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Landfills and waste water treatment plants as sources of polyfluorinated compounds, polybrominated diphenyl ethers and synthetic musk fragrances to ambient air

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

Author:

I. Weinberg

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Ingo Weinberg

150 pages with 35 figures and 39 tables

Abstract

Polyfluorinated compounds (PFCs), polybrominated diphenyl ethers (PBDEs) and synthetic musk fragrances are frequently used and applied in a variety of consumer and industrial products as surfactants and surface coating agents (PFCs), flame retardants (PBDEs) and odourous substances (musk fragrances). Due to their persistence, bioaccumulation potential and toxicity they have been reported to be chemicals of emerging environmental concern. However, their sources to the environment are not fully understood yet. All of the three substance classes were reported to accumulate in waste water treatment plants (WWTPs) or disposed to landfills as final sinks. Several efforts have been made to investigate the fate of PFCs, PBDEs and musk fragrances at these potential sources. However, the potential for atmospheric release was less investigated. Therefore, the aim of this study was to elucidate whether landfills and WWTPs can be sources for these substances to ambient air.

Airborne PFCs, PBDEs and musk fragrances were determined at two landfills and two WWWPs in Northern Germany. Samples were analysed for neutral and ionic PFCs (five fluorotelomer alcohols (FTOHs), three fluorotelomer acrylates, three perfluoroalkylsulfonamido ethanols, three perfluoralkyl sulfonamides, five perfluorosulfonates and nine perfluorocarboxylates), eight PBDE congeners and seven musk fragrances. Air samples were taken simultaneously at reference sites that were supposed not to be influenced by these potential sources. Airborne PFCs, PBDEs and musk fragrances were accumulated in cartridges containing polyurethane foam and XAD-2 resin (gas-phase) and on glass fibre filters (particle-phase).

Results of this study suggest that landfills and particularly WWTPs are significant point sources for musk fragrances ambient air. The source strength of the active landfill was higher than for the inactive landfill for musk fragrances. The source character of PFCs at WWTPs and landfills was less pronounced. As for the musk fragrances, statistical analysis indicated that FTOHs are mainly responsible for the significantly elevated PFC gas-phase concentrations observed at landfills and WWTPs. The emissions from WWTPs seemed to vary strongly depending on the waste water contributors and the population equivalents of the respective treatment plant. In contrast to volatile PFCs, removal of ionic PFCs from waste water by aerosol formation did not appear to be an important loss mechanism. Air samples were only slightly contaminated with PBDEs displaying low air contamination in central Europe. Only at one WWTP and one landfill significantly elevated concentrations of particle-associated BDE183 were detected suggesting their origin from these sites.

Deponien und Kläranlagen als Quellen für polyfluorierte Verbindungen, polybromierte Diphenylether und synthetische Moschusverbindungen in die Umgebungsluft

Zusammenfassung

Polyfluorierte Alkylverbindungen (PFCs), polybromierte Diphenyl Ether (PBDEs) und synthetische Moschusverbindungen werden in einer Vielzahl von Industrie- und Haushaltsprodukten zur Oberflächenbeschichtung (PFCs), als Flammschutzmittel (PBDEs) und als Duftstoffe (Moschusverbindungen) eingesetzt und verwendet. Aufgrund ihrer Persistenz, ihres Bioakkumulationspotentials und ihrer toxischen Eigenschaften wird diesen Substanzen eine erhebliche Umweltrelevanz zugesprochen. Vorhergehende Studien weisen Kläranlagen und Deponien als wichtige Eintragspfade in die Umwelt durch Abwassereinleitung oder durch Deponierung der Produkte, die diese Stoffe enthalten, aus. Dadurch wurde der Verbleib dieser Substanzen in Wasser an diesen Standorten bereits häufig untersucht. Weniger bekannt ist, ob PFCs, PBDEs und Moschusverbindungen von dort in die Atmosphäre emittiert werden können. Ziel dieser Arbeit ist aufzuklären, inwiefern Deponien und Kläranlage eine Quelle für PFCs, PBDEs und Moschusverbindungen darstellen können.

Probenahmestandorte waren zwei Deponien und zwei Kläranlagen in Norddeutschland. Die Luftproben wurden auf neutrale und ionische PFCs (fünf Fluortelomeralkohole (FTOHs), drei Fluortelomerakrylate, drei Perfluoralkylsulfonamide und drei Perfluoralkylsulfonamidoethanole, fünf Perfluorsulfonate und neun Perfluorcarboxylate), acht Hauptkongenere der PBDEs und sieben Moschusverbindungen untersucht. Gleichzeitig wurden Referenzstandorte beprobt, die nicht von den Deponien und Klärwerken beeinflusst waren. Die PFCs, PBDEs und Moschusverbindungen wurden in Säulen bestehend aus Polyurethanschaum und XAD-2-Adsorberharz (Gasphase) und Glasfaserfiltern (Partikelphase) angereichert.

Die Ergebnisse dieser Studie weisen Deponien und insbesondere Kläranlagen als signifikante Quellen für Moschusverbindungen für die Umgebungsluft aus. Die Quellenstärke der aktiven Deponie war für Moschusverbindungen jedoch größer als die der geschlossenen Deponie. Für die PFCs ist der Quellencharakter von Deponien und Kläranlagen weniger ausgeprägt. Wie schon für die Moschusverbindungen ergab die statistische Auswertung, dass vor allem die FTOHs verantwortlich für den signifikanten Anstieg der PFC Konzentrationen sind. Die Emissionen von Moschusverbindungen und PFCs veränderten sich mit den verschiedenen Abwassereinleitern und den Einwohnergleichwerten der jeweiligen Kläranlage. Im Gegensatz zu den neutralen PFCs sind die Emissionen von aerosolgebundenen PFCs keine entscheidende Quelle für die Atmosphäre. Die PBDE Konzentrationen waren auf einer Deponie und einer Kläranlage signifikant erhöht. Dies könnte ein Hinweis darauf sein, dass diese von dem jeweiligen Standort emittiert wurden.

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Abbreviations

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
10:2 FTA	10:2 fluorotelomer acrylate
10:2 FTOH	10:2 fluorotelomer alcohol
12:2 FTOH	12:2 fluorotelomer alcohol
^{13}C 4:2 FTOH	2-perfluorobutyl-[1,1-2H2, 1,2-$^{13}C_2$] ethanol
^{13}C 6:2 FTOH	2-perfluorohexyl-[1,1-2H2, 1,2-$^{13}C_2$] ethanol
^{13}C 8:2 FTOH	2-perfluorooctyl-[1,1-2H2, 1,2-$^{13}C_2$]ethanol
^{13}C 10:2 FTOH	2-perfluorodecyl-[1,1-2H2, 1,2-$^{13}C_2$]ethanol
^{13}C HCB	[$^{13}C_6$]hexachlorobenzene
^{13}C PFBA	perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoate
^{13}C PFDA	perfluoro-n-[1,2-$^{13}C_2$]decanoate
^{13}C PFDoDA	perfluoro-n-[1,2-$^{13}C_2$]dodecanate
^{13}C PFHxA	perfluoro-n-[1,2-$^{13}C_2$]hexanoate
$^{18}O_2$ PFHxS	perfluoro-1-hexane[$^{18}O_2$]sulfonate
^{13}C PFNA	perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoate
^{13}C PFOA	perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoated
^{13}C PFOS	perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate
^{13}C PFUnDA	perfluoro-n-[1,2-$^{13}C_2$]undecanate
AbfAblV	Abfallablagerungsverordnung
ADBI	4-acetyl-1,1-dimethyl-6-tert-butylindane, Celestolide®
AHMI	6-acetyl-1,1,2,3,3,5-hexamethylindane, Phantolide®
AHTN	7-Acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-Tetrahydronaphthalene, Tonalide®
AHTN D_3	7-Acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-Tetrahydronaphthalene
ASE	Accelerated Solvent Extraction
ATII	5-Acetyl-1,1,2,6-tetrametyl-3-isopropyl-dihydroindene, Traseolide®
BDE28	2,4,4'-Tribromodiphenylether

BDE47	2,2',4,4'-Tetrabromodiphenyl ether
BDE99	2,2',4,4',5-Pentabromodiphenyl ether
BDE100	2,2',4,4',6-Pentabromodiphenyl ether
BDE153	2,2',4,4',5,5'-Hexabromodiphenyl ether
BDE154	2,2',4,4',5,6'-Hexabromodiphenyl ether
BDE183	2,2',3,4,4',5',6-Heptabromodiphenyl ether
BDE209	decabromodiphenyl ether
BFR	brominated flame retardantse
BG	Bestimmungsgrenze
BLK	field blank
BP	boiling point
C	concentration
C(g)	gas-phase concentration
C(p)	particle-phase concentration
LB	landfill site LB
DCM	dichloromethane
DepV	Deponieverordnung
LA	landfill site LA
DIN	Deutsche Industrienorm
EC	European Commission
EI	electron impact ionisation
ESI	electrospray ionisation
EtFOSA D_5	ethyl-[$^2H_5$]perfluorooctane sulfonamide
EtFOSAA D_5	n-deuterioethylperfluoro-1-octanesulfonamidoacetic acid
EU	European Union
FTA	fluorotelomer acrylate
FTOH	fluorotelomer alcohol
ECF	electrochemical fluorination
FASA	n-alkylated fluoroalkyl sulfamide
FASE	n-alkylated fluoroalkyl sulfonamido ethanols
FB	filter blank
FBE	fluidized bed extraction
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry

GDAS	Global Data Assimilation System
GFF	glass fibre filter
HHCB	1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran, Galaxolide®
HPLC	high performance liquid chromatography
HPLC-MS/MS	high performance liquid chromatography-tandem mass spectrometry
IFRA	International Fragrance Association
IS	internal standard
K_H	Henry's law constant
K_{OA}	octanol-air partition coefficient
K_{OW}	octanol-water partition coefficient
LOD	instrumental detection limits
LOQ	instrumental quantification limit
Max	maximum
MBDE28	2,4,4'-Tribromo[$^{13}C_6$]diphenyl ether
MBDE47	2,2',4,4'-Tetrabromo[$^{13}C_6$]diphenyl ether
MBDE99	2,2',4,4',5-Pentabromo[$^{13}C_6$]diphenyl ether
MBDE153	2,2',4,4',5,5'-Hexabromo[$^{13}C_6$]diphenyl ether
MBDE183	2,2',3,4,4',5',6-Heptabromo[$^{13}C_6$]diphenyl ether
MBDE209	decabromo[$^{13}C_6$]diphenyl ether
MDL	method detection limit
MeFOSA D_3	methyl-[$^2H_3$]perfluorooctanesulfonamide
MeFOSE D_7	methyl-[$^2H_7$]perfluorooctanesulfonamido ethanol
MeFOSE D_9	ethyl-[$^2H_9$]perfluorooctanesulfonamido ethanol
MeOH	methanol
MeO-PBDE	methoxylated polybrominated diphenyl ether
Min	minimum
MK	1-tert.-butyl-3,5-dimethyl-2,6-dinitro-4-acetyl-benzene
MP	melting point
MQL	method quantification limit
MRM	multiple reaction monitoring mode
MS	mass spectrometry
MS/MS	tandem mass spectrometer
MTBE	methyl tert-butyl ether

MW	molecular weight
MX	1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene
m/z	mass-to-charge ratio
NCI	negative chemical ionisation
N-MeFBSA	n-Methyl-perfluorobutane sulfonamide
N-MeFBSE	n-Methyl-perfluroctane sulfonamido ethanol
N-MeFOSA	n- Methyl-perfluoroctane sulfonamide
N-MeFOSE	n-Methyl-perfluoroctane sulfonamido ethanol
N-Me$_2$FOSA	n-2-Methyl-perfluoroctane sulfonamide
N-EtFOSE	n-Ethyl-perfluoroctane sulfonamido ethanol
OH	hydroxyl radical
OH-PBDE	hydroxylated polybrominated diphenyl ether
OSPAR	Oslo Paris Commision
PAH	polycyclic aromatic hydrocarbons
PCI	positive chemical ionisation
PBDE	polybrominated diphenyl ethers
PFA	perfluorinated acid
PFBA	perfluorobutanoate
PFBS	perfluorobutane sulfonate
PFC	poly- and perfluorinated alkyl substances
PFCA	perfluorinated carboxylic acids
PFDA	perfluorodecanoate
PFDoDA	perfluorododecanooate
PFDS	perfluorodecane sulfonate
PFHpA	perfluoroheptanooate
PFHpS	perfluoroheptane sulfonate
PFHxA	perfluorohexanooate
PFHxS	perfluorohexane sulfonate
PFNA	perfluorononanooate
PFNS	perfluorononane sulfonate
PFOA	perfluorooctanooate
PFOS	perfluorooctane sulfonate
PFOSA	perfluoroctane sulfonamide
PFPA	perfluoropentanooate

PFPS	perfluoropentane sulfonate
PFUnDA	perfluoroundecanooate
PFSA	perfluorinated sulfonates
PLE	pressurized liquid extraction
PSOF	perfluorooctanesulfonyl fluoride
POP	persistent organic pollutant
PTV	programmed temperature vaporisation
PUF	polyurethane foam
R	recovery rate
RF	reference site
RSD	relative standard deviation
Q	qualifier ion
SB	solvent blank
SD	standard deviation
SD abs.	absolute standard deviation
SIM	selected ion-monitoring mode
S_W	water solubility
S/N	signal-to-noise ratio
TCB D_3	$[^2H_3]$1,3,5-trichlorobenzene
TI	target ion
TNT	trinitrotoluol
UBA	German Federal Environmental Agency (Umweltbundesamt)
UK	United Kingdom
USA	United States of America
USEPA	Untited States Environmental Protection Agency
VOC	volatile organic compound
VP	vapor pressure
v:v	volume by volume
WWTP	waste water treatment plant

1. Introduction

1.1 General information on PFCs, PBDEs and musk fragrances

Per- and polyfluorinated compounds (PFCs) are a diverse substance class that are usually characterized by carbon chain lengths equal or greater than three, whereas the majority of hydrogen atoms are exchanged by fluorine (Kissa 2001). Beside the lipophilic fluorinated alkyl chain there is typically a hydrophilic functional group, which may be a carboxylate, a sulfonate, phosphorate or an alcohol. The combination of those properties results in the amphiphilic character of PFCs which combines both oil and water repellence (Kissa 2001; Jensen et al. 2008). Furthermore, the strong carbon bond (460 kJ mol^{-1}) makes PFCs very stable against UV radiation, chemical and physical degradation as well as metabolic transformation (Kissa 2001; Schultz et al. 2003).

To date, several hundred different PFCs have been produced and applied. Analytically relevant are two main classes, generally separated by their properties into ionic and neutral PFCs (see section 1.2) (Kissa 2001). Ionic PFCs consists of the groups of perfluorocarboxylates (PFCAs) and –sulfonates (PFSAs). Their main characteristics comprise ionic properties as well as their persistent (Prevedouros et al. 2006), bioaccumulative (Conder et al. 2008) and toxic properties (Roos et al. 2008) accompanied by low vapour pressure and moderately high water solubility (Jensen et al. 2008). Among these PFCs there are most investigated perfluorooctanoate (PFOA) and perfluorosulfonate (PFOS) that raised broad environmental concerns in recent years in the scientific community as well as political stakeholders (USEPA 2002; Clara et al. 2008). Neutral PFCs comprise semi-volatile and volatile molecules that are not persistent and are quickly degraded to ionic PFCs (Dinglasan et al. 2004; Ellis et al. 2004; Martin et al. 2006). Semi-volatile and volatile PFCs which are part of this study are fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAs), perfluoroalkyl sulfonamides (FASAs) and pefluoroalkyl sulfonamido ethanols (FASEs). FTOHs and FTAs consist of even-numbered carbon chains which are partially fluorinated and either a hydroxyl (FTOHs) or an acrylate (FTAs) moiety. FASAs and FASEs analysed in this study consist of either four (FBSA/ FBSE) or eight (FOSA/ FOSE) carbon atoms. All neutral and ionic PFCs which are part of this study are presented in table 1.

Flame retardants are chemicals that are added or applied to materials in order to increase the fire resistance of the corresponding product (WHO 1997). In the past decades, increasing use of flammable polymer-based materials in construction, electronics, vehicles, furniture or clothing enhanced the global demand of flame retardants (Alaee et al. 2003). Today, there are

175 chemicals classified as flame retardants (WHO 1997). Besides inorganic and nitrogen-based flame retardants, there is a major group of halogenated flame retardants in use. Among halogenated flame retardants, brominated flame retardants (BFRs) are the most important ones. This is particularly because of high efficiency of bromine in trapping free radicals produced during combustion processes and the low decomposition temperatures, compared to other halogens such as fluorine. Furthermore, bromines bound to organic carbons are characterized by a long-lasting stability during lifetime of the products as well as sufficient compatibility to the target polymer. This suitability of bromine results in more than 75 different aliphatic and aromatic BFRs (Alaee et al. 2003). Among BFRs, polybrominated diphenyl ethers (PBDEs) are widely applied as flame retardants. Beside their favourable properties as flame retardants, PBDEs are reported to be persistent in the environment, have low water solubility as well as high lipohilicy and tend therefore to accumulate in biota and sediments (De Wit 2002). Since they are simply blended to the product to be protected, they have a strong potential of being released throughout the lifecycle. The chemical structures of PBDEs consist of diphenyl ether molecules containing 10 hydrogen atoms, which can be exchanged with bromine to varying degrees. This results in 209 possible congeners. Due to structural similarities to polychlorinated diphenyl ethers (PCBs), the same nomenclature is used as introduced by Ballschmiter and Zell (1980). The majority of PBDEs were produced in three commercial formulations: pentaBDE, octaBDE and decaBDE. These three formulations contain varying proportions of the respective PBDE congeners. PBDE congeners analysed in this study (table 2) were selected according to the three commercial formulations and their main ingredients as suggested by Law et al. (2006).

Basically, musk is a naturally gland secretion of the male musk deer (Moschus moscherifus L.) that has been used as fragrance for centuries. Until the 19th century musk fragrances were completely obtained from those natural sources. However, since the 1950s musk compounds are almost completely of artificial origin (Sommer 2004). They have been used in various personal care products and household commodities, such as deodorants, shampoos, perfumes, detergents and washing powders. After their use they are predominantly discharged into the sewage system and can finally reach aquatic ecosystems. Due to their high lipophilicy, musk fragrances tend to accumulate in aquatic biota (Rimkus 1999). In general, musk fragrances can be divided in three substance classes (aromatic nitro musks, polycyclic musks and macrocyclic musk fragrances) that exhibit a common flavour, the distinct musk flavour. Nitro musks are two or three-folded nitrated benzenes that comprise alkyl-, keto- or methoxy moieties (Sommer 2004). Compared to the nitro musks, polycyclic musk fragrances are characterised by increased light and alkali resistance as well as the ability to adsorb to fabrics (Sommer 2004). The chemical structure of polycyclic musk fragrances consists of polycyclic properties in combination with several methyl groups and either an ether or a carbonyl oxygen. Due to these structures they are capable to form different stereoisomers which determine their odourous character. Macrocyclic musks contain at least 14 carbon atoms and are characterized by a ring structure. Due to high production costs their commercial importance is still limited. Therefore, this study focuses on the two main nitro musks, musk ketone (MK) and musk xylene (MX) as well as five polycyclic musks that are frequently used. Chemical structures are given table 3.

Table 1: Per- and polyfluorinated compounds analysed in this study

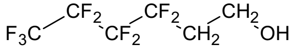
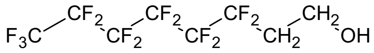
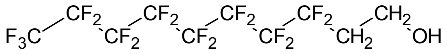
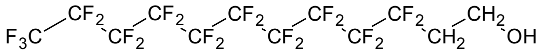
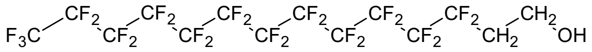
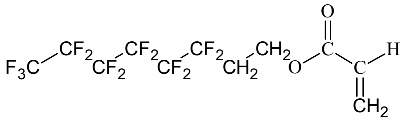
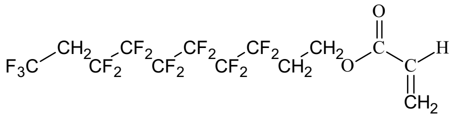
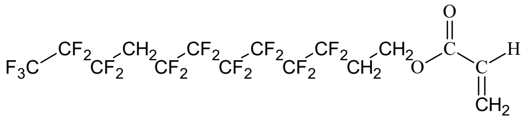
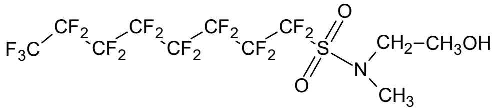
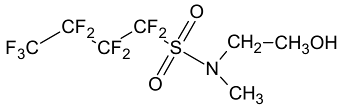
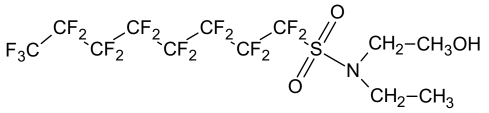
Analytes	Acronym	CAS-Nr.	Chemical structure
			Fluorotelomer alcohols (FTOHs)
4:2 fluorotelomer alcohol	4:2 FTOH	2043-47-2	
6:2 fluorotelomer alcohol	6:2 FTOH	647-42-7	
8:2 fluorotelomer alcohol	8:2 FTOH	678-39-7	
10:2 fluorotelomer alcohol	10:2 FTOH	865-86-1	
12:2 fluorotelomer alcohol	12:2 FTOH	3929-77-5	
			Fluorotelomer acrylates (FTAs)
6:2 fluorotelomer acrylate	6:2 FTA	17527-29-6	
8:2 fluorotelomer acrylate	8:2 FTA	27905-45-9	
10:2 fluorotelomer acrylate	10:2 FTA	17741-60-5	
			Perfluoroalkyl sulfonamido ethanols (FASEs)
N-methyl-perfluorooctane sulfonamido ethanol	MeFOSE	24448-09-7	
N-methyl-perfluorobutane sulfonamido ethanol	MeFBSE	34454-97-2	
N-ethyl-perfluorooctane sulfonamido ethanol	EtFOSE	1691-99-2	

Table 1 cont.

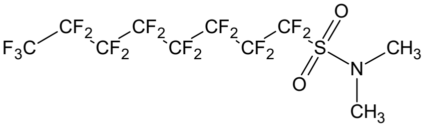
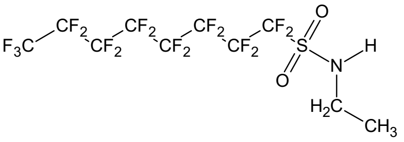
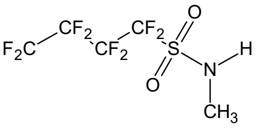
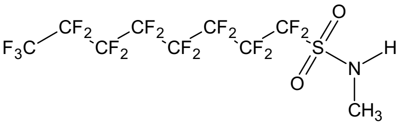
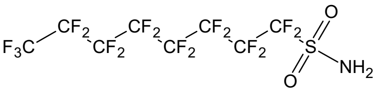
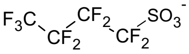
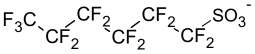
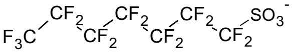
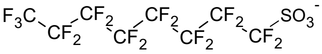
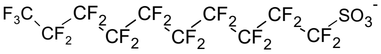
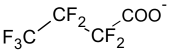
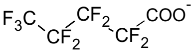
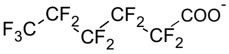
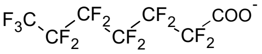
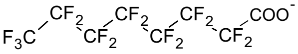
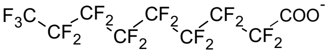
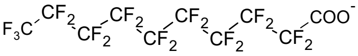
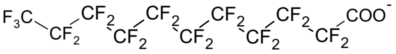
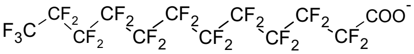
Analytes	Acronym	CAS-Nr.	Chemical structure
Perfluoroalkyl sulfonamides (FASAs)			
N,N-dimethyl-perfluoroocatane sulfonamide	Me_2FOSA	-	
N-ethyl-perfluorooctane sulfonamide	EtFOSA	4151-50-2	
N-methyl-perfluorobutane sulfonamide	MeFBSA	68298-12-4	
N-methyl-perfluorooctane sulfonamide	MeFOSA	31506-32-8	
perfluorooctane sulfonamide	PFOSA	754-91-6	
Perfluoroalkyl sulfonamides (PFSAs)			
perfluorobutane sulfonate	PFBS	29240-49-3	
perfluorohexane sulfonate	PFHxS	355-46-4	
perfluoroheptane sulfonate	PFHpS	-	
perfluorooctane sulfonate	PFOS	2795-39-3	
perfluorodecane sulfonate	PFDS	335-77-3	
Perfluoroalkyl carboxylates (PFCAs)			
perfluorobutanoate	PFBA	375-22-4	
perfluoropentanoate	PFPA	2706-90-3	
perfluorohexanoate	PFHxA	307-24-4	
perfluoroheptanoate	PFHpA	375-85-9	
perfluorooctanoate	PFOA	335-67-1	
perfluorononanoate	PFNA	375-95-1	
perfluorodecanoate	PFDA	335-76-2	
perfluorododecanoate	PFUnDA	2058-94-8	
perfluoroundecanoate	PFDoDA	307-55-1	

Table 2: Polybrominated diphenyl ethers analysed in this study

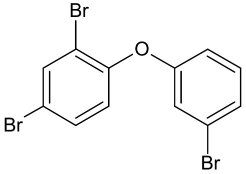
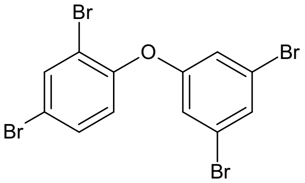
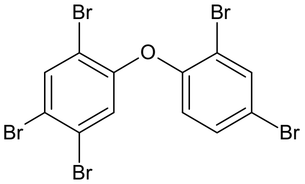
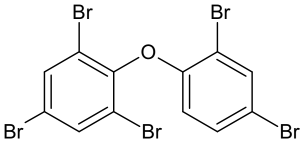
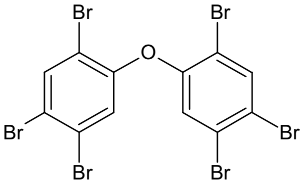
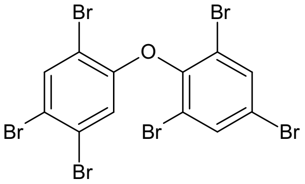
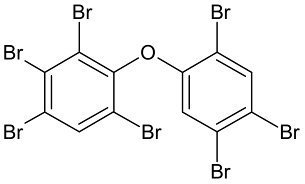
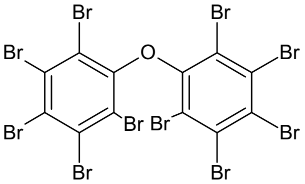
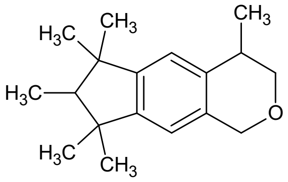
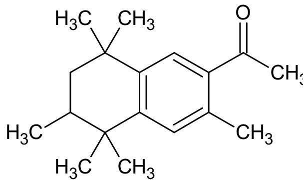
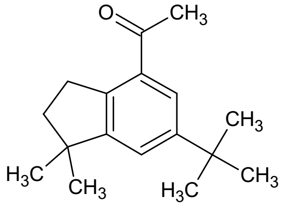
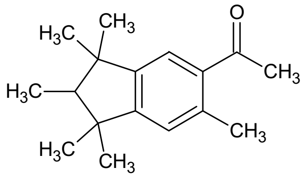
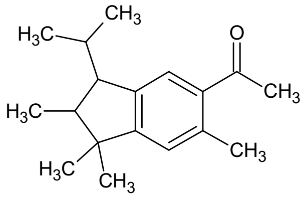
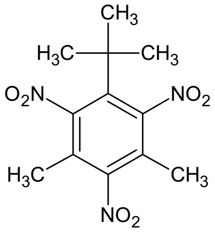
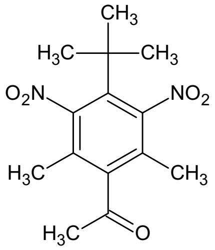
Analytes	Acronym	CAS-Nr.	Chemical structure
2,4,4'-tribromodiphenyl ether	BDE28	41318-75-6	
2,2',4,4'-tetrabromodiphenyl ether	BDE47	5436-43-1	
2,2',4,4',5-pentabromodiphenyl ether	BDE99	60348-60-9	
2,2',4,4',6-pentabromodiphenyl ether	BDE100	189084-64-8	
2,2',4,4',5,5'-hexabromodiphenyl ether	BDE153	68631-49-2	
2,2',4,4',5,6'-hexabromodiphenyl ether	BDE154	207122-15-4	
2,2',3,4,4',5',6-heptabromodiphenyl ether	BDE183	68928-80-3	
Decabromodiphenyl ether	BDE209	1163-19-5	

Table 3: Polycyclic musk fragrances and nitro musks analysed in this study

Analytes	Acronym	CAS-Nr.	Chemical structure
Polycyclic musks			
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(*γ*)-2-benzopyran, (Galaxolide®)	HHCB	1222-05-5	
7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-Tetrahydronaphthalene, (Tonalide®)	AHTN	1506-02-1	
4-acetyl-1,1-dimethyl-6-tert-butylindane, (Celestolide®)	ADBI	13171-00-1	
6-acetyl-1,1,2,3,3,5-hexamethylindane, (Phantolide®)	AHMI	15323-35-0	
5-Acetyl-1,1,2,6-tetrametyl-3-isopropyl-dihydroindene, (Traseolide®)	ATII	68140-48-7	
Nitro aromatic musks			
1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene, musk xylene	MX	81-15-2	
1-tert.-butyl-3,5-dimethyl-2,6-dinitro-4-acetyl-benzene, musk ketone	MK	81-14-1	

1.2 Production and use

Production of PFCs started in the late 1940s with the development of electro-chemical-fluorination (ECF) by J.H. Simons (Simons 1950). The process mechanism of ECF is rather unspecific and leads to various number of PFCs with chain lengths usually ranging between 4 to 13 carbon atoms as well as several by-products (Kissa 2001). Basic product within the ECF is the perfluorooctanesulfonyl fluoride (PSOF) which is used as intermediate for the production of other PFCs, such as PFSAs, FASAs and FASEs. Besides ECF, there is another important production process of PFCs: the telomerisation. It was invented by Hazeldine in 1947 and is applied since the 1960s (Kissa 2001; Hekster et al. 2002). Telomerisation results in linear carbon chains with even number of usually 4 to 14 carbon atoms (De Voogt et al. 2006). Typical products of telomerisation process are FTOHs, FTAs and PFCAs.

The application of PFCs implicate protection of products from grease and dirt, such as carpets, clothing and papers as well as the usage as surfactants and agents in aqueous fire-fighting foams (Hekster et al. 2002; Prevedouros et al. 2006). The different classes of PFCs can be attributed to various capabilities. PSOF-based PFCs were predominantly used in metal plating, photographics, floor polishes, lubricants, semi conductor production, galvanic processes, polymerisation emulsions and fire-fighting foams (Prevedouros et al. 2006). FASAs and FASEs were in most cases applied as additional agents in polymer-related proceedings or intermediates for other PSOF related PFCs (3M 1999). FTOHs are mainly applied to papers, food packaging and carpet treatment (Kissa 2001; Sinclair et al. 2007) as well as impregnating agents (Fiedler et al. 2008). FTAs are predominantly used within polymer-related processes (Van Zelm et al. 2008).

Specific data on production and use of PFCs are rather rare, since publication is incumbent on the producers them selves. However, there are several estimates available that quantified the manufacture and consumption of PFCs. Prevedouros et al. (2006) estimated the worldwide production of PFCAs to 4400-8000 t. Historical manufacture of PSOF-related PFCs were estimated with 122500 t, including unusable waste (Paul et al. 2009). In general, PFC production increased through the years with a PSOF production maximum in the 1990s. Due to the voluntarily phase-out of some PSOF-based products by the 3M Company, one of the main producer, in 2000, production declined since then (Paul et al. 2009). However, manufacture of PSOF-based PFCs is still going on and is estimated to be about 1000 t a^{-1} (Paul et al. 2009). Worldwide FTOH production reached 5000 t a^{-1} (Ellis et al. 2004). More recently, FTOH production was estimated to be 11000-14000 t a^{-1} (Dinglasan-Panlilio and

Mabury 2006). This increase is probably related to the withdrawal of PSOF-based products by the 3M Company (Stock et al. 2004).

Since the 1960s, PBDEs are produced by bromination of diphenyl ether in the presence of an Friedel-Craft catalyst in a solvent (Alaee et al. 2003). The bromination process is fairly specific due to the directing oxygen atom and steric hindrance, resulting in a limited number of PBDE congeners. Therefore, commercial formulations that are manufactured contain specified congeners of brominated diphenyl ethers (BDEs) (Rahman et al. 2001). Commercial pentaBDE mixture usually consists of BDE47 (24- 38 %), BDE82, BDE85, BDE99, BDE100 (50- 62 %), BDE153 and BDE154 (4-8 %). OctaBDE mixtures comprise congeners BDE153, BDE154 (10-12 %), BDE183 (43-44 %), octaBDE (31-35 %) and nonaBDE (9-11 %) as well as around 1 % of BDE209. In contrast, decaBDE is predominantly composed of BDE209 (97-98 %) with small amounts of nonaBDE (Darnerud et al. 2001).

In general, the use of PBDEs as flame retardants is in relation to their bromination level. PentaBDE mixtures are mainly added to polyurethane foams (PUF). PUF are applied to car interiors, carpets, furniture and pillows (Prevedouros et al. 2004). Furthermore, small amounts of pentaBDE have been applied to electronic housings, textiles and packaging. In contrast, highly brominated mixtures such as octa- and decaBDE are almost entirely used in dense thermoplastics, such as television and computer housings (Hale et al. 2002; Alaee et al. 2003). The worldwide consumption of PBDEs in 2001 was 67000 t (Watanabe 2003). DecaBDE accounted for 83 % whereas pentaBDE and octaBDE account for a smaller proportion with 12 % and 5 %, respectively (Watanabe 2003). In 2003, the production volume of decaBDE mixture was estimated to be 56000 t (Christiansson et al. 2009). The usage of PBDE products differ considerably between the continents. Compared to North America, Europe and Asia have rather low consumption of penta- and octaBDE mixtures (Kierkegaard et al. 2009). In contrast to PFCs, estimates on the historical production of PBDEs are very limited. However, Prevedouros et al. (2004) calculated the European production and consumption of pentaBDE from 1970 to 2000 between 3000 and 5000 t. Furthermore 9000 to10000 t were imported in finished products. Starting in 1980, consumption of pentaBDE increased rather constantly to 1200 t in the mid of the 1990s. From thereon, a rapid decline to about 200 t in 2000 was estimated. Overall, production in North America and Europe is about to decline, due to voluntary and restrictive phase-outs (see section 1.4.6) of octa- and pentaBDE (and partly decaBDE) (de Wit et al. 2009).

Synthetic musk fragrances were synthesized for the first time by Albert Bauer at the end of 19th century. His ongoing research with nitro organics lead to the invention of nitro musks such as MX and MK (Rowe 2005). Industrial production of polycyclic musk fragrances started in the late 1960s. They are manufactured by automated organic synthesis in either continuous or batch reactions processed in close systems.

Musk fragrances were manufactured because of their pleasant odour and their abilities to bind to fabrics. Thus, they are not only added to cosmetics but also to detergents (Rowe 2005). Musk fragrances are used in a variety of different household, sanitation and personal care products, such as detergents, lotions, perfumes, deodorants, shampoos and hair care products (Reiner and Kannan 2006; Roosens et al. 2007).

Over the past fifty years musk fragrances have been produced in increasing amounts (Hutter et al. 2009). Until the 1980s, nitro musks were predominantly produced due to their low production costs and intensive musk scent (Rowe 2005). Since 1980s, production rate of these compounds decline because of emerging health and environmental concerns (Sommer 2004). As substitutes polycyclic musks were produced with increasing volumes. In 1998 world wide production of polycyclic musks was 5600 t with HHCB and AHTN accounting for approximately 95 % (Rimkus 1999). According to the International Fragrance Association (IFRA), about 100 t nitro musks (MX 86 t, MK 40 t) and 1800 t polycyclic musks were used in Europe in 2000. Predominantly consumed polycyclic musks are HHCB (1427 t), followed by AHTN (359 t), AHMI (19 t), ADBI (18 t) and ATII (2 t) (OSPAR 2004).

1.3 Physico-chemical properties

Ionic and neutral PFCs, PBDEs and musk fragrances have considerably different physico-chemical properties that determine their partitioning behaviour in the environment. In general, those properties are determined by their functional groups within the molecule as well as carbon-fluorine chain lengths (PFCs) or bromine content (PBDEs). Physico-chemical constants of substances investigated in this study are presented in table 4.

The vapour pressures of PFSAs and PFCAs are generally low (Rayne and Forest 2009). In contrast, vapour pressures of neutral PFCs are more than 1000 times higher than those of ionic PFCs (Hekster et al. 2002; Rayne and Forest 2009). Vapour pressures of PBDEs are directly linked to the bromine content of the congener. Each additional bromine substitution causes a decline of vapour pressures by factors of 6-9 (Wong et al. 2001). Musk fragrances have comparable vapour pressures as FASEs. Therefore, neutral PFCs, BDE28 and BDE47 as well as musk fragrances are likely being transported as gaseous compounds in the atmosphere. Ionic PFCs and higher-brominated BDE congeners are not primarily expected in the gas phase, but atmospheric transport may still be possible if compounds adsorb to particles.

The water solubilities of ionic PFCs are several orders of magnitude higher than those of neutral PFCs. Solubility decreases with increasing chain length of the both neutral and ionic PFCs (Rayne and Forest 2009). In contrast, musk fragrances are fairly well soluble in water. It is assumed that PBDEs are not predominantly transported via the water phase, whereas musk fragrances are more likely entering aqueous media (Rimkus 1999; Wania and Dugani 2003). Ionic PFCs are predominantly dissolved in the aqueous phase and/or bound to particles (especially long-chained PFSAs) (Rayne and Forest 2009).

Polycyclic musk fragrances and FTOHs have relatively high Henry's law constants that exceed those of PBDEs and nitro musks. For PBDEs, the tendency to volatilize from the water phase is influenced by the degree of bromination (Wong et al. 2001). In contrast to FTOHs, ionic PFCs have lower Henry constants (OECD 2002). Overall, it can be concluded that particularly FTOHs and polycyclic musk fragrances may volatilize from the aqueous phase to the atmosphere, whereas PBDEs and ionic PFCs rather partition to the water phases.

It has been reported that K_{OA} values for PBDEs, FTOHs, FASAs and FASEs are increasing with decreasing of temperatures (Harner and Shoeib 2002; Thuens et al. 2008; Dreyer et al. 2009a). Particularly highly brominated congeners are expected in the particle phase (Harner and Shoeib 2002). For musk fragrances K_{OA} values have not yet been reported. However, several studies observed those compounds predominantly in the gas phase (Peck and Hornbuckle 2004; Xie et al. 2007).

A substance is bioaccumulative with a log K_{OW} value greater than 5 (UNEP 2010). On the basis of this criterion, almost all substances of this study are assumed to be bioaccumulative. Due to the amphipilic character of ionic PFCs it is not possible to determine their K_{OW}. However, their potential of bioaccumulation has been demonstrated (Conder et al. 2008).

Table 4: Physico-chemical properties of semi-volatile and volatile PFCs, PBDEs and musk fragrances analysed in this study. MW: molecular weight, MP: melting point, VP: vapor pressure, K_{OW}: octanol-water partition coefficient, K_{OA}: octanol-air partition coefficient, S_W: water solubility, k_H: Henry's law constant.

Analyte	MW ($g\ mol^{-1}$)	MP (°C)	VP at 25 °C (Pa)	log K_{OW} at 25 °C	log K_{OA} at 25 °C	S_W ($mg\ L^{-1}$)	k_H ($Pa\ m^3\ mol^{-1}$)
Per- and polyfluorinated compounds (PFCs)							
4:2 FTOH	264	-	252^{1}	3.28^{2}	4.57^{4}	974^{5}	174^{1}
6:2 FTOH	364	-	145.2^{1}	4.7^{2}	4.84^{4}	18.8^{5}	240^{1}
8:2 FTOH	464	-	45.9^{1}	6.14^{2}	5.58^{4}	0.194^{23}	650^{1}
10:2 FTOH	564	-	13.27^{1}	7.57^{2}	5.71^{4}	0.006^{5}	-
12:2 FTOH	664	-	-	-	6.2^{4}	-	-
6:2 FTA	418	-	-	-	4.4^{3}	-	-
8:2 FTA	518	-	-	-	5.2^{3}	-	-
10:2 FTA	618	-	-	-	5.7^{3}	-	-
Me2FOSA	527	-	-	-	-	-	-
EtFOSA	527	-	-	-	6.6^{3}	-	-
MeFBSA	313	-	-	-	-	-	-
MeFOSA	513	-	-	-	6.3^{3}	-	-
PFOSA	499	-	-	-	-	-	-
EtFOSA	527	-	2.38^{1}	-	-	-	-
MeFOSE	557	-	0.33^{1}	-	6.4^{3}	-	-
MeFBSE	357	-	-	-	-	-	-
EtFOSE	571	-	0.19^{1}	-	6.7^{3}	-	-
Polybrominated Diphenyl Ethers (PBDEs)							
BDE28	407	$64\text{-}64.5^{6}$	0.0016^{7}	5.94^{8}	9.5^{13}	0.07^{6}	4.83^{11}
BDE47	486	78.75^{9}	0.00025^{7}	6.81^{8}	10.53^{13}	0.0146^{10}	0.85^{11}
BDE99	565	92.3^{12}	0.000018^{7}	7.32^{8}	11.31^{13}	0.009^{6}	0.6^{11}
BDE100	565	97^{9}	0.00005^{7}	7.24^{8}	11.31^{13}	0.00786^{10}	0.24^{11}
BDE153	644	$160\text{-}163^{6}$	0.0000058^{7}	7.9^{8}	11.82^{13}	0.001^{6}	0.26^{11}
BDE154	644	142^{9}	0.0000034^{6}	7.82^{8}	11.92^{13}	0.001^{6}	0.08^{11}
BDE183	722	$171\text{-}173^{6}$	$0.0000066\ (21\ °C)^{16}$	8.27^{8}	11.96^{13}	0.0005^{16}	0.0074^{6}
BDE209	960	$300\text{-}310^{14}$	$0.0000046\ (21\ °C)^{14}$	8.7^{15}	15.27^{22}	$<0.0001^{14}$	0.04^{11}
Musk Fragrances							
HHCB	258	-57.9^{17}	0.0727^{18}	5.9^{18}	-	1.75^{19}	11.3^{18}
AHTN	258	54.5^{18}	0.0682^{18}	5.7^{18}	-	1.25^{20}	12.5^{18}
ADBI	244	77.9^{18}	0.0192^{18}	5.4^{20}	-	0.22^{18}	1801^{17}
AHMI	244	61.5^{18}	0.132^{20}	4.9^{20}	-	0.027^{24}	646^{17}
ATII	258	-127.3^{17}	0.0091^{18}	5.4^{20}	-	0.085^{24}	85.1^{17}
MX	297	114^{21}	0.00003^{20}	4.3^{20}	-	0.15^{20}	0.018^{21}
MK	294	137^{21}	0.00004^{20}	4.9^{20}	-	0.46^{20}	0.0061^{21}

^{1}Lei et al. (2004), ^{2}Arp et al. (2006), ^{3}Dreyer et al. (2009a), ^{4}Thuens et al. (2008), ^{5} Liu and Lee (2007), ^{6}Tittlmeier et al. (2002), ^{7}Wong et al. (2001), ^{8}Braekevelt et al. (2003) , ^{9}Marsh et al. (1999), ^{10}Palm et al. (2002), ^{11}Cetin and Odabasi (2005), ^{12}Örn et al. (1996), ^{13}Harner and Shoeib (2002), ^{14}EU (2002), ^{15}Hardy (2002), ^{16}EU (2003), ^{17}Paasivirta et al. (2002), ^{18}Balk and Ford (1999), ^{19}Van de Plassche and Balk (1997), ^{20}OSPAR (2004), ^{21}Tas et al. (1997), ^{22}Wania and Dugani (2003), ^{23}Liu and Lee (2005), ^{24}Peck and Hornbuckle (2004)

1.4 Environmental concerns

1.4.1 Persistence

On the basis of today's knowledge, ionic PFCs are not degradable in the environment (Hekster et al. 2002). Due to its strong carbon-fluorine bond PFCAs and PFSAs are resistant against oxidants, reductants, acids, bases, photolysis and metabolic processes (Schultz et al. 2003). In contrast, neutral PFCs are subject to biodegradation and atmospheric degradation (Jensen et al. 2008). Metabolic transformation of FTOHs and FASAs to PFCAs and PFSAs was observed in various studies (Dinglasan et al. 2004; Wang et al. 2009). Atmospheric degradation by OH radical of neutral PFCs to persistent PFCAs and PFSAs was demonstrated in several studies under laboratory conditions, mainly using smog chambers (Ellis et al. 2004; Sulbaek Andersen et al. 2005; D'Eon et al. 2006; Martin et al .2006). In contrast to neutral PFCs, ionic PFCs are removed from the atmosphere via dry and wet deposition (Hurley et al. 2003; Dreyer et al. 2010). On the basis of these processes, neutral PFCs are often named as "precursor compounds" for persistent ionic PFCs.

Although it is often concluded that PBDE degradation is negligible and a rather slow process (Vonderheide et al. 2008), photochemical and biological degradation in air, water, soils, sediments and house dust have been reported (Eriksson et al. 2004; Gerecke et al. 2005; He et al. 2006; Vonderheide et al. 2006). It is reported that photolysis is the predominant PBDE degradation mechanism. For example, Raff and Hites (2007) estimated that about 90 % of low molecular weight PBDEs are removed from the atmosphere by this process, whereas BDE209 is predominantly subject to wet and dry deposition. Nevertheless, the completely brominated BDE209 is regarded as remarkable photolabile and tends to form lighter PBDEs in various environmental compartments (Christiansson et al. 2009; Söderström et al. 2004; La Guardia et al. 2007). Schenker et al. (2008b) estimated that about 50 % of the hexa- and heptaBDE homologues in the environment originate from the debromination of decaBDE. However, the contribution for tetra- and pentaBDE is distinctly lower. Moreover, oxidation of OH radicals may also be of importance (Ueno et al. 2008). So far, there are two groups of PBDE degradation products known. The first one are methoxylated PBDEs (MeO-PBDEs), that have been detected in various marine biota, such as fish (Sinkkonen et al. 2004) and sea lions (Stapleton et al. 2006). However, MeO-PBDEs can also have natural origin (Teuten et al. 2005). The second degradation products are hydroxylated PBDEs (OH-PBDEs), that have recently been detected at elevated concentrations in surface water near to a WWTP (Ueno et al. 2008). It is suggested that these degradation products mainly originated from reactions with OH radicals (Ueno et al. 2008).

For musk fragrances, data on the degradation potential and products are rather limited in comparison to PFCs and PBDEs. However, a risk assessment of both nitro musks and polycyclic musks HHCB and AHTN revealed that they can be biotransformed in activated sludge and fish as well as by abiotic factors such as UV radiation and the reaction with OH radicals (OSPAR 2004). The main MX and MK degradation mechanism is the reduction of nitro-moieties resulting to amino-metabolites (Peck 2006). Biotransformation of polycyclic HHCB and AHTN occurs in fungi through hydroxylation at different carbon positions (Martin et al. 2007). Most investigated degradation product is the HHCB-lactone that was reported to be formed during waste water treatment (Bester 2004; Kupper et al. 2004; Bester 2005).

Several studies examined the atmospheric lifetimes of PFCs, PBDEs and musk fragrances using smog chamber experiments or modelling approaches. FASEs and FTAs were reported to have a lifetime of about one to two days in the atmosphere (D'Eon et al. 2006; Butt et al. 2009). In contrast, FTOHs and FASAs are much more stable in air and they degrade within approximately 20 days (Ellis et al. 2004). However, estimates from field measurements of Dreyer et al. (2009c) and Piekarz et al. (2007) indicated residence times of FTOHs to be even longer. Raff and Hites (2007) calculated atmospheric lifetimes of gas-phase PBDEs ranging from 0.1 h (BDE209) to more than 20 h to for congeners with 1-2 bromines. In the gas phase, reactivity to photolysis increased with increasing bromine content, whereas OH radical reactivity followed the opposite trend (Raff and Hites 2007). Lifetimes of particle-associated lower brominated congeners, such as BDE47 and BDE99, are estimated to be below 12 h whereas the lifetime of BDE209 is higher than 2 days (Raff and Hites 2007). The overall atmospheric lifetime, including wet and dry deposition, of particle-bound PBDEs is estimated to be less than one day (Raff and Hites 2007). Regarding musk fragrances, only one study has been published on the atmospheric lifetimes (Aschmann et al. 2001). In this experimental approach HHCB is predominantly degraded by OH radical and not by photolysis with an atmospheric lifetime of 5.3 h.

1.4.2 Bioaccumulation

In recent years, various biomonitoring studies around the globe have been conducted on the bioaccumulation potential of PFCs, PBDEs and musk fragrances (Yamagishi et al. 1981; Yamagishi et al. 1983; Draisci et al. 1998; Allchin et al. 1999; Franke et al. 1999; Fromme et al. 1999; Gatermann et al. 1999; She et al. 2002; Rayne et al. 2004; Smithwick et al. 2005;

Chen et al. 2007a; Hart et al. 2008; Löfstrand et al. 2008; Ahrens et al. 2009d; Hutter et al. 2009; Kelly et al. 2009). However, for musk fragrances the availability of biomonitoring data is rather limited compared to the other substance classes.

Bioaccumulation and bioconcentration of PFCs are directly connected to the carbon chain length and increase with increasing number of fluorinated carbons (Conder et al. 2008). PFSAs are more bioaccumulative than its corresponding PFCAs of same chain length (Houde et al. 2006) PFCAs with chain length shorter than eight carbons are reported not to be bioaccumulative according to current regulatory criteria (Conder et al. 2008). The potential for bioaccumulation of PBDEs is directly linked to the size of the molecule. Therefore, lower brominated congeners (four to seven bromines) are more bioaccumulative with bioconcentration factors of higher than 5000 (Birnbaum and Staskal 2004). BDE209 has only limited bioavailability (De Wit 2002).

Whereas, PBDEs and musk fragrances accumulate primarily in fatty tissues of animals and humans, PFCs are stored in protein-rich repositories such as liver, gall bladder and blood proteins (Hites 2004; Conder et al. 2008). For example, concentrations of PFOS and PFOA in liver from Artic polar bears ranged from 263-6340 and 2-9 ng g^{-1}, respectively (Smithwick et al. 2005). PBDEs were recently detected in adipose tissue of polar bears from various arctic locations and ranged from 2.91-132 ng g^{-1} dominated by BDE47 (Muir et al. 2005). Kannan et al. (2005) observed polycyclic musk HHCB between 4 and 25 ng g^{-1} in the blubbers of dolphins and whales.

Half-life time of PFOS in monkeys is reported to be 150 days, whereas that of PFOA was 30 and 21 days for female and male, respectively (Lau et al. 2007). Half-lives in rats of commercial pentaBDE congeners were determined between 19-105 days and were increasing with increased degree of bromination (Birnbaum and Cohen Hubal 2006). MX has a calculated half-life time in humans of 100 days (Kokot-Helbling et al. 1995). In fish they are rather short (3 d for MX and MK) (Tas et al. 1997).

Furthermore, PFCs and PBDEs were reported to accumulate in the marine food web with significant increases towards higher trophic levels (Sørmo et al. 2006; Kelly et al. 2009). In contrast, biomagnification of musk fragrances to higher trophic levels was less pronounced (Kannan et al. 2005; Nakata 2005).

1.4.3 Toxicity

PFCs, PBDEs and musk fragrances are subject to various toxicologically effects in humans and animals. In general, acute toxicities of PFCs are moderate but increase with chain-length

(Lau et al. 2007). In animal studies mainly on PFOS and PFOA, it was observed that PFCs induce a number of adverse effects. PFOS and PFOA were reported to cause increased liver weight and hepatocytic hypertrophies (Kennedy et al. 2004). Favoured by their molecular structure those substances were observed to bind to proteins in cell membranes, where they influence the fluidity of the membranes (Hu et al. 2003). Although not genotoxic, PFOS and PFOA promoted tumour growth in rats (Roos et al. 2008). Some PFCs, e.g. 6:2 and 8:2 FTOH induce breast cancer proliferation probably because of biodegradation to PFCAs (Jensen and Leffers 2008). In addition, PFCs can act as endocrine disruptors (Jensen and Leffers 2008). On the basis of experimental approaches with test animals, the impact on human health was assessed. The risks for the general population are expected to be low (Fromme et al. 2006). However, Fromme et al. (2006) reported that that elevated occupational exposure can be within the magnitude of toxicological relevant concentrations.

There is growing concern about the toxicology of PBDEs because of their structural similarities to other polyhalogenated aromatic hydrocarbons, such as polychlorinated biphenyls and dioxins. Although, some PBDEs have comparable structures, they are not supposed to be dioxin-like (Birnbaum et al. 2006). Although, congener specific data is still lacking, PBDE toxicity depends on the bromine content of the respective congeners. Toxicity decreases in the order of pentaBDE> octaBDE> decaBDE (Darnerud et al. 2001). Acute toxicities for all PBDE congeners are reported to be low (Hardy 2002). There is no evidence on BDE209 carcinogenicity as well as effects on reproduction and development in rats, probably because 99 % of this congener is rapidly discreted by faeces (Hardy 2002). In contrast, octa- and pentaBDE were well absorbed and only slowly eliminated. They are expected to be carcinogenic and exposure has been linked to tumour formation, but clear evidence has not been published yet (Vonderheide et al. 2008). Penta- and octaBDE mixtures are reported to have thyroid-disrupting properties which are likely due to structural similarities to the endogenous hormones (Vonderheide et al. 2008). PentaBDE have also been perceived to interfere the sexual and fetal development as well as the ability for reproduction in males (Stoker et al. 2005; Lilienthal et al. 2006).

Toxicological studies on musk fragrances revealed no severe health risks for aquatic organisms since environmental concentration are under the threshold for acute or chronic toxicity (Tas et al. 1997; Balk and Ford 1999; HERA 2004; Gooding et al. 2006). Nevertheless, nitro musks MK and MX are reported to induce toxifying liver enzymes in mice and rats and can therefore act as a cogenotoxicants (Mersch-Sundermann et al. 1996). Both, nitro musks and polycyclic musk are inhibitors for efflux transport proteins that normally prevent xenobiotica from entering the cell (Luckenbach et al. 2004; Luckenbach and Epel 2005) resulting in increased accumulation of musk fragrances. Recently, a study of Schnell et al. (2009) demonstrated that musk fragrances can inhibit the catalytic activities of several xenobiotica-metabolizing enzymes. Furthermore, it was demonstrated that especially polycyclic musks are endocrine active substances (Bitsch et al. 2002; Schreurs et al. 2004). Although, there is clear evidence that musk fragrances occur in human blood (Hutter et al. 2005; Hutter et al. 2009), adipose tissue (Rimkus et al. 1994) and breast milk (Lignell et al. 2008; Reiner et al. 2007), there is still a lack on toxicological data for humans.

1.4.4 Policies and regulation

In recent years, PFCs, PBDEs and musk fragrances were reported to have risk-entailing properties. This created awareness to political stakeholders as well as producers limiting the environmental risk as well as human impact of those compounds. Special attention was raised to PFCs, particularly to PFOS and PFOA, and PBDEs due to their extraordinary persistence, bioaccumulation potential and toxic properties. Regarding musk fragrances, only nitro musks are subject to fortified restrictions.

3M, the main producer of PFOS, has voluntarily phased-out its production of PFOS-based chemistry from 2000 till 2002. This is regarded as remarkable step in regulation of PFCs and marking the starting point for other legislative actions (see below). Furthermore, all major producers have joined a global PFOA stewardship program which claims to reduce production PFOA and PFOA-related PFCs as well as their elimination in 2015 (USEPA 2006). Additionally, PFOS and PFOA were replaced by shorter chained PFCs which are not supposed to be bioaccumulative but are still persistent (3M 2002; Hekster et al. 2002).

In 2004, production of penta- and octaBDE were voluntarily stopped in USA, whereas decaBDE production is still going on since this mixture is less toxic and bioaccumulative than its lower brominated counterparts (Vonderheide et al. 2008). Starting from 1983, with the first detections of nitro musks in fish and health concerns, fragrances industry was replacing these compounds by polycyclic musks (Sommer 2004).

Besides voluntary production stops, various efforts were made on legal actions on international and domestic levels. The United Nations Stockholm convention on persistent organic pollutants is an international treaty that forces the member states to take legal action on the application, productions and elimination of persistent organic pollutants (POP). Since 2009, penta- and octaBDE are listed in the Annex A of the convention. This means that member states must take measures to eliminate the production and use of such substances. At the same time, PFOS was listed under Annex B, that claims to reduce unintentional releases, minimisation and, when feasible, the elimination of those chemicals (UNEP 2010). Since 2001, the Oslo Paris Commission (OSPAR) set out a list of priority action for substances with emerging concern for the marine environment of the North-Atlantic. Among the 315 substances, PFOS, PBDEs and MX are listed (OSPAR 2007).

The European Community prohibited the marketing and use of PFOS as well as of PFOS containing preparations (EC 2006). However, exceptions are industrial processes where substitution is not available. The phase-out of PFOA is still under discussion. According to the European Commission (EC) the use and marketing of penta- and octaBDE was banned in 2004 (EC 2003). Additionally, articles are not to be placed on the market if they contain more as 0.1 % in mass of those compounds. In contrast, decaBDE was excluded from this directive, e.g. for their essential role in fire safety in electronic housings. However, Sweden and Norway introduced a complete ban of decaBDE in all products entering the respective country (Kemmlein et al. 2009). Currently, there are not any regulations for polycyclic musk fragrances in the EU. However, after risk assessment of MK and MX, European Commission banned the use of those compounds from almost all cosmetics (EC 2004).

Regarding regulation in Germany, the target state of surface waters is estimated with 0.5 $\mu g\ L^{-1}$ of pentaBDE mixture (UBA 2006a). According to the German Federal Environmental Agency (UBA) a health based precautionally value for PFOS and PFOA in drinking water is suggested with 0.1 $\mu g\ L^{-1}$ (UBA 2006b). For musk fragrances national regulations are not available.

1.4.5 Transport in the environment

Long-range transport via the atmosphere and/or water phase was indicated by numerous studies for all substance classes investigated in this thesis (Oros et al. 2005; Wang et al. 2005; Wurl et al. 2006; Stock et al. 2007; Su et al. 2007; Wei et al. 2007; Xie et al. 2007; Yamashita et al. 2008; Ahrens et al. 2009a; Ahrens et al. 2009b; Dreyer et al. 2009c; Sumner et al. 2010). However, transport mechanism can differ considerably for the different compound classes.

PFCs are being transported according to their chain lengths and functional groups. The primary transport pathway of ionic PFCs, preferably those with less than ten carbon atoms, occurs via the water phase (Wania 2007). However, ionic PFCs may also leave the water body through aerosol formation (McMurdo et al. 2008) or are deposited from the atmosphere (Scott et al. 2006). In contrast, neutral precursors such as FTOHs, FTAs, FASAs and FASEs are primarily transported via the atmosphere (Shoeib et al. 2006; Stock et al. 2007; Dreyer et al. 2009c) and being degraded to persistent ionic PFCs such as PFOS and PFOA (Ellis et al. 2004; Lei et al. 2004; Stock et al. 2007; Schenker et al. 2008a). A selection of typical gas-phase concentration is given in table 5. The contribution of atmospheric PFCAs and PFSAs to is rather limited since air concentrations are low (Dreyer et al. 2009b) and those compounds are rapidly wash-out (Kim and Kannan 2007). Regarding the relevance for long-range transport to remote regions such as the Arctic and Antarctica, the contribution of precursor degradation to the sum of PFCAs and PFSAs is still under discussion. Some authors conclude that this pathway is subordinate (Prevedouros et al. 2006; Wania 2007). However, findings at areas that experience their contamination solely from the atmospheric sources such as polar ice caps (Young et al. 2007) and lake water of remote mountains (Loewen et al. 2008) revealed the importance for their occurrence in pristine regions.

The transport for individual PBDEs is basically driven by their bromine content. Highly brominated PBDEs in the water phase are primarily associated to suspended matter (XiaoJun et al. 2007) and subsequently sedimented (De Wit et al. 2006). In the atmosphere, they are more likely adsorbed to aerosols (Gouin et al. 2005). Since the half-life times of particle-bound PBDEs are rather short (see section 1.4.1), they are rapidly deposited from the atmosphere (Wania and Dugani 2003; Raff and Hites 2007). In contrast, lower brominated congeners, such as BDE47 reside predominantly in the gas phase and are more mobile in the water phase (Palm et al. 2002; Watanabe 2003). Numerous studies revealed the ubiquitous occurrence of PBDEs in the atmosphere even in remote regions (Su et al. 2007; Wang et al. 2007; Bossi et al. 2008a; Noël et al. 2009). Table 6 presents exemplary air concentrations in gas- and particle phase.

The water phase is the major pathway for the release of musk fragrances in the environment (Heberer 2002). They have been detected in WWTP effluents (Simonich et al. 2000; Zeng et al. 2007), adjacent rivers (Osemwengie and Gerstenberger 2004; Bester 2005) and coastal waters (Rimkus 1995; Bester et al. 1998; Sumner et al. 2010). Furthermore, several studies revealed that musk fragrances are reported to be transported via the atmosphere (Table 7). In spite of these detections in water and the atmosphere, there is currently little evidence for long-range transport due to their short half-lives in water (Buerge et al. 2003) and atmosphere (Aschmann et al. 2001). Nevertheless, Xie and Ebinghaus (2008) detected HHCB and AHTN in the atmosphere and water phase in the Arctic revealing that they may have potential for long-range transport. However, there is currently limited data available in order to evaluate this issue sufficiently.

Table 5: Selection of neutral PFC concentrations (pg m^{-3}) frequently detected in ambient air (gas-phase)

Source	Location	Description	n	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$_2$FOSA	EtFOSA	MeFBSA	MeFOSA	PFOSA	MeFOSE	MeFBSE	EtFOSE
Shoeib et al. (2006)	Canadian Arctic	remote	20	n.a.	3	11	6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2	n.a.	1
	Toronto, Canada	urban	3	n.a.	18	40	21	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	8	n.a.	2
Barber et al. (2007)	Hazelrigg, UK (spring)	semi-rural	2	57	81	102	75	n.a.	n.a.	n.a.	n.a.	n.a.	8	n.a.	6	n.a.	24	n.a.	9
	Manchester, UK (spring)	urban	2	3	187	237	65	n.a.	n.a.	n.a.	n.a.	n.a.	10	n.a.	6	n.a.	24	n.a.	6
	Mace Head, Ireland (spring)	rural	4	1	5	11	8	<25	n.a.	n.a.	n.a.	n.a.	<2	<1	<5	n.a.	<80	<15	<52
	Kjeller, Norway (fall)	rural	1	<1	12	34	17	n.a.	n.a.	n.a.	n.a.	n.a.	5	n.a.	6	n.a.	49	n.a.	30
	Hazelrigg, UK (fall)	semi-rural	10	26	32	67	21	8	n.a.	n.a.	n.a.	n.a.	<4	<1	<5	n.a.	<54	<3	<66
	Manchester, UK (fall)	urban	2	<16	61	237	62	21	n.a.	n.a.	n.a.	n.a.	<4	<1	<5	n.a.	<54	<3	<2
Jahnke et al. (2007)	Hamburg, Germany	urban	7	54	66	119	35	n.a.	n.a.	n.a.	n.a.	n.a.	3	n.a.	9	n.a.	30	n.a.	8
	Waldhof, Germany	rural	4	19	64	75	23	n.a.	n.a.	n.a.	n.a.	n.a.	3	n.a.	7	n.a.	7	n.a.	11
Piekarz et al. (2007)	Mount Bachelor, USA	remote	34	n.a.	5	24	15	n.a.	n.a.	n.a.	n.a.	n.a.	<3	n.a.	n.a.	n.a.	<11	n.a.	<4
Dreyer and Ebinghaus (2009)	North Sea, Germany	ocean	7	2	8	37	9	27	5	4	2	<1	1	5	3	4	2	1	<1
Oono et al. (2008)	Japan	variable	19	n.a.	18	90	19	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Dreyer et al. (2009b)	Barsbüttel, Germany	semi-rural	117	<1	22	62	21	13	2	4	3	1	1	3	3	1	2	3	1
	Geesthacht, Germany	semi-rural	121	<1	23	50	21	16	2	3	3	1	2	4	3	2	2	2	1
Dreyer et al. (2009c)	Baltic Sea	ocean	24	n.d.	11	29	10	3	1	1	<1	1	2	2	2	n.d.	2	1	1
	European Artic	ocean	3	n.d.	18	11	2	1	1	<1	<1	n.d.	n.d.	1	1	n.d.	1	<1	<1
	Atlantic (France, Spain)	ocean	5	n.d.	14	24	7	7	5	2	n.d.	1	2	2	3	n.d.	2	1	1
	Atlantic (North Africa)	ocean	6	n.d.	7	40	15	10	4	4	2	<1	13	3	4	9	4	3	3
	Atlantic (West/ Africa)	ocean	29	n.d.	3	9	4	4	3	1	1	n.d.	1	1	1	n.d.	2	2	2
	Atlantic (South America)	ocean	3	n.d.	4	16	11	3	3	4	n.d.	n.d.	1	1	1	n.d.	10	9	1
	South Africa/Antarctica	ocean	14	n.d.	1	6	2	<1	<1	<1	<1	n.d.	<1	<1	1	n.d.	1	<1	<1

Table 6: Selection of PBDE concentrations (pg m^{-3}) frequently detected in ambient air. C(g): concentration gas phase, C(p): concentration particle phase

Source	Location	Description	n	BDE28		BDE47		BDE99		BDE100		BDE153		BDE154		BDE183		BDE209	
				C(g)	C(p)	C(g)	C(p)	C(g)	C(p)	C(g)	C(p)	C(g)	C(p)	C(g)	C(p)	C(g)	C(p)	C(g)	C(p)
Agrell et al. (2004)	Malmö, Sweden	urban[b]	17[a]	0.4	-	2.3	-	3	-	1.4	-	0.3	-	0.2	-	0.2	-	20.3	-
	Malmö, Sweden	urban[b]	19[a]	0.3	-	1.6	-	2.1	-	0.8	-	0.1	-	0.2	-	0.1	-	39.6	-
Jaward et al. (2004a)	Europe	mixed	71	0.3	n.a.	2.9	n.a.	4.2	n.a.	0.8	n.a.	0.4	n.a.	0.3	n.a.	5.5	n.a.	n.a.	n.a.
	Germany	mixed	3	0.11	n.a.	<1	n.a.	n.d.	n.a.	<0.3	n.a.	0.12	n.a.	<0.1	n.a.	n.a.	n.a.	n.a.	n.a.
Lee et al. (2004)	Hazelrigg, UK	rural	43[a]	0.49	-	5.2	-	2.7	-	0.74	-	0.31	-	0.2	-	n.a.	n.a.	n.a.	n.a.
Hoh and Hites (2005)	Lake Michigan, USA	remote	35[a]	n.a.	-	6.2	-	5.1	-	1.1	-	n.a.	-	n.a.	-	n.a.	-	3.6	-
	Chicago, USA	urban	28[a]	n.a.	-	17.4	-	7.4	-	1.8	-	n.a.	-	n.a.	-	n.a.	-	60.1	-
	Bloomington, USA	semi-urban	38[a]	n.a.	-	7	-	5.1	-	1	-	n.a.	-	n.a.	-	n.a.	-	3.2	-
	Rohwer, USA	rural	30[a]	n.a.	-	9.2	-	5.4	-	1.2	-	n.a.	-	n.a.	-	n.a.	-	11.7	-
	Cocodrie, USA	remote	26[a]	n.a.	-	6.9	-	3	-	0.7	-	n.a.	-	n.a.	-	n.a.	-	4	-
Chen et al. (2006)	Guangzhou, China	urban	8	13.5	0.5	23.4	5.8	8.3	13	1.6	1.4	0.9	5.1	0.8	2.1	n.d.	4.5	n.d.	264
	Baiyun Mountain, China	rural	8	10.9	0.4	25.6	3.5	28.3	7.3	4.6	0.9	28.3	4.4	2.3	1.6	0.2	4.1	n.d.	478
	Chilton, UK	semi-rural	43[a]	0.69	-	2.6	-	3.5	-	0.61	-	0.38	-	0.9	-	n.a.	n.a.	n.a.	n.a.
	Mace Head, Ireland	remote	25[a]	0.09	-	1.1	-	0.75	-	0.2	-	0.1	-	0.08	-	n.a.	n.a.	n.a.	n.a.
Su et al. (2007)	Canadian Artic	remote	104[a]	0.18	-	2.5	-	2.4	-	0.45	-	0.17	-	0.17	-	0.15	-	1.6	-
Bossi et al. (2008a)	Nuuk, Greenland	remote	11[a]	0.05	-	0.46	-	0.36	-	0.08	-	0.05	-	0.03	-	0.02	-	n.a.	n.a.
St-Amand et al. (2008)	Ottawa, Canada	urban[c]	140	0.16	0.06	0.78	1.24	0.42	2.34	n.a.	n.a.	0.03	o.48	n.a.	n.a.	n.a.	n.a.	n.d.	12.74

[a] gas and particle phase not analysed separately, [b] nearby a waste incineration plant, [c] nearby a sanitary landfill

Table 7: Selection of polycyclic- and nitro musks concentrations (ng m^{-3}) frequently detected in ambient air (gas-phase)

Source	Location	Description	n	HHCB	AHTN	ADBI	AHMI	ATII	MX	MK
Kallenborn et al. (1999b)	Kjeller, Norway	Semi-urban	4	0.145	0.052	n.a.	n.a.	0.01	0.05	0.04
Peck and Hornbuckle. (2004)	Milwaukee, USA	Urban	26	4.1	2.5	0.19	0.24	0.17	0.03	0.09
	Lake Michigan, USA	Urban	11	1.1	0.49	0.042	0.039	0.04	n.d.	n.d.
Peck and Hornbuckle (2006).	Hills, USA	Rural	41	0.036^{e}	0.032^{e}	0.01^{e}	n.q. ^{e}	n.q.	0.02^{e}	n.d.
	Iowa City, USA	Urban	85	0.13^{e}	0.1^{e}	n.a.	n.a.	n.q.	n.d.	n.d.
	Cedar Rapids, USA	Urban	10	0.8^{e}	0.33^{e}	0.1^{e}	n.a^{e}.	n.q.	n.d.	n.d.
	Lake Erie, USA	Rural	5	0.12^{e}	0.15^{e}	n.q.	n.a.	n.q.	n.d.	n.d.
	Lake Ontario, USA	Rural	3	0.37^{e}	0.16^{e}	n.q.	n.a.	n.q.	n.d.	n.d.
Chen et al. (2007b)	GuangZhou, China	Indoor^{a}	7	4505	724.82	34.45	32.63	n.a.	n.a.	n.a.
	GuangZhou, China	Indoor^{b}	7	84.32	84.32	0.5	0.23	n.a.	n.a.	n.a.
	GuangZhou, China	Semi-urban^{c}	7	11.52	2.51	0.31	n.d.	n.a.	n.a.	n.a.
	GuangZhou, China	Semi-urban^{d}	7	2.14	1.01	0.24	n.d.	n.a.	n.a.	n.a.
Xie et al. (2007)	Geesthacht, Germany	Semi-rural	9	0.068	21	n.a.	n.a.	n.a.	n.a.	n.a.
	North Sea, Germany	ocean	10	0.027	0.021	n.a.	n.a.	n.a.	n.a.	n.a.
	European Arctic	ocean	6	4	0.017	n.a.	n.a.	n.a.	n.a.	n.a.

^{a}cosmetic plant (workshop), ^{b}cosmetic plant (out of workshop), ^{c}200m downwind to cosmetic plant, ^{d}25 km upwind to cosmetic plant, ^{e}median values

1.5 Sources

Sources of PFCs, PBDEs and musk fragrances can be divided into direct and indirect sources. Direct sources are production plants that emit these substances either in the atmosphere or as waste water into rivers (Dinglasan-Panlilio and Mabury 2006; Prevedouros et al. 2006; Chen et al. 2007b). Indirect sources are the release of those contaminants from products by volatilisation and during use, application and cleaning into waste water (Simonich et al. 2000; Hale et al. 2002; Heberer 2002; Palm et al. 2002; Agrell et al. 2004; Prevedouros et al. 2004; Dinglasan-Panlilio and Mabury 2006; Kim et al. 2006b; Sinclair et al. 2007; Chen et al. 2009; Choi et al. 2009; Paul et al. 2009).

Direct emissions of ionic PFCs have been identified as the major source to surface water (Prevedouros et al. 2006; Paul et al. 2009). Ionic PFCs in the atmosphere are predominantly particle-bound and thus subject to rapid deposition (Barton et al. 2006). In contrast, semi-volatile and volatile PFCs are emitted directly from production processes of fluorosurfactants (Dinglasan-Panlilio and Mabury 2006; Prevedouros et al. 2006). However, indirect emissions by volatilisation and application from consumer products that have been reported to contain semi-volatile and volatile PFCs (Dinglasan-Panlilio and Mabury 2006; Sinclair et al. 2007; Fiedler et al. 2008; Jensen et al. 2008; Langer 2010) are regarded as the dominating source. Paul et al. (2009) estimated that 85 % of total neutral PFC emissions are likely due to these releases.

So far, the direct emission sources for PBDEs into water and air are not well known. Since PBDEs are simply blended to polymers, plastics and electronic housings indirect emissions are regarded as the major sources for PBDEs into the atmosphere (Palm et al. 2002; Prevedouros et al. 2004). This is supported by studies that have been performed on the leaching characteristics of PBDEs from fabrics, such as plastics, TV housings, and polyurethane foams (Hale et al. 2002; Kim et al. 2006b; Choi et al. 2009) In 2000, indirect emissions in Europe were estimated to be 750 kg for BDE47 whereas BDE99 accounts only for about 1 kg (Prevedouros et al. 2004). In two coherent studies from southern Sweden waste incineration facilities were identified as point sources for PBDEs to ambient air (Agrell et al. 2004; Ter Schure et al. 2004). In contrast, Prevedouros et al. (2004) estimated BDE47 emissions by this route into the UK atmosphere to be less than 1 kg a^{-1} and concluded that waste incineration is a negligible PBDE source. Recently, Chen et al. (2009) and Cahill et al. (2007) reported elevated air concentrations at electronic waste dismantling and recycling facilities. These findings further support the ability of PBDEs to volatilise from electronic products.

Regarding musk fragrances, only little is known about their emission sources. However, a study conducted at a Chinese cosmetic plant revealed elevated musk fragrance concentrations in the surrounding ambient air and in the waste water of this plant (Chen et al. 2007b). Indirect diffuse emissions of musk fragrances are due to their widespread use and application such as cleaning and personal care (Reiner and Kannan 2006; Roosens et al. 2007). Therefore, those compounds may either be released into the atmosphere during use or, more important, are discharged with the waste water (Bridges 2002; Heberer 2002).

Overall, several efforts has been made on the characterisation of point sources for PFCs, PBDEs and musk fragrances. Due to the widespread everyday use of all substances, air concentrations are distinctly elevated in urban areas identifying those regions as diffuse source (Agrell et al. 2004; Peck and Hornbuckle 2004; Peck and Hornbuckle 2006; Barber et al. 2007; St-Amand et al. 2008; Dreyer et al. 2009b).

2. Objectives

In recent years, intensive efforts have been made on the identification of point sources for PFCs, PBDEs and musk fragrances (Agrell et al. 2004; Prevedouros et al. 2006; Chen et al. 2007b). After usage and application in consumer and industrial products these substances are disposed to landfills as final sink. Additionally, PFCs, PBDEs and musk fragrances end up in waste water by textile cleaning or the use of personal care products. Various studies characterized landfills and/or WWTPs as potential sources for PFCs, PBDEs and musk fragrances to the aquatic environment (Simonich et al. 2000; Bester et al. 2004; North et al. 2004; Osako et al. 2004; Prevedouros et al. 2004; Prevedouros et al. 2006; Schultz et al. 2006; Slack et al. 2007; Wang et al. 2007; Becker et al. 2008; Bossi et al. 2008b; Ahrens et al. 2009c; Busch et al. 2010). However, the release of PFCs, PBDEs and musk fragrances from these sources to the atmosphere is less investigated so far. Therefore, the objective of this study was to elucidate if landfills and WWTPs are sources of PFCs, PBDEs and musk fragrances to ambient air.

Specifically, the objectives are:

1. The optimisation of an analytical method for the simultaneous determination of PBDEs and musk fragrances in air. In order to be able to analyse PBDEs and musk fragrances, a selective method with low detection limits had to be developed. PFCs were analyzed separately with a previously validated method.

2. The assessment of air concentrations of PFCs, PBDEs and musk fragrances at landfills. Are the concentrations determined at landfills different than those detected at a reference site? Comparison of concentrations within substance groups: Are there any differences in concentration levels?

3. The assessment of air concentrations of PFCs, PBDEs and musk fragrances at waste water treatment plants. Are the concentrations determined at waste water treatment plants different than those detected at a reference site? Comparison of concentrations within substance groups: Are there any differences in concentration levels?

4. The evaluation of source strengths of landfills and waste water treatment plants for PFCs, PBDEs and musk fragrances to ambient air.

3. Method optimisation for the determination of PBDEs and musk fragrances

3.1 Introduction

For the sampling of PBDEs and musk fragrances in ambient air, high volume samplers are the most commonly applied sampling techniques (Lee et al. 2004; Peck and Hornbuckle 2004; Su et al. 2007; Xie et al. 2007). However, for PBDEs and PFCs passive sampling devices were also used (Jaward et al. 2004a; Gouin et al. 2005; Shoeib et al. 2005). PUF and XAD-2 resin are the sorbents most typically applied to accumulate airborne PFCs, PBDEs and musk fragrances (Agrell et al. 2004; Fromme et al. 2004; Peck and Hornbuckle 2004; Hoh and Hites 2005; St-Amand et al. 2008; Regueiro et al. 2009). Usually, a glass fibre filter (GFF) is additionally used to collect airborne particles.

Solvents for extraction of PUF/XAD-2/PUF and GFF include mixtures of hexane, diethyl ether, dichloromethane and acetone (Covaci et al. 2007; Bester 2009). Soxhlet extraction is widely used as a robust and effective extraction technique for PBDEs and musk fragrances. In recent studies, the long extractions times and large solvent volumes were partially avoided by the use of alternative extraction techniques, such as pressurized liquid extraction (PLE) (Wise et al. 2005).

Synthetic musk fragrances have a sufficient vapour pressure, temperature stability and lipophilicy and can therefore be separated by gas chromatography (GC) (Tas et al. 1997). The numbers of analytical methods for the determination of PBDEs increased over past years and were in most cases established on the basis of methods for chlorinated organic pollutants, such as polychlorinated biphenyls (Covaci et al. 2003). The most applied instrumental method is GC.

Separation of musk fragrances and PBDEs can be performed using non-polar or semi-polar capillary columns with films containing 5 % phenyl-dimethylpolysiloxane (DB-5 MS, HP-5 MS) and 100 % methyl-polysiloxane (DB-1 MS) (Strandberg et al. 2001; Stevens et al. 2003; Bester 2004; Covaci et al. 2005; Gouin et al.2005). Frequently, a length of 30 m and inner diameters of 0.25 mm with film thickness 0.25 μm is used. However, for determination of thermo-labile BDE209 it is suggested to apply columns with a lengths of 15 m or even shorter (Bjorklund et al. 2004; Kierkegaard et al. 2009).

Except for on-column inlets, all currently available inlets have been successfully applied in the analysis of musk fragrances since these substances are not thermo-labile (Rimkus 1999;

Simonich et al. 2000; Bester 2004; Peck 2006). For determination of PBDEs the most frequently used injection systems are splitless and on-column injection (Covaci et al. 2003). Highly brominated PBDEs (octa- to decaBDE) are reported to be degraded during analytical process. Björklund et al. (2004) described the influence of GC settings on the determination of highly brominated PBDEs. If not selected properly, particularly column length and injection technique may reduce the accuracy of the analytical method. Björklund et al. (2004) tested several inlets for the analysis of PBDEs. The authors concluded that the PTV inlet is the most suitable inlet for the analysis since the degradation of thermo-labile PBDEs is avoided.

Due to the lack of functional groups which allows detection by other commonly applied detectors, all musk fragrances are routinely detected by mass spectrometry (MS) (Yamagishi et al. 1981; Bester 2004; Peck et al. 2006; Lignell et al. 2008). Nitro musks have successfully been analysed with electron impact ionisation (EI) as the nitro groups give sufficient response (Rimkus 1999). In the EI mode of MS, usually three mass fragments from the musk fragrances are produced as result of a cleavage between one or more methyl groups. So far, indications of co-elution of other substances within the mass spectra were not observed (Bester 2009). However, musk fragrances often contain impurities (stereoisomers) which cannot be detected properly even if advanced technologies such as tandem MS or high resolution MS are applied (Bester 2009).

Detection of PBDEs was performed using MS either in the EI mode or the negative chemical ionisation mode (NCI) (Eljarrat 2003). Mass spectrometry in the EI mode produces a good selectivity through the formation of M^+ and the $[M\text{-}2\ Br]^+$ which are used for identification and quantification. However, EI mode has a low sensitivity for higher brominated congeners, such as penta-, octa-, and decaBDE and is therefore not routinely applied (Covaci et al. 2003). Benefit of the NCI mode is the enhanced sensitivity towards the Br^- ions (mass-to-charge-ratio, m/z= 79, 81) and is therefore widely applied to detect PBDEs. However, the quantification with compound-specific mass-labelled standards is not possible, since they exhibit the same mass signal. In trace analysis it is strongly suggested to apply mass-labelled standards for quantification. Furthermore, due to the low selectivity using two bromine ions, coelutions of other brominated compounds such as polybrominated biphenyls and MeO-PBDEs were reported (Stapleton 2006).

For the quantification of musk fragrances only two mass-labelled internal standards (IS) are commercially available. Those are the deuterated musk xylene (MX D_{15}) and the deuterated

7-Acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-Tetrahydronaphthalene, (AHTN D_3). However, the applicability of AHTN D_3 is under discussion since proton exchange during sample handling and storage was observed in several studies (Buerge et al. 2003; Bester 2004). This results in reduced concentration of AHTN D_3 and elevated concentration of AHTN in real samples. Mass-labelled PBDEs are commercially available and are frequently applied as internal standard for quantification. Furthermore, several native PBDE congeners which are not present in technical mixtures or environmental matrices were applied as IS (Gouin et al. 2005; Covaci et al. 2007).

The objective of this study was to optimize an analytical method that allows simultaneous extraction of PBDEs and musk fragrances from air sampling media. Although there are currently various individual extraction methods of both substance groups available, a combined method for PBDEs and musk fragrances have not been published, yet. Therefore, several extraction techniques were tested and evaluated. Furthermore, a GC-MS method to determine PBDEs and musk fragrances simultaneously was developed. Mass-labelled compound-specific internal standards should be included to the analytical method in order to increase analytical precision. As first step, the GC oven temperature program was optimized in order to achieve sufficient selectivity for each substance. To prevent thermal degradation of certain PBDE congeners during injection, inlet temperature was thoroughly optimised and evaluated.

3.2 Experimental section

3.2.1 Chemicals

Except for HHCB (51 % purity), all solvents, native and mass-labelled analytical standards and gases were of highest purity. A detailed table of all compounds, suppliers and qualities is listed in supporting information.

3.2.2 Determination of mass-to-charge ratio of PBDEs and musk fragrances

For determination of m/z of PBDEs and musk fragrances a 6890N GC (Agilent, Waldbronn, Germany) coupled to a 5973N inert mass spectrometer was used. The GC was equipped with a PTV inlet containing a multi-baffle liner (Agilent). The PTV inlet was run with the following parameters: Initial inlet temperature 50 °C, heating rate 300 °C min^{-1} and final inlet temperature 300 °C. Injection was performed using an autosampler and a 10 µL syringe. Separation was conducted on a HP-5 MS capillary column (Agilent, 30 m x 0.25 mm) coated with 5% phenyl-dimethylpolysiloxane stationary phase (0.25 µm film thickness). Helium was used as carrier gas at a constant flow of 1.3 mL min^{-1}. 2 µL of a standard solution (c=1 ng $µL^{-1}$) of each target analyte was injected to the GC-MS using EI in the full scan mode. For PBDE m/z determination in the NCI mode (full scan) a 15 m HP-5 MS column with same diameter and film thickness as described above was also used. The following oven program was applied: initial temperature 40 °C, 30 °C min^{-1} to 130 °C; 2 °C min^{-1} to 240 °C; 30 °C min^{-1} to 300 °C, hold for 20 min). This assured the elution of all analytes in the chromatogram. The fragment occurring in highest abundance was depicted as target ion (TI). In addition to each TI, at least one qualifier ion (Q) was selected according to abundance and m/z difference to TI.

3.2.3 Optimisation of the oven program

In order to achieve a sufficient chromatographic separation for all analytes, the oven temperature program was optimized. 2 µL of a standard solution containing all native and mass-labelled PBDEs and musk fragrances (c=800 pg $µL^{-1}$) was injected to GC-MS (EI mode, full scan). Separation was conducted on a HP-5 MS capillary column (Agilent, 30 m x 0.25 mm x 0.25 µm).
During optimisation, special attention was given to those substances that were detected with similar m/z. Particularly, these are musk fragrances (ADBI, AHMI m/z = 229 and HHCB, AHTN m/z = 243) as well as PBDE congeners (BDE99, BDE100 m/z = 404 and BDE154, BDE153 m/z = 484). Furthermore, attention was given to fronting and tailing of peaks.

Initial oven temperature (60 °C, hold for 2 min) and (30 °C min^{-1} to 130 °C) were fixed parameters and not changed during the experiments. Temperature program for musk fragrances (ramp II) and PBDEs (ramp III) were evaluated stepwise. An overview about oven temperature programs tested in this study is presented in table 8.

Table 8: Overview about oven temperature programs. Parameters printed in bold were changed during experiments.

Exp.	Ramp I	Ramp II	Ramp III
A	30 °C min^{-1} to 130 °C, hold 2 min	**5 °C min^{-1}** to 200 °C	**10 °C min^{-1}** to 300 °C, hold 20 min
B	30 °C min^{-1} to 130 °C, hold 2 min	**10 °C min^{-1}** to 200 °C	10 °C min^{-1} to 300 °C, hold 20 min
C	30 °C min^{-1} to 130 °C, hold 2 min	**15 °C min^{-1}** to 200 °C	**15 °C min^{-1}** to 300 °C, hold 20 min
D	30 °C min^{-1} to 130 °C, hold 2 min	**20 °C min^{-1}** to 200 °C	**20 °C min^{-1}** to 300 °C, hold 20 min
E	30 °C min^{-1} to 130 °C, hold 2 min	**5 °C min^{-1} to 170 °C, hold 3 min** **5 °C min^{-1} to 200 °C**	**15 °C min^{-1}** to 300 °C, hold 20 min

3.2.4 Optimisation of the inlet program

Inlet temperature was optimized in three steps as suggested by Godula et al. (2001). For three steps 2 µL of a standard solution containing all native and mass-labelled PBDEs and musk fragrances (c=800 pg µL^{-1}) were injected. GC-MS was operated in the EI mode using the selected ion monitoring mode (SIM). Inlet parameters were adjusted according to table 9.

Table 9: Overview about the inlet temperature programs. Parameters printed in bold were adjusted during the three steps.

Step	Initial inlet temperature (°C)	Inlet heating rate (°C min^{-1})	Final inlet temperature (°C)	Pulse pressure (psi)	Pulse time (min)	Initial oven temperature (°C)
A	**50**	300	300	40	2	**40**
	60	300	300	40	2	**40, 50**
	70	300	300	40	2	**40, 50, 60**
B	60	300	**200**	40	2	50
	60	300	**250**	40	2	50
	60	300	**300**	40	2	50
C	60	**100**	300	40	2	50
	60	**200**	300	40	2	50
	60	**300**	300	40	2	50
	60	**400**	300	40	2	50
	60	**500**	300	40	2	50

3.2.5 Determination of the instrumental detection and quantification limits

For determination of the instrumental limits of detection (LOD) and limits of quantification (LOQ) of PBDEs and musk fragrances 2 µL of a standard solution containing native and mass-labelled analytes were spiked to the GC system. Ionisation modes were EI and NCI. In order to include thermo-labile BDE209 in the analysis, a 15 m HP-5 MS capillary column was used in the NCI mode. PBDEs and musk fragrances in the EI mode were separated on a 30 m HP-5 MS capillary column. LOD and LOQ were determined using optimized oven and inlet settings from section 3.4. The LOD was set to signal-to-noise ratio (S/N) of 3, the LOQ was set to S/N=10.

3.3 Extraction experiments

3.2.5 Extraction method for PBDEs and musk fragrances of gas-phase samples

Prior to the extraction experiments, precleaned PUF/XAD-2/PUF cartridges (n=3) were spiked with 50 µL of an internal standard solution containing mass-labelled MBDE27, MBDE47, MBDE99, MBDE153, MBDE183 as well as both musk fragrances AHTN D_3 and MX D_{15} (c=200 pg μL^{-1}). PUF/XAD-2/PUF cartridges were cold-column extracted in three cycles (1 h, 1 h, 30 min) using hexane/acetone 1:1 (v:v). After each cycle, solvent was blown out with nitrogen. The volume of the solvent (approximately 450 mL) was reduced using Synchore polyvap (Büchi, Essen, Germany) at a temperature of 45 °C and 415-380 mbar. Samples were further evaporated to 150 µL by a gentle stream of nitrogen. Finally, extracts were transferred to GC vials. Prior to the measurements using GC-MS, 50 µL of an injection standard solution (^{13}C HCB and Fluoranthene D_{10}, c=400 pg μL^{-1}) was added to the samples. For quantification a seven point calibration was used (2, 4, 10, 20, 50, 80, 100, 200 pg μL^{-1}). Linearity of calibration was checked as described in DIN 32645 (1994). Peaks were quantitated based on their peak areas and calculated using the internal standard method.

3.2.6 Extraction method for PBDEs and musk fragrances of particle-phase samples

Accelerated solvent extraction (ASE)

GFF (n=3) were folded and filled into extraction cells (stainless steel, volume= 22 mL) of an accelerated solvent extractor (ASE, ASE 200, Dionex, Idstein, Germany). 50 µL of an internal standard solution containing mass-labelled MBDE27, MBDE47, MBDE99, MBDE153, MBDE183 as well as both musk fragrances AHTN D_3 and MX D_{15} (c=200 pg μL^{-1}) was added. Remaining space in the cells was filled up with precleaned diatomite (Fluka, Germany). Filters were extracted with hexane/acetone and pressurized to 140 bar at 100 °C. Two static cycles (5 min, hold time 5 min) were performed. After the first extraction cycle cell volume was rinsed and refilled with solvent. The purge time was set to 60 s. The volume of the extract (about 35 mL) was reduced to 1 mL using Synchore polyvap. Extracts were further concentrated to 150 µL under a gentle stream of nitrogen. Prior to the measurement using GC-MS, 50 µL of an injection standard solution containing ^{13}C HCB and Fluoranthene D_{10} (c=400 pg μL^{-1}) was added to the samples. For quantification a seven point calibration was used (2, 4, 10, 20, 50, 80, 100, 200 pg μL^{-1}). Linearity of calibration was checked as described in DIN 32645 (1994). Peaks were quantitated based on their peak areas and calculated using the internal standard method.

Fluidized bed extraction (FBE)

In order to determine the extraction efficiency of fluidized bed extraction (FBE, IKA GmbH, Staufen, Germany) using hexane/acetone 1:1 (v:v). GFF (n=3) were folded and inserted into glass tubes. Three extraction cycles of 30 min with a maximum temperature of 75 °C, hold for 30 min, were used. After each cycle, solvent was allowed to cool down to 30 °C. Extracts were evaporated to 1 mL using a synchore polyvap and further reduced to 150 µL with nitrogen. Final extracts were transferred to GC vials and determined by GC-MS. Prior to the measurements, 50 µL of an injection standard solution (^{13}C HCB and Fluoranthene D_{10}, c=400 pg µL^{-1}) was added to the samples. According to DIN 32645 (1994) linearity of a seven point calibration curve (2, 4, 10, 20, 50, 80, 100, 200 pg µL^{-1}) was tested. Peaks were quantitated by peak area and calculated with the internal standard method.

3.2.7 Clean-up of PBDEs in the particle phase

Eight air samples were taken at GKSS for one day each using high volume samplers. GFF (150 mm in diameter) were extracted with ASE using the method described in section 3.2.6. The extracts were combined and used for the purification experiments (n=2). Prior to the clean-up, 60 mL of the combined extract were evaporated to about 1 mL and used as reference material for the tests. Clean-up of the extracts was performed using the method of Kaupp for PAH from aerosols (Kaupp 1996). 5 g of silica gel (0 % deactivated) was filled in a glass column (d = 1 cm) and covered by 3 g aluminium oxide (15 % deactivated). Hexane was added for equilibration. Evaporated extracts were transferred to the glass columns and eluted with 35 mL hexane (fraction 1) and 30 mL hexane/dichloromethane 3:1 (v:v) (fraction 2). Finally, the different fractions were rotary evaporated at 30 °C and 240 mbar to about 1 mL, and further reduced to 150 µL using nitrogen and transferred to GC vials. Prior to the measurements using GC-MS, 50 µL of an injection standard solution (^{13}C HCB and Fluoranthene D_{10}, c=400 pg µL^{-1}) was added to the samples. For quantification a seven point calibration was used (2, 4, 10, 20, 50, 80, 100, 200 pg µL^{-1}). Linearity of calibration was checked according to DIN 32645 (1994). Peaks were quantitated based on their peak area and calculated using the internal standard method.

3.3 Results

3.3.1 Determination of mass-to-charge ratio of PBDEs and musk fragrances

Table 10: Mass-to-charge-ratio (m/z) of PBDEs and musk fragrances determined with GC-MS in the EI and NCI mode, respectively. MW: molecular weight, TI: Target Ion, Q1: Qualifier 1, Q2: Qualifier 2.

		EI mode			NCI mode		
Analyte	**MW**	**TI**	**Q1**	**Q2**	**TI**	**Q1**	**Q2**
^{13}C HCB	291	290	255	-	290	256	-
ADBI	244	229	244	173	-	-	-
AHMI	244	229	244	187	-	-	-
MX D_{15}	294	294	248	-	-	-	-
HHCB	258	243	213	258	-	-	--
ATII	258	215	173	258	-	-	-
AHTN D_{13}	271	246	261	-	-	-	-
MX	297	282	297	-	-	-	-
AHTN	258	243	258	159	-	-	-
MK	294	279	294	128	-	-	-
Fluoranthene D_{10}	212	212	106	-	212	211	-
BDE28	407	248	408	139	327	328	326
MBDE28	419	260	418	150	339	337	338
MBDE47	498	338	498	228	417	419	415
BDE47	486	326	486	406	407	405	404
BDE100	565	404	564	484	405	403	484
MBDE99	577	416	576	496	417	415	496
BDE99	565	404	564	484	405	403	484
BDE154	644	484	644	404	564	562	563
MBDE153	656	496	656	416	496	494	498
BDE153	644	484	644	404	564	562	563
MBDE183	734	574	734	414	574	576	572
BDE183	722	562	724	484	564	562	484
MBDE 209	972	-	-	-	495	497	-
BDE209	960	-	-	-	487	489	485

3.3.2 Optimisation of the GC oven program

In order to asses the selectivity of the chromatographic process, separation factor α for each analyte was calculated using following equation: $\alpha = k_2/k_1$, whereas k_1 and k_2 are the retention times of two peaks succeeding one another. For example, in the case where $\alpha=1$, the two compounds are not separated, whereas $\alpha=1.10$ means that compounds differ in 10 % of relative retention time and are well separated. Table 11 displays α values of each analyte at the tested parameters from section 3.2.3. It should be noted that mass-labelled PBDEs were observed at same retention times as their native substances and are therefore not discussed separately.

Table 11: Separation factors (α) of PBDEs and musk fragrances obtained by experiments A-E as well as direct comparison of α values of pairs of analytes that were problematic to separate (for details see 3.2.3).

	Separation factor α				
Analyte	**Experiment A**	**Experiment B**	**Experiment C**	**Experiment D**	**Experiment E**
^{13}C HCB	-	-	-	-	-
ADBI	1.00	1.00	1.00	1.00	1.02
AHMI	1.04	1.04	1.03	1.03	1.08
MX D_{15}	1.08	1.08	1.07	1.06	1.16
HHCB	1.00	1.00	1.00	1.00	1.00
ATII	1.00	1.00	1.00	1.00	1.00
AHTN D_{13}	1.01	1.01	1.01	1.01	1.02
MX	1.00	1.00	1.00	1.00	1.00
AHTN	1.00	1.00	1.00	1.00	1.00
MK	1.11	1.09	1.08	1.07	1.16
Fluoranthene D_{10}	1.06	1.05	1.05	1.05	1.07
BDE28	1.12	1.09	1.10	1.08	1.12
BDE47	1.14	1.09	1.11	1.10	1.09
BDE100	1.09	1.05	1.07	1.06	1.05
BDE99	1.02	1.01	1.02	1.02	1.01
BDE154	1.06	1.04	1.05	1.05	1.04
BDE153	1.03	1.02	1.03	1.03	1.02
BDE183	1.08	1.09	1.10	1.11	1.08
ADBI, AHMI	1.04	1.04	1.03	1.03	1.08
HHCB, AHTN	1.00	1.01	1.01	1.01	1.03
BDE100, BDE99	1.02	1.01	1.02	1.02	1.02
BDE154, BDE153	1.03	1.02	1.03	1.03	1.03

Separation factors of musk fragrances ranged from 1.00 to 1.16 in all experiments. However, low retention factors of most musk fragrances (ADBI, HHCB, ATII, AHTN D_{13}, MX, and AHTN) were observed in experiments A-D. Experiment E revealed elevated retention factors for some musk fragrances, such as AHMI and MK. Retentions factors of musk fragrances with same m/z were slightly elevated in experiment E. For PBDEs significant differences in retentions factors could not be observed in one of the experiments.

For musk fragrances and PBDEs peak abundances were elevated with increasing heating rates. Concurrently, decreasing peak widths were detected at higher heating rates. Fronting or tailing of musk fragrances during different oven parameters were not observed. However, a slight tailing was detected for low brominated congeners BDE28 and BDE47 in all experiments.

3.3.3 Optimisation of the GC inlet parameters

Figure 1 displays peak abundances of native musk fragrances and PBDEs obtained by injections of standard solution at different oven and inlet temperature settings as described in table 8 (section 3.2.4). Settings at low oven temperatures (50 °C, 60 °C) resulted in low peak abundances. Maximum peak abundances were observed for the most volatile analytes (ADBI

AHMI). For less volatile analytes such as BDE153 and BDE154 peak abundances were rather low. An oven temperature of 70 °C and an inlet temperature 60 °C lead to highest abundances. At different final inlet temperatures peak heights did not vary significantly (figure 1b). There is no significant change in peak abundance of musk fragrances at heating rates. PBDEs are increased with higher heating rates (figure 1c). For example, best responses for BDE99 and BDE100 were achieved for temperatures equal to 300 °C min^{-1} or even higher as demonstrated in figure 2.

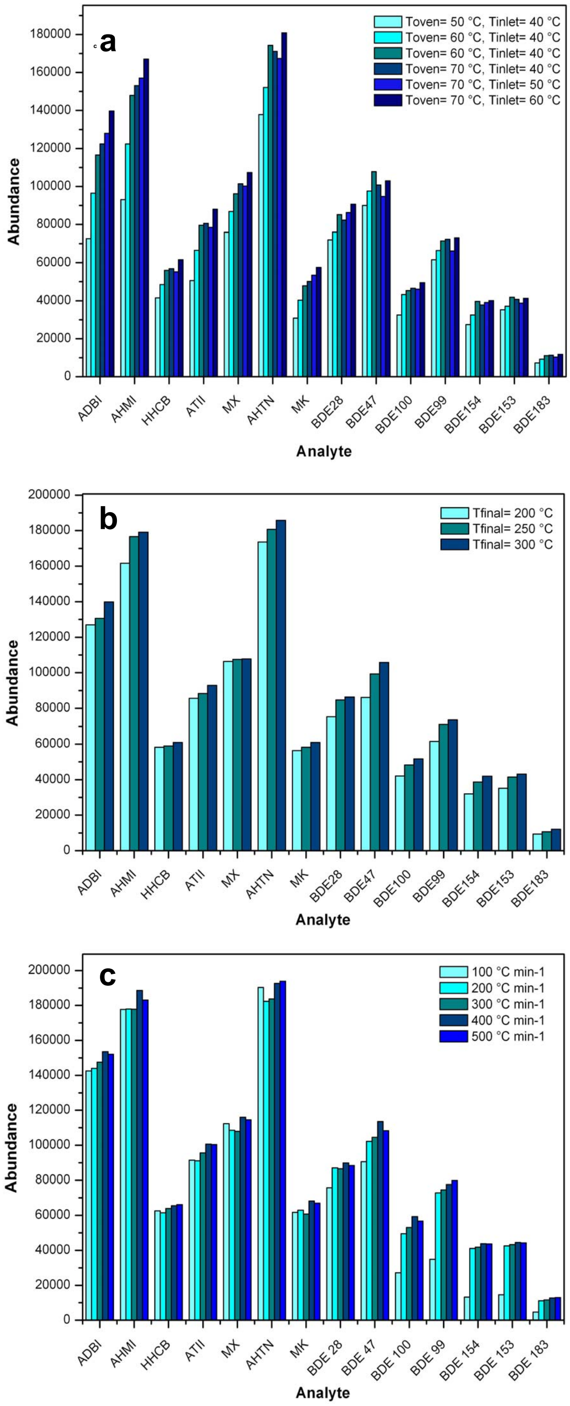


Figure 1: Differences of peak abundance obtained with varying oven (a), inlet temperatures (b) and heating rates (c) according to experiments 3A-C (section 3.2.4).

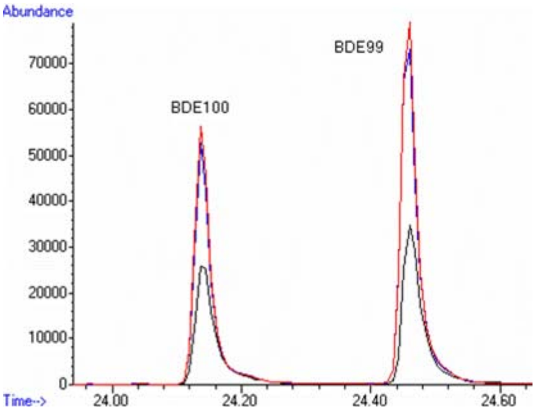


Figure 2: GC-MS chromatogram of BDE100 and BDE99) at 100 °C min^{-1} (black line), 300 °C min^{-1} (blue line) and 500 °C min^{-1} (red line) according to experiment C from section 3.2.4

3.3.4 Limits of detection and quantification of PBDEs and musk fragrances

LOD and LOQ of musk fragrances were below 1 pg µL^{-1}. Only HHCB and MX D$_{15}$ were detected with LOQ and LOD of 1.8 pg µL^{-1}and 6.6 pg µL^{-1}, respectively. With increasing molecule mass of PBDEs, LOD and LOQ increased in the EI mode. With the exception of BDE209, PDBE detection limits were below 1 pg µL using NCI mode. A detailed list of LOD and LOQ of PBDEs and musk fragrances in EI and NCI mode is presented in table 12.

Table 12: Limits of detection (LOD) and limits of quantification (LOQ) on the basis of a S/N= 3 (LOD) and S/N= 10 (LOQ), respectively.

	EI mode					NCI mode			
	LOQ pg µL^{-1}	LOQ pg abs.	LOD pg µL^{-1}	LOD pg abs.		LOD pg µL^{-1}	LOD pg abs.	LOQ pg µL^{-1}	LOQ pg abs.
ADBI	0.1	0.2	0.3	0.6		-	-	-	-
AHMI	0.1	0.2	0.3	0.7		-	-	-	-
MX D$_{15}$	6.6	13.2	3.3	6.6		-	-	-	-
HHCB	1.8	3.6	0.9	1.8		-	-	-	-
ATII	0.1	0.3	0.4	0.8		-	-	-	-
AHTN D$_{13}$	0.1	0.2	0.3	0.7		-	-	-	-
MX	0.3	0.7	1.1	2.3		-	-	-	-
AHTN	0.2	0.4	0.6	1.3		-	-	-	-
MK	0.1	0.3	0.5	0.9		-	-	-	-
BDE28	0.1	0.2	0.3	0.6		0.4	0.7	1.2	2.4
MBDE28	0.1	0.2	0.4	0.8		0.6	1.1	1.9	3.8
MBDE47	0.2	0.3	0.5	1.0		0.4	0.7	1.2	2.4
BDE47	0.1	0.3	0.4	0.8		1.0	2.0	3.3	6.6
BDE100	2.3	4.5	4.5	9.0		0.0	0.1	0.1	0.3
MBDE99	2.2	4.3	4.3	8.6		0.1	0.2	0.4	0.8
BDE99	2.3	4.6	4.6	9.2		0.2	0.4	0.6	1.2
BDE154	2.5	4.9	4.9	9.8		0.1	0.1	0.2	0.4
MBDE153	2.5	4.9	4.9	9.8		0.0	0.1	0.2	0.3
BDE153	2.6	5.2	5.2	10.4		0.1	0.2	0.3	0.6
MBDE183	13.5	27.0	27.0	54.0		0.0	0.0	0.1	0.1
BDE183	13.5	27.0	27.0	54.0		0.0	0.1	0.1	0.2
MBDE209	-	-	-	-	-	0.6	1.2	2.1	4.1
BDE209	-	-	-	-	-	0.4	0.9	1.4	2.8

3.3.5 Extraction experiments

Extraction of PBDEs and musk fragrances from PUF/XAD-2/PUF cartridges

Average recovery rates, absolute and relative standard deviations, medians as well as minimum and maximum recovery rates of PBDEs and musk fragrances obtained from PUF/XAD-2/PUF extraction tests are listed in table 13.

Table 13: Recovery rates (R, %) of PBDEs and musk fragrances obtained from extraction of PUF/XAD-2/PUF cartridges (n=3); SD abs.: absolute standard deviation, RSD: relative standard deviation, Min: minimum, Max: maximum.

	AHTN D_{13}	MX D_{15}	MBDE28	MBDE47	MBDE99	MBDE153	MBDE183
R (Average)	69	87	88	84	82	94	92
SD abs.	7	3	4	1	2	3	2
RSD	10	4	5	2	2	4	2
R (Median)	67	85	89	84	82	95	92
R (Min)	63	85	84	82	81	90	90
R (Max)	77	90	92	85	84	96	94

Extraction of PBDEs and musk fragrances from GFF

Average recovery rates of musk fragrances and PBDEs determined by the two different extraction methods (FBE, ASE) are presented in figure 3.

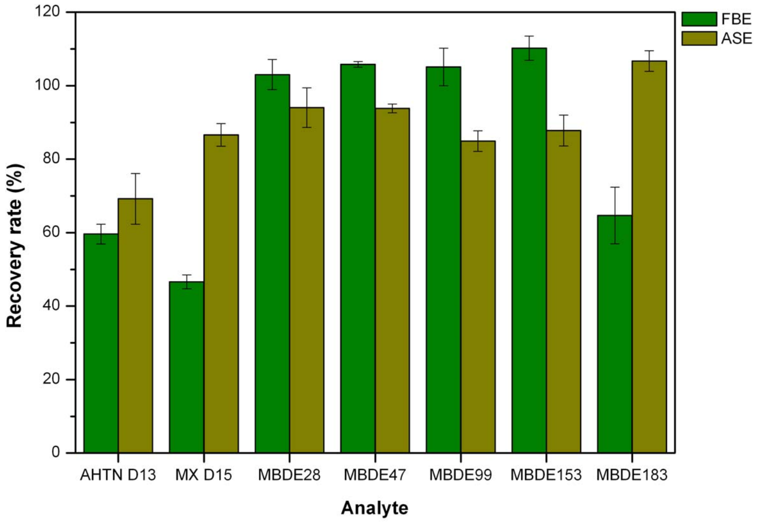


Figure 3: Average recovery rates (n=3) of mass-labelled musk fragrances and PBDEs using FBE and ASE. Error bars display absolute standard deviations.

Recovery rates for PBDEs were between 85 % and 107 % (ASE) and 65 % to 106 % (FBE). Recovery rates of low and middle molecular weight PBDEs of FBE extracts were constantly observed above 100 %. In contrast, recovery rates of MBDE183 were low (65 %). Compared to ASE, average recovery rate of nitro musk MX D_{15} in FBE extracts was lower by a factor of 2. A detailed chart of individual recovery rates, their minimum and maximum recovery rates and standard deviations are presented in table 14.

Table 14: Recovery rates (R, %) of PBDEs and musk fragrances obtained from extraction of GFF using FBE and ASE (n=3); SD abs.: absolute standard deviation, RSD: relative standard deviation, Min: minimum, Max: maximum.

	AHTN D_{13}	MX D_{15}	MBDE28	MBDE47	MBDE99	MBDE153	MBDE183
R (FBE1)	61	45	112	88	102	93	51
R (FBE2)	61	49	106	110	106	111	83
R (FBE3)	56	46	91	120	107	126	60
R (Average)	60	47	103	106	105	110	65
SD abs.	3	2	11	16	3	17	16
R (RSD)	5	4	11	16	3	15	25
R (Min)	56	45	91	88	102	93	51
R (Max)	61	49	112	120	107	126	83
R (ASE1)	63	85	94	94	85	92	107
R (ASE2)	77	90	99	92	88	84	109
R (ASE3)	67	85	89	95	82	87	104
R (Average)	69	87	94	94	85	88	107
SD abs.	7	3	5	1	3	4	3
R (RSD)	10	4	6	1	3	5	3
R (Min)	63	85	89	92	82	84	104
R (Max)	77	90	99	95	88	92	109

3.3.6 Clean-up of PBDEs from particle-phase samples

Almost all PBDE congeners were detected in fraction 1. Only 2-3 % MBDE183 were observed in fraction 2. Average recovery rates of the purification step were 92 % (MBDE28), 86 % (MBDE47), 85 % (MBDE99), 99 % (MBDE153), 115 % (MBDE183), 91 % (MBDE209). Detailed results are given in figure 4.

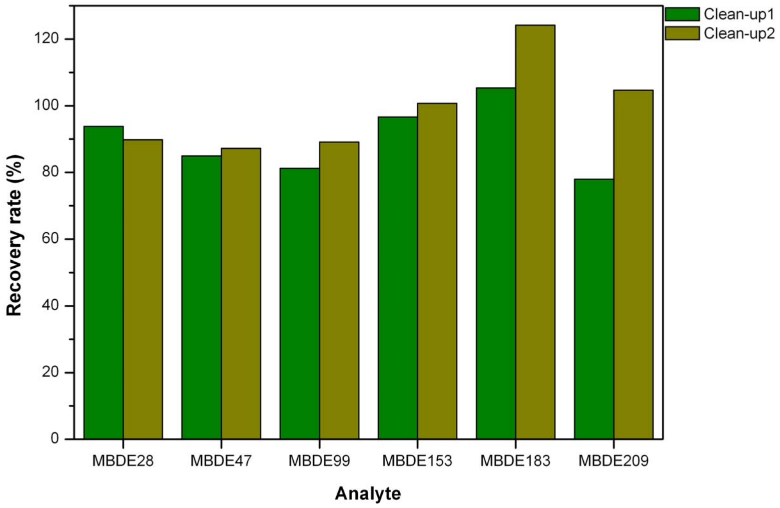


Figure 4: Recovery rates (%) of mass-labelled musk fragrances and PBDEs determined after clean-up step described in section 3.2.7.

3.4 Discussion

Main characteristics for a good chromatographic separation are a sufficient peak performance without fronting or tailing and high selectivity. After modification of oven program parameters, musk fragrances HHCB and AHTN were finally separated when temperature plateau was included (experiment E section 3.2.3). However, other musk compounds such as ATII and MX still coelute with MX D_{15}, HHCB, and AHTN D_{13}. These results corroborate with other studies (Kallenborn and Gatermann 2004; Peck and Hornbuckle 2004; Peck et al. 2007). Nevertheless, it was possible to quantify the co-eluting substances by their different m/z. Good chromatographic separation of all PBDE congeners was achieved in every single experiment. Except for the slight tailing of BDE28 and BDE47 all peak performances for PBDEs and musk fragrances were acceptable. Figure 5 displays the final chromatogram for PBDEs and musk fragrances using GC-MS in the EI mode.

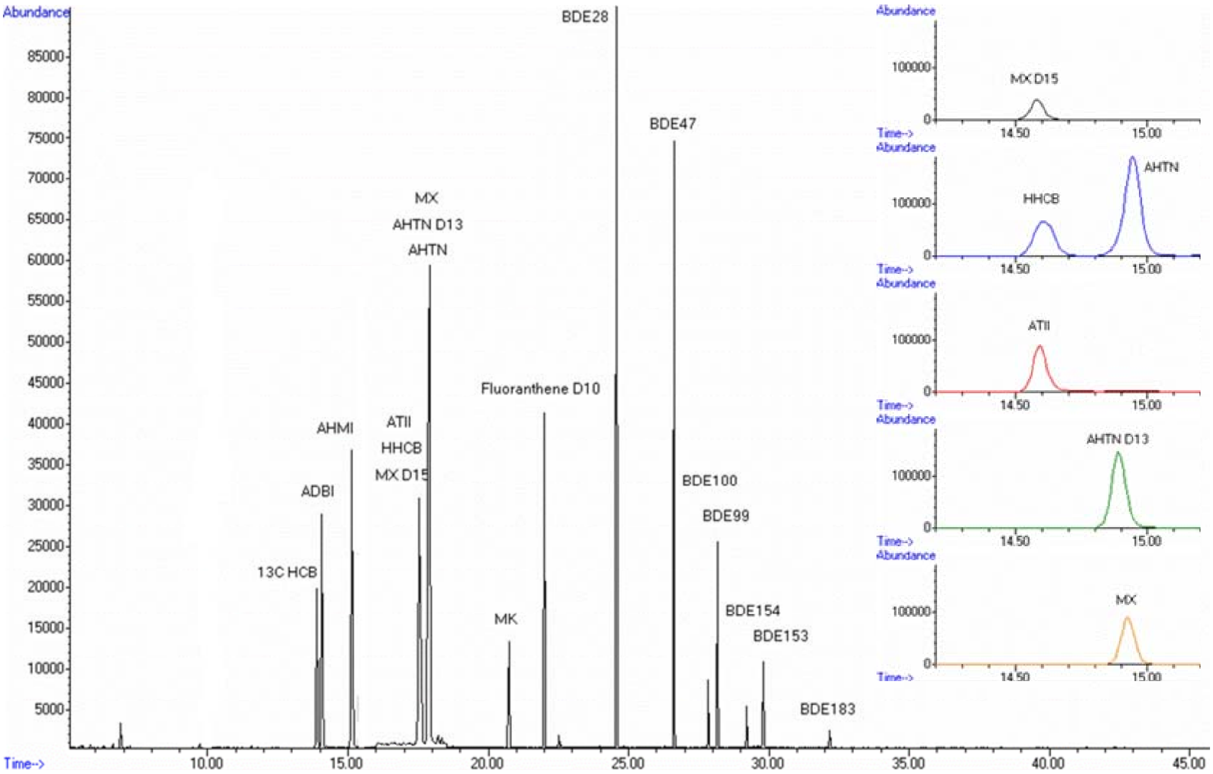


Figure 5: Total ion chromatogram (TIC) of GC-MS in the EI mode for musk fragrances and PBDEs after optimisation of oven temperature settings. The close-up displays musk fragrances that obtained insufficient separation (for details see section 3.3.4).

In order to separate BDE209 a 15 m HP5-MS column had to be applied. This is caused by thermal degradation on columns of more than 15 m BDE209 is thermally degraded (Binelli et al. 2006). Different studies revealed the importance of inlet optimisation for PBDE trace analysis due to inherent thermal degradation of octa- to decaBDE (Eljarrat et al. 2002;

Kierkegaard et al. 2009). By inlet optimisation conducted in this thesis, an increase of sensitivity particularly for PBDE congeners with high boiling points, such as BDE99, BDE154 and BDE183 was observed (see sections 3.2.4 and 3.3.3). In particular, significant improvements of peak abundance and shape were obtained by application of increased heating rates. This result is confirmed by the study of Björklund at al (2004). For more volatile BDE28 and BDE47 enhanced sensitivity at elevated initial oven and inlet temperatures were observed. For early eluting musk fragrances initial inlet- and oven temperatures seemed to be the most important parameters. A significant increase of abundance with elevated temperatures could be observed for those compounds. Inlet heating rates did not reveal a distinct increase of selectivity for musk fragrances.

Higher abundances of musk fragrances and PBDEs with increasing final inlet temperature was not observed. However, it is suggested to set this parameter as possible at high values in order to bake out co-eluting matrix components during measurement of environmental samples (Godula et al. 2001)

Different studies indicated that PBDEs from European air samples are to be expected in the range of a few pg m^{-3} (De Boer et al. 2006). Therefore, the method should include low detection limits in order to determine ultra-traces. Low sensitivities of highly brominated PBDEs (BDE153, BDE154, and BDE183) in the EI mode resulted in insufficient detection limits (section 3.3.4) for the analysis of air samples. Thus, EI is not the adequate ionisation mode for determination of high molecular weight PBDEs at ultra-trace levels. Due to considerably lower LOD and LOQ for PBDEs, detection by NCI mode is supposed to be the more sensitive ionisation method and thus more suitable. This corroborates with other studies (Covaci et al. 2003; Covaci et al. 2007).

Cold-column extraction of PUF/XAD-2/PUF cartridges using hexane/acetone as extraction solvent resulted in high recovery rates with low standard deviations (table 13 in section 3.3.5). Furthermore, short extraction times (2.5 h) support the suitability of this method compared to soxhlet extraction (> 12 h) which was used in many other studies (Peck and Hornbuckle 2004; Hoh and Hites 2005; Covaci et al. 2007; Xie et al. 2007). Therefore, cold column extraction was selected as the final extraction method for the determination of musk fragrances and PBDEs in air samples.

Results of particle-phase extraction tests revealed varying recovery rates for musk fragrances and PDBEs extracted by FBE and ASE (figure 3 in section 3.3.5). In general, recovery rates of musk fragrances were lower than those of PBDEs for both extraction methods. This may partly due to higher vapour pressures and therefore the increased volatility of those compounds (for details see table 4 in section 1.3). Compared to FBE, higher recovery rates of musk fragrances were obtained with ASE. This may be explained by volatilisation of musk fragrances during relatively long FBE extraction cycles (3 h). Furthermore, ASE is a “closed” system where analyte losses are minimized. The low recovery rate of MBDE183 in FBE extracts may be caused by the lower extraction strength of this technique. ASE operates at high temperatures and high pressures and is therefore assumed to be the stronger extraction technique. Nevertheless, both techniques were suitable for extraction of musk fragrances and PBDEs from GFF. However, the shorter extraction time of ASE (20 min) and lower amount of solvent underline the suitability of ASE that is therefore applied for further analysis.

The clean-up step for PBDEs using silica gel and aluminium oxide revealed good recovery rates as displayed in figure 4 (section 3.3.6) and was therefore applied for further analysis. Musk fragrances were not included into the purification experiment because they were estimated to be detected primarily in the gas phase (Kallenborn and Gatermann 2004; Peck and Hornbuckle 2006; Xie et al. 2007). Therefore, further optimisation of clean-up step for musk fragrances was not considered.

3.5 Conclusions

First objective of this study was to develop and optimize an analytical method that can efficiently and simultaneously extract PBDEs and musk fragrances from air sampling media. High recovery rates with low standard deviations for both substance groups revealed the high precision and good suitability of evaluated methods.

For simultaneous determination of PBDEs and musk fragrances GC oven program and inlet parameters were optimized. Separation factors revealed good chromatographic separation for most of the target analytes. However, some musk fragrances could not be sufficiently separated but it was possible to quantify those compounds by different m/z. Inlet parameter optimisation revealed a distinct increase of PBDE and musk fragrances sensitivity. With these inlet modifications an average improvement of sensitivity of 9 % for PBDEs and musk fragrances was achieved if compared to the starting PTV settings in section 3.2.2. Figure 6 demonstrates improvements in sensitivity for each compound.

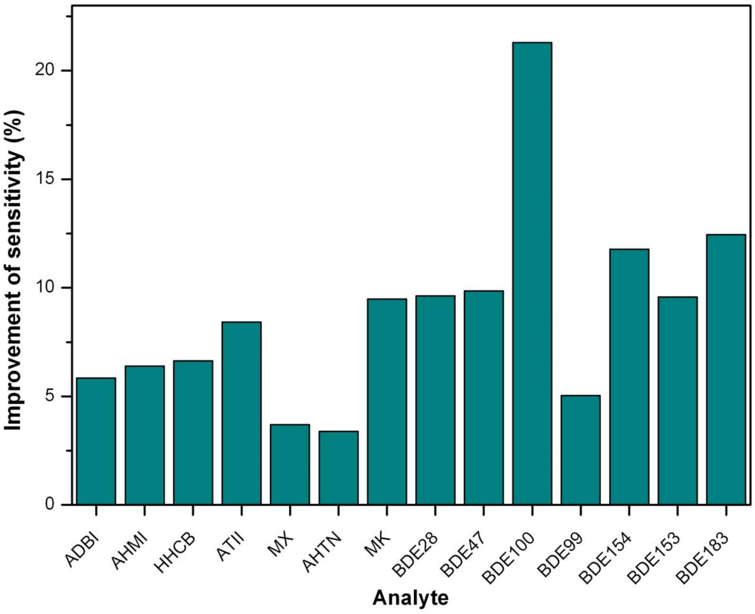


Figure 6: Improvements of sensitivity (%) of PBDEs and musk fragrances after optimisation of PTV inlet on the basis of previous PTV inlet settings in section 3.2.2

Further objective was the optimisation of an instrumental method that is sensitive for PBDEs and musk fragrances. Due to the high LOD and LOQ in the EI mode for higher brominated PBDE congeners it was not possible to determine these compounds at low concentration levels. Thus the objective to develop a simultaneous detection method was not achieved and NCI mode was selected as the adequate ionisation mode for PBDEs. For further analysis, PBDEs had to be separately determined in the NCI mode and musk fragrances in the EI mode. Finally, following optimized inlet parameter were used: Initial inlet temperature 70 °C, initial oven temperature 60 °C, final inlet temperature 300 °C, inlet heating rate 400 °C, initial oven temperature: 60 °C. Final optimized oven temperature programs and final chromatograms are displayed in table 15 and figure 7, respectively.

Table 15: Final oven temperature programs for the determination of PBDEs and musk fragrances using GC-MS

NCI (PBDEs)			EI (Musk fragrances)		
heating rate °C min^{-1}	**final temperature °C**	**hold time min**	**heating rate °C min^{-1}**	**final temperature °C**	**hold time min**
30	130	0	30	130	0
5	170	3	5	170	3
5	200	0	5	200	0
15	300	20	15	300	5

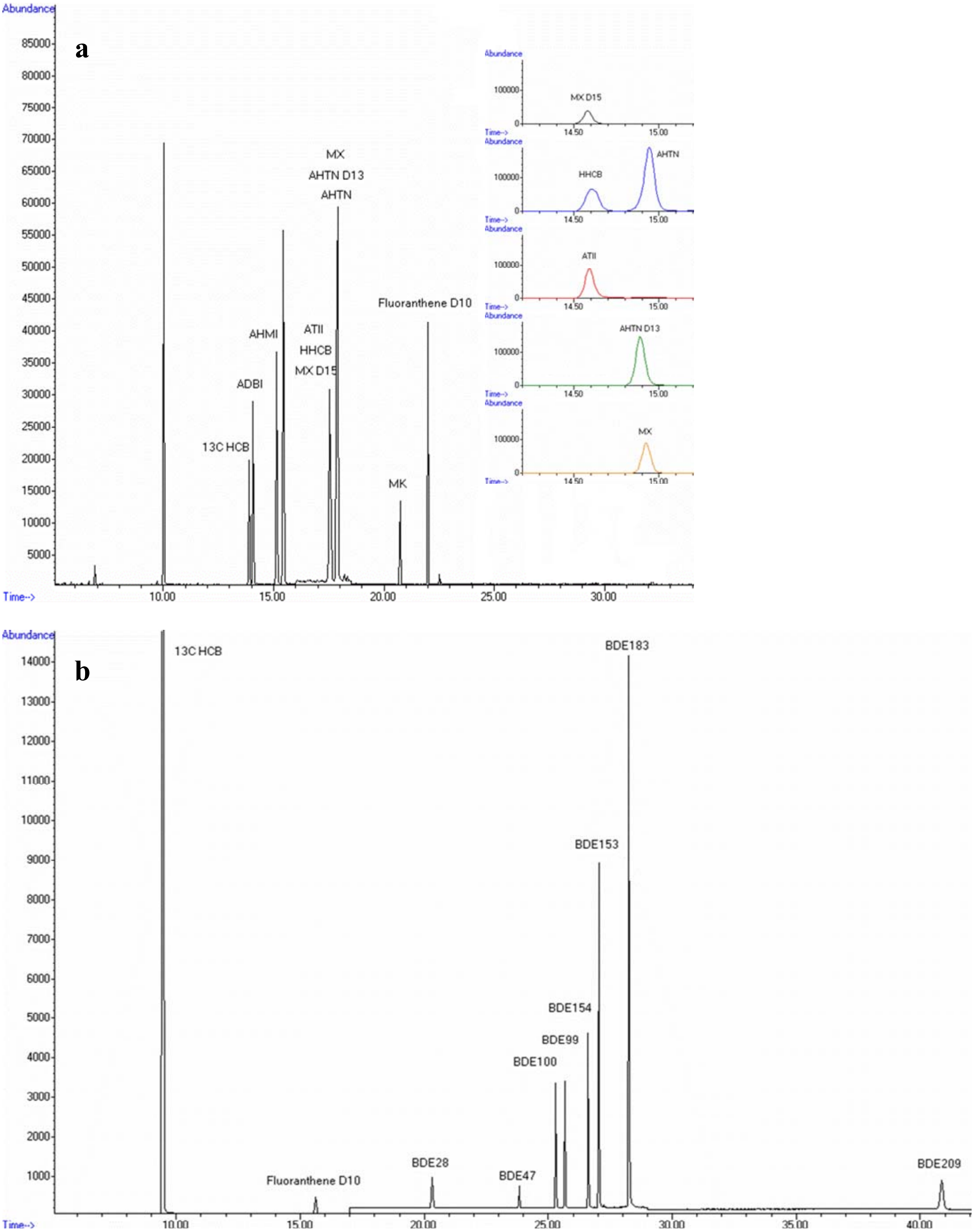


Figure 7: Final GC-MS chromatograms for (a) musk fragrances (EI) and (b) PBDEs (NCI). The close-up in 8a displays musk fragrances of insufficient separation (for details see section 3.3.2).

4. Study 1: Landfills as sources of polyfluorinated compounds, polybrominated diphenyl ethers and synthetic musk fragrances to ambient air

4.1 Introduction

According to the German Ordinance on Compatible Storage of Waste from Human Settlements and on Biological-Treatment Facilities (Abfallablagerungsverordung, AbfAblV) a landfill is defined as “waste-management facility for the storage of waste above the earth's surface (above-ground)”(AbfAblV 2001). In general, landfills contain a variety of different types of waste including household waste and waste from industrial sources and products. Household waste represents two-thirds of the municipal solid waste stream. Almost 70 % of municipal solid waste is disposed to landfills (OECD 2001). In particular, sanitary landfills accumulate huge quantities of a wide variety of consumables, including general and hazardous wastes, electric and electronic equipment and compost (St-Amand et al. 2008). Since the European Commission Directive 99/31/EC which constituted the classification and separation of waste prior to the deposit, waste treatment is strongly regulated in the European Union. In Germany for example, the Ordinance on Landfills and Long-Term Storage Facilities (Deponieverordnung, DepV), demands separation and pre-treatment of waste either thermically by incineration or mechanically-biologically in order to reduce the volume prior to the storage on landfill sites (DepV 2002). Therefore the total amount of waste is supposed to decrease overtime (Slack et al. 2004). On the other hand, alternative disposal practices, such as recycling and incineration, still generate waste that is to be landfilled (Slack et al. 2004). Figure 8 displays how a product is predominantly disposed to a landfill and can be released into the environment via different pathways.

In general, emissions from landfills can be addressed to different forms of release: gaseous emissions, formation of particulate matter and lecheate (Slack et al. 2005). In this thesis the focus is on atmospheric emissions from landfill sites. The other emission pathways are not discussed in detail. Various studies have been conducted on the environmental fate and release of volatile organic compounds (VOC) from landfills to the atmosphere (Allen et al. 1997; James and Stack 1997; Kim et al. 2006a). Studies about semi-volatile organic compounds, such as PCBs and PAHs usually focus on leachate concentrations (Vollmuth and Niessner 1995; Marttinen et al. 2003; Herbert et al. 2006) and the impact of waste incineration plants (Dyke 2003; Capuano et al. 2005). However, little is known about the volatalisation of PFCs, PBDEs and musk fragrances from landfills. Since PFCs, PBDEs and musk fragrances are substances of emerging concern (see section 1.4) it is essential to understand their environmental fate.

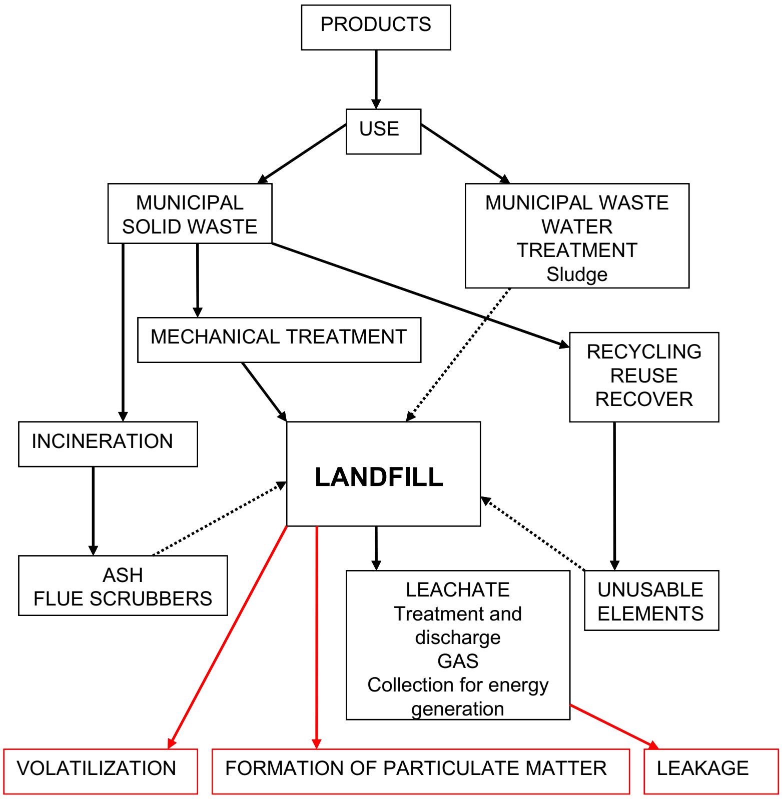


Figure 8: General lifecycle of products prior to the storage in landfills. Continuous arrows mark a direct to the next step in process; dotted arrows display indirect contributions of product disposals to landfills. Red boxes are relevant pathways for release of pollutants from landfills into the environment. Scheme adapted from Slack et al. 2004, modified.

Currently, five studies have been conducted on the occurrence of PFCs in landfills. All of them focused on leachates concentrations (3M 2001; Kallenborn et al. 2004; Bossi et al. 2008b; Woldegiorgis et al. 2008; Busch et al. 2010). In the most recent study, sum concentrations of 40 PFCs in landfill leachates ranged from <MQL to ~8000 ng L^{-1}. The authors conclude that landfills are sources for PFCs to the environment (Busch et al. 2010).

Several studies have been conducted on the fate of PBDEs in waste streams and related processes, such as waste treatment and recycling (Kim et al. 2006b; Chen et al. 2009; Choi et al. 2009; Petreas and Oros 2009; Zhao et al. 2009). Regarding PBDEs on landfills most studies focus on leachates concentrations (Osako et al. 2004; Odusanya et al. 2009) or atmospheric release during incineration processes (Agrell et al. 2004; Ter Schure et al. 2004). However, studies on PBDE emissions from sanitary landfills into the atmosphere were rarely performed. St-Amand et al. (2008) investigated seasonality and temperature dependence of PAHs and PBDEs close to a sanitary landfill in Ottawa, Canada. Trajectory as well as statistical and meteorological analysis revealed that gaseous PBDE concentrations predominantly depend on air mass origin (long-range transport). In contrast, particle-bound PBDEs are mainly released by local sources, such as the landfill itself. However, atmospheric emissions from landfills in Germany remain still unknown.

Beside the occurrence in waste water treatment plants (Simonich et al. 2000; Bester 2004; Zeng et al. 2007), it is estimated that synthetic musk fragrances are further emitted indirectly from leaching out of landfill sites (Slack et al. 2007). Although, several studies focus on the occurrence of musk fragrances in ambient air (Kallenborn et al. 1999a; Kallenborn and Gatermann 2004; Peck and Hornbuckle 2004; Chen et al. 2006; Peck and Hornbuckle 2006; Xie et al. 2007; Regueiro et al. 2009), it is still unknown if landfills are important point sources for those compounds.

Due to the lack of data for all of these semi-volatile organic contaminants, it is necessary to evaluate their occurrence in the ambient air at sanitary landfills. Therefore objective of this study was to elucidate whether landfills can be a significant source of airborne PFCs, PBDEs and synthetic musk fragrances to ambient air.

4.2 Materials and methods

4.2.1 Sampling

Air sampling was conducted at two landfill sites of Northern Germany from 11.08.-18.08.2009 (landfill LA) and 27.08.-02.09.2009 (landfill LB). LA is a sanitary landfill in a rural area and was closed in 2003. The former waste site is covered to prevent atmospheric emissions and sealed to the ground to avoid uncontrolled leakage. However, LA is still in operation for regional electronic waste, compost and plastic diminishments for pre-treatment and further transport. Landfill LB is situated close to a city and serves about 170000 inhabitants. This landfill consists of an old, inactive part and an active part that is still in use. The waste from the inactive part was transferred to another section which is subsequently sealed due to legal assignments. After pre-treatment, waste is deposited to the active section. LB deposits waste from almost all categories, such as sanitary waste, compost, plastics and electronic devices.

Two reference sites (RFs) were sampled simultaneously to LA and LB. The RFs were assumed not to be contaminated by landfills themselves. Since this part of northern Germany receives winds primarily from west- and south-western directions, RFs were chosen as sites located west of the landfills.

On each landfill and each reference site two high volume samplers were deployed and operated for one week. Airborne PBDEs/musk fragrances and PFCs were sampled separately. Four daily air samples (Monday, Tuesday, Wednesday, Thursday) and one three-day sample (Friday-Monday) were taken. The average sampling rate was about 350 m^3 d^{-1}. In total, 40 air samples and six field-blanks were taken.

Semi-volatile PFCs, PBDEs and musk fragrances were enriched in cartridges filled with PUF/XAD-2/PUF (Supelco, Germany). Particle-associated ionic PFCs, PBDEs and musk fragrances were accumulated on glass fibre filters (150 mm, Macherey&Nagel, Germany). Prior to the sampling, cartridges for PFCs were spiked on the upper PUF slice with 50 µL of an mass-labelled internal standard solution containing, ^{13}C 4:2 FTOH, ^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH, MeFOSA D_3, EtFOSA D_5, MeFOSE D_7, and MeFOSE D_9 (c=200 pg µL). PBDE and musk fragrances' cartridges were spiked with an internal standard solution containing ATHN D_{13}, MX D_{15}, MBDE28, MBDE47, MBDE99, MBDE153, MBDE183 and MBDE209 (c=200 pg μL^{-1}). After sampling, cartridges and GFF were separately packed in aluminium-coated polypropylene bags, sealed and stored at -20 °C until analysis.

4.2.2 Chemicals

Except for HHCB (51 % purity), all solvents, native and mass-labelled analytical standards and gases were of highest purity. A detailed table of all compounds, suppliers and qualities is listed in supporting information.

4.2.3 Extraction of semi-volatile PFCs in gas-phase samples

Extraction procedure and sample treatment of PFC samples were adopted from Dreyer et al. (2008). Briefly, PFC gas-phase samples were defrost and cold extracted three times (1 h, 1 h, 30 min) using acetone/Methyl tert-buthyl ether (MTBE) 1:1 (v:v). After each step, remaining solvent was blown out using nitrogen. Prior to the volume reduction, ethyl acetate was added as a keeper. The solvent was evaporated to approximately 2 mL using rotary evaporators (Buechi, R-210, Essen, Germany) at 30 °C and 430-390 mbar. The extracts were transferred to glass vials and reduced to 150 µL by a gentle stream of nitrogen (Barkey optocontrol 8s, Leopoldshöhe, Germany). Final extracts were transferred to measurement vials. Prior to measurement with GC-MS, 50 µL of an injection standard solution was added containing ^{13}C HCB and TCB D_3 (c=200 pg μL^{-1}).

4.2.4 Extraction of ionic PFCs in particle-phase samples

Ionic PFCs were extracted applying the method of Dreyer et al. (2009b). After unfreezing the GFF, FBE was performed using 150 mL methanol (MeOH). GFF were folded and inserted to the glass tubes. Prior to extraction 50 µL of an internal standard solution containing $^{18}O_2$ PFHxS, ^{13}C PFOS, ^{13}C PFBA, ^{13}C PFHxA, ^{13}C PFOA, ^{13}C PFNA, ^{13}C PFDA, ^{13}C PFUnDA and ^{13}C PFDoDA (c=200 pg μL^{-1}) was added. Three extraction cycles were run with a maximum temperature of 100 °C and hold for 30 min. Between each cycle solvent was allowed to cool down to 30 °C. After extraction, extracts were transferred and evaporated to about 1 mL (Synchore polyvap) at 190 mbar at a temperature of 45 °C. Extracts were transferred and reduced to 150 µL under a gentle flow of nitrogen. Prior to the measurement, 50 µL of an injection standard solution was added containing EtFOSAA D_5 (c=400 pg μL^{-1}).

4.2.5 Extraction and clean-up for PBDEs and musk fragrances from the gas- and particle phase

Details of extraction and clean-up procedures for PBDEs and musk fragrances from sampling devices are described in section 3.2.5 and 3.2.6. Briefly, air samples from the gas phase were defrosted and cold extracted using hexane/acetone 1:1 (v:v). Extracts were evaporated to about 1 mL using Synchore polyvap and further reduced to 150 µL by a stream of nitrogen. Finally, extracts were spiked with 50 µL of an injection standard solution containing Fluoranthene D_{15} and ^{13}C HCB (c=400 pg μL^{-1}).

GFF were extracted using ASE and hexane/acetone 1:1 (v:v). Prior to extraction, 50 µL of an internal standard solution containing mass-labelled MBDE27, MBDE47, MBDE99, MBDE153, MBDE183 as well as both musk fragrances AHTN D_3 and MX D_{15} (c=200 pg μL^{-1}) was added. Clean-up was performed using silica gel (0 % deactivated) covered by a layer of 3 g alumina oxide (15 % deactivated). Samples were eluted with 35 mL hexane and 30 mL hexane/DCM 3:1. Fractions were combined, evaporated to 1 mL using Synchore polyvap and further reduced to 150 µL. Prior to the measurement, 50 µL of an injection standard solution containing Fluoranthene D_{15} and ^{13}C HCB (c=400 pg μL^{-1}) was added.

4.2.6 Instrumental analysis

Analysis of PFC gas-phase samples was performed on an Agilent 6890N gas chromatograph connected to a PTV inlet and coupled to a 5975 inert mass spectrometer. Samples were quantified using the positive chemical ionisation (PCI). MS was run in the SIM mode. Chromatographic separation of target compounds was applied using a Wax capillary column

(Supelco, Munich, Germany; 30 m x 0.25 mm x 0.25 µm). Samples were also measured in NCI to confirm FASAs. Details on instrumental conditions were reported by Dreyer et al. (2008).

PFC air samples from the particle phase were analysed using high performance liquid chromatography (HPLC, HP100, Agilent, Waldbronn, Germany) coupled to an triple-quadrupole tandem mass spectrometer (MS/MS, Applied Biosystems, MDS SCIEX, Darmstadt, Germany) using negative electrospray ionisation and the multiple reaction monitoring (MRM) mode. Separation was done on a Phenomenex Synergi Hydro RP 80A column (Phenomenex, Aschaffenburg, Germany) with a length of 150 mm and a inner diameter of 2 mm connected to a guard column Phenomenex Synergi 2µ Hydro RO Mercury (200 mm lengths and 2 mm inner diameter). Detailed instrumental conditions can be found in Ahrens et al. (2007).

Measurement of PBDEs and musk fragrances from gas- and particle-phase samples was performed separately using GC-MS in the EI mode (musk fragrances) and NCI mode (PBDEs) using the previously optimized instrumental method described in chapter 3.

4.2.7 Quantification

Quantification was based on peak areas. Peak integration was done using MSD Chemstation (Agilent Technologies, version D.02.00.275) for all samples measured by GC-MS. HPLC samples were integrated and quantitated with Analyst (Applied Biosystems, MSD SCIEX, version 1.4.1). Mass fragments of PBDEs and musk fragrances used for quantification are listed in section 3.3.1 (musk fragrances, PBDEs) and in the supporting information (PFCs). Analyte concentrations were calculated using the internal standard method and a seven point calibration. Target compounds were quantified with an S/N>10 and detected with S/N>3. The PFC method quantification limits (MQL) were <1 pg m^{-3} and 23 pg m^{-3} for PFOSA (Dreyer et al. 2008). MQL and MDL of ionic PFCs were below 1 pg m^{-3} and 1 pg m^{-3}, respectively (Ahrens et al. 2007). A detailed list of PFC detection and quantification limits is given in supporting information (PFCs) and in section 3.3.4 (PBDEs and musk fragrances).

4.2.8 Quality assurance and quality control

All experiments were conducted in a clean lab (class 10000) at the GKSS research centre. For PFC analysis, PFC containing materials were avoided during sampling and preparation. Prior to the sampling PUF/XAD-2/PUF cartridges were soxhlet-cleaned for 24 h using acetone (PFCs) and hexane/acetone 1:1 (PBDEs and musk fragrances). GFF were baked at 400 °C for at least 12 h. Glassware was dish-washed and heated for 10 h at 250 °C. All standard solutions were only used at room temperature. Seven point calibrations (GC-MS: 2, 4, 10, 20, 50, 100, 200 pg µL^{-1}; HPLC-MS/MS: 1, 5, 10, 25, 50, 100, 500 pg µL^{-1}) were used to quantify target analytes. Linearity was tested according to DIN 32645 (1994). Mass-labelled standards were used to correct for analyte losses during analysis and measurements.

Average recovery rates for PFCs, PBDEs and musk fragrances spiked to the PUF/XAD-2/PUF cartridges prior to sampling are presented in table 16. Table 17 displays recovery rates of particle-phase samples. A list of individual recovery rates can be obtained from the supporting information.

Table 16: Average recovery rates (R, %) standard deviations (SD), relative standard deviations (RSD), median, minima (Min), and maxima (Max) values for semi-volatile PFCs, PBDEs and musk fragrances from gas-phase samples taken at landfills and reference sites. If not marked separately mean recoveries are referred to n=20.

	R (Average)	SD abs.	RSD	R(Median)	R(Min)	R(Max)
^{13}C 4:2 FTOH	10	7	1	9	2	30
^{13}C 6:2 FTOH^{a}	43	10	4	45	24	57
^{13}C 8:2 FTOH	47	14	6	45	27	78
^{13}C 10:2 FTOH	55	12	7	51	34	78
EtFOSA D_5	44	13	6	43	23	75
MeFOSA D_3	41	11	5	40	17	66
MeFOSE D_7	57	11	6	60	35	76
EtFOSE D_9	58	13	8	59	37	89
MBDE28^{b}	78	23	29	74	37	138
MBDE47^{c}	88	35	40	86	0	176
MBDE99	95	20	21	91	68	162
MBDE153^{d}	137	23	17	140	104	173
MBDE183	103	23	22	104	70	164
AHTN D_3	92	14	15	96	43	109
MX D_{15}^{e}	100	40	40	114	28	150

[a] n=11, [b] n=17, [c] n=17, [d] n=18, [e] n=18; note: Differences are due to matrix problems.

Table 17: Average recovery rates (R, %) standard deviations (SD), relative standard deviations (RSD), median, minima (Min), and maxima (Max) values for semi-volatile PFCs, PBDEs and musk fragrances from particle-phase samples taken at landfills and reference sites.

	R (Average)	SD abs.	RSD	R(Median)	R(Min)	R(Max)
$^{18}O_2$ PFHxS	51	26	51	40	15	125
^{13}C PFOS	71	19	27	67	23	104
^{13}C PFBA	53	29	54	45	18	137
^{13}C PFHxA	27	17	64	22	9	86
^{13}C PFOA	58	29	51	52	15	143
^{13}C PFNA	51	17	34	49	21	99
^{13}C PFDA	58	16	27	58	23	85
^{13}C PFUnDA	64	19	30	67	22	98
^{13}C PFDoDA	56	22	40	60	4	90
MBDE28	73	17	24	68	50	103
MBDE47	76	14	18	73	54	103
MBDE99	77	13	17	73	59	110
MBDE153	95	13	13	98	69	117
MBDE183	91	15	17	93	58	127
MBDE209	121	34	28	115	61	186
AHTN D_3	62	18	30	65	39	95
MX D_{15}	67	23	34	67	36	106

In order to determine possible contaminations during sampling procedure and sample handling, field blanks on each sampling site were taken. Additionally, solvent blanks (gas phase) and filter blanks (particle phase) were applied with each set of samples during extraction. Individual blank contamination of field blanks, filter and solvent blanks are given in the supporting information. Field blanks were occasionally contaminated with HHCB and AHTN in the low pg m^{-3} and ranged up to 4.7 pg m^{-3} for HHCB. However, all other field blanks were not contaminated with PFCs or PBDEs. Only some neutral PFCs were occasionally detected in solvent blanks ranging from 0.9 to 2.6 pg m^{-3} (8:2 FTOH, 10:2 FTOH and 12:2 FTOH). Ionic PFC concentrations in filter blanks were generally below 1 pg m^{-3}. Filter blanks of musk fragrances revealed a slight contamination with HHCB (about 1 pg m^{-3}) and MX (4 pg m^{-3}). All PBDE filter blanks were contaminated with BDE183 in the range of 2 to 3 pg m^{-3}. All filter blanks were highly contaminated with elevated concentrations of BDE209 ranging from 608 to 1943 pg m^{-3}. Therefore, BDE209 was excluded from further analysis. Concentrations for the remaining analytes were blank-corrected by subtraction of peak area.

4.2.9 Trajectory analysis

To investigate air mass origin during air sampling, air mass back trajectory were calculated by Hysplit 4.8 (Draxler and Rolph 2003) for an arriving height of 2 m using NCEP's Global Data Assimilation System (GDAS) with a resolution of one degree latitude/longitude. Seven-days back trajectories were calculated for 3 h intervals (one day samples) and 6 h intervals (three day samples).

4.2.10 Statistical analysis

Statistical analysis was performed using Winstat (version 2007.1). Due to the limited number of samples, data was not tested for normal distribution. The significance ($p<0.05$) of concentration differences was evaluated between landfill samples and their corresponding RFs using the Mann-Whitney-U-test.

4.3 Results

4.3.1 Air concentrations of PFCs in the gas- and particle phase

Volatile and semi-volatile PFCs were in detected all air samples. Figure 9 demonstrates total PFC concentrations of gas-phase samples from landfills and their RFs. Individual concentrations of neutral PFCs are given in the supporting information. PFC concentrations at LA ranged from 84 (LA5) to 126 pg m^{-3} (LA2). PFC concentrations at corresponding RF ranged from 42 (RF8) to 80 pg m^{-3} (RF9). PFC concentrations at LB were between 134 (LB2) and 706 pg m^{-3} (LB1). Those of corresponding RF ranged from 54 (RF17) to 284 pg m^{-3} (RF16). With an average contribution of 82 % FTOH were the most frequently detected class of volatile PFCs in all samples in the gas phase, followed by FASA (5 %), FASE (4 %) and FTA (3 %). Proportions of all gas-phase samples from landfills and corresponding RFs are displayed in figure 10.

Ionic PFCs bound to particles were detected in all samples. Figure 11 demonstrates concentrations of ionic PFCs in the particle phase from landfill sites and RFs. Individual concentrations of ionic PFCs are given in the supporting information. Sum concentrations of particulate PFCs ranged from 6 to 15 pg m^{-3} at LA as well as from <1 to 15 pg m^{-3} at corresponding RF. At LB ionic PFCs were detected at sum concentrations of <MQL to 42 pg m^{-3}. PFC concentrations observed at RF were between 11 and 16 pg m^{-3}. PFOS, PFBA, PFHxA, and PFOA were detected in all samples. Ionic PFCs, PFOSA, PFBS and PFHxS and those with chain length longer than C_8 were only occasionally detected at low concentration levels (<1 pg m^{-3}). Except for samples LB4, LA3 and LA4, PFBA was the predominant ionic PFC with average proportions of 59 %, followed by PFHxA (16 %), PFOS (11 %) and PFOA (9 %). Proportions of particle-phase samples from landfills and corresponding RFs are displayed in figure 12.

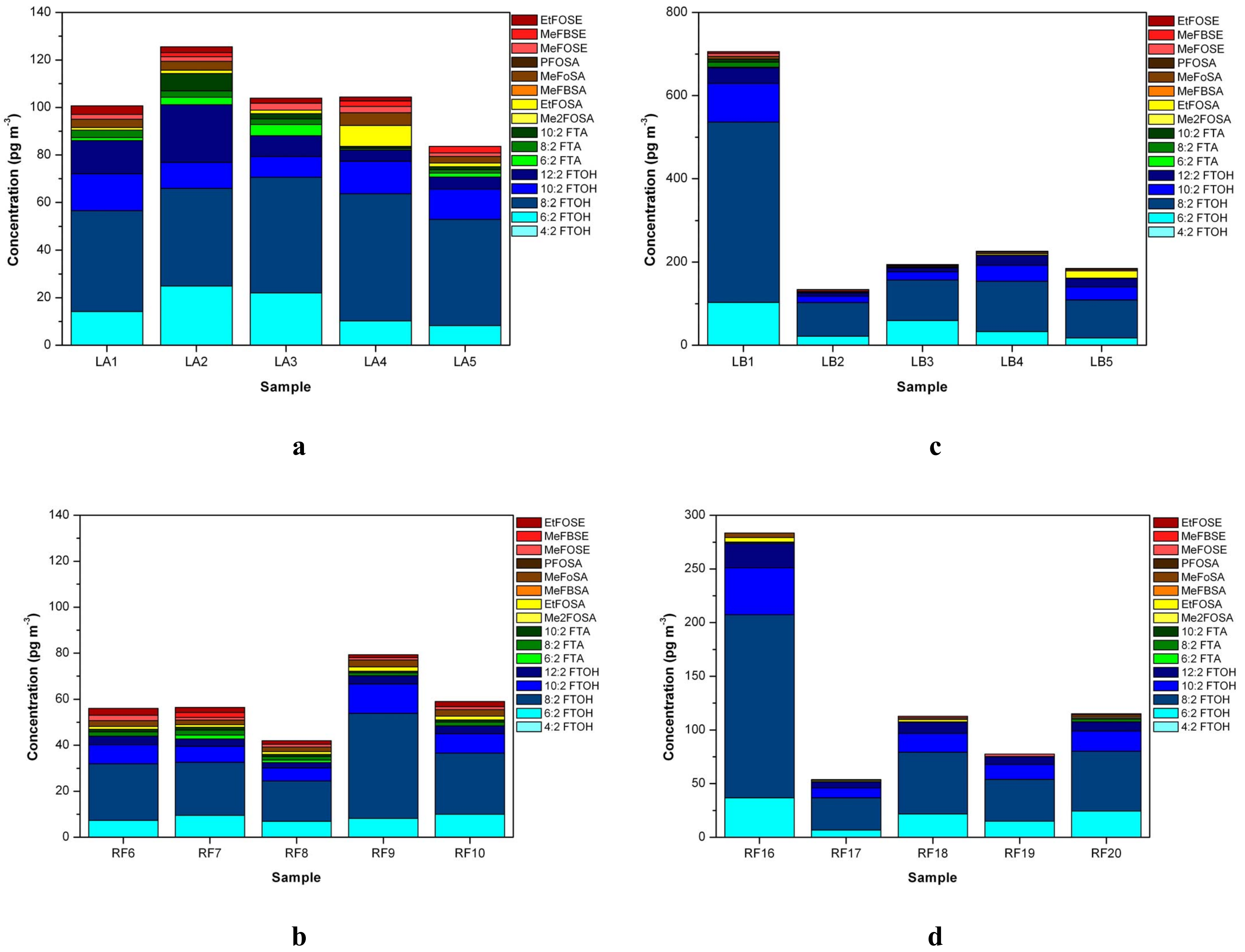


Figure 9: Concentrations (pg m^{-3}) of airborne PFCs in gas-phase samples taken at landfills LA (a) and LB (c) and at the corresponding reference sites (b, d). Sampling periods: 11.08.-18.08.2009 (LA) and 27.08.-02.09.2009 (LB). Note the different scales.

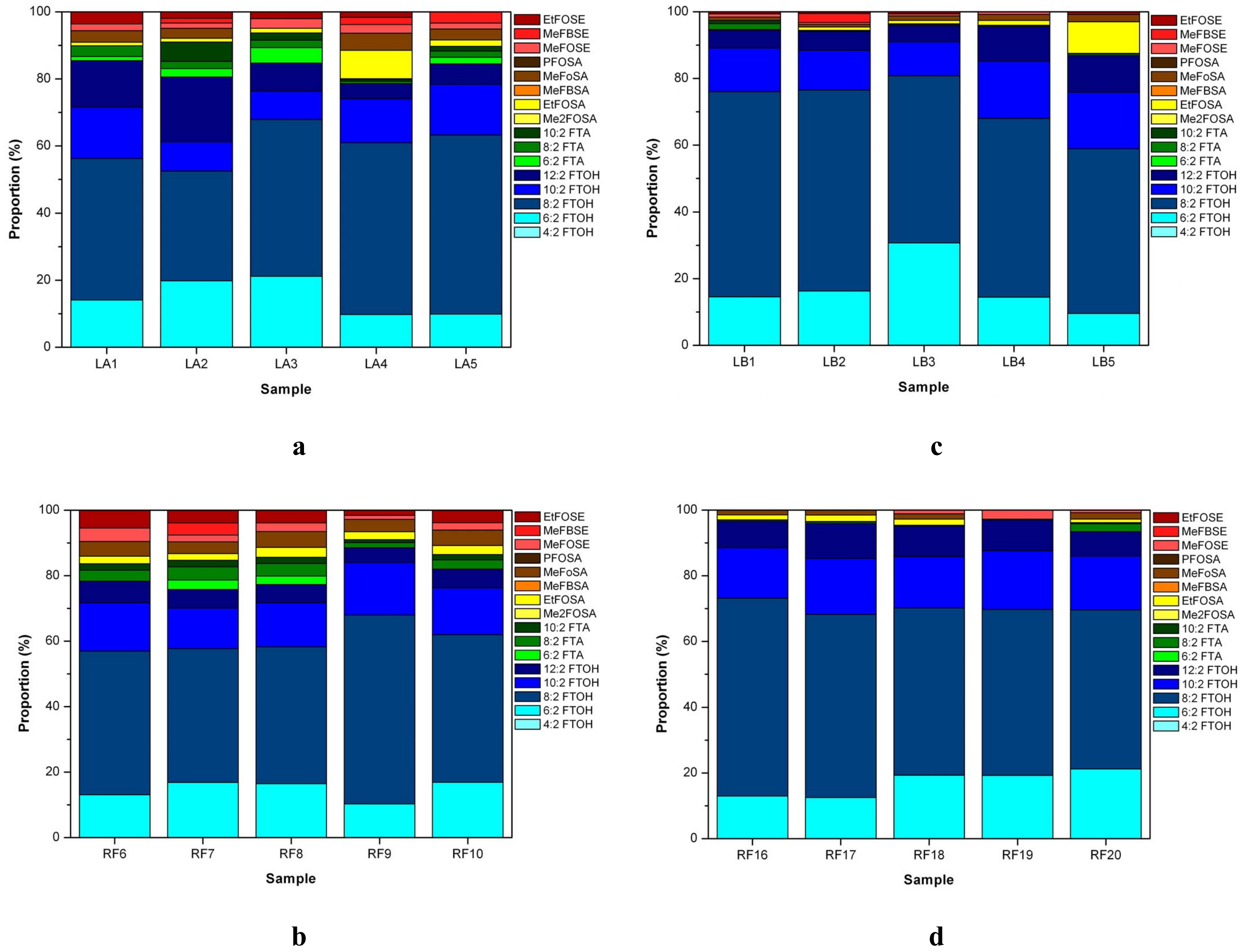


Figure 10: Proportions (%) of airborne PFCs in gas-phase samples taken at landfills LA (a) and LB (c) and at the corresponding reference sites (b, d). Sampling periods: 11.08.-18.08.2009 (LA) and 27.08.-02.09.2009 (LB).

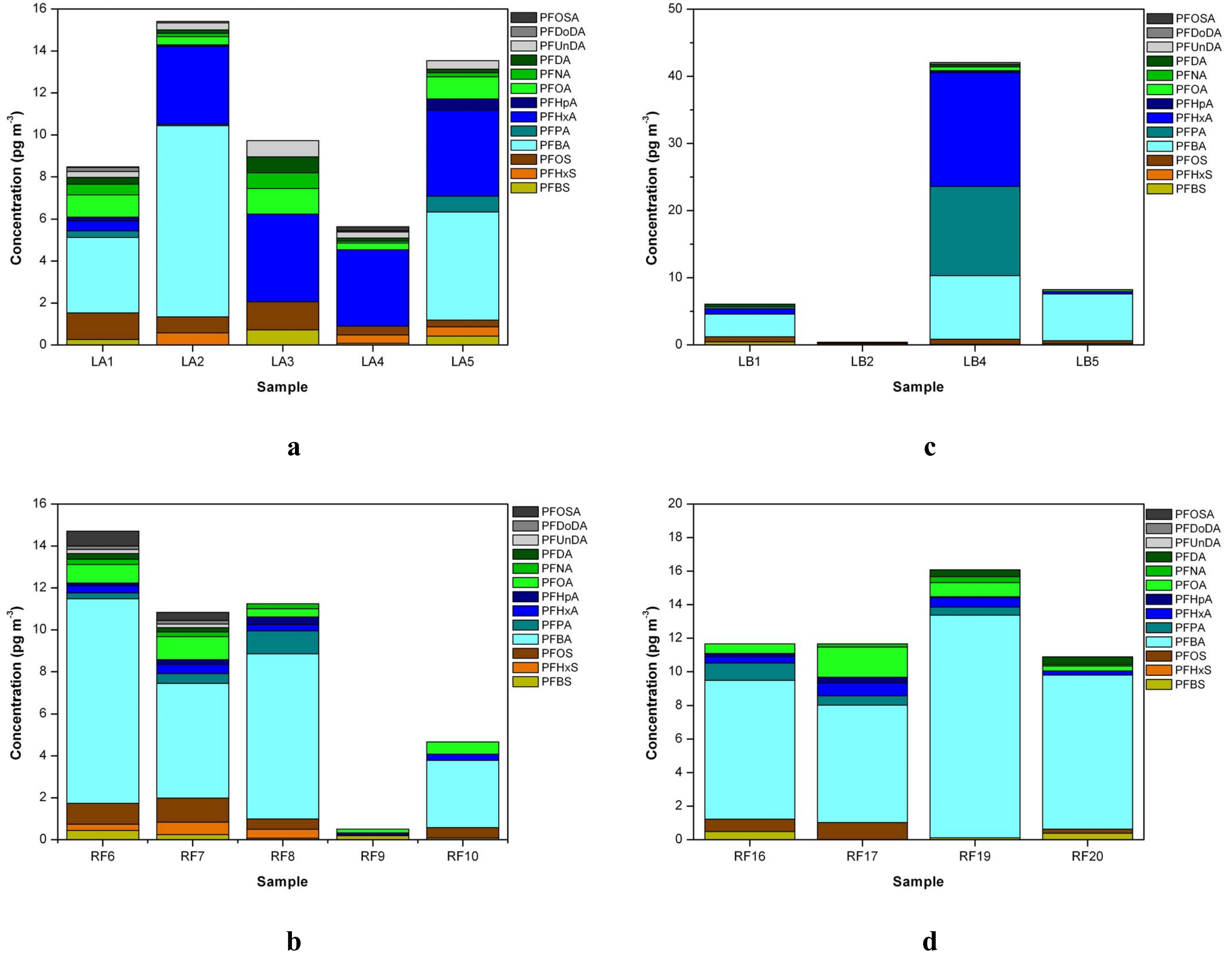


Figure 11: Concentrations (pg m^{-3}) of airborne PFCs in particle-phase samples taken at landfills LA (a) and LB (c) and at the corresponding reference sites (b, d). Sampling periods: 11.08.-18.08.2009 (LA) and 27.08.-02.09.2009 (LB). Note the different scales.

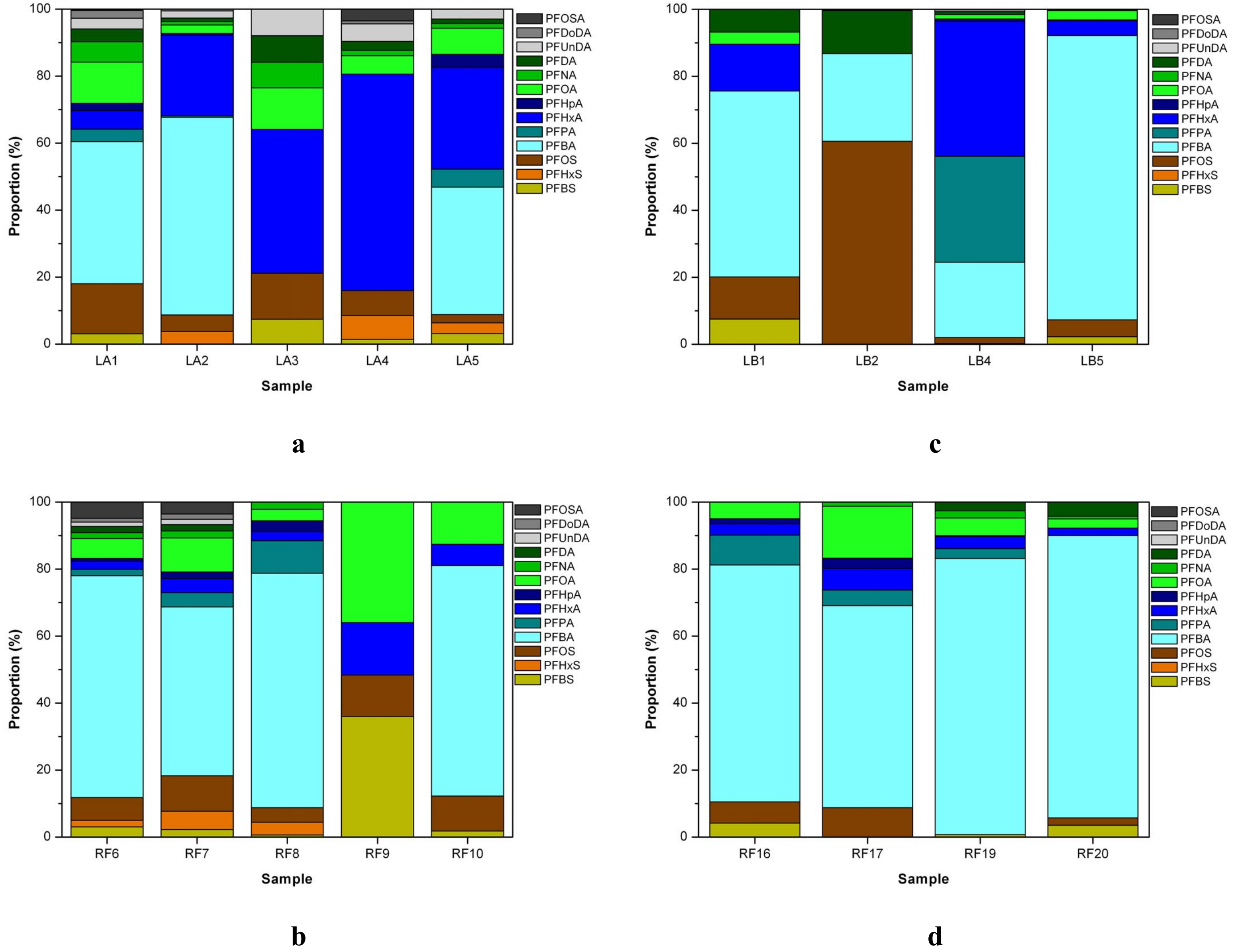


Figure 12: Proportions (%) of airborne PFCs in particle-phase samples taken at landfills LA (a) and LB (c) and at the corresponding reference sites (b, d). Sampling periods: 11.08.-18.08.2009 (LA) and 27.08.-02.09.2009 (LB).

4.3.2 Air concentrations of musk fragrances in the gas- and particle phase

Musk fragrances in the gas phase were detected in all air samples. Figure 13 demonstrates musk fragrance concentrations at landfill sites and their corresponding RFs. Individual concentrations of musk fragrances are given in the supporting information. Musk fragrance concentrations at landfill LA ranged from146 (LA3) to 990 pg m^{-3} (LA1). In corresponding RF, these compounds were observed at 47 (RF9) and 84 pg m^{-3} (RF8). Concentrations at LB were observed from 579 (LB5) to 1947 pg m^{-3} (LB2). Concentrations of musk fragrances taken in air samples at RF simultaneously ranged from 50 to 1016 pg m^{-3}. HHCB and AHTN were the only compounds detected in all air samples. ADBI was only occasionally observed (LA1, LA3, LA4, and RF20). AHMI was only detected in sample LA4 (8 pg m^{-3}). ATII as well as both nitro musks were not observed in one of the samples. The average proportions in gas-phase samples were 85 % (HHCB) and 14 % (AHTN). Proportions of all gas phase samples from landfills and corresponding RF are displayed in figure 14.

Musk fragrances in the particle phase were constantly detected in samples from LB and its corresponding RF. LA samples were not contaminated with musk fragrances. In samples RF9 and RF10 musk fragrances were observed. Sum concentrations at LB and its RF ranged from 3 to 103 pg m^{-3}. Sum concentrations in RF9 and RF10 were of 20 and 30 pg m^{-3}, respectively. HHCB and AHTN were the only observed substances bound to particles. The proportions were dominated by AHTN (60 % or even higher) in the majority of particle phase samples. In samples LB3 and RF20 proportion of HHCB succeeds those of AHTN. In samples RF9 and LB4 ratios of AHTN and HHCB are quite similar.

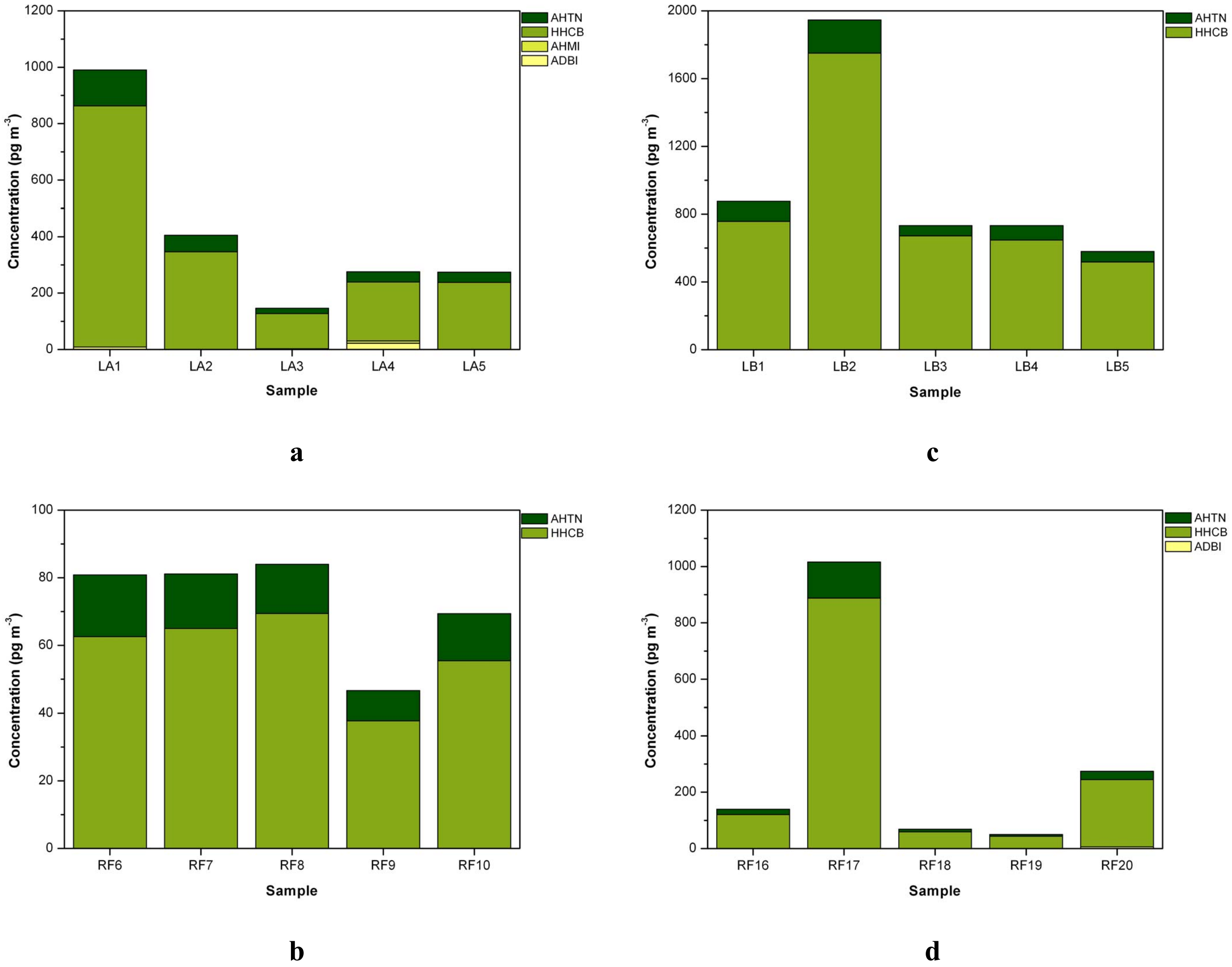


Figure 13: Concentrations (pg m^{-3}) of airborne musk fragrances in gas-phase samples taken at two landfills LA (a) and LB (c) and at the corresponding reference sites (b, d). Sampling periods: 11.08.-18.08.2009 (LA) and 27.08.-02.09.2009 (LB). Note the different scales.

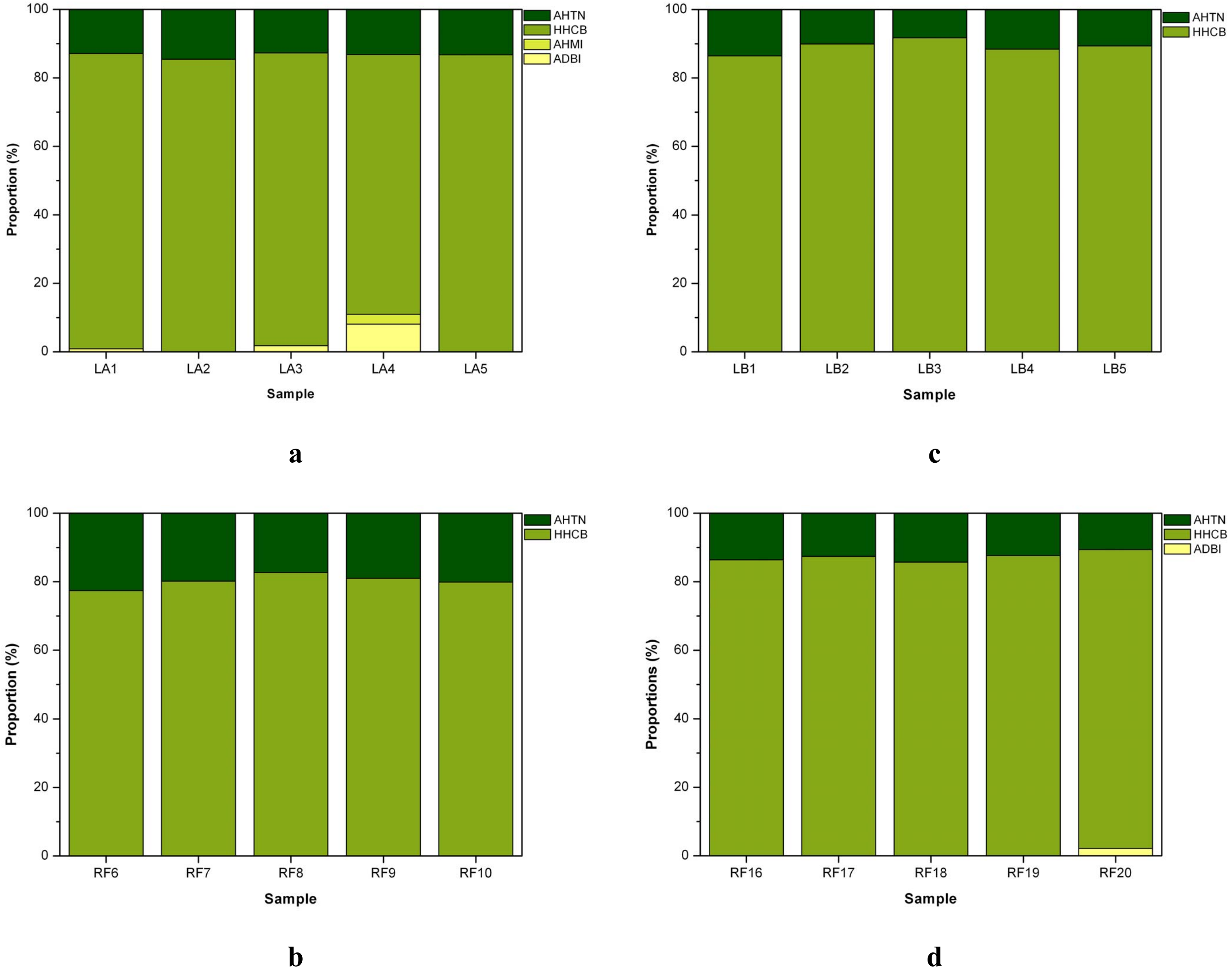


Figure 14: Proportions (%) of airborne musk fragrances in gas-phase samples taken at two landfills LA, (a) and LB (b) and at the corresponding reference sites (b, d). Sampling periods: 11.08.-18.08.2009 (LA) and 27.08.-02.09.2009 (LB).

4.4.3 Air concentration of PBDEs in the gas- and particle phase

None of the PBDE congeners was detected in any of the gas phase samples. BDE183 was detected in all particle-phase samples. Concentrations at LA3, LA4, RF6 and RF9 were lower than filter blanks. BDE183 concentrations in remaining LA samples and corresponding RF were between 1 and 3 pg m^{-3}. Figure 15 presents BDE183 concentration in the particle phase from landfill LB and its corresponding RF. Concentrations in samples in landfill LB ranged from 1 to 11 pg m^{-3}. In corresponding RF, BDE183 was constantly observed at concentrations in the range of <1 to 3 pg m^{-3}. In this sample RF16 BDE47 (20 pg m^{-3}), BDE100 (6 pg m^{-3}), BDE99 (15 pg m^{-3}) and BDE154 (2 pg m^{-3}) were observed. BDE209 was detected in all samples from the particle phase. Due to the high blank values, as described in section 4.2.8, it was decided to exclude this substance from further interpretations.

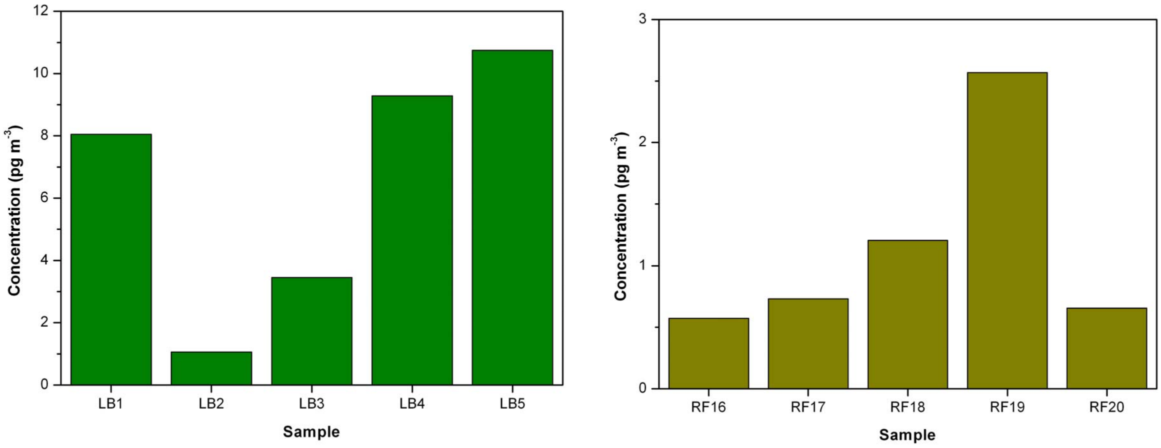


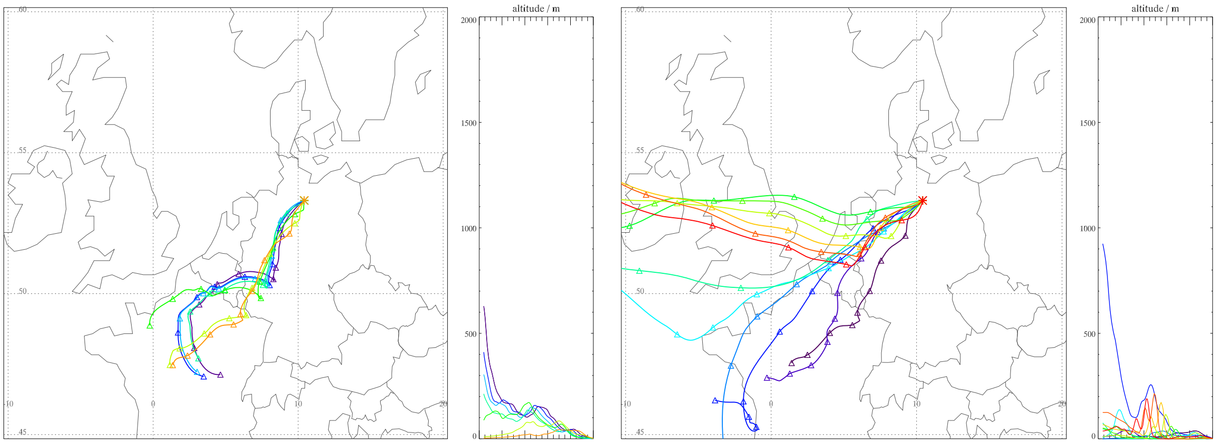
Figure 15: Concentrations (pg m^{-3}) of BDE183 in the particle phase in air samples from landfill LB and the corresponding RF. Sampling period: 27.08.-02.09.2009. Note the different scales.

4.5 Discussion

Concentrations of FTOHs, FASAs and FASEs determined here, were in the same range as those determined in compared to other studies from rural and semi-rural areas in Europe (Barber et al. 2007; Jahnke et al. 2007; Dreyer et al. 2009b). However, it should be mentioned that studies from Barber et al. (2007) and Jahnke et al. (2007) differed in the spectrum of analytes. As reported in other studies (Barber et al. 2007; Jahnke et al. 2007; Dreyer and Ebinghaus 2009; Dreyer et al. 2009b; Jahnke et al. 2009), FTOH were the predominant substance class and 8:2 FTOH detected in highest amounts in this study.

Compared to the corresponding RFs, air concentrations of volatile and semi-volatile PFCs were 1.5 to 3 times higher. Proportion analysis revealed FTOHs to be responsible for the concentration enhancement. Statistical analysis revealed that concentrations of 6:2, 8:2, 10:2, and 12:2 FTOH were significantly higher at landfill LA ($p < 0.05$). In contrast to LA, only concentrations of 8:2 FTOH were significantly higher at LB than at its corresponding RF ($p<0.05$). Concentrations of FTAs, FASAs and FASEs did not differ significantly between landfills and their corresponding RFs. Therefore, in particular FTOHs and less FASAs and FASEs may subject to volatilisation from landfills. This may be attributed to the lower volatility of FASEs and FASAs and therefore limited potential of being released (see section 1.3). FTOHs are incorporated in polymers in a wide array of products such as plastics, paper packaging and surfactants (Jensen et al. 2008; Kissa 2001). A laboratory study revealed that PFCs can be released from those products (Dinglasan-Panlilio and Mabury 2006). These processes may also occur during the storage in landfills.

Several studies demonstrated the importance of air mass origin regarding PFC concentrations in ambient air. For central Europe it was reported that higher PFC concentrations coincided with air masses from westerly regions such as UK, Netherlands, Benelux and Western Germany (Jahnke et al. 2007; Dreyer and Ebinghaus 2009; Dreyer et al. 2009b). In this study analysis of back trajectories revealed that air masses originate constantly from potential source regions west of the sampling sites. This is reflected by the rather constant PFC air concentrations and proportions of volatile PFCs observed these sites. However, PFC concentrations in samples LB1 and RF16 were elevated. These may caused either by other local sources, since sampling sites were situated close to a city, or subject to air transport from far away source regions. Dreyer et al. (2009b) and Primbs at al. (2008) reported that PFC concentrations increased significantly with the time air masses spend over urban areas. Since air masses of samples LB1 and RF2 arrived with low velocities (figure 16a), high concentrations may be explained by passing over highly populated and industrial areas west from the sites. This is supported by Dreyer et al. (2009b) in air samples from the same region. In contrast, the rapid decline in PFC concentrations in samples LB2 and RF17 can likely be attributed to air masses that arrived with high velocities from coastal regions and thus shorter residence time over those source regions (figure 16b).



a b

Figure 16 a, b: Selected seven days air mass back trajectories calculated for three hours intervals (arrival height 2 m). Generated by Hysplit 4.8 using GDAS data for sample LB1 (a) (ΣPFCs= 706 pg m^{-3}) and sample LB2 (b) (ΣPFCs= 134 pg m^{-3}). Triangles represent 12 h tags of every trajectory. In addition, trajectory heights are plotted.

Taken the prevailing wind direction in account, it can be assumed that during the sampling periods RFs were not contaminated by the landfills itsselves or by other potential sources that are located between these sites. Thus, trajectory analysis supports the assumption that volatile and semi-volatile PFCs originated from the landfills.

Ionic PFCs from particle phase determined in this study are in the same range as those observed by Harada et al. (2005) for a rural region of Japan. However, PFOS and PFOA concentrations were more than two orders of magnitude lower than those of Barber at al. (2007) and Harada et al. (2005) in urban areas of UK and Japan, respectively. In contrast to other studies of Dreyer et al. (2009b) and Barber et al. (2007), who observed PFOS and PFOA in maximum proportions, PFBA was the most dominant compound in this study. However, in samples LA3, LA4 and LB4 PFHxA was detected in highest proportions. For ionic PFCs distinct differences between landfills and their corresponding RFs were not observed. Moreover, samples are characterized with high variation in concentrations and proportions indicating an enhanced uncertainty of these data, probably due to revolatilisation of PFCAs from GFF (Arp and Goss 2008).

Musk fragrances were detected predominantly in the gas phase which confirms other studies (Peck and Hornbuckle 2004; Peck and Hornbuckle 2006; Xie et al. 2007). In general, total concentrations of gas-phase musk fragrances were in about the same range as reported in other studies from comparable rural to suburban locations in Northern Germany (Xie et al. 2007), Norway (Kallenborn et al.1999a) and North America (Peck and Hornbuckle 2004; Peck and Hornbuckle 2006). However, elevated concentrations of samples LA1, LB5 and RF17 were comparable to those reported for urban sites in North America (Peck and Hornbuckle 2006).

As presented in other studies (Kallenborn et al. 1999a; Peck and Hornbuckle 2004; Peck and Hornbuckle 2006; Chen et al. 2007b), HHCB and AHTN were the predominant substances in all samples. Xie et al. (2007) reported mean ratio of HHCB/AHTN of 3.5 which is comparable to that of the European market volumes in 2000 (ratio 3.9) (OSPAR 2004). However, mean ratio of HHCB/AHTN observed in this study was 6.5. This may be due to the enormous variability of HHCB and AHTN content in personal care products, as demonstrated by Roosens et al. (2007) and Reiner and Kannan (2006). They revealed that concentrations of HHCB and AHTN can vary with every product type by several orders of magnitude. The variety of personal care products containing different quantities of musk fragrances which are possibly disposed on landfills, may explain differences in HHCB/AHTN ratios. That other compounds such as ADBI and AHMI were only occasionally observed, may be due to the distinctly lower production volumes of those compounds compared to HHCB and AHTN (OSPAR 2004). That MX and MK were not detected in any of the samples is in contrast to the findings of Kallenborn et al. (1999a) who detected those nitro musks constantly in the atmosphere of Norway. However, nitro musk's phase out in the 1990s and restrictions in the EU may be responsible for the decline of the compounds' atmospheric concentrations.

Musk fragrance concentrations of all samples of landfill LA and LB were significantly higher than those of corresponding RFs ($p<0.05$). Trajectory analysis revealed that air masses arrived from predominantly westerly to south-westerly directions in both sampling periods. Elevated concentrations of musk fragrances at landfills are not displayed by trajectories. A modelling study by Aschmann et al. (2001) revealed atmospheric lifetime of HHCB of 5.3 h due to gas-phase reactions with the OH radical. It can be assumed that structurally similar musk fragrances are degraded in a same way, however this is not known yet. Aschmann et al. (2001) concluded that HHCB will not undergo long-range transport. Highest concentration of LB2 was accompanied simultaneously by strongly elevated concentrations at corresponding RF (RF17) probably due to unknown local sources. Trajectories were not able to elucidate these variations. However, the concentration difference between the RF and landfill is about the same extent as in the other samples. On the basis of this data set, it can be assumed that musk fragrances are emitted from waste accumulated at landfills but the air concentrations may partly be interfered by other (local) sources.

Except for sample RF16, PBDEs from gas-phase samples were not detected in this study. These findings are in contrast to those of St-Amand et al. (2008) who detected air concentrations of PBDEs up to 7 pg m^{-3} near to a sanitary landfill in Ottawa, Canada. However, several studies from Europe revealed that airborne PBDEs generally decrease from urban sites as local sources to more rural areas (Jaward et al. 2004a; Jaward et al. 2004b; Lee et al. 2004; Gioia et al. 2006). UK is regarded as regional source for continental Europe (Law et al. 2008). As trajectory revealed, air masses were arriving partly from these directions. However, elevated concentration could not be observed on landfills and RFs. Therefore neither landfills nor nearby local sources or long-range transport influenced PBDE air concentrations.

BDE183 was the only congener that was detected in particle-phase samples. The concentration differences between samples of LA and the corresponding RF were not significantly different. In contrast, concentrations of LB samples were significantly higher than those of the corresponding RF ($p<0.05$). Due to the low potential of long-range transport it can be assumed that this compound originated from the landfill or other local sources in that region.

Overall, concentrations of analysed substances decreased in the order of musk fragrances > PFCs > PBDEs. Air concentrations of musk fragrances usually exceed those of PFC by factors of 3 to 14 ($p<0.05$). However, musk fragrance of samples LA3 and LB1 were in the same order as PFC concentrations. PFCs and musk fragrances air concentrations at RF were quite uniform displaying background concentration at those sites. Nevertheless, sample RF17 revealed occasionally elevated concentrations which can be attributed to an additional local source (see above). None of the substance classes was correlated to each other. This might be explained by varying contaminant contents of products disposed at the landfill sites or their different release mechanisms. Furthermore, different contributions of local sources as well as atmospheric transport from distant source regions may have influenced the gas-phase composition of those substances. Samples from LB were significantly higher concentrated with PFCs, particle-bound PBDEs and musk fragrances than those from LA ($p<0.05$). Therefore it can be assumed that principally the source strength of an active landfill (LB) is higher than those of an inactive landfill (LA). Furthermore, different types of waste may have influenced the emissions from these sites, since proportions of PFCs and musk fragrances were different.

4.6 Conclusion

The analysis of PFCs, PBDEs and musk fragrances in air at two landfills and two corresponding reference sites that were not influenced by landfills indicated that landfills are sources for volatile and semi-volatile PFCs and musk fragrances. Significant concentration differences were mainly driven by FTOHs. PBDE concentrations and concentrations of particle-bound ionic PFCs did not differ between sites revealing that source strength of landfills regarding these compounds is rather low. The source strength for musk fragrances is higher than for volatile PFCs. Furthermore, the source strength for airborne PFCs, PBDEs and musk fragrances of the active landfill is higher than those of the inactive landfill.

5. Study 2: Waste water treatment plants as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air

5.1 Introduction

For many industrial chemicals WWTPs are filters between technosphere and the environment. Release mechanisms of chemicals within a WWTP are volatilisation from the waste water, aerosol formation, adsorption to sewage sludge, degradation during the treatment process or discharge to effluents due to incomplete removal. Waste water contains elevated concentration of non-polar substances, such as fat and oils, which form surface films at the air-water interface. Lipophilic trace compounds are accumulated in this micro layer to a significant amount compared to the bulk phase (Sauer et al. 1989; Hardy et al. 1990). It was reported that these compounds are typical waste water constituents such as aliphatic hydrocarbons and estrogenic substances as well as pollutants like PAHs and pharmaceuticals (Radke and Herrmann 2003).

At WWTPs, aerosols are formed during bubble bursting in the aeration tanks (Radke and Herrmann 2003; Beck and Radke 2006). The action of water movement forms air bubbles under/at the air-water surface. Afterwards, the trapped bubbles burst and release aerosol droplets into the atmosphere (Oppo et al. 1999; McMurdo et al. 2008) (figure 17).

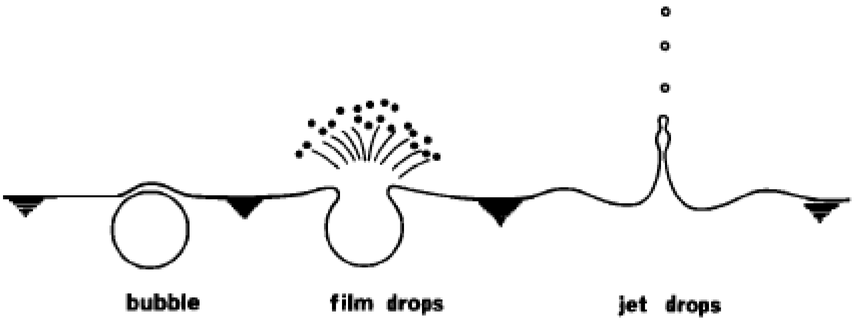


Figure 17: Schematic aerosol production (film- and jet drops) from bursting air bubbles at the air-water interface. Figure adapted from Resch et al. (1986).

Aerosols emitted via this mode may contain contaminants which are usually found in waste water such as PAHs or sterols (Lepri 2000; Radke and Herrmann 2003). Thus PFCs, PBDEs and musk fragrances may be emitted to the atmosphere as well. Besides the aerosol formation at aeration tanks direct emissions of organic trace compounds by volatilisation should be considered. Several measurements and modelling studies revealed that volatile organic compounds (VOC) are released during waste water treatment (Roberts and Daendliker 1983; Namkung and Rittmann 1987; Zhu et al. 1998; Chern and Yu 1999; Sree et al. 2000).

Due to their use in numerous products (see section 1.2), PFCs, PBDEs and musk fragrances were often detected in waste water (Simonich et al. 2000; Simonich et al. 2002; Bester 2004; North 2004; Boulanger et al. 2005; Sinclair and Kannan 2006; Loganathan et al. 2007; Zeng et al. 2007; Arnold et al. 2008; Becker et al. 2008; Ying et al. 2009).

The discharge of waste water is the major route of introducing PFCs into the environment (Prevedouros et al. 2006; Becker et al. 2008). Several studies investigated concentrations and behaviour of ionic PFCs during waste water treatment process (Schultz et al. 2006; Sinclair and Kannan 2006; Longanathan et al. 2007; Becker et al. 2008). These studies revealed that concentrations of particular PFC species such as PFOS and PFOA were increasing from influent to effluent. This has been linked to metabolic transformation of precursors (Lange 2002; Dinglasan et al. 2004; Boulanger et al. 2005; Rhoads et al. 2008). Thus, WWTPs may be a source for volatile and semi-volatile PFCs. Processes at the air-water interface of aeration tanks may promote volatilisation of precursor compounds and emissions of particle-bound PFCAs and PFSAs.

Several studies investigated concentrations and fate of PBDEs during waste water treatment process (North 2004; Goel et al. 2006; Song et al. 2006). Due to their physico-chemical properties PBDEs are particularly removed from waste water by sorption to sewage sludge (Arnold et al. 2008; North 2004; Knoth et al. 2007; Ricklund et al. 2008). The removal efficiency by this mechanism is supposed to be more than 90 % (North 2004; Song et al. 2006). Remaining fraction of PBDEs leaves the plant unaltered into the effluent. However, currently it is not well known, whether particularly low brominated PBDEs can volatilise from waste water into the atmosphere during aeration process.

Various studies investigated the occurrence and behaviour of musk fragrances in the process of water treatment (Kanda et al. 2003; Bester 2004; Kupper et al. 2004; Osemwengie and Gerstenberger 2004; Yang and Metcalfe 2006; Zeng et al. 2007). Main removal mechanism of musk fragrances from waste water is the sorption to sewage sludge (Bester 2004; Kupper et al. 2004; Yang and Metcalfe 2006). However, the removal efficiency varies with the design and operation of the plant (Simonich et al. 2000). Overall, waste water treatment results in removal efficiencies of musk fragrances of about >70 % (Simonich et al. 2000; Bester 2004; Yang and Metcalfe 2006). Due to their comparative high Henry's law constant (see section 1.3) musk fragrances have the strong potential to be emitted from waste water in particular at aeration tanks into the atmosphere (Yang and Metcalfe 2006). Although several studies focus on the occurrence of musk fragrances in ambient air (Kallenborn et al. 1999a; Peck and Hornbuckle 2004; Chen et al. 2006; Peck and Hornbuckle 2006; Xie et al. 2007), their emission potential from WWTPs is not known yet.

Therefore, objective of this study is to determine whether PFCs, PBDEs and musk fragrances can be emitted from waste water treatment plants during treatment process and therefore contribute to the total burden of atmospheric contaminants.

5.2 Materials and methods

5.2.1 Sampling

Air sampling was conducted at two WWTPs in Northern Germany from 04.08.-11.08.2009 (WWTP WA) and 20.08.-27.08 2009 (WWTP WB) (figure 18). WA is located in the vicinity of the town Lüchow in the federal state of Lower Saxony, Germany. One-third of the waste water originate from households; two-thirds from industrial processes resulting in 86500 population equivalents. WB is located in the outskirts of the city of Lüneburg, Lower Saxony, Germany. The mean population equivalent is estimated to 210000. Two-thirds of the waste water originates from private households and one-third from industrial processes.

At each site, two high volume samplers were operated simultaneously directly above the aeration tanks in order to collect gas-phase and particle-phase PFCs, PBDEs and musk fragrances. At each site (RF and WWTP) four daily (Monday, Tuesday, Wednesday, Thursday) and one three-day (Friday-Monday) air samples were taken. Average sampling volume was about 350 m^3 d^{-1}. Six field blanks were taken in order to determine sample contamination of analytes during sample handling and transport. Neutral PFCs, PBDEs and musk fragrances were enriched on PUF/XAD-2/PUF cartridges. Particle-associated ionic PFCs, PBDEs and musk fragrances were accumulated on glass fibre filters (150 mm, Macherey&Nagel, Germany). Prior to the sampling, cartridges for PFCs were spiked on the upper PUF slice with 50 µL of an internal standard solution containing, ^{13}C 4:2 FTOH, ^{13}C 6:2 FTOH, ^{13}C 8:2 FTOH, ^{13}C 10:2 FTOH, MeFOSA D_3, EtFOSA D_5, MeFOSE D_7, and MeFOSE D_9 (c=200 pg µL^{-1}). PBDE and musk fragrances' cartridges were spiked with an IS containing ATHN D_{13}, MX D_{15}, MBDE28, MBDE47, MBDE99, MBDE153, MBDE183 and MBDE209 (c=200 pg µL^{-1}). After sampling cartridges and GFF were packed separately in alumina-coated polypropylene bags, sealed airtightly, and stored at -20 °C.

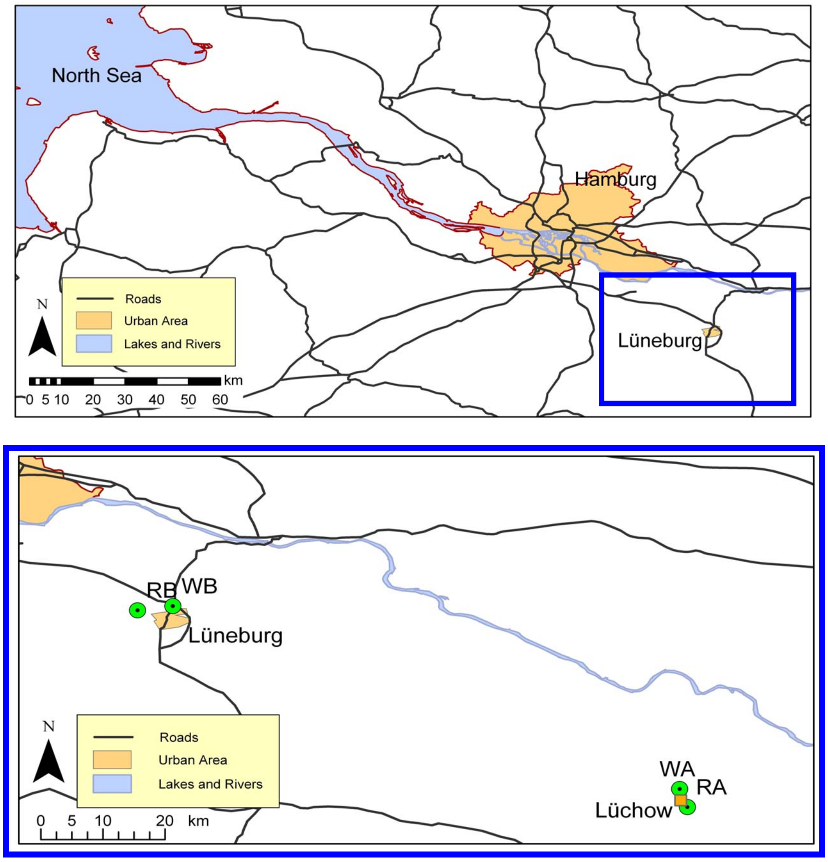


Figure 18: Sampling locations of two WWTPs: WA and WB and the corresponding RFs (RA, RB).

5.2.2 Chemicals

Except for HHCB (51 % purity), all solvents, native and mass-labelled analytical standards and gases were of highest purity. A detailed table of all compounds, suppliers and qualities is listed in supporting information.

5.2.3 Extraction of semi-volatile PFCs, PBDEs and musk fragrances in gas-phase samples

PFCs in gas-phase samples were extracted according to the method of Dreyer et al. (2008). Details on sample preparation can be found in section 4.2.3. Gaseous PBDEs and musk fragrances extraction procedures are described in section 3.

Briefly, PUF/XAD-2/PUF cartridges were cold extracted three times (1 h, 1 h, 30 min) using MTBE/acetone 1:1 (v:v) for PFCs and hexane/acetone 1:1 (v:v) for PBDEs and musk fragrances. The volume of the extracts was reduced to 150 µL and extracts were transferred to measurement vials. Prior to the measurement, 50 µL of an injection standard solution containing ^{13}C HCB and TCB D_3 (c=400 pg µL^{-1}; PFC analysis) or ^{13}C HCB and Fluoranthene D_{15} (c=400 pg µL^{-1}, PBDEs and musk fragrance analysis) was added.

^{13}C PFUnDA and ^{13}C PFDoDA (c=200 pg µL^{-1}; PFCs) or MBDE27, MBDE47, MBDE99, MBDE153, MBDE183, AHTN D_3 and MX D_{15} (c=200 pg µL^{-1}; PBDEs and musk fragrances) was added to correct for analyte losses during sample handling and extraction. The volume of the extracts was reduced to about 1 mL. PBDE and musk fragrance extracts were purified by silica gel and alumina oxide. Samples were eluted with hexane and hexane/DCM. The eluates were evaporated and transferred to measurement vials. Prior to the GC-MS measurements, 50 µL of an injection standard solution containing Fluoranthene D_{15} and ^{13}C HCB (c=400 pg µL^{-1}) was added. PFC samples were spiked with 50 µL of an injection standard solution containing EtFOSAA D_5 (400 pg µL^{-1}). After spiking PFC extracts with the injection standard, white solids was formed. Therefore, sample vials were centrifuged at 5000 rpm for 15 min (Hettich, Universal 320, Tuttlingen, Germany). The remaining liquid fraction was measured.

5.2.5 Instrumental analysis

Semi-volatile and volatile PFCs were measured by GC-MS using the PCI and SIM mode. Samples were also measured in NCI to confirm FASAs. Chromatographic separation was performed on a Supelco Wax column (30 m x 0.25 mm x 0.25 µm). Ionic PFCs were analysed by HPLC-MS/MS using an ESI source (MRM mode). Separation was performed by a Phenomenex Synergi Hydro RP 80A column connected to a guard column. Measurement of PBDEs was performed by GC-MS. MS was run in the NCI using SIM mode. Separation was conducted using a HP5-MS column (15 m x 0.25 mm x 0.25 µm). For determination of musk fragrances GC-MS was operated in the EI mode (SIM). Analytes were separated by HP-5 MS column (30 m x 0.25 mm x 0.25 µm). Detailed instrumental conditions of GC-MS and HPLC MS/MS can be obtained from Dreyer et al. (2008) and Ahrens et al. (2007) for PFCs and section 3 for PBDEs and musk fragrances.

5.2.6 Quantification

Peak integration was performed using MSD Chemstation (version D.02.00.275) for all samples analysed by GC-MS. HPLC-MS/MS peaks were integrated with Analyst software (version 1.4.1). Mass fragments that were used for determination and quantification are presented in section 3.3.1 (PBDEs and musk fragrances) and in the supporting information (PFCs). The internal standard method was used for the calculation of analytes. Target compounds were quantified with an S/N>10 and detected with S/N>3. The PFC method quantification limits (MQL) were <1 and 23 pg m^{-3} for PFOSA (Dreyer et al. 2008). MQL and MDL of ionic PFCs were below 1 and 1 pg m^{-3}, respectively (Ahrens et al. 2007). A detailed list of PFC detection and quantification limits is given in supporting information (PFCs) and in section 3.3.4 (PBDEs and musk fragrances).

5.2.7 Quality assurance and quality control

All sample preparations and extractions were performed in a clean lab class 10000. PFC containing labware were avoided. Glassware was dish-washed and heated at 250 °C for at least 10 h. Prior to the sampling, GFF were baked at 400 °C for at least 12 h. PUF/XAD-2/PUF cartridges were thoroughly cleaned using acetone/MTBE 1:1 for PFC samples and hexane/acetone 1:1 for PBDE and musk fragrance samples. All standard solutions were only used at room temperature. Seven point calibrations (GC-MS: 2, 4, 10, 20, 50, 100, 200 pg μL^{-1}; HPLC-MS/MS: 1, 5, 10, 25, 50, 100, 500 pg μL^{-1}) were used to quantify target analytes. Linearity was tested according to DIN 32645 (1994). Mass-labelled standards were used to correct for analyte losses during analysis and measurements.

Mean recovery rates, standard deviations, median as well as their minima and maxima values of PFCs, PBDEs and musk fragrances spiked to the PUF/XAD-2/PUF cartridges prior to sampling are given in table 18. Table 19 displays recovery rates of particle-phase samples. A list of all recovery rates of gas-phase samples can be obtained from the supporting information.

Table 18: Average recovery rates (R, %) standard deviations (SD), relative standard deviations (RSD) median and minima (Min) and maxima (Max) values for semi-volatile PFCs, PBDEs and musk fragrances in gas-phase samples taken at WWTPs and RFs. If not marked separately mean recoveries are referred to n=20.

	R (Average)	SD abs.	RSD	R(Median)	R(Min)	R(Max)
^{13}C 4:2 FTOH	13	15	2	7	2	60
^{13}C 6:2 FTOH[a]	45	22	10	43	0	89
^{13}C 8:2 FTOH	40	15	6	40	5	68
^{13}C 10:2 FTOH	57	33	19	51	3	131
EtFOSA D_5	41	12	5	43	2	55
MeFOSA D_3	40	16	7	39	8	73
MeFOSE D_7	56	16	9	58	4	79
EtFOSE D_9	57	17	10	59	9	89
MBDE 28	97	39	41	97	46	175
MBDE 47	83	17	20	81	65	122
MBDE 99	99	32	32	90	46	176
MBDE 153	156	82	52	120	46	326
MBDE 183	119	49	41	106	30	219
AHTN D_3[b]	97	11	12	96	76	123
MX D_{15}	79	48	61	66	26	181

[a] n=8, [b] n=15; note: Differences are due to matrix problems.

Table 19: Average recovery rates (R, %) standard deviations (SD), relative standard deviations (RSD) median and minima (Min) and maxima (Max) values for semi-volatile PFCs, PBDEs and musk fragrances in particle-phase samples taken at WWTPs and RFs. If not marked separately mean recoveries are referred to n=20.

	Average	SD abs.	RSD	Median	Min	Max
$^{18}O_2$ PFHxS[a]	54	23	44	46	31	118
^{13}C PFOS[a]	75	14	18	78	56	103
^{13}C PFBA[a]	50	23	45	45	28	118
^{13}C PFHxA[a]	32	22	68	20	16	83
^{13}C PFOA[a]	57	21	36	52	36	111
^{13}C PFNA[a]	53	17	32	46	35	93
^{13}C PFDA[a]	59	12	20	56	45	91
^{13}C PFUDA[a]	67	18	27	64	27	103
^{13}C PFDoA[a]	57	20	35	54	2	95
MBDE 28	65	17	26	63	36	93
MBDE 47	65	16	25	63	36	90
MBDE 99	67	13	20	64	42	87
MBDE 153	88	20	23	81	57	135
MBDE 183	90	21	23	84	56	122
MBDE 209	103	36	35	103	47	162
AHTN D_3	81	18	22	83	49	106
MX D_{15}	81	22	27	82	40	119

[a] n=16; note: Differences are due to breaking of measurement vials during centrifugation.

In order to determine possible contaminations during sampling procedure and sample handling, field blanks on each sampling site were taken. Additionally, solvent blanks (gas phase) and filter blanks (particle phase) were applied with each set of samples during extraction. Individual blank contamination of field blanks, filter and solvent blanks are given in the supporting information. Field blanks were occasionally contaminated with HHCB and AHTN in the low pg m^{-3} and ranged up to 3 pg m^{-3} for HHCB. However, all other field blanks were not contaminated with PFCs or PBDEs. Two solvent blanks were contaminated with ADBI, HHCB and MX at the low pg m^{-3} range. Some PFC solvent blanks contained small amounts of 8:2 FTOH and 10:2 FTOH ($\leq$ 1 pg m^{-3}). Ionic PFC concentrations in filter blanks were generally below 1 pg m^{-3}. Filter blanks of musk fragrances revealed a slight contamination with HHCB (about 1 pg m^{-3}) and MX (4 pg m^{-3}). All PBDE filter blanks were contaminated with BDE183 in the range of 2 to 3 pg m^{-3}. All filter blanks were highly contaminated with elevated concentrations of BDE209 ranging from 647 to 1202 pg m^{-3}. Therefore, BDE209 was excluded from further analysis. Concentrations for the remaining analytes were blank-corrected by subtraction of peak area.

5.2.8 Trajectory analysis

To investigate air masses origin during air sampling, air mass back trajectory were calculated using Hysplit 4.8 (Draxler and Rolph 2003) using NCEP's GDAS with a resolution of one degree latitude/longitude. Seven-days back trajectories were calculated for 3 h intervals (one day samples) and 6 h intervals for three day samples, respectively. Arriving sampling heights varied according to the sites between 4 m (WB) and 8 m (WA), 2 m (RFs).

5.2.9 Statistical analysis

Statistical analysis was performed using Winstat (version 2007.1). Due to the limited number of samples, data was not tested for normal distribution. The significance ($p<0.05$) of concentration differences was evaluated between landfill samples and their corresponding RF using the Mann-Whitney-U-test.

5.4 Results

5.4.1 Air concentration of PFCs in the gas- and particle phase

Volatile and semi-volatile PFCs were detected in all gas-phase samples. Figure 19 displays total PFC air concentrations at both WWTPs and the corresponding RFs. Individual concentrations of neutral PFCs are given in the supporting information. Air concentrations of airborne PFCs at WA ranged from 97 (WA4) to 228 pg m^{-3} (WA1). Total PFC concentrations at corresponding RF were between 74 (RF4) and 193 pg m^{-3} (RF2). Total PFC concentrations at WB ranged from 290 (WB2) to 1004 pg m^{-3} (WB5) and from 23 (RF15) to 345 pg m^{-3}(RF14). Only 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH and EtFOSA were detected continuously in all samples. Compositions of semi-volatile and volatile PFCs in gas-phase samples are given in figure 20. At WA, FTOH (76 %) were the most abundant proportion, followed by FTA (10 %), FASA (9 %) and FASE (6 %). At WB, average proportion was 76 % for FTOH, 17 % for FASA, 5 % for FTA and for 2 % FASE. At corresponding RFs, average contribution decreased in the order of FTOH (88 %), FTA (5 %), FASA (4 %) and FASE (3 %).

Ionic PFCs were detected in all particle-phase samples (figure 21). Individual concentrations of ionic PFCs are given in the supporting information. Total concentrations at WA and corresponding RF ranged from 2 to 13 pg m^{-3} and <1 to 25 pg m^{-3}, respectively. At WB concentrations were between <MQL and 5 pg m^{-3} and at the corresponding RF between 2 and 42 pg m^{-3}. Compositions of PFSAs and PFCAs are given in figure 22. PFBA, PFOS and PFOA were the most abundant compounds and were detected in more than two-thirds of the samples. With exceptions of WB1, WB5, RF5 and RF11 the proportion of PFBA was observed at >60 %. At WA and WB proportion of PFOSA was 17 % and 26 %, respectively. Contributions of other compounds varied but were usually ≤ 10 %.

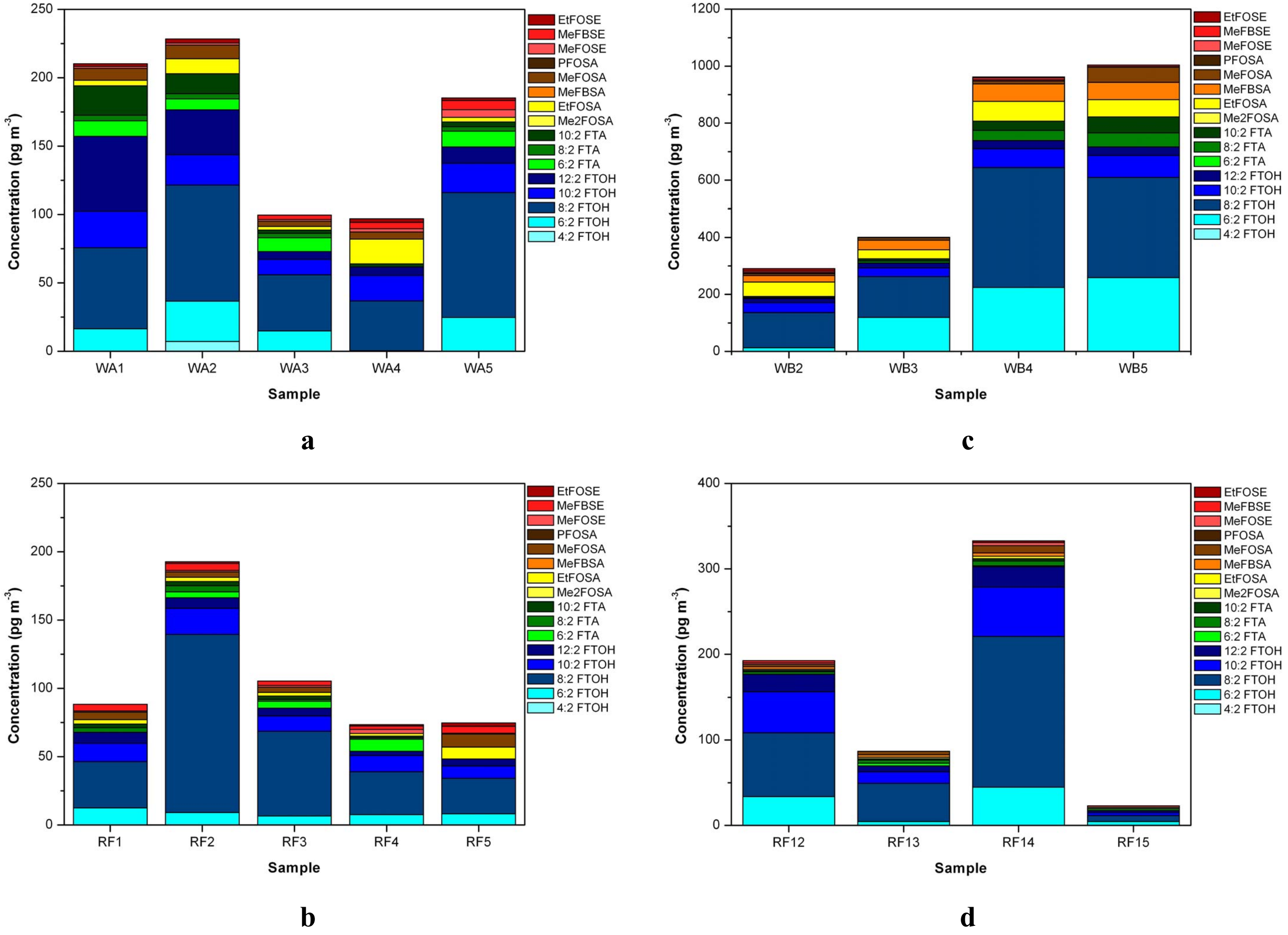


Figure 19: Concentrations (pg m^{-3}) of semi-volatile and volatile PFCs in gas-phase samples taken at two WWTPs WA (a) and WB (b) and at the corresponding reference sites (b, d). Sampling periods: 04.08.- 11.08.2009 (WA) and 20.08.–27.08.2009 (WB). RF11 was not analysed due to high water content. RF15 may not be representative due to technical problems with the high-volume sampler. Note the different scales.

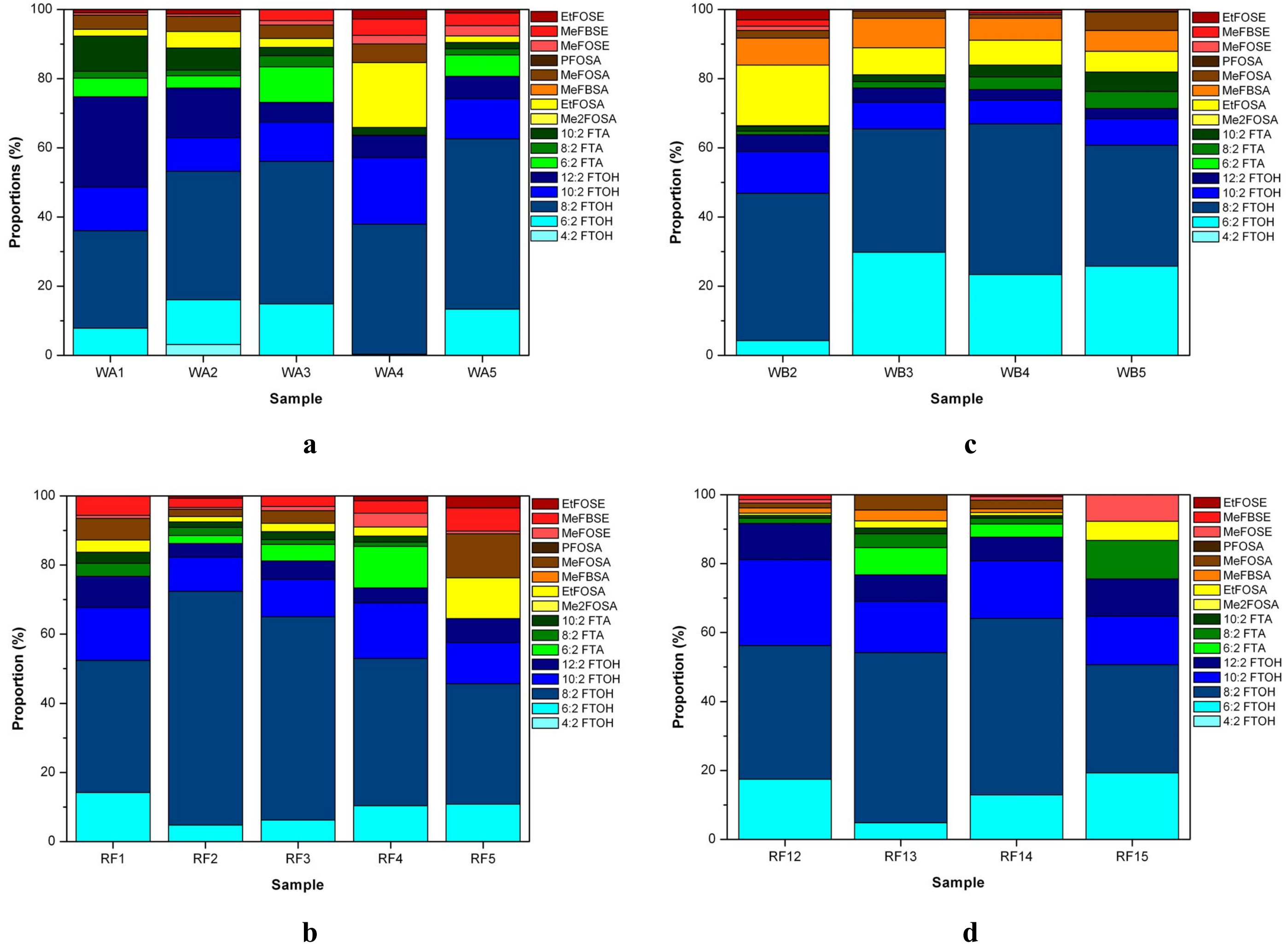


Figure 20: Proportions (%) of semi-volatile and volatile PFCs in gas-phase samples taken at two WWTPs WA (a) and WB (b) and at the corresponding reference sites (b, d). Sampling periods: 04.08- 11.08.2009 (WA) and 20.08.- 27.08.2009 (WB). RF11 was not analysed due to high water content. RF15 may not be representative due to technical problems with the high-volume sampler.

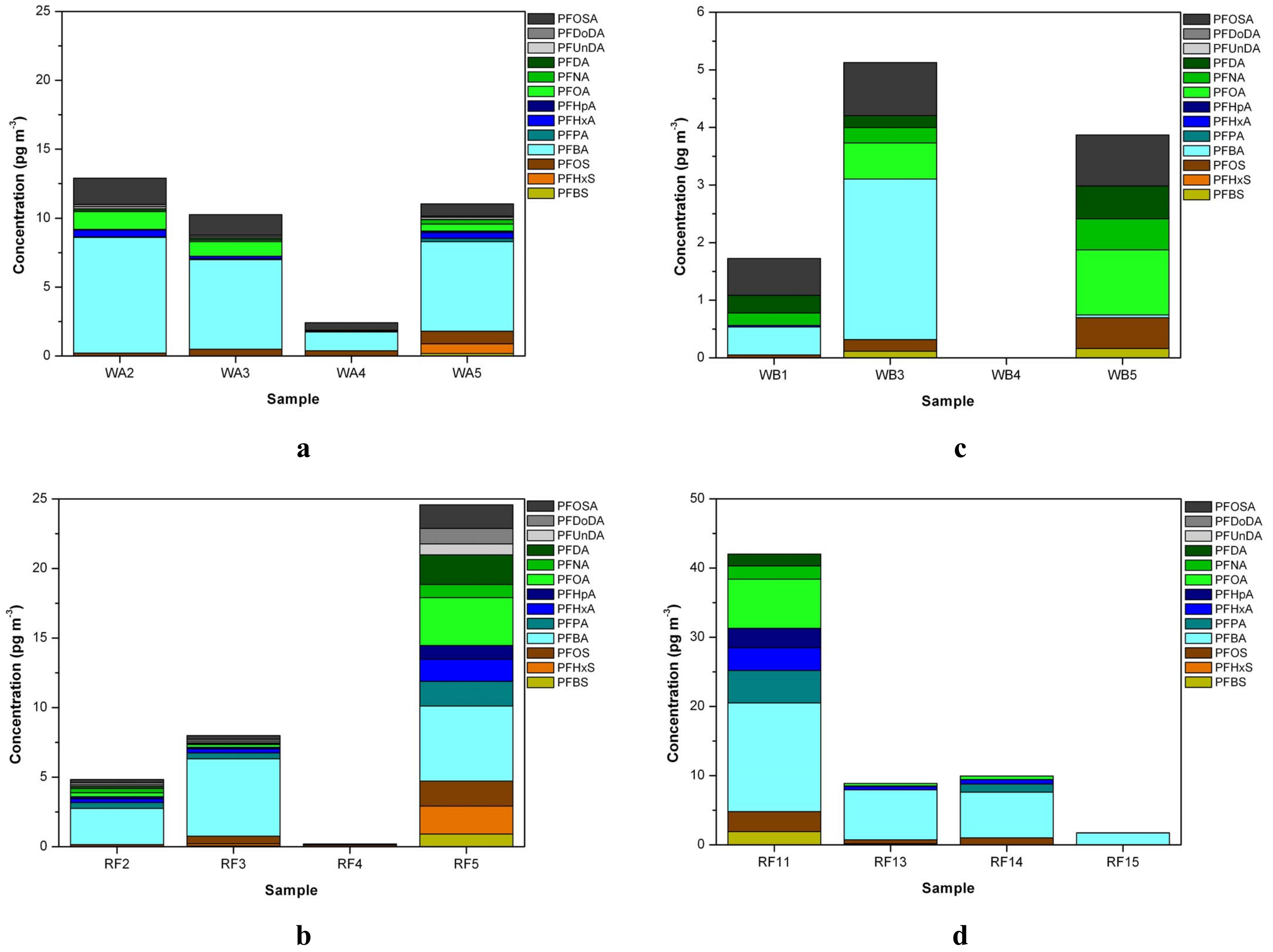


Figure 21: Concentrations (pg m^{-3}) of ionic PFCs in particle-phase samples taken at two WWTPs WA (a) and WB (b) and at the corresponding reference sites (b, d). Sampling periods: 0.4.08.-11.08.2009 (WA) and 20.08.-27.08.2009 (WB). Samples WA1, RF1, WB2 and RF12 were not analysed because of breaking of measurement vials during centrifugation. WB4 is <MQL. Note the different scales.

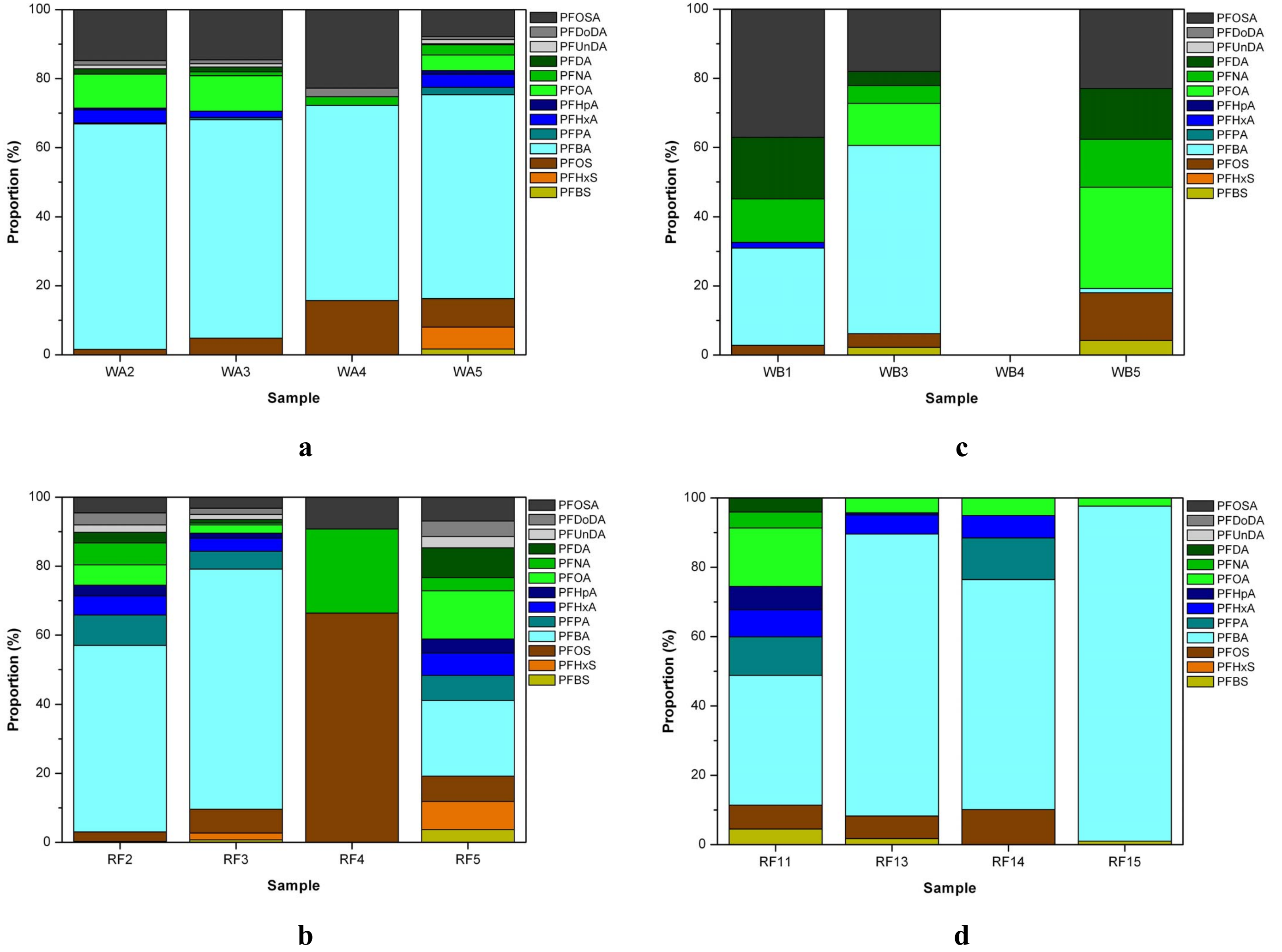


Figure 22: Proportions (%) of ionic PFCs in particle-phase samples taken at two WWTPs WA (a) and WB (b) and at the corresponding reference sites (b, d). Sampling periods: 04.08.- 11.08.2009 (WA) and 20.08.- 27.08. 2009 (WB). Samples WA1, RF1, WB2, and RF12 were not analysed because of breaking of measurement vials during centrifugation. WB4 is <MQL.

5.4.2 Air concentration of musk fragrances in the gas- and particle phase

Musk fragrances in the gas phase were observed in all samples. Figure 23 displays concentrations of all musk fragrances at WA and WB as well as their corresponding RFs. Individual concentrations are given in the supporting information. Total musk fragrances concentrations at WA ranged from 5.5 (WA1) to 127.7 ng m^{-3} (WA4). At corresponding RF, concentrations between 0.1 (RF3) and 0.9 ng m^{-3} (RF4) were observed. At WB, musk fragrances total concentrations were between 75.4 (WB1) and 480.6 ng m^{-3} (WB5). Air concentrations of musk fragrances ranged from 0.1 (RF11) and 0.8 ng m^{-3} (RF15) at corresponding RF. HHCB and AHTN were the only analytes that were detected in all air samples. ADBI and AHMI were consequently detected on both WWTPs with concentrations ranging from 0.02 to 1.7 ng m^{-3} (ADBI) and from 0.01 to 6.6 ng m^{-3} (AHMI). At RF, only ADBI was detected occasionally at about 0.01 ng m^{-3}. ATII as well as both nitro musks were not detected. Proportions of musk fragrances in gas-phase samples taken at the two WWTPs and its corresponding RFs are displayed in figure 24. The average proportions of analytes decreased in the order of HHCB (88 %), AHTN (10.8 %), AHMI (0.8 %), and ADBI (0.5 %). At RFs composition was 87 % for HHCB and 13 % for AHTN.

Musk fragrances in the particle phase were only detected in air samples from sites WA, WB and the corresponding RF (figure 25). Individual concentrations of musk fragrances are given in the supporting information. Total particle-phase concentrations ranged from 49 to 534 pg m^{-3} at WA, 152 to 1615 pg m^{-3} at WB and 7 to 24 pg m^{-3} at the corresponding RF: HHCB and AHTN were the predominant analytes and detected in all particle samples. Except for WB2, ADBI and AHMI were continuously detected in air samples of both WWTPs ranging from 3 to 22 pg m^{-3}. These compounds were not observed in RF samples. ATII, MX and MK were not observed in particle phase in any sample. Proportions of musk fragrances in the particle phase are displayed in figure 26. With the exception of sample WB2, HHCB occurred in highest mean proportions at both WWTPs (WA: 73 %) and WB (85 %), followed by AHTN (WA: 18 %, WB: 12 %). Musk fragrances ADBI and AHMI accounted for 5 % and 4 % (WA) and 2 % and 1 % (WB), respectively. The mean composition of samples RF11-RF15 was dominated by AHTN (57 %) followed by HHCB (43 %).

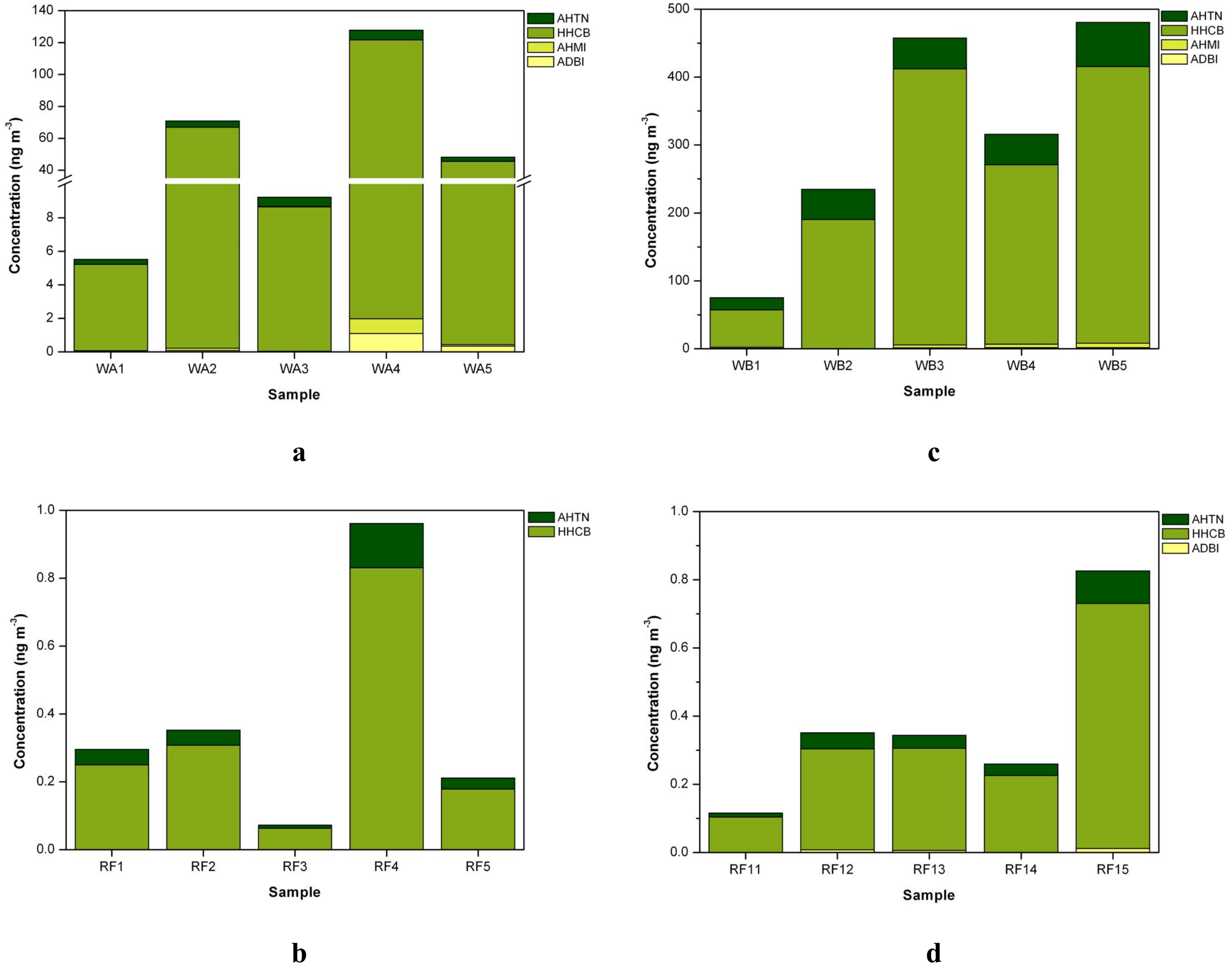


Figure 23: Concentrations (ng m^{-3}) of musk fragrances in gas-phase samples taken at two WWTPs WA (a) and WB (b) and at the corresponding reference sites (b, d). Sampling periods: 04.08.- 11.08.2009 (WA) and 20.08.- 27.08.2009 (WB). Note the different scales.

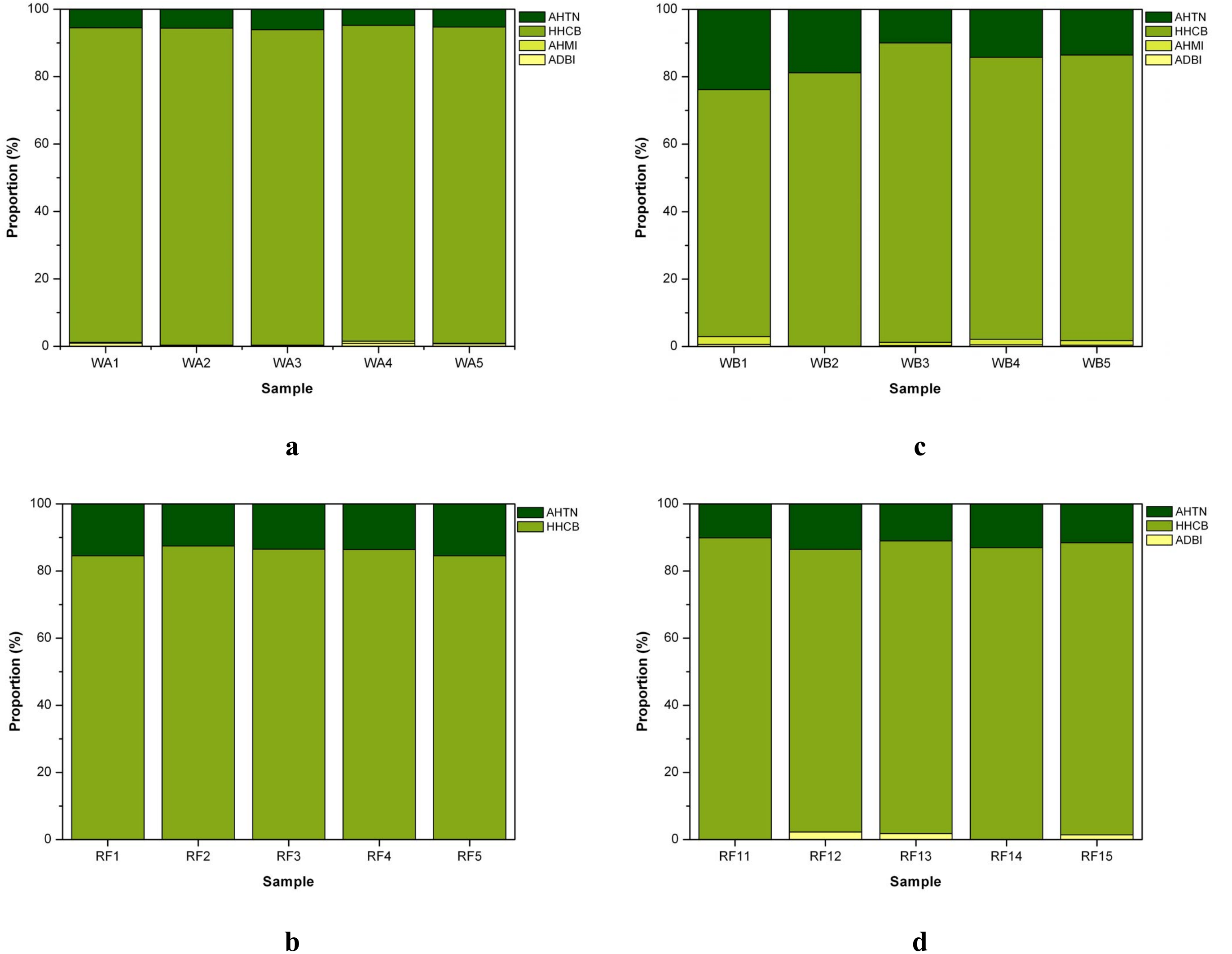


Figure 24: Proportions (%) of musk fragrances in gas-phase samples taken at two WWTPs WA (a) and WB (b) and at the corresponding reference sites (b, d). Sampling periods: 04.08- 11.08.2009 (WA) and 20.08-27.08.2009 (WB).

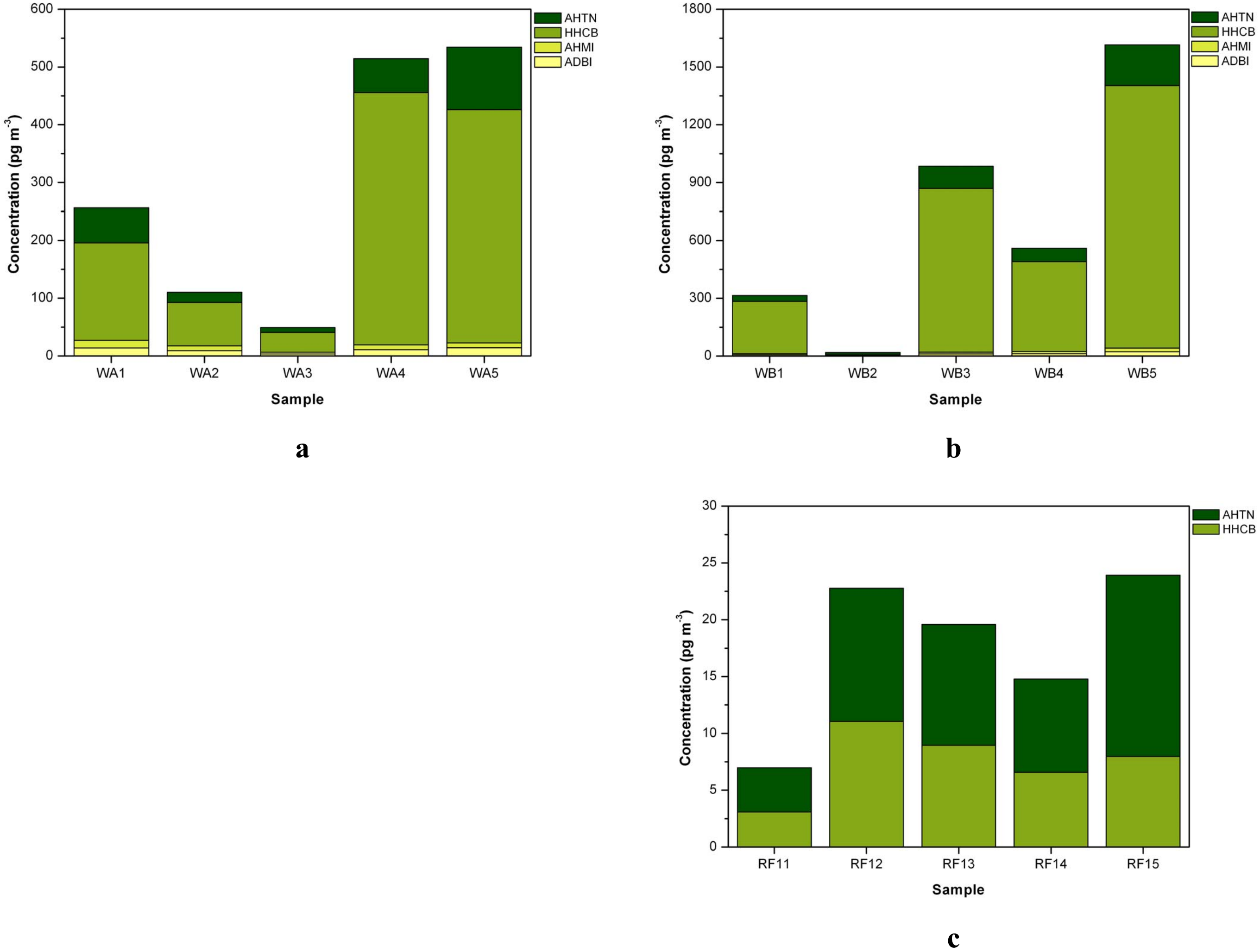


Figure 25: Concentrations (pg m^{-3}) of musk fragrances in particle-phase samples taken at two WWTPs WA (a) and WB (b) and at the corresponding reference site (c). Sampling periods: 04.08- 11.08. 2009 (WA) and 20.08.- 27.08.2009 (WB). In samples RF1-RF5 musk fragrances were <LOD. Note the different scales.

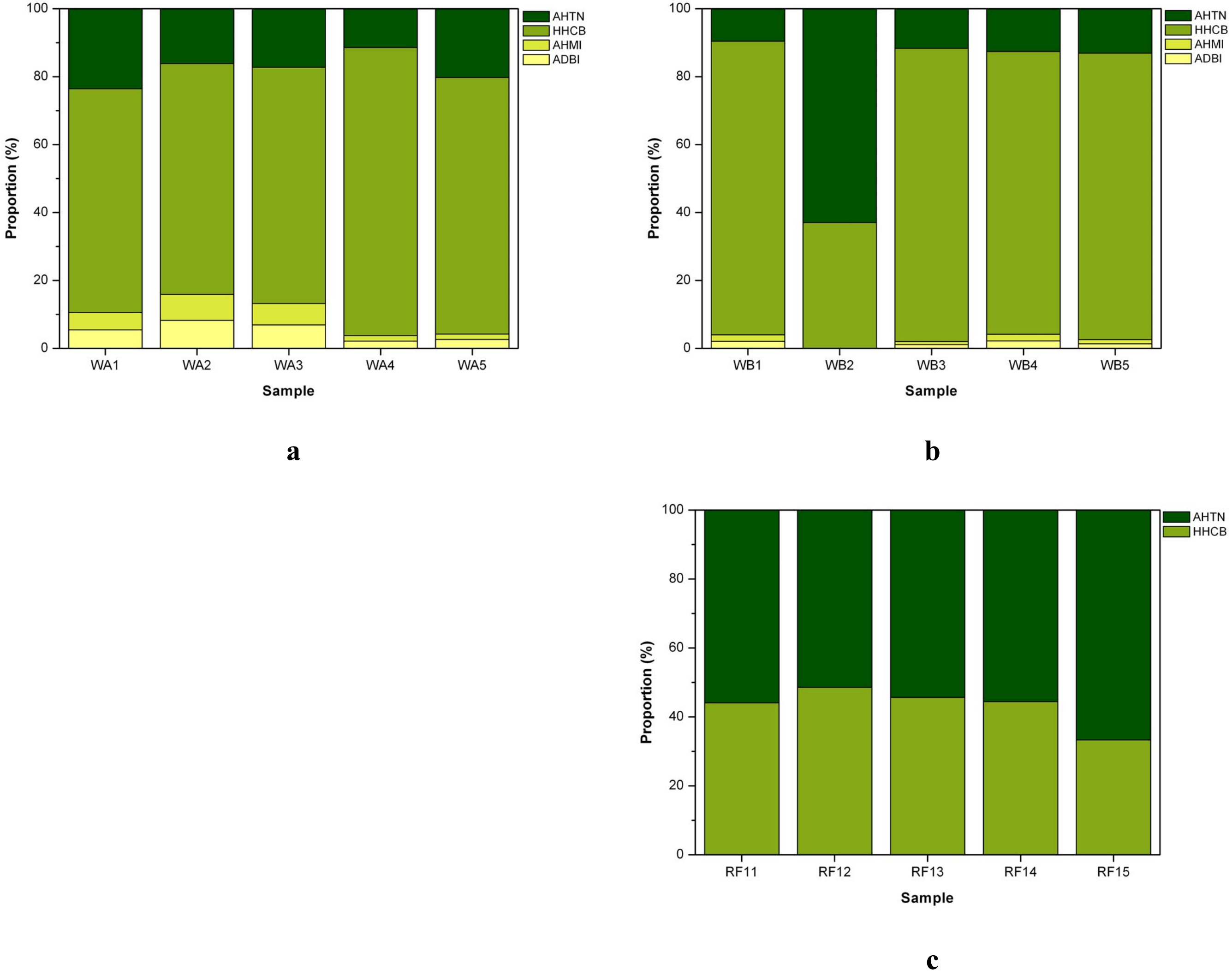


Figure 26: Proportions (%) of musk fragrances in particle-phase samples taken at two WWTPs WA (a) and WB (b) and their corresponding reference site (c). Sampling periods: 04.08.- 11.08.2009 (WA) and 20.08.- 27.08.2009 (WB). In samples RF1-RF5 musk fragrances were <LOD.

5.4.3 Air concentration of PBDEs from gas- and particle phase

With the exception of BDE154 and BDE183, PBDEs were not detected in gas-phase samples. BDE154 was observed in samples WA2 and RF5 at concentration of 2 pg m^{-3}. BDE183 was only observed in samples RF3 and RF5 (4 pg m^{-3}). BDE28, BDE48, BDE99, BDE100, BDE153, BDE154 were not detected in the particle phase in samples of WWTPs and their corresponding RFs. BDE209 was detected in all particle-phase samples. Due to the high contamination of filter blanks (see section 5.2.7), this compound is not further discussed. BDE183 was detected in all samples of WWTPs and RFs. Concentrations of samples RF4 and RF15 were lower than filter blanks. BDE183 concentrations in remaining RF samples were constantly about 1 pg m^{-3}. In sample RF5 a slightly elevated concentration of BDE183 (5 pg m^{-3}) was observed. Concentration of particle-phase BDE183 at WA ranged between <1 and 2 pg m^{-3} and between 2 and 27 pg m^{-3} at WB.

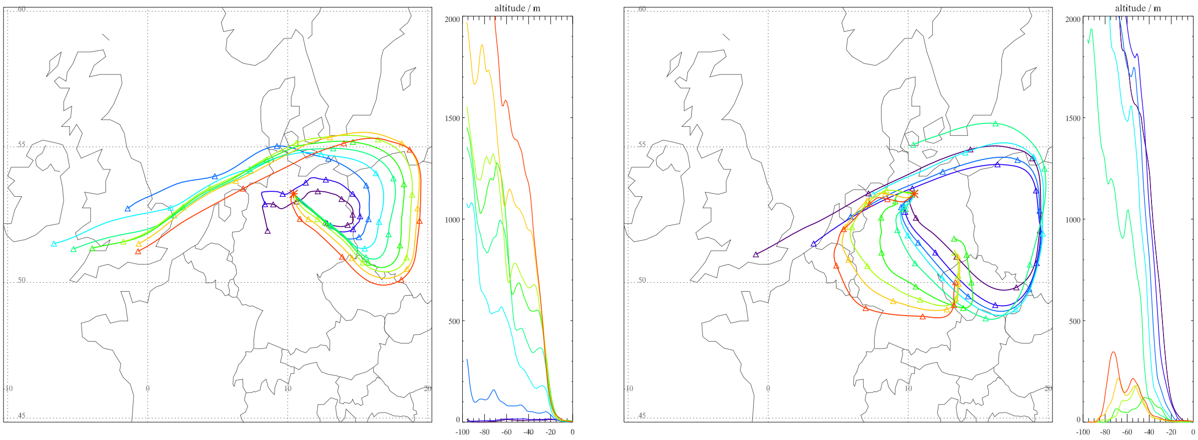
5.5 Discussion

PFC gas-phase concentrations of this thesis are in the same order of magnitude as observed in other studies of Northern Germany, (Jahnke et al. 2007; Dreyer and Ebinghaus 2009; Dreyer et al. 2009b). As reported in these studies, FTOH were the predominant substance class with 8:2 FTOH detected in highest quantities in all samples.

Concentration levels of PFCs at WA were 1.5 to 2 times higher as those of corresponding RF. These differences were mainly driven by increased concentrations of FTOHs at WA. However, FTOH concentrations were not significantly different as those of the RF. PFC concentrations of WB were 1.5 to 4 times as high as those of the corresponding RF. In contrast to WA samples, ΣFTOH concentrations were significantly higher at WB ($p<0.05$). Proportions of FTOHs and FTAs in WA samples and its corresponding RF were quite uniform suggesting common sources. In samples WA1 and WA2 an elevated proportion of 12:2 FTOH was observed which was in contrast to corresponding RF. In contrast to WA, a different substance pattern between WWTP and RF was observed in WB samples (figure 21). Concentrations of EtFOSA and MeFBSA were significantly higher than those of the corresponding RF ($p<0.05$) suggesting their emission from the aeration tank to ambient air. Furthermore, higher proportion of particle-bound PFOSA (figure 23) was observed suggesting that this precursor compound occurs in waste water and can be emitted by aerosol formation at the aeration tanks. PFOSA was not detected in the gas phase. The occurrence of precursor compounds such as EtFOSA in waste waters was demonstrated by several authors (Schultz et al. 2006; Sinclair and Kannan 2006; Becker et al. 2008; Ahrens et al. 2009c).

Furthermore, occurrence of FTOHs in effluents of WWTPs was reported by Mahmoud et al. (2009). Due to their high air water partition coefficients and the aeration process these precursors may easily volatilise from the waste water into the atmosphere. In three-day samples WA4 and WB2 higher EtFOSA concentrations and proportions and lower FTA concentrations and proportions as the one-day samples were observed (figures 20 and 21). These altered proportions may have resulted from different discharger profiles on weekends (e.g. a shift of incoming waste waters from industrial sources to households).

Several studies demonstrated the importance of air mass origin regarding PFC concentrations in ambient air. For central Europe it was reported that higher PFC concentrations coincided with air masses from westerly regions such as UK, Netherlands, Benelux and Western Germany (Jahnke et al. 2007; Dreyer and Ebinghaus 2009; Dreyer et al. 2009b). In this thesis analysis of back trajectories revealed high variability of the origin of air masses. Samples WB3 and WB4 revealed that air masses basically passed over coastal regions but arrived at sampling site from easterly- (figure 27a) and in part westerly directions at low altitudes (figure 27b). Having regard to the potential source regions in the west, the increase of PFC air concentrations in WB4 and the corresponding RF may be explained. Furthermore, other local or diffuse sources of the nearby city of Lüneburg may have had an influence on the concentration in WB samples. However, due to the high variability of circulating air masses during this sampling campaign trajectories cannot fully elucidate this issue.



a b

Figure 27 a, b: Selected seven days air mass back trajectories calculated for three hours intervals (arrival height 5 m). Generated by Hysplit 4.8 using GDAS data for sample WB3 (a) (ΣPFCs= 401 pg m^{-3}) and sample WB4 (b) (ΣPFCs= 962 pg m^{-3}). Triangles represent 12 h tags of every trajectory. In addition, trajectory heights are plotted.

Concentrations of PFCAs and PFSAs determined in this study are in the same range as reported by Dreyer et al. (2009) from air samples in Northern Germany and German Bight, Harada et al. (2006) in rural areas of Japan, and Kim and Kannan (2007) from an urban area in USA. High-concentration samples (RF11 and RF5) were distinctly lower than those of Barber et al. (2007) from UK and Harada et al. (2005) from Japanese urban region. PFBA, PFOA and PFOS were the predominant substances. Highest proportions were usually observed for PFBA. These findings are in contrast to Dreyer et al. (2009b) who detected PFOS in highest proportions as well as Barber et al. (2007) and Harada et al. (2005) who observed mostly particle-bound PFOA. Concentrations of PFCA and PFSA were characterized with high variability at all sites indicating an enhanced uncertainty of these data, probably due to revolatilisation of PFCAs from GFF (Arp and Goss 2008). Therefore, WWTPs seem to be a rather minor source for particle-bound PFCAs and PFSAs into the atmosphere.

Air concentrations of musk fragrances at both RFs were in good agreement with those reported by Xie et al. (2007) from coastal areas and semi-rural area in Northern Germany, Kallenborn et al. (1999a) in ambient air samples from Norway, and Peck and Hornbuckle (2004) over Lake Michigan, USA. It should be mentioned that Peck and Hornbuckle (2004) observed increased proportions of ADBI, AHMI, MX and MK in most samples. Low concentrations of musk fragrances detected at WA (WA1, WA3) are similar to maximum values reported by Peck and Hornbuckle (2006) from an urban site in USA. Concentrations of the remaining WWTP samples were at least one order of magnitude higher. Musk fragrances concentrations in WA samples were in the same range as those reported by Chen et al. (2007b) who sampled musk fragrances in ambient air close to a cosmetic plant in China. Concentrations of WB samples were higher those but still lower than in the cosmetic plant (table 7). The observed musk fragrance profile with HHCB and AHTN as predominant compounds corroborate with production data from Europe (OSPAR 2004) as well as findings of other authors (Chen et al. 2007b, Kallenborn and Gatermann 2004; Peck and Hornbuckle 2004; Peck and Hornbuckle 2006) That nitro musks were not detected is likely due to the voluntary phase out of these compounds in the 1990s (Käfferlein and Angerer 2001).

Musk fragrances concentrations were significantly higher in WWTPs than in RFs ($p<0.05$) revealing that musk fragrances volatilise from waste water into the local atmosphere. This is corroborated by studies reporting that WWTPs are the major source for musk fragrances for the aquatic environment and that these compounds occur in waste waters in high quantities (Rimkus 1999; Simonich et al. 2000; Bester 2004; Osemwengie and Gerstenberger 2004; Bester 2005; Chen et al. 2007b). In addition to concentration differences, WWTPs and RFs also differed with regard to the proportions of ADBI and AHMI (Figure 24, 26). In contrast to studies reporting ATII frequently in waste water, it was not observed in air samples at WA and WB (Heberer 2002). Since only 6 % of the musk fragrances were detected in the particle phase it can be concluded that aerosol formation is not the primary removal of fragrances compounds from waste water into the atmosphere.

PBDEs were not detected in gas-phase samples at WWTPs. Furthermore, only two samples of corresponding RFs revealed slight concentrations of BDE154 and BDE183. Although PBDEs were observed in gas-phase samples in EU (Jaward et al.2004a; Law et al. 2008) at low concentrations (<2 pg m^{-3}) they were almost not detected in this theses. Particle-bound BDE183 was detected constantly in all samples of this sampling campaign. Samples from WA were not significantly higher than those determined at corresponding RF. However, BDE183 concentrations at WB were significantly increased as its RF ($p<0.05$). Thus, BDE183 might be subject to aerosol formation at the water surface promoted by the aeration process.

Sum concentrations of PFCs and musk fragrances at WB were higher than those of WA ($p<0.05$). These differences may point to the importance of populated areas as atmospheric sources for PFCs and musk fragrances. More likely, this might be explained by different population equivalents or ratios of waste water contributors. Waste waters originating primarily from households (more than two-thirds) may have resulted in elevated concentrations at WB since domestic waste water was reported to be the most important source for musk fragrances (Kallenborn et al. 1999b; OSPAR 2004; Reiner and Kannan 2006). Obviously, composition of dischargers and population equivalents or other factors such as plant operation (e.g. aeration power) seem to be important factors leading to increased volatilisation of musk fragrances. In contrast, an influence of waste water flow-through at both WWTPs could not be demonstrated.

Generally air concentrations increased in the order of PBDEs < PFCs < musk fragrances. Except for a very few samples, musk fragrances air concentrations at RFs usually exceeded those of semi-volatile and volatile PFCs by a factor of 2 to 3 (figures 20 and 24). Therefore, air concentrations at RFs of those compounds may be regarded as background concentrations for this region. At WWTPs air concentrations of musk fragrances exceed those of semi-volatile and volatile PFCs by several orders of magnitude. However, air concentrations of musk fragrances and PFCs from both WWTPs were not correlated to each other. This gives further evidence of different sources and/or different release mechanisms and substance behaviour at aeration tanks.

5.6 Conclusion

For the first time, it was demonstrated that that musk fragrances and precursor compounds of persistent PFCAs and PFSAs may be released by waste water through volatilisation and can therefore be regarded as sources to the atmosphere. Concentrations of FASAs and FTOHs were significantly higher than those at the corresponding RFs. Aerosol formation is not an important release mechanism of PFCs from waste water. Gas-phase PBDEs were not observed in any sample, but particle-bound PBDEs may have been emitted emitted from aeration tanks. Musk fragrances were observed at significantly elevated concentrations and enhanced substance spectra at both WWTPs by several orders of magnitude as the corresponding RFs. Source strength for gas-phase musk fragrances was significantly higher than for volatile and semi-volatile PFCs. Pronounced differences of the concentrations between the two WWTPs may suggest a strong influence of waste water origin and operational conditions. An influence of waste water flow-through at both WWTPs could not be demonstrated.

6. Conclusions and Outlook

In this study PFCs, PBDEs and musk fragrances were determined in air samples from two landfills and two waste water treatment plants from Northern Germany and simultaneously sampled reference sites. A previously developed analytical method for PBDEs and musk fragrances revealed high precision and repeatability as well as good suitability. However, simultaneous determination of PBDEs and musk fragrances using GC-MS in the EI mode resulted in low sensitivities of highly brominated PBDE congeners. Thus, PBDE measurement had to be performed in the NCI mode that was more sensitive and resulted in sufficiently low detection limits.

PFCs and musk fragrances were detected in all air samples. PBDEs were less often detected and predominantly bound to particles. Air concentrations of PFCs, PBDEs and musk fragrances at landfills and WWTPs were generally higher than those at corresponding RFs. However these concentration differences were not significant for all analytes. Generally, concentrations decreased in the order musk fragrances > PFCs > PBDEs.

The PFC composition at of gas-phase samples from landfills was quite similar suggesting common PFC sources. The detection of PFCs at landfills and corresponding RFs corroborates previous assumptions of diffuse sources located west of the sites in industrialized and populated regions. Significantly elevated FTOH concentrations at both landfills suggest landfills as additional PFC source to ambient air. Furthermore, the PFCA and PFSA precursors 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, EtFOSA, MeFBSA and particle-bound PFOSA were detected at elevated concentrations at at least one WWTP revealing that those compounds can be emitted from waste water of aeration tanks. Concentrations of ionic PFCs such as particle-associated PFOA were not significantly elevated suggesting that the aeration process is not an important release mechanism for these substances from waste water.

Musk fragrances were detected at significantly higher concentrations at both landfills compared to their corresponding RFs indicating the source character for these compounds. At both WWTPs concentrations of musk fragrances were several orders of magnitude higher than these at the corresponding RFs. Therefore, WWTPs are not only the primary source for musk fragrances to the aquatic environment as described in various studies but also an important source to ambient air.

PBDEs were less often detected suggesting a generally low contamination of the sampled air masses. Nevertheless, at one WWTP and one landfill concentrations of the particle-associated

BDE183 were significantly higher than those at the corresponding RFs indicating that this congener has the potential of being emitted from waste disposed at landfills or from waste water at WWTPs.

Overall, landfills and particularly WWTPs are sources for musk fragrances to ambient air. Compared to the tremendously elevated concentrations of musk fragrances at WWTPs and landfills these sites appeared to be rather minor sources for PFCs and PBDEs.

Further research efforts should include the quantification of the source strengths for PFCs, PBDEs and musk fragrances of landfills and WWTPs. Therefore longer time series are needed. For emission estimates of PFCs, PBDEs and musk fragrances from these sites, air sampling campaigns should be intensified by application of an increased number of air samplers surrounding the target site in order to differentiate between site-specific emissions and those from surrounding sources. Additionally, potential seasonal effects (e.g. temperature dependence) promoting the volatilisation should be investigated at landfills. This study clearly revealed WWTPs as point sources for musk fragrances. Therefore, future comprehensive studies such as mass balances should include the atmospheric pathway as an important loss mechanism for these compounds. Furthermore, the influence of operational parameters on the air concentrations of musk fragrances and PFCs e.g. flow velocities, aeration power and the origin of waste water should be investigated.

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8. Supporting information

Figure S1: High volume sampler deployed at reference site in region Wendland.

Figure S2: High volume sampler deployed at waste water treatment plant WA.

Figure S3: High volume sampler deployed at landfill LA.

Figure S4: High volume sampler deployed at waste water treatment plant WB.

Figure S5: High volume sampler deployed at reference site in region Lüneburg.

Figure S6: High volume sampler deployed at landfill LB.

Table S1: Table of solvents, native and mass-labelled analytical standards and gases

Substance	Acronym	Purity	Supplier
2-Perfluorohexyl-($^{13}C_2$)-ethanol	^{13}C 6:2 FTOH	> 98	Wellington, Guelph, Canada
2-Perfluorooctyl-($^{13}C_2$)-ethanol	^{13}C 8:2 FTOH	> 98	Wellington, Guelph, Canada
2-Perfluorodecyl-($^{13}C_2$)-ethanol	^{13}C 10:2 FTOH	> 98	Wellington, Guelph, Canada
methyl-D_3-perfluorooctane sulfonamide	MeFOSA D_3	> 98	Wellington, Guelph, Canada
ethyl-D_5-perfluorooctane sulfonamide	EtFOSA D_5	> 98	Wellington, Guelph, Canada
methyl-D_7-perfluorooctane sulfonamido ethanol	MeFOSE D_7	> 98	Wellington, Guelph, Canada
ethyl-D_9-perfluorooctane sulfonamidoethanol	MeFOSE D_9	> 98	Wellington, Guelph, Canada
perfluoro-(^{13}C4)-butanoic acid	^{13}C PFBA	>98	Wellington, Guelph, Canada
perfluoro-(^{13}C4)-hexanoic acid	^{13}C PFHxA	>98	Wellington, Guelph, Canada
perfluoro-(^{13}C4)-octanoic acid	^{13}C PFOA	>98	Wellington, Guelph, Canada
perfluoro-(^{13}C4)-nonanoic acid	^{13}C PFNA	>98	Wellington, Guelph, Canada
perfluoro-(^{13}C4)-decanoic acid	^{13}C PFDA	>98	Wellington, Guelph, Canada
perfluoro-(^{13}C4)-undecanoic acid	^{13}C PFUnDA	>98	Wellington, Guelph, Canada
perfluoro-(^{13}C4)-dodecanoic acid	^{13}C PFDoA	>98	Wellington, Guelph, Canada
sodium perfluoro-(^{18}O2)-hexane sulfonate	$^{18}O_2$-PFHxS	>99	Wellington, Guelph, Canada
sodium perfluoro-(^{13}C4)-octane sulfonate	^{13}C-PFOS	>98	Wellington, Guelph, Canada
sodium perfluoro-(^{13}C4)-octane sulfinate	^{13}C-PFOSi	~90	Wellington, Guelph, Canada
hexachlorobenzene $^{13}C_6$	^{13}C HCB	97	Dr. Ehrenstorfer, Augsburg, Germany
1,3,5-trichlorobenzene D_3	TCB D_3	98	Aldrich, Munich, Germany
perfluorooctane sulfonamido-D_5-acetic acid	EtFOSAA D_5	>98	Wellington, Guelph, Canada
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 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, Guelph, Canada
n-methyl perfluorobutane sulfonamido ethanol	MeFBSE	-	donated by 3M, USA
n-methyl perfluorooctane sulfonamido ethanol	MeFOSE	-	donated by 3M, USA
n-ethyl perfluorooctane sulfonamido ethanol	EtFOSE	-	donated by Toronto University, 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, Frankfurt, Germany
perfluorooctanoic acid	PFOA	95	Lancaster, Frankfurt, Germany

Table S1 cont.

Substance	Acronym	Purity	Supplier
perfluorooctanoic acid	PFOA	95	Lancaster, 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
2,4,4'-Tribromo[$^{13}C_6$]diphenyl ether	MBDE28	>98	Wellington, Guelph, Canada
2,2',4,4'-Tetrabromo[$^{13}C_6$]diphenyl ether	MBDE47	>98	Wellington, Guelph, Canada
2,2',4,4',5-Pentabromo[$^{13}C_6$]diphenyl ether	MBDE99	>98	Wellington, Guelph, Canada
2,2',4,4',5,5'-Hexabromo[$^{13}C_6$]diphenyl ether	MBDE153	>98	Wellington, Guelph, Canada
2,2',3,4,4',5',6-Heptabromo[$^{13}C_6$]diphenyl ether	MBDE183	>98	Wellington, Guelph, Canada
Decabromo[$^{13}C_6$]diphenyl ether	MBDE209	>98	Wellington Guelph, Canada
2,4,4'-Tribromodiphenyl ether	BDE28	>98	Wellington, Guelph, Canada
2,2',4,4'-Tetrabromodiphenyl ether	BDE47	>98	Wellington, Guelph, Canada
2,2',4,4',5-Pentabromodiphenyl ether	BDE99	>98	Wellington , Guelph, Canada
2,2',4,4',6-Pentabromodiphenyl ether	BDE100	>98	Wellington , Guelph, Canada
2,2',4,4',5,5'-Hexabromodiphenyl ether	BDE153	>98	Wellington , Guelph, Canada
2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE154	>98	Wellington , Guelph, Canada
2,2',3,4,4',5',6-Heptabromodiphenyl ether	BDE183	>98	Wellington , Guelph, Canada
Decabromodiphenyl ether	BDE209	>98	Wellington , Guelph, Canada
Fluoranthene-d10	Fluoranthene D_{10}	>98	Dr. Ehrenstorfer, Augsburg, Germany
1-tert-Buthyl-3,5-dimethyl-2,4,6-trinitrobenzene	MX	>99	Ehrenstorfer, Augsburg, Germany
1-tert.-butyl-3,5-dimethyl-2,6-dinitro-4-acetyl-benzene	MK	98	Dr. Ehrenstorfer, Augsburg, Germany
Musk xylene D15	MX D_{15}	>97	Dr. Ehrenstorfer, Augsburg, Germany
7-Acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-Tetrahydronaphthalene	AHTN D_3	99	Dr. Ehrenstorfer, Augsburg, Germany
7-Acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-Tetrahydronaphthalene	AHTN	98	Dr. Ehrenstorfer, Augsburg, Germany
5-Acetyl-1,1,2,6-tetrametyl-3-isopropyl-dihydroindene	ATII	98	Dr. Ehrenstorfer, Augsburg, Germany
4-acetyl-1,1-dimethyl-6-*tert*-butylindane	ADBI	98	Dr. Ehrenstorfer, Augsburg, Germany
6-acetyl-1,1,2,3,3,5-hexamethylindane	AHMI	98	Dr. Ehrenstorfer, Augsburg, Germany
1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran	HHCB	51	Dr. Ehrenstorfer, Augsburg, Germany
hexane	-	picograde	Promochem, Wesel, Germany
ethyl acetate	-	picograde	Promochem, Wesel, Germany
acetone	-	picograde	Promochem, Wesel, Germany
methyl-tert-butylether	MTBE	picograde	Promochem, Wesel, Germany
methanol	MeOH	residual analysis	J.T. Baker, Griesheim, Germany
Helium	-	5.0	Air Liquide, Germany
nitrogen	-	5.0	Air Liquide, Germany
methane	-	5.0	Air Liquide, Germany

Table S2: Mass-to-charge-ratio (m/z) of semi-volatile PFCs determined with GC-MS. MW: molecular weight, TI: Target Ion, Q: Qualifier. PCI: positive chemical ionisation; NCI: negative chemical ionisation. IS: internal standard used for correction

Analyte	MW	TI	Q1 (PCI)	Q2 (Carballa Omil Lema)	IS
4:2 FTOH	264	265.0	227.0	-	^{13}C 6:2 FTOH
6:2 FTOH	364	365.0	327.0	-	^{13}C 6:2 FTOH
8:2 FTOH	464	465.0	493.1	-	^{13}C 8:2 FTOH
10:2 FTOH	564	565.0	527.0	-	^{13}C 10:2 FTOH
12:2 FTOH	664	665.1	627.0	-	^{13}C 10:2 FTOH
6:2 FTA	418	419.0	447.1	-	^{13}C 6:2 FTOH
8:2 FTA	518	519.1	547.1	-	^{13}C 8:2 FTOH
10:2 FTA	618	619.1	647.1	-	^{13}C 10:2 FTOH
EtFOSA	527	528.0	508.0	507.0	EtFOSA D_5
EtFOSE	571	554.0	572.1	508.0	EtFOSE D_9
MeFOSA	513	514.0	494.0	493.0	MeFOSA D_3
MeFOSE	557	540.0	558.0	494.0	MeFOSE D_7
MeFBSA	313	314.0	294.0	292.9	MeFOSA D_3
MeFBSE	357	340.0	358.0	293.2	MeFOSE D_7
Me2FOSA	527	528.0	444.0	483.0	^{13}C 8:2 FTOH
PFOSA	499	500.0	381.0	478.9	EtFOSE D_9

Table S3: Mass-to-charge-ratio (m/z) and product ion of ionic PFCs determined at HPLC-MS/MS

analyte	m/z	product ion
PFBS	298.877	80
PFHxS	398.894	80
PFOS	498.971	80
PFBA	112.9	169
PFPA	262.825	219
PFHxA	312.934	269
PFHpA	362.95	319
PFOA	412.987	369
PFNA	462.908	419
PFDA	512.876	469
PFUnDA	562.865	519
PFDoDA	612.991	569
PFOSA	497.896	78
MeFBSA	311.914	219
MeFBSE	416.047	59
$^{18}O_2$-PFHxS	402.981	84
^{13}C PFOS	502.899	80
^{13}C PFBA	216.823	172
^{13}C PFHxA	314.891	270
^{13}C PFOA	416.978	372
^{13}C PFNA	467.907	423
^{13}C PFDA	514.944	470
^{13}C PFUnDA	564.959	520
^{13}C PFDoDA	614.913	570
EtFOSAA D_5	589.015	419

Table S4: Instrumental detection limits (LOD), instrumental quantification limits (LOQ), method quantification limits (MQL), and method detection limits (MDL) of semi-volatile and ionic PFCs from the gas phase (g) and particle phase (p).

	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
Me$_2$FOSA	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	4.2	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
PFBS	0.3	0.1	0.05	0.02	0.5	5.0	0.3	0.1
PFHxS	0.2	0.1	0.05	0.02	0.5	5.0	0.2	0.1
PFHpS	0.3	<0.3	0.05	0.02	0.5	5.0	0.3	<0.3
PFOS	0.1	<0.05	0.1	0.05	1.0	10	0.1	<0.05
PFBA	0.1	<0.1	0.2	0.2	2.0	20	0.1	<0.1
PFPA	0.4	<0.05	0.1	0.05	1.0	10	0.4	<0.05
PFHxA	<0.05	<0.05	0.1	0.05	1.0	10	<0.05	<0.05
PFHpA	0.1	<0.1	0.1	0.05	1.0	10	0.1	<0.1
PFOA	<<1.8	<<1.8	0.1	0.05	1.0	10	<<1.8	<<1.8
PFNA	<0.05	<0.05	0.1	0.05	1.0	10	<0.05	<0.05
PFDA	0.1	0.05	0.1	0.05	1.0	10	0.1	0.05
PFUnDA	<0.1	<0.1	0.2	0.1	2.0	20	<0.1	<0.1
PFDoDA	<0.2	<0.2	0.1	0.05	1.0	10	<0.2	<0.2

Table S5: Table of recovery rates (%) obtained in gas-phase samples from landfills LB and LA as well as the reference sites.

	^{13}C 4:2 FTOH	^{13}C 6:2 FTOH	^{13}C 8:2 FTOH	^{13}C 10:2 FTOH	EtFOSA D$_5$	MeFOSA D$_3$	MeFOSE D$_7$	EtFOSE D$_9$	MBDE28	MBDE47	MBDE99	MBDE153	MBDE183	AHTN D$_3$	MX D$_{15}$
LA1	16	24	48	72	51	44	57	42	37	76	69	106	101	86	33
LA2	6	34	39	62	40	36	69	57	73	124	105	161	108	97	
LA3	9	57	55	38	41	39	67	72	69	103	97	155	116	93	86
LA4	2	50	37	48	26	32	46	44	-	-	103	149	109	109	127
LA5	11	-	43	49	44	57	64	72	72	94	84	-	121	43	28
LB1	-	-	27	52	31	17	37	50	79	100	89	157	113	100	150
LB2	7	-	28	47	26	34	45	38	86	96	90	156	104	90	101
LB3	3	-	40	50	47	47	62	68	84	176	162	122	164	97	129
LB4	5	45	42	50	43	38	48	60	74	85	91	122	78	105	138
LB5	8		49	47	40	34	58	89	-	-	89	173	118	96	148
RF6	13	43	54	63	58	51	76	68	138	0	71	104	71	88	68
RF7	11	35	47	55	47	45	61	60	74	112	104	140	105	99	86
RF8	17	52	66	72	59	51	62	69	100	66	101	122	82	95	51
RF9	2	32	32	39	23	25	46	48	112	73	112	156	98	100	43
RF10	9	47	56	65	46	41	67	66	59	76	92	106	84	77	-
RF16	9	-	41	50	40	36	47	49	63	85	88	141	80	98	130
RF17	5	-	33	34	37	32	35	37	-	-	105	-	110	95	124
RF18	14	-	50	62	50	47	61	51	62	54	68	111	94	75	125
RF19	15	54	70	66	60	50	58	58	75	93	90	169	130	96	103
RF20	30	-	78	78	75	66	70	68	70	86	83	122	70	97	135

Table S6: Table of recovery rates (%) obtained in particle-phase samples from landfills LB and LA as well as the reference sites.

	$^{18}O_2$-PFHxS	**^{13}C PFOS**	**^{13}C PFBA**	**^{13}C PFHxA**	**^{13}C PFOA**	**^{13}C PFNA**	**^{13}C PFDA**	**^{13}CPFUDA**	**^{13}CPFDoA**	**MBDE28**	**MBDE47**	**MBDE99**	**MBDE153**	**MBDE183**	**MBDE209**	**AHTN D_3**	**MX D_{15}**
LA1	30	53	34	18	40	34	46	52	49	81	83	75	89	90	127	-	-
LA2	41	61	43	20	42	45	63	72	66	91	85	91	102	104	156	-	-
LA3	40	98	33	17	39	51	55	53	46	98	94	110	101	98	105	-	-
LA4	33	76	20	16	35	46	55	61	53	98	103	93	104	105	186	-	-
LA5	15	23	18	9	15	21	23	22	22	67	77	74	74	78	145	-	-
LB1	38	63	54	19	53	39	43	43	44	50	62	68	102	96	105	-	36
LB2	46	79	38	20	51	49	54	68	60	52	67	70	107	98	117	95	53
LB3	79	83	76	30	81	59	63	76	70	66	54	72	113	127	83	65	106
LB4	50	64	55	31	56	50	60	75	71	58	69	69	117	107	125	78	93
LB5	59	75	67	28	73	60	66	83	80	52	60	64	102	90	111	-	42
RF6	39	81	48	35	56	73	85	89	82	103	93	91	89	96	151	-	-
RF7	32	59	39	24	40	48	62	68	60	85	80	88	91	90	165	-	37
RF8	62	71	76	34	66	49	63	82	77	96	99	92	100	100	169	-	-
RF9	35	58	32	10	36	31	38	50	40	66	71	70	90	82	113	66	82
RF10	40	62	30	14	38	37	50	67	61	66	70	64	76	64	114	50	74
RF16	90	95	82	34	96	67	80	98	90	69	70	73	83	80	92	-	-
RF17	-	-	-	-	-	-	-	-	-	72	80	67	96	93	99	41	56
RF18	-	-	-	-	-	-	-	-	-	70	74	79	104	92	131	39	71
RF19	125	104	137	86	143	99	84	36	4	52	56	59	69	58	61	50	63
RF20	63	64	78	33	75	55	56	60	30	60	65	70	93	81	65	69	85

Table S7: Blank contamination of semi-volatile PFCs in samples in the gas phase (pg m^{-3}). SB: Solvent blank, BLK: field blank, n.d.: not detected.

	6:2 FTA	4:2 FTOH	6:2 FTOH	8:2 FTA	8:2 FTOH	Me2FOSA	10:2 FTA	10:2 FTOH	12:2 FTOH	EtFOSA	MeFBSA	MeFOSA	MeFOSE	MeFBSE	EtFOSE	PFOSA
PFC_SB1	n.d.	n.d.	n.d.	n.d.	1.9	n.d.	n.d.	2.3	2.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFC_SB2	n.d.	n.d.	n.d.	n.d.	2.1	n.d.	n.d.	2.6	2.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFC_SB3	n.d.	n.d.	n.d.	n.d.	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFC_SB4	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.	n.d.
PFC_SB5	n.d.	n.d.	n.d.	n.d.	0.9	n.d.	n.d.	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFC_SB6	n.d.	n.d.	n.d.	n.d.	0.9	n.d.	n.d.	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFC_SB7	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.	n.d.
PFC_SB8	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.	n.d.
PFC_BLK1	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.	n.d.
PFC_BLK2	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.	n.d.
PFC_BLK3	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.	n.d.
PFC_BLK4	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.	n.d.
PFC_BLK5	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.	n.d.

Table S8: Blank contamination of ionic PFCs in particle-phase samples (pg m^{-3}). FB: filter blank. n.d.: not detected, n.q.: not quantified.

	PFBS	PFHxS	PFOS	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFOSA	MeFBSA	MeFBSE
PFC_FB1	0.1	0.2	0.2	1.1	0.4	0.3	0.2	0.1	0.1	0.3	0.2	0.3	n.d.	n.q.	n.q.
PFC_FB2	0.1	0.0	0.1	0.5	0.4	0.2	0.2	0.6	n.q.	0.3	0.1	0.1	n.d.	n.q.	n.q.
PFC_FB3	0.1	0.1	0.2	0.5	0.1	0.1	0.1	0.5	n.d.	0.1	0.1	0.1	n.q.	n.q.	n.q.
PFC_FB4	n.q.	n.q.	0.1	0.2	0.1	0.1	0.1	0.2	n.q.	n.q.	0.0	0.0	n.d.	n.d.	n.q.
PFC_FB5	n.q.	n.q.	0.2	n.q.	0.4	0.1	0.2	0.4	0.1	n.q.	n.q.	0.1	0.1	n.d.	0.1
PFC_FB6	n.q.	n.q.	0.2	n.q.	0.3	0.1	0.1	0.3	0.1	0.1	n.q.	0.1	0.1	n.q.	0.1
PFC_FB7	n.q.	n.q.	0.2	n.q.	0.7	0.3	0.2	0.5	0.1	0.2	n.q.	0.1	n.q.	n.d.	0.1
PFC_FB8	n.q.	n.q.	0.1	n.q.	0.3	0.1	0.1	0.2	n.q.	n.q.	n.q.	n.q.	0.1	n.q.	0.1
PFC_FB9	0.1	n.q.	n.q.	n.q.	0.7	0.1	0.1	0.3	0.1	0.1	n.q.	n.q.	0.1	n.q.	0.1

Table S9: Blank contamination of musk fragrances in samples in the gas-and particle phase (pg m^{-3}). SB: Solvent blank, BLK: field blank, FB: filter blank, n.d.: not detected.

	ADBI	AHMI	HHCB	ATII	MX	AHTN	MK
SB1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SB2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SB3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SB4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SB5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SB6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SB7	2.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SB8	n.d.	n.d.	1.1	n.d.	1.3	n.d.	n.d.
BLK1	n.d.	n.d.	2.8	n.d.	n.d.	2.9	n.d.
BLK2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BLK3	n.d.	n.d.	4.7	n.d.	n.d.	1.8	n.d.
BLK4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BLK5	n.d.	n.d.	1.0	n.d.	n.d.	1.5	n.d.
FB1	n.d.	n.d.	0.1	n.d.	3.1	n.d.	n.d.
FB2	n.d.	n.d.	0.9	n.d.	3.8	n.d.	n.d.
FB3	n.d.	n.d.	0.9	n.d.	3.6	n.d.	n.d.
FB4	n.d.	n.d.	1.2	n.d.	3.3	n.d.	n.d.

Table S10: Blank contamination of PBDEs in samples in the particle phase (pg m^{-3}). FB: filter blank, n.d.: not detected.

	BDE28	BDE47	BDE100	BDE99	BDE154	BDE153	BDE183	BDE209
FB1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.9	1234.6
FB2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.3	608.4
FB3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.5	1943.1
FB4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.1	646.7
FB5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.8	1202.9

Table S11: PFC concentrations (pg m^{-3}) in gas-phase samples from landfills LB and LA and the corresponding RFs. n.d.: not detected, [a] values are corrected by mean recovery rates of ^{13}C 6:2 FTOH as described in section 4.3.7.

	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_2FOSA	EtFOSA	MeFBSA	MeFOSA	PFOSA	MeFOSE	MeFBSE	EtFOSE
LA1	n.d.	14.2	42.4	15.4	14.0	1.3	3.2	n.d	n.d	1.1	n.d	3.4	n.d	2.1	n.d	3.6
LA2	n.d.	24.9	41.0	11.0	24.3	3.2	2.7	7.3	n.d	1.4	n.d	3.7	n.d	2.0	1.7	2.4
LA3	n.d.	22.0	48.5	8.8	8.7	4.8	2.4	2.2	n.d	1.5	n.d	n.d	n.d	2.9	n.d	2.1
LA4	n.d.	10.2	53.4	13.6	4.8	n.d	0.8	0.6	0.2	8.9	n.d	5.3	n.d	2.7	2.3	1.7
LA5	n.d.	8.2	44.7	12.6	5.1	1.6	1.6	1.2	n.d	1.6	n.d	2.7	n.d	1.5	2.8	n.d
LB1	n.d.	102.8	433.6	92.7	38.0	1.1	12.6	6.9	n.d	n.d	n.d	6.9	n.d	6.9	n.d	4.3
LB2	n.d.	21.8	80.5	15.9	7.7	n.d	0.2	0.1	n.d	1.3	n.d	1.1	n.d	0.7	3.6	0.7
LB3	n.d.	59.6	97.1	19.8	9.3	n.d	0.8	0.3	n.d	2.0	n.d	2.6	n.d	1.2	n.d	1.2
LB4	n.d.	32.7	121.0	38.8	23.6	n.d	0.7	0.0	n.d	3.3	n.d	4.0	n.d	1.8	n.d	n.d
LB5	n.d.	17.7	90.9	31.5	20.2	n.d	0.9	0.4	n.d	17.5	n.d	4.0	n.d	n.d	n.d	1.5
RF6	n.d.	7.4	24.6	8.3	3.7	n.d.	1.9	1.1	n.d.	1.3	n.d.	2.5	n.d.	2.3	n.d.	3.1
RF7	n.d.	9.5	23.1	7.0	3.2	1.7	2.3	1.1	n.d.	1.1	n.d.	2.0	n.d.	1.2	2.1	2.2
RF8	n.d.	6.9	17.6	5.7	2.3	1.1	1.6	0.8	n.d.	1.3	n.d.	2.0	n.d.	1.1	n.d.	1.6
RF9	n.d.	8.2	45.7	12.7	3.6	n.d.	1.3	0.7	n.d.	1.9	n.d.	3.0	n.d.	1.0	n.d.	1.2
RF10	n.d.	10.0	26.6	8.5	3.4	n.d.	1.6	1.0	n.d.	1.6	n.d.	2.8	n.d.	1.3	n.d.	2.3
RF16	n.d.	36.8[a]	154.0	43.7	22.6	n.d.	1.5	0.4	n.d.	1.8	n.d.	1.7	n.d.	n.d.	n.d.	n.d.
RF17	n.d.	8.4[a]	27.4	9.2	5.7	n.d.	1.2	0.1	n.d.	1.1	n.d.	0.8	n.d.	n.d.	n.d.	n.d.
RF18	n.d.	21.8[a]	56.2	17.6	10.5	n.d.	0.4	n.d	n.d.	1.1	n.d.	0.9	n.d.	0.7	n.d.	n.d.
RF19	n.d.	14.9[a]	39.5	13.9	7.3	n.d.	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.9	n.d.	n.d.
RF20	n.d.	24.4[a]	55.6	18.9	8.6	n.d.	1.9	0.4	n.d.	1.1	n.d.	2.0	n.d.	0.8	n.d.	n.d.

Table S12: PFC concentrations (pg m^{-3}) in particle-phase samples from landfills LB and LA and the corresponding RFs. n.d.: not detected, n.q.: not quantified

	PFBS	PFHxS	PFOS	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFOSA
LA1	0.3	n.d.	1.3	3.6	0.3	0.5	0.2	1.0	0.5	0.3	0.3	0.2	n.q.
LA2	n.d.	0.6	0.8	9.1	0.1	3.7	0.1	0.4	0.2	0.2	0.3	0.1	n.d.
LA3	0.7	n.d.	1.3	n.d.	n.d.	4.2	n.d.	1.2	0.7	0.8	0.8	n.q.	n.d.
LA4	0.1	0.4	0.4	n.d.	n.d.	3.6	n.d.	0.3	0.1	0.2	0.3	0.0	0.2
LA5	0.4	0.4	0.3	5.1	0.7	4.1	0.5	1.1	0.2	0.2	0.4	n.d.	n.d.
LB1	0.46	n.d.	0.76	3.37	n.d.	0.85	n.d.	0.22	n.d.	0.41	n.d.	n.d.	n.d.
LB2	n.d.	n.d.	0.23	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.q	n.d.	0.00	n.d.
LB3	n.d.	n.d.	n.q.	4.0	n.d.	n.q.	n.q.	n.q.	n.d.	n.q.	n.d.	n.d.	n.d.
LB4	0.1	n.d.	0.8	9.5	13.3	16.9	0.3	0.6	n.d.	0.3	n.d.	0.3	n.d.
LB5	0.2	n.d.	0.4	7.0	n.d.	0.4	n.q.	0.2	n.d.	n.q.	n.d.	n.d.	n.d.
RF6	0.4	0.3	1.0	9.7	0.3	0.4	0.1	0.9	0.3	0.3	0.2	0.2	0.7
RF7	0.2	0.6	1.1	5.5	0.5	0.4	0.2	1.1	0.2	0.2	0.2	0.2	0.4
RF8	0.1	0.4	0.5	7.9	1.1	0.3	0.4	0.4	0.2	n.d.	n.d.	n.d.	n.d.
RF9	0.2	n.d.	0.1	n.d.	n.d.	0.1	n.d.	0.2	n.d.	n.d.	n.d.	n.d.	n.d.
RF10	0.1	n.d.	0.5	3.2	n.d.	0.3	n.d.	0.6	n.d.	n.d.	n.d.	n.d.	n.d.
RF16	0.5	n.d.	0.7	8.3	1.0	0.4	0.2	0.6	n.d.	n.d.	n.d.	n.d.	n.d.
RF17	n.d.	n.d.	1.0	7.0	0.5	0.8	0.4	1.8	0.2	n.d.	n.d.	n.q	n.d.
RF19	0.1	n.d.	n.d.	13.3	0.5	0.6	n.q	0.8	0.3	0.4	n.d.	n.d.	n.d.
RF20	0.4	n.d.	0.2	9.2	n.d.	0.2	n.d.	0.3	0.1	0.5	n.d.	n.d.	n.d.

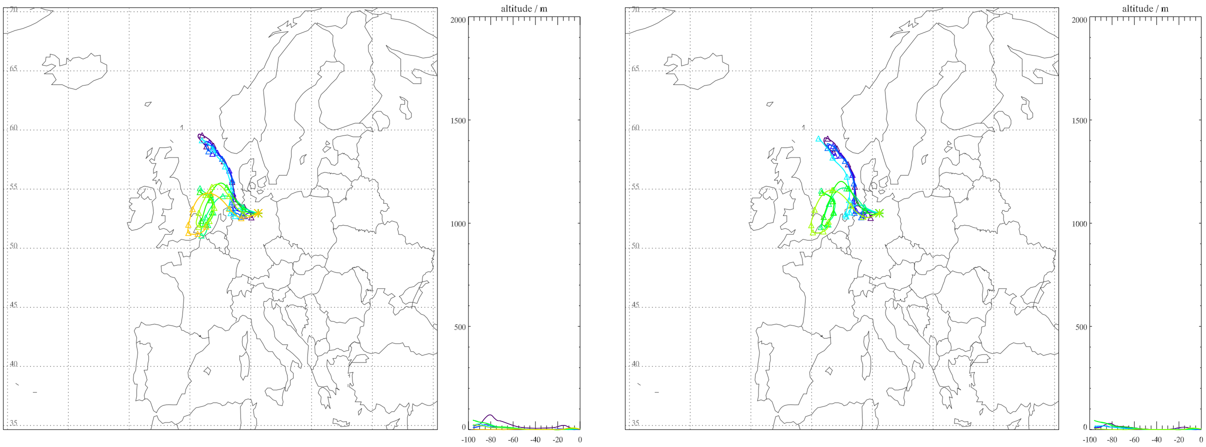
Table S13: Musk fragrance concentrations (pg m^{-3}) in gas-phase samples from landfills LB and LA and the corresponding RFs. n.d.: not detected.

	ADBI	AHMI	HHCB	ATII	MX	AHTN	MK
LA1	9	n.d.	854	n.d.	n.d.	127	n.d.
LA2	n.d.	n.d.	346	n.d.	n.d.	59	n.d.
LA3	3	n.d.	125	n.d.	n.d.	19	n.d.
LA4	22	8	209	n.d.	n.d.	36	n.d.
LA5	n.d.	n.d.	238	n.d.	n.d.	36	n.d.
LB1	n.d.	n.d.	758	n.d.	n.d.	119	n.d.
LB2	n.d.	n.d.	1751	n.d.	n.d.	195	n.d.
LB3	n.d.	n.d.	672	n.d.	n.d.	60	n.d.
LB4	n.d.	n.d.	648	n.d.	n.d.	85	n.d.
LB5	n.d.	n.d.	518	n.d.	n.d.	62	n.d.
RF6	n.d.	n.d.	63	n.d.	n.d.	18	n.d.
RF7	n.d.	n.d.	65	n.d.	n.d.	16	n.d.
RF8	n.d.	n.d.	69	n.d.	n.d.	15	n.d.
RF9	n.d.	n.d.	38	n.d.	n.d.	9	n.d.
RF10	n.d.	n.d.	55	n.d.	n.d.	14	n.d.
RF16	n.d.	n.d.	120	n.d.	n.d.	19	n.d.
RF17	n.d.	n.d.	888	n.d.	n.d.	128	n.d.
RF18	n.d.	n.d.	59	n.d.	n.d.	10	n.d.
RF19	n.d.	n.d.	44	n.d.	n.d.	6	n.d.
RF20	6	n.d.	239	n.d.	n.d.	29	n.d.

Table S14: Musk fragrance concentrations (pg m^{-3}) in particle-phase samples from landfills LB and LA and the corresponding RFs. n.d.: not detected.

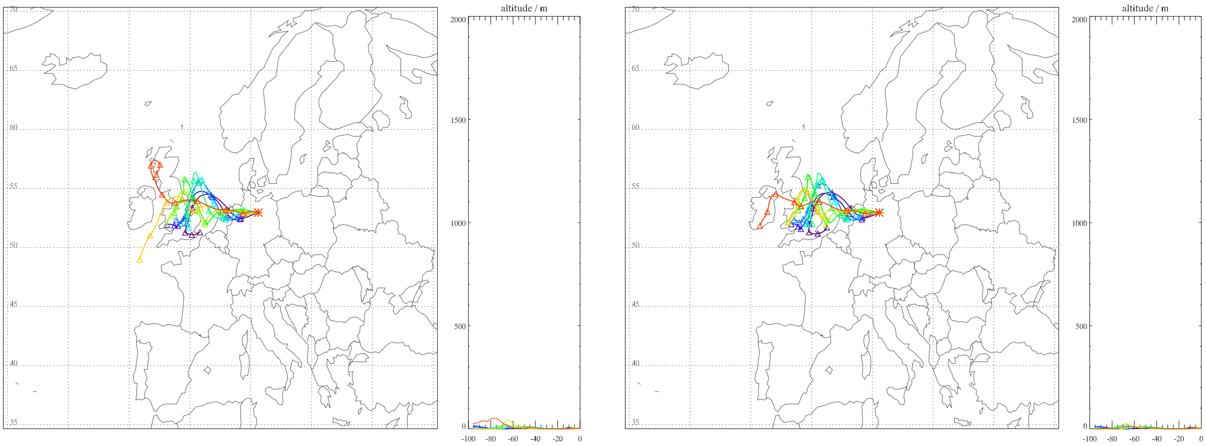
	ADBI	AHMI	HHCB	ATII	MX	AHTN	MK
LB1	n.d.	n.d.	3	n.d.	n.d.	5	n.d.
LB2	n.d.	n.d.	5	n.d.	n.d.	11	n.d.
LB3	n.d.	n.d.	34	n.d.	n.d.	23	n.d.
LB4	n.d.	n.d.	17	n.d.	n.d.	15	n.d.
LB5	n.d.	n.d.	7	n.d.	n.d.	15	n.d.
LA1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
LA2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
LA3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
LA4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
LA5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RF16	n.d.	n.d.	2	n.d.	n.d.	4	n.d.
RF17	n.d.	n.d.	38	n.d.	n.d.	65	n.d.
RF18	n.d.	n.d.	24	n.d.	n.d.	41	n.d.
RF19	n.d.	n.d.	12	n.d.	n.d.	16	n.d.
RF20	n.d.	n.d.	25	n.d.	n.d.	14	n.d.
RF6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RF7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RF8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RF9	n.d.	n.d.	9	n.d.	n.d.	11	n.d.
RF10	n.d.	n.d.	12	n.d.	n.d.	18	n.d.

Figure S7: Seven days air mass back trajectories calculated for three hours intervals (arrival height 2 m), generated by Hysplit 4.8 using GDAS data for samples from landfill sites LA and LB and the corresponding RF. Sampling periods were 11.08.2009- 18.08.2009 (LA) and 27.08.2009- 02.09.2009 (LB). Triangles represent 12 h tags. In addition, trajectory heights are plotted.



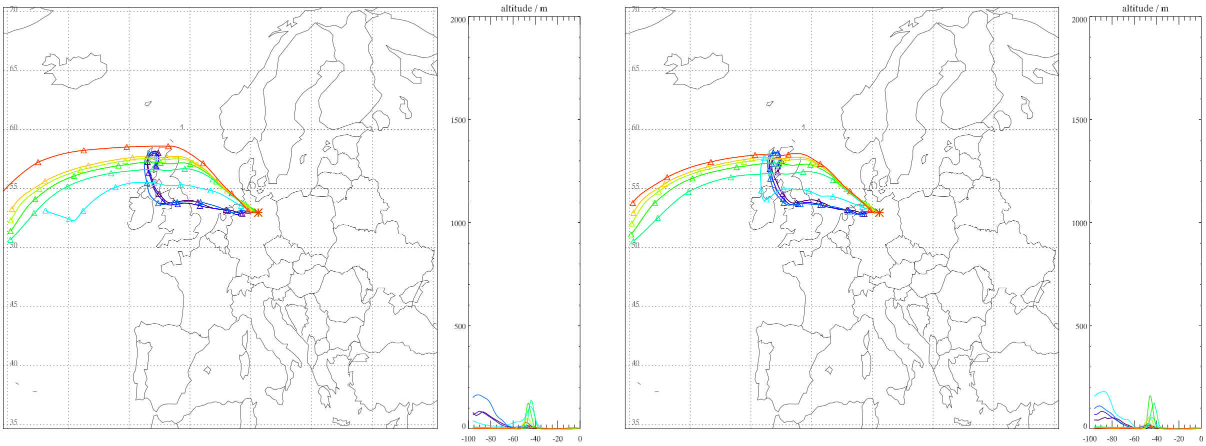
Sample LA1

Sample RF6



Sample LA2

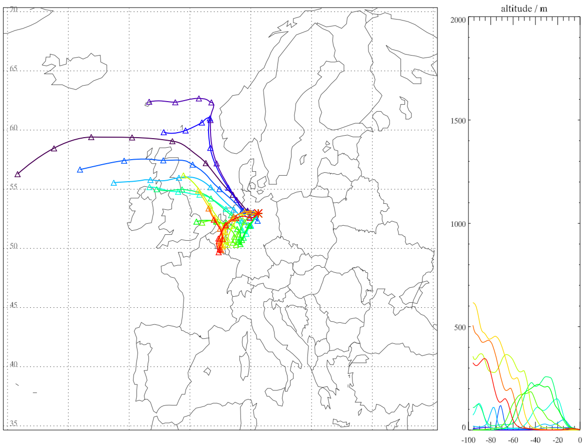
Sample RF7



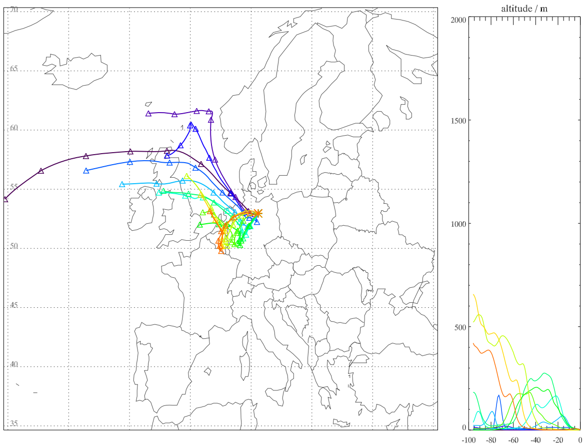
Sample LA3

Sample RF8

Figure S7 cont.



Sample LA4



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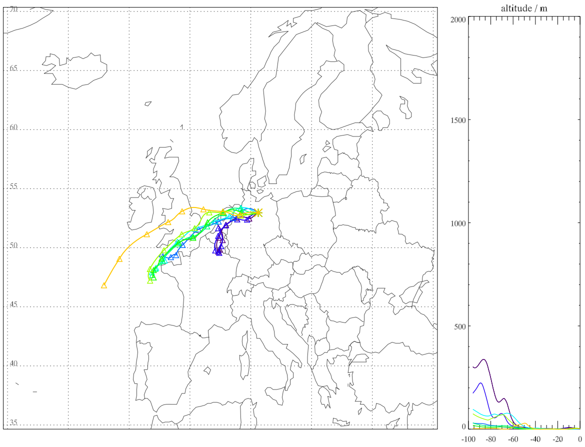
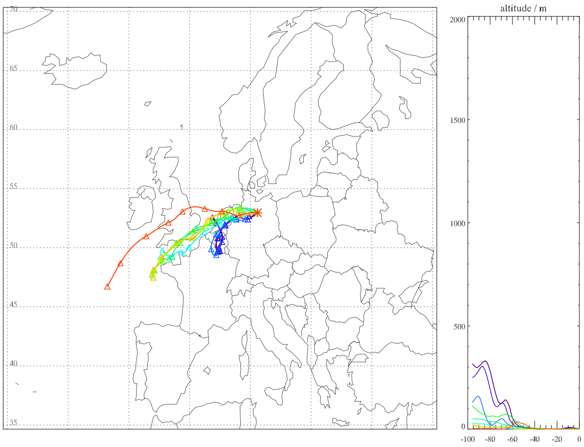


Sample LA5



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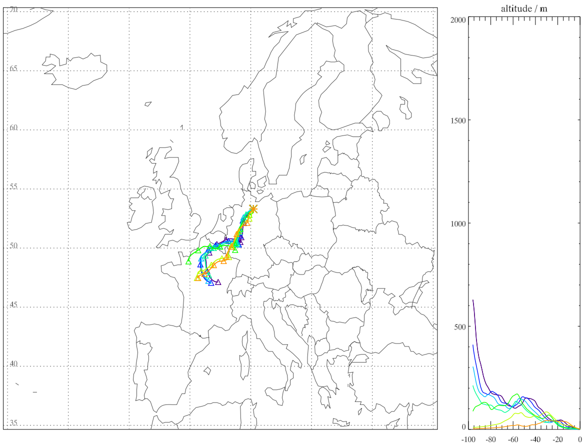

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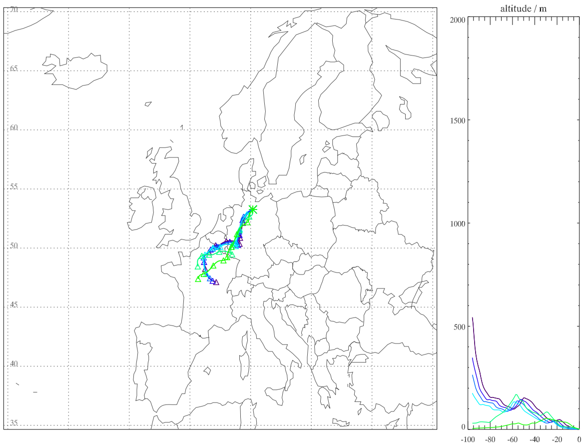
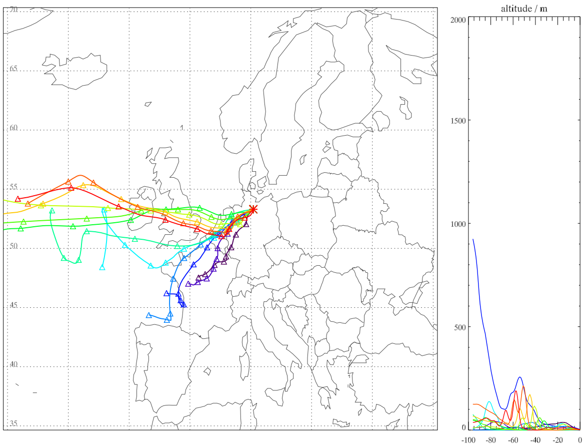
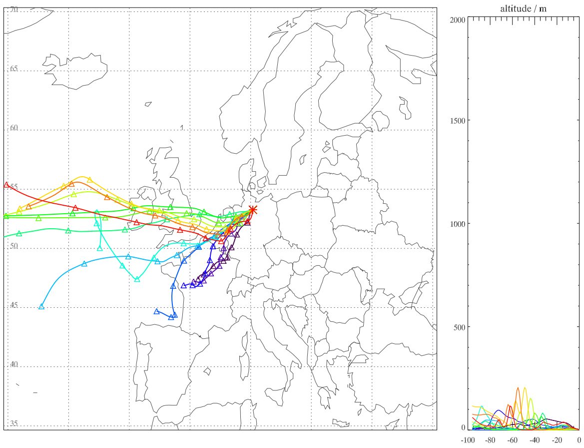


Sample RF16

Figure S7 cont.



Sample LB2



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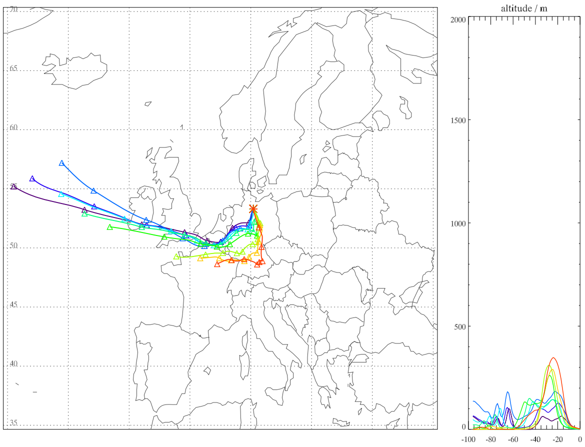
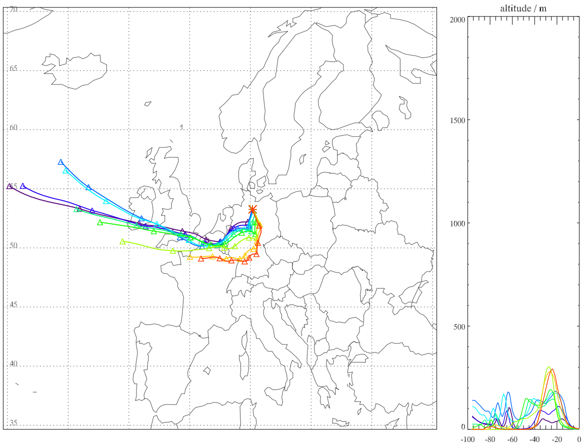
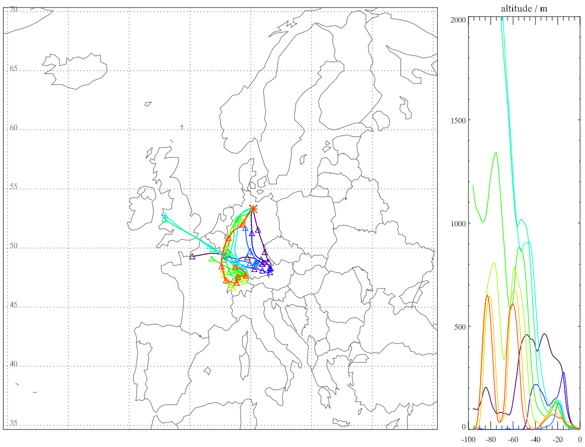


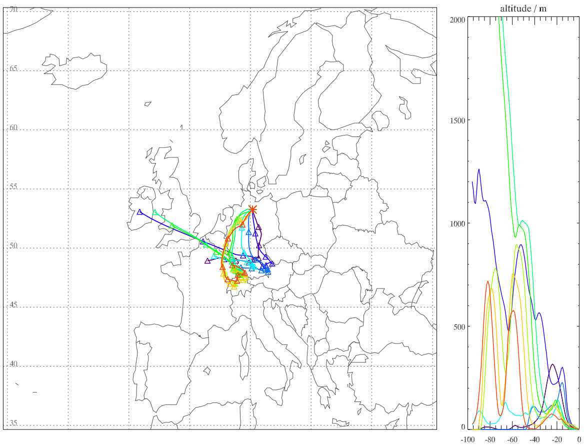
Sample LB3



SampleRF18

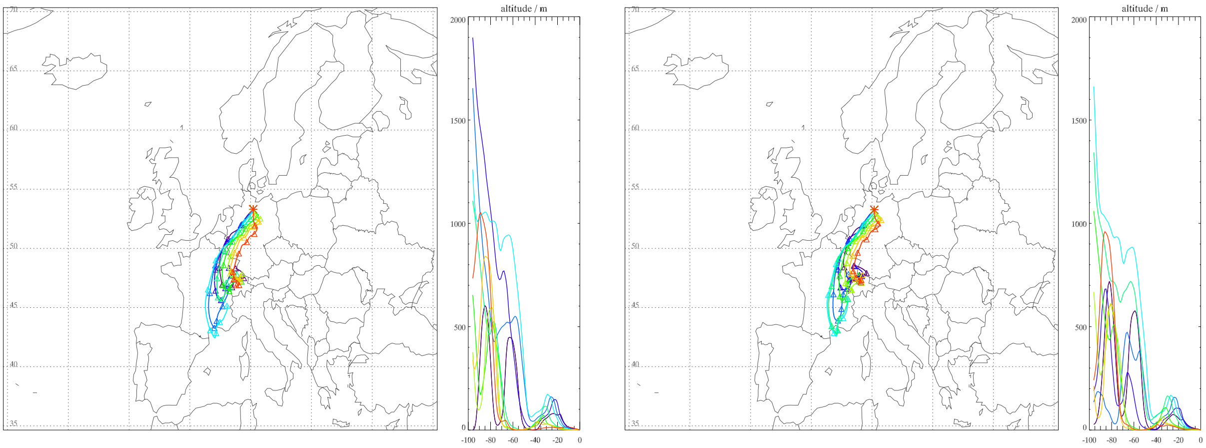


Sample LB4



Sample RF19

Figure S7 cont.



Sample LB5 **Sample RF20**

Table S15: Table of recovery rates (%) obtained in gas-phase samples from waste water treatment plants WA and WB and the reference sites.

	^{13}C 4:2 FTOH	**^{13}C 6:2 FTOH**	**^{13}C 8:2 FTOH**	**^{13}C 10:2 FTOH**	**EtFOSA D_5**	**MeFOSA D_3**	**MeFOSE D_7**	**EtFOSE D_9**	**MBDE 28**	**MBDE 47**	**MBDE 99**	**MBDE 153**	**MBDE 183**	**AHTN D_3**	**MX D_{15}**
WA1	7	34	47	6	44	35	77	59	99	81	97	116	161	123	47
WA2	12	42	44	11	50	58	79	68	93	68	90	105	136	106	71
WA3	6	40	40	36	44	53	71	75	76	84	93	100	115	99	47
WA4	2	0	28	17	20	31	29	23	55	-	46	46	30	88	59
WA5	6	47	34	39	49	73	56	71	84	84	90	100	107	85	66
WB1	8	-	34	75	40	30	52	54	-	-	130	267	204	-	-
WB2	5	-	53	71	36	53	53	54	-	-	158	299	219	-	-
WB3	5	-	30	65	39	34	57	51	171	122	176	306	177	-	-
WB4	5	-	49	108	45	46	68	51	-	-	101	180	114	-	-
WB5	4	-	26	62	38	8	59	43	175	109	154	326	186	-	-
RF1	18	34	46	54	52	52	66	71	97	82	95	120	103	100	26
RF2	18	47	29	49	49	60	64	71	97	75	78	119	90	93	66
RF3	15	40	38	54	53	63	66	74	104	68	87	116	102	102	133
RF4	3	89	16	40	37	46	48	46	-	-	77	80	71	110	43
RF5	60	79	59	67	53	29	55	58	101	73	86	108	106	96	33
RF11	-	-	-	-	-	-	-	-	-	-	80	142	88	98	70
RF12	-	-	5	3	2	8	4	9	-	-	-	-	-	76	48
RF13	22	-	68	131	55	49	62	60	46	88	76	139	93	95	146
RF14	13	48	52	108	42	40	57	65	-	65	88	146	86	92	181
RF15	51	-	67	114	50	33	60	68	56	-	86	150	73	89	150

Table S16: Table of recovery rates (%) obtained in particle phase samples from waste water treatment plants WA and WB and the reference sites.

	$^{18}O_2$ PFHxS	^{13}CPFOS	^{13}C PFBA	^{13}C PFHxA	^{13}C PFOA	^{13}C PFNA	^{13}C PFDA	^{13}C PFUDA	^{13}C PFDoA	MBDE 28	MBDE 47	MBDE 99	MBDE 153	MBDE 183	MBDE 209	AHTN D_3	MX D_{15}
WA1	-	-	-	-	-	-	-	-	-	93	90	83	110	113	162	55	104
WA2	42	59	54	32	55	37	58	87	67	88	83	87	110	117	132	93	94
WA3	38	60	39	19	39	35	58	70	54	80	85	76	96	93	129	69	102
WA4	32	88	35	16	45	53	53	47	35	91	87	84	135	122	130	88	119
WA5	44	80	46	28	51	63	73	88	73	85	88	84	113	114	141	106	-
WB1	65	63	85	46	77	41	52	63	59	40	44	56	92	116	69	55	76
WB2	-	-	-	-	-	-	-	-	-	36	36	42	57	56	60	95	40
WB3	47	66	53	18	55	38	45	51	48	54	61	65	110	122	67	99	101
WB4	118	72	44	83	96	70	65	83	79	46	44	49	75	76	47	83	85
WB5	55	87	48	19	58	42	47	64	54	51	57	61	103	99	87	70	81
RF1	48	77	55	40	54	61	76	84	74	60	65	59	70	68	103	-	48
RF2	43	79	35	27	49	57	69	76	68	80	76	80	89	89	150	-	70
RF3	35	56	28	17	36	41	50	59	51	78	76	77	84	84	144	-	66
RF4	31	87	35	17	39	48	52	49	43	70	72	77	79	83	131	-	48
RF5	43	91	35	21	38	55	60	63	53	65	66	61	61	64	113	-	61
RF11	92	85	118	61	111	93	68	27	2	53	49	48	76	75	48	101	97
RF12	48	83	30	18	43	43	55	66	54	52	59	64	73	75	76	78	82
RF13	52	60	48	18	52	44	51	59	55	62	59	63	73	84	82	93	103
RF14	44	62	42	19	49	39	46	58	53	56	52	59	70	73	80	83	89
RF15	91	103	77	82	81	87	91	103	95	65	60	67	75	72	103	49	74

Table S17: PFC concentrations (pg m^{-3}) in gas-phase samples from WWTP WA and WB and the corresponding RFs. n.d.: not detected, [a] values are corrected by mean recovery rates of ^{13}C 6:2 FTOH as described in section 5.3.7.

	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$_2$FOSA	EtFOSA	MeFBSA	MeFOSA	PFOSA	MeFOSE	MeFBSE	EtFOSE
WB1	n.d.	112[a]	216	51	34	n.d.	20	28	n.d.	55	27	16	n.d.	7	n.d.	3
WB2	n.d.	12[a]	124	35	14	n.d.	3	4	n.q.	51	23	6	n.d.	4	5	9
WB3	n.d.	120[a]	143	31	17	n.d.	7	8	n.d.	31	34	8	n.d.	2	n.d.	n.d.
WB4	n.d.	225[a]	419	66	29	n.d.	35	33	n.d.	69	61	10	n.d.	4	7	3
WB5	n.d.	259[a]	350	77	30	n.d.	49	56	n.d.	61	60	54	n.d.	2	5	n.d.
WA1	n.d.	16	59	27	55	11	4	21	n.d.	4	n.d.	9	n.d.	1	n.d.	2
WA2	7	29	85	22	33	8	4	15	n.d.	11	n.d.	10	n.d.	2	n.d.	3
WA3	n.d.	15	41	11	6	10	3	2	n.d.	3	n.d.	4	n.d.	1	3	n.d.
WA4	n.d.	0	36	19	6	n.d.	n.d.	2	n.d.	18	n.d.	5	n.d.	2	5	3
WA5	n.d.	25	91	22	12	11	3	3	n.d.	3	n.d.		n.d.	6	7	2
RF1	n.d.	13	34	14	8	n.d.	3	3	n.d.	3	n.d.	6	n.d.	1	5	n.d.
RF2	n.d.	9	130	19	8	4	4	3	n.d.	3	n.d.	4	n.d.	1	5	1
RF3	n.d.	7	62	11	6	5	1	2	n.d.	3	n.d.	4	n.d.	1	3	n.d.
RF4	n.d.	8	31	12	3	9	1	1	n.d.	2	n.d.		n.d.	3	3	1
RF5	n.d.	8	26	9	5	n.d.	n.d.	n.d.	n.d.	9	n.d.	10	n.d.	1	5	3
RF12	n.d.	34[a]	75	48	20	n.d.	3	2	n.d.	1	3	3	n.d.	2	3	n.d.
RF13	n.d.	4[a]	45	14	7	7	4	2	n.d.	2	3	4	n.d.	n.d.	n.d.	n.d.
RF14	n.d.	45	176	58	24	13	6	3	n.d.	3	4	9	n.d.	4	n.d.	2
RF15	n.d.	4[a]	7	3	2	n.d.	3	n.d.	n.d.	1	n.d.	n.d.	n.d.	2	n.d.	n.d.

Table S18: PFC concentrations (pg m^{-3}) in particle-phase samples from WWTP WA and WB and the corresponding RFs. n.d.: not detected, n.q.: not quantified

	PFBS	PFHxS	PFOS	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFOSA
WA2	n.d.	n.d.	0.2	8.4	0.0	0.5	0.1	1.3	n.d.	0.2	0.1	0.2	1.9
WA3	n.d.	n.d.	0.5	6.5	0.1	0.2	n.d.	1.1	0.1	0.1	0.1	0.1	1.5
WA4	n.d.	n.d.	0.4	1.4	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	0.1	0.6
WA5	0.2	0.7	0.9	6.5	0.2	0.4	0.1	0.5	0.3	0.0	0.1	0.1	0.9
WB1	n.d.	n.d.	0.0	0.5	n.d.	0.0	n.d.	n.d.	0.2	0.3	n.d.	n.d.	0.6
WB3	0.1	n.d.	0.2	2.8	n.d.	n.d.	n.d.	0.6	0.3	0.2	n.d.	n.d.	0.9
WB4	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.
WB5	0.2	n.d.	0.5	0.0	n.d.	n.d.	n.d.	1.1	0.5	0.6	n.d.	n.d.	0.9
RF2	n.d.	0.0	0.1	2.6	0.4	0.3	0.1	0.3	0.3	0.1	0.1	0.2	0.2
RF3	0.1	0.2	0.6	5.6	0.4	0.3	0.1	0.2	0.0	0.1	0.1	0.1	0.3
RF4	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	0.0	n.d.	n.d.	n.d.	0.0
RF5	0.9	2.0	1.8	5.4	1.8	1.6	1.0	3.4	0.9	2.1	0.8	1.1	1.7
RF11	1.9	n.d.	2.9	15.7	4.7	3.3	2.8	7.1	1.9	1.7	n.d.	n.d.	n.d.
RF13	0.2	n.d.	0.6	7.2	n.d.	0.5	0.1	0.4	n.d.	n.d.	n.d.	n.d.	n.d.
RF14	n.d.	n.d.	1.0	6.6	1.2	0.6	n.d.	0.5	n.d.	n.d.	n.d.	n.d.	n.d.
RF15	n.q.	n.d.	n.d.	1.7	n.d.	n.q.	n.d.	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.

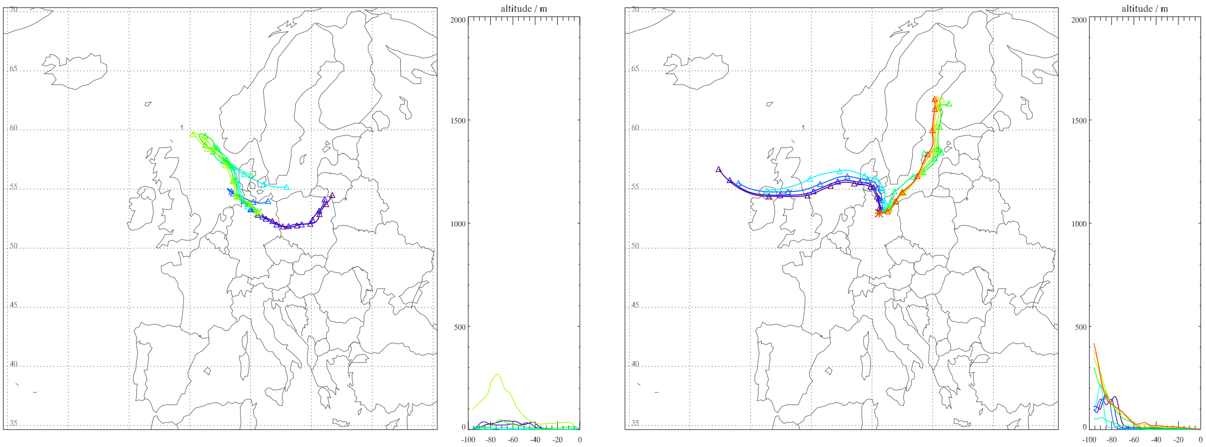
Table S19: Musk fragrance concentrations (ng m^{-3}) in gas-phase samples from WWTP WA and WB and the corresponding RFs. n.d.: not detected.

	ADBI	AHMI	HHCB	ATII	MX	AHTN	MK
WA1	0.048	0.016	5.157	n.d.	n.d.	0.304	n.d.
WA2	0.076	0.142	66.715	n.d.	n.d.	3.972	n.d.
WA3	0.011	0.020	8.621	n.d.	n.d.	0.556	n.d.
WA4	1.097	0.880	119.644	n.d.	n.d.	6.106	n.d.
WA5	0.348	0.090	45.128	n.d.	n.d.	2.539	n.d.
WB1	0.454	1.760	55.181	n.d.	n.d.	17.967	n.d.
WB2	0.181	0.088	190.216	n.d.	n.d.	44.126	n.d.
WB3	1.328	4.213	406.625	n.d.	n.d.	45.556	n.d.
WB4	1.576	5.164	264.112	n.d.	n.d.	44.831	n.d.
WB5	1.741	6.551	407.194	n.d.	n.d.	65.063	n.d.
RF1	n.d.	n.d.	0.250	n.d.	n.d.	0.046	n.d.
RF2	n.d.	n.d.	0.308	n.d.	n.d.	0.044	n.d.
RF3	n.d.	n.d.	0.063	n.d.	n.d.	0.010	n.d.
RF4	n.d.	n.d.	0.831	n.d.	n.d.	0.131	n.d.
RF5	n.d.	n.d.	0.179	n.d.	n.d.	0.033	n.d.
RF11	n.d.	n.d.	0.104	n.d.	n.d.	0.012	n.d.
RF12	0.008	n.d.	0.296	n.d.	n.d.	0.047	n.d.
RF13	0.006	n.d.	0.300	n.d.	n.d.	0.038	n.d.
RF14	n.d.	n.d.	0.226	n.d.	n.d.	0.034	n.d.
RF15	0.012	n.d.	0.718	n.d.	n.d.	0.096	n.d.

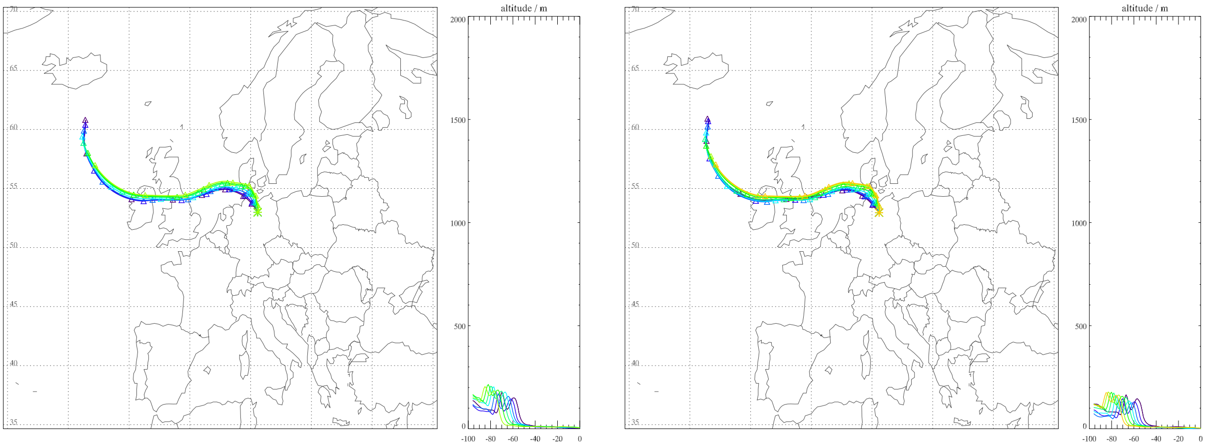
Table S20: Musk fragrance concentrations (pg m^{-3}) in particle-phase samples from WWTP WA and WB and the corresponding RFs. n.d.= not detected.

	ADBI	AHMI	HHCB	ATII	MX	AHTN	MK
WA1	14	13	169	n.d.	n.d.	60	n.d.
WA2	9	8	75	n.d.	n.d.	18	n.d.
WA3	3	3	34	n.d.	n.d.	8	n.d.
WA4	11	8	436	n.d.	n.d.	59	n.d.
WA5	14	9	404	n.d.	n.d.	108	n.d.
WB1	7	6	272	n.d.	n.d.	30	n.d.
WB2	n.d.	n.d.	6	n.d.	n.d.	11	n.d.
WB3	11	9	850	n.d.	n.d.	115	n.d.
WB4	12	11	467	n.d.	n.d.	70	n.d.
WB5	22	20	1362	n.d.	n.d.	211	n.d.
RF11	n.d.	n.d.	3	n.d.	n.d.	4	n.d.
RF12	n.d.	n.d.	11	n.d.	n.d.	12	n.d.
RF13	n.d.	n.d.	9	n.d.	n.d.	11	n.d.
RF14	n.d.	n.d.	7	n.d.	n.d.	8	n.d.
RF15	n.d.	n.d.	8	n.d.	n.d.	16	n.d.
RF1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RF2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RF3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RF4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RF5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

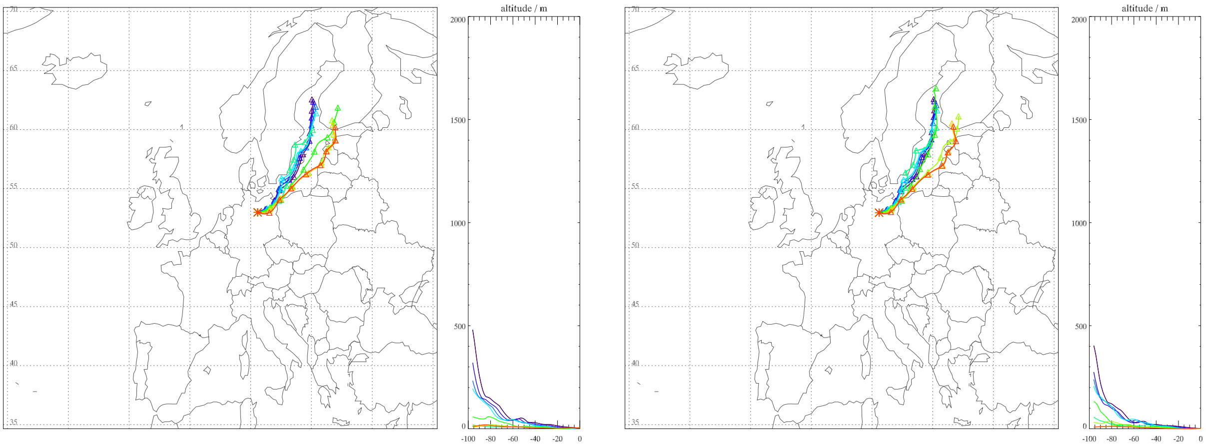
Figure S8: Seven days air mass back trajectories calculated for three hours intervals (arrival height s: 5m (WA) 3 m (WB)), generated by Hysplit 4.8 using GDAS data for samples from waste water treatment plants WA and WB and the corresponding RF. Sampling periods were 04.08.2009- 11.08.2009 (WA) and 20.08.2009- 27.08.2009 (WB). Triangles represent 12 h tags of every trajectory. In addition, trajectory heights are plotted.



Sample WA1 **Sample RF1**

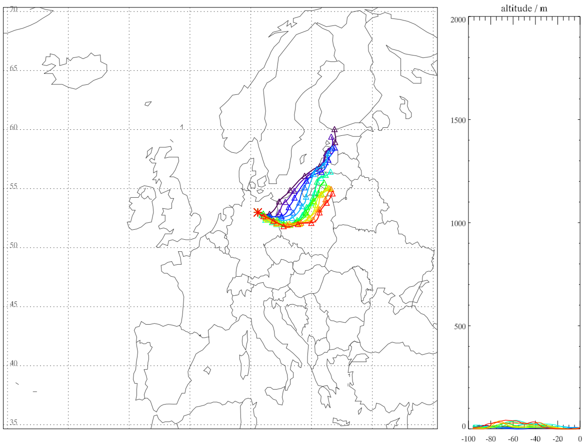


Sample WA 2 **Sample RF2**



Sample WA 3 **Sample RF3**

Figure S8 cont.



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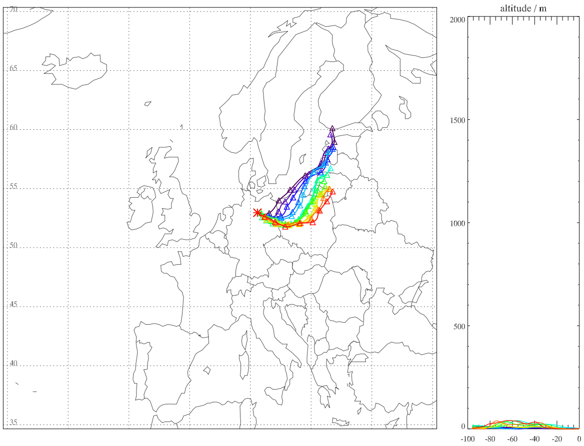

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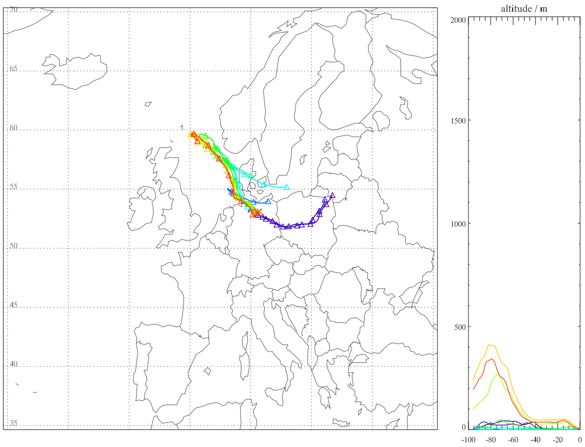
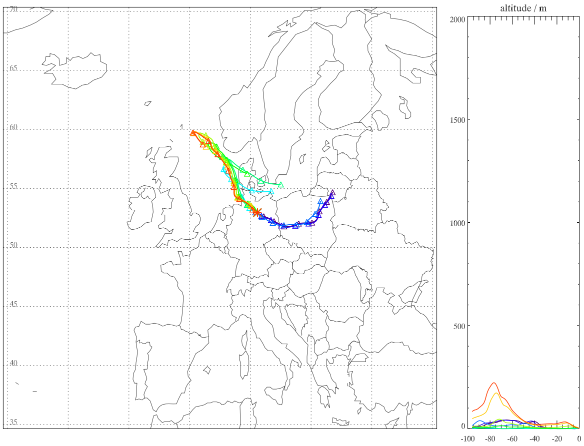


Sample WA 5



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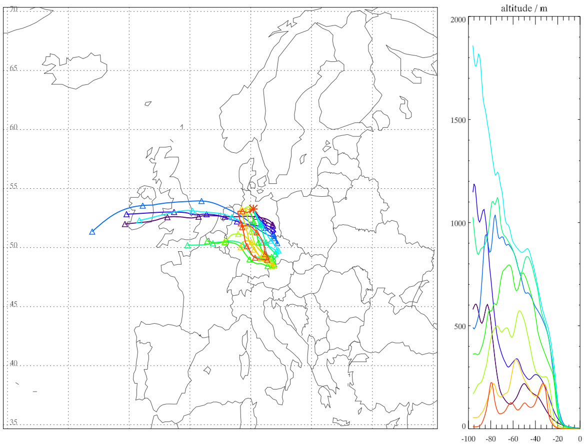
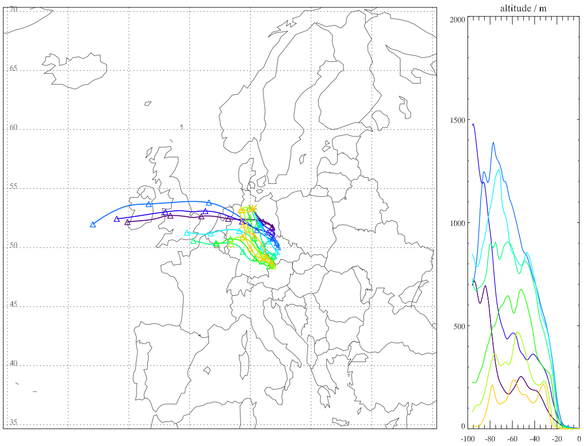
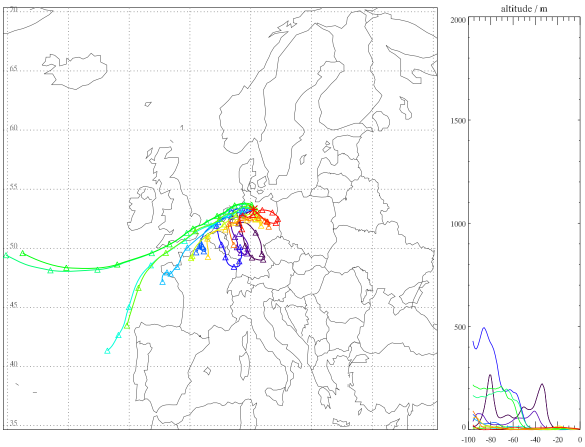


Sample WB1



Sample RF11

Figure S8 cont.



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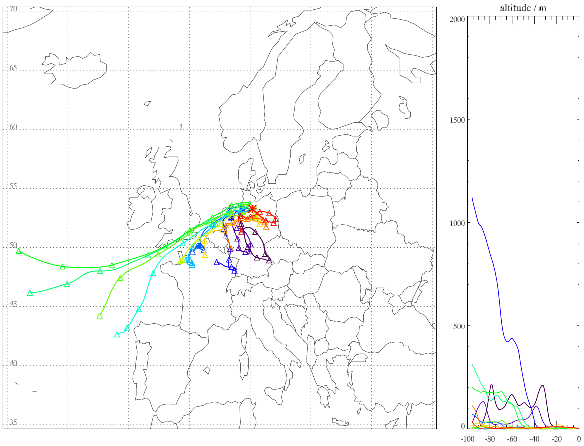

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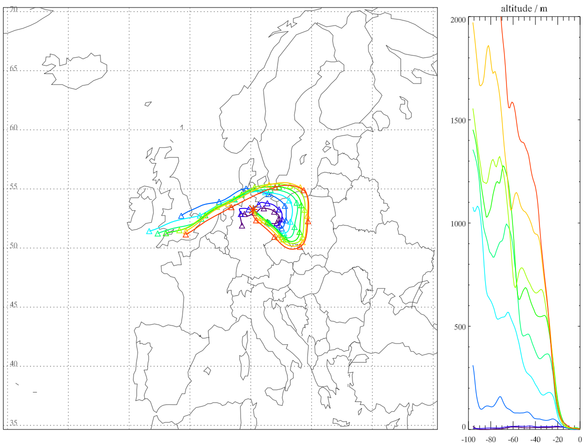

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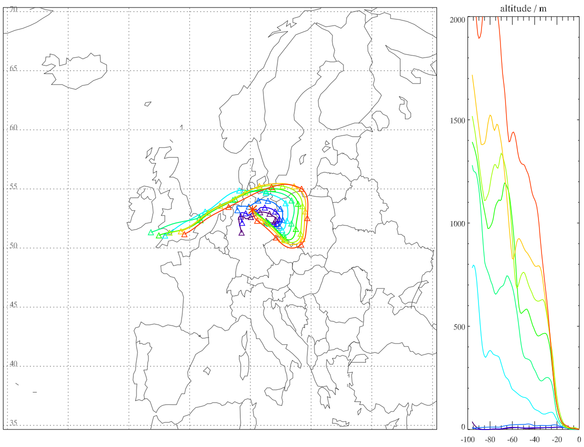

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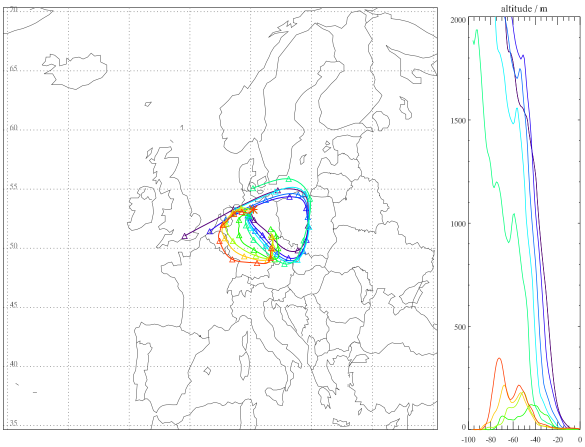

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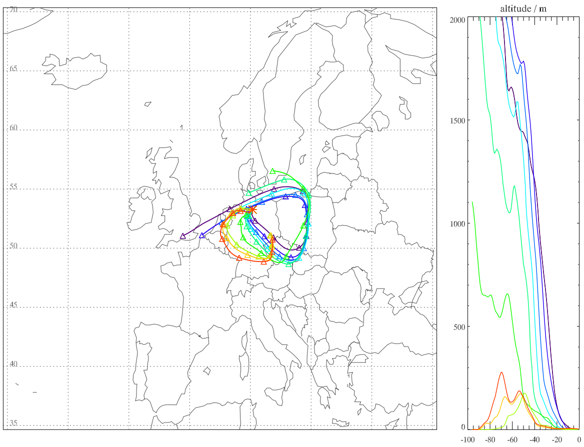
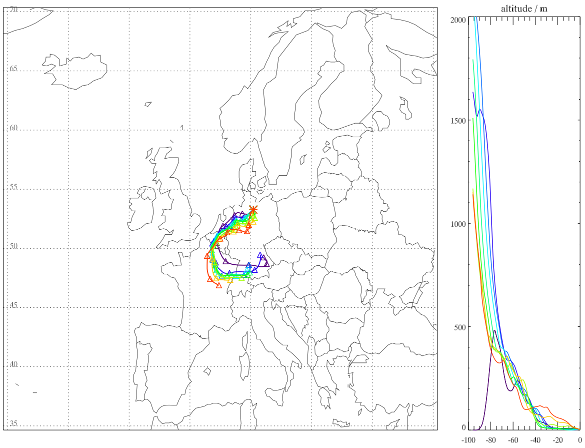


Sample RF14

Figure S8 cont.



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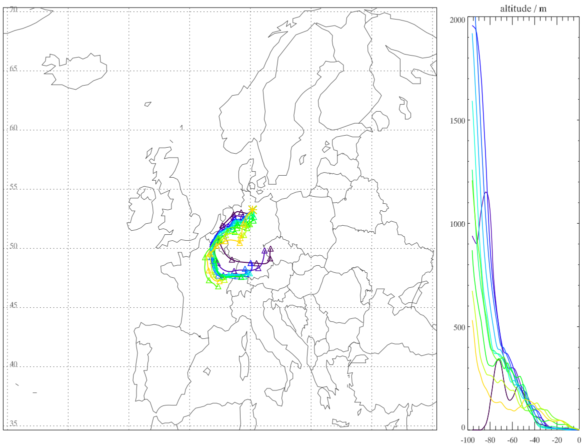

Sample RF15

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