]	0.14	0.67[a]
10:2 FTA							0.41[a]	0.29[a]	0.46[a]	0.42[a]	0.03	0.52[a]
MeFBSA								0.72[a]	0.35[a]	0.49[a]	0.18	0.50[a]
MeFOSA									0.45[a]	0.61[a]	0.44[a]	0.67[a]
EtFOSA										0.53[a]	0.08	0.56[a]
MeFBSE											0.55[a]	0.87[a]
MeFOSE												0.61[a]

References

ISO-20988 Air quality - Guidelines for estimating measurement uncertainty, 2007.

ISO-2533 Standard Atmosphere, 1975-05.

Herzlichen Dank

allen, die mir während der Zeit meiner Doktorarbeit zur Seite standen. Mein besonderer Dank gilt:

Prof. Ralf Ebinghaus, der mir die Möglichkeit gab, am Institut für Küstenforschung des GKSS Forschungszentrums meine Promotion durchzuführen. Er ließ mir stets die Freiräume, die nötig waren, um meine Ideen zu verwirklichen. Danke Ralf! Es war ein Privileg, all dies machen zu können.

Michael Radke und Prof. Hartmut Frank für die Auseinandersetzung mit diesem Thema und die Betreuung der Doktorarbeit auf universitärer Seite.

Volker Matthias, Hans Herbert Kock, Michael Radke und Christian Temme für die hilfreichen Diskussionen, Kommentare und Anregungen. Volker, vielen lieben Dank auch für Einführung in der Welt der Trajektorien und das unermüdliche Plotten derselben.

Armando Caba, der immer da war, wenn man ihn brauchte, sowohl an Land als auch auf See. Ohne ihn wäre diese Arbeit weitaus weniger reibungslos verlaufen.

Ingo Weinberg, Sabine Struwe, Torben Kirchgeorg und Vera Langer für die helfenden Hände in Barsbüttel und bei der GKSS, ob bei der Probenahme oder bei nicht gerade ereignisreichen Trajektorienberechnungen. Und natürlich für die stets heitere Büroatmosphäre, die so manchen trüben Tag aufgehellt hat.

Petra Günnewig, John Barber, Zhiyong Xie, Gesine Witt und Ingo Weinberg für die Probenahme während einiger Seereisen.

Mahiba Shoeib, Tom Harner, John Barber, and Stefan Fiedler for the exchange of good ideas and the good cooperation during expeditions or our field intercomparison study.

dem Alfred Wegener Institut für Polar und Meeresforschung, dem Bundesamt für Seeschiffahrt und Hydrographie (BSH) sowie den Fahrtenleitern Prof. Monika Rhein, Prof. Detlef Quadfasel, Prof. Colin Devy, Prof. Sigrid Schiel, Prof. Gerhard Kattner, Olaf Böbel und Joanna Wanieck, die die Probenahme und/oder Teilnahme an den fantastischen Expeditionen auf See ermöglichten. Ein großer Dank gilt auch den Kapitänen und Crews der Forschungsschiffe Polarstern, Maria S. Merian, L'Atalante und Atair ohne deren Unterstützung jeder Wissenschaftler verloren wäre.

Uwe Eckermann vom Staatlichen Umweltamt Itzehoe sowie Christian Wollny von den Wasserwerken Hamburg für die Möglichkeit auf dem Gelände der Luftmonitoring Station Barsbüttel Proben zu nehmen.

Prof. Justus Notholt, Michael Radke und Christian Temme für anregende Diskussionen, auch wenn die “PhD-Panel-Treffen” nie so stattgefunden haben wie sie eigentlich vorgesehen gewesen wären.

Jan Bödewadt für die Programmierung und Einrichtung der windabhängigen Steuerung der Probenahme auf Forschungsschiffen sowie Nadine Golumbek für die vielen Stunden über meinen Fracht- und Packlisten und die Abwicklung des ganzen Zollzeugs.

der gesamten KSC Familie und allen anderen aus Gebäude 14, die immer für einen Schnack zu haben waren und einfach mit angepackt haben, wenn es notwendig war.

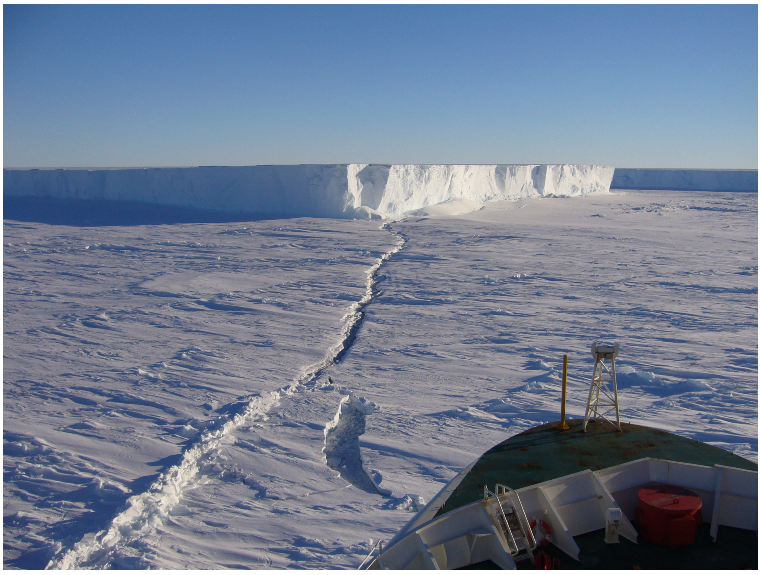
Petra, Claudia, Anja, Hermann, Ruth, Olli, Viky, Felicitas, Christoph, Holger, Armando… Was wären die Forschungsexpeditionen und langen Tage auf See oder im Eis ohne Euch! Vielen Dank für die einzigartigen Augenblicke sowie Diskussionen über „Schiff und die Welt“, die solche Seereisen zu so außergewöhnlichen Erlebnissen machen.

meinen Freunden Melanie, Sibylle, Hanna, Petra, Jenny, Carmen und Matthias, die so manche Höhen und Tiefen während dieser Zeit miterlebt haben.

meiner Familie, die mir andauernden Rückhalt gegeben und immer an mich geglaubt hat und mich unterstützte, wo sie nur konnte.

meinem Freund Stefan, der jede Gemütslage, ob gut oder schlecht, jedes „ich will Schiff fahren“ oder „Eisberge sehen“ geduldig ertragen hat, der mir mit Rat und Tat zu Seite stand und einfach immer da war, wenn ich ihn brauchte. Danke dafür!

nicht zuletzt der Deutschen Bundesstiftung Umwelt, deren Stipendium es mir überhaupt erst ermöglichte, diese Arbeit anzufertigen.



This extraordinary barrier of ice,
of probably more than a thousand
feet in thickness, crushes the
undulations of the waves, and
disregards their violence: it is a
mighty and wonderful object, far
beyond anything we could have
thought or conceived.
(James Clark Ross, 1847)