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Fluorotelomer alcohols, perfluoroalkyl acids and semifluorinated alkanes in the house dust, air and sediment

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For My parents

And

My husband Lingxiangyu

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Summary

Per– and polyfluorinated compounds (PFCs), such as semifluorinated alkanes (SFAs), fluorotelomer alcohols (FTOHs), perfluoroalkyl acids including perfluorinated carboxylates (PFCAs) and perfluorinated sulfonates (PFSAs) are anthropogenic compounds, and have been generally produced and applied over 50 years. SFAs are applied in ski wax products to reduce friction and repel dirt. The limited number of publications has shown their high levels in snow and soil in skiing tracks. FTOHs are prone to be dominant in the atmosphere due to their high volatility, and they could be transformed to PFCAs via atmospheric degradation. FTOHs can undergo long range atmospheric transport (LRAT) reaching to remote regions, and thus are considered as a potential source of PFCAs in remote areas. PFCAs and PFSAs are highly persistent and have a potential of accumulation in biota. Thus, it is of high importance to investigate the environmental behavior of PFCs.

In this PhD thesis, the presence and distribution of FTOHs in house dust were investigated. More than 70% of the house dust samples contained 6:2 FTOH, 8:2 FTOH and 10:2 FTOH, whereas 4:2 FTOH was not detected in any of the samples. The total concentrations varied from 4.8 to 734 ng/g. On the basis of FTOH concentrations in house dust, the human exposure to FTOHs via dust ingestion was evaluated. The total FTOH intake was 0.1 - 40.4 ng/d for adults, and 1.6 - 73.4 ng/d for toddlers, indicating that house dust imposes more potential health risk on toddlers due to their hand-to-mouth contact. In addition, the highest 8:2 FTOH-based perfluorooctanoate (PFOA) intake via indoor dust was estimated to be 0.24 ng/d for adults and 0.44 ng/d for toddlers.

A clean-up method using silica gel deactivated with 10% H_2O was developed, and applied to the active air samples to explore the occurrences of FTOHs in the Alpine atmosphere. Air masses from four potential source regions (NW, NE, S and UND) were sampled separately at two Alpine summits (Sonnblick and Zugspitze) during 2007-2010. 6:2, 8:2, and 10:2 FTOH were all detected with 8:2 FTOH being the dominant compound. Air mass origin was an important factor determining the atmospheric FTOH levels at Zugspitze, and air mass from NE (regions in the Northeast of the Alps) led to the highest median ΣFTOH concentration (34.8 pg/m^3), followed by NW (regions in the Northwest of the Alps), S (the Po basin in Italy) and UND (the Atlantic or the Arctic). However, this trend was not pronounced at Sonnblick.

Time-averaged ΣFTOH was calculated to be 7.5 - 41.3 pg/m^3, showing low FTOH concentrations in the Alpine atmospheric environment and contributing to 0.1 - 1.4 ng/m^2/d of PFOA deposition fluxes.

The potential of FTOH migration to the groundwater was assessed. FTOHs could be detected in groundwater collected in Berlin, Germany. However, the differences between samples and procedure blank were not significant. The results might imply that FTOHs have a potential of migration to groundwater. This needs to be further investigated.

PFSAs and PFCAs were investigated in sediment cores from the Yangtze River. Among the 12 congeners analyzed, PFOA was the compound with the highest detection rate, followed by perfluorooctane sulfonate (PFOS) and perfluoroundecanoate (PFUnDA). The total concentrations ranged from non-detection to 724.7 pg/g dry weight. As for the profiles with depth in sediment cores, the relative standard deviation (RSD) values implied that the differences in concentrations of PFSAs and PFCAs among layers were not significant and thus average concentration values were used to track the distribution of analytes along the Yangtze River. In the main stream of the Yangtze River, the total concentrations were the highest at WZ (Wanzhou), decreased by 40% towards YY (Yunyang), increased by 23% at FJ (Fengjie), and stayed comparable at BD (Badong), GJB (Guojiaba) and MP (Maoping).

PFSAs and PFCAs were also investigated in the biota from the Yangtze River. Long-chain PFSAs and PFCAs were detected in fish samples. PFOS was the dominant compound with concentrations in the range of non-detection to 11.9 ng/g, followed by PFUnDA.

Finally, a method was developed for the detection of SFAs by GC-PCI-MS. Fragments of $[M\text{-}H]^+$ and $[MH\text{-}HF]^+$ were used as quantifier and qualifier in the measurement. No SFAs were detected in tested ski wax products; therefore, only SFA congeners (F_6H_{16}, F_8H_{16}, $F_{10}H_{16}$, $F_{12}H_{16}$, $F_{12}H_{16}$ene and $F_{12}H_{14}$) with available standard solutions were investigated in active air samples from Sonnblick and Zugspitze. SFAs were sparsely detected in the air, with concentrations up to 10.7 pg/m^3.

Zusammenfassung

Per– und polyfluorierte Verbindungen (engl. per- and polyfluorinated compounds, PFCs), wie teilfluorierte Alkane (engl. semifluorinated alkanes, SFAs), Fluortelomeralkohole (engl. fluorotelomer alcohols, FTOHs), perfluorierte Karboxylate (engl. perfluorinated carboxylates, PFCAs) und perfluorierte Sulfonate (engl. perfluorinated sulfonates, PFSAs) sind anthropogene Substanzen, die seit über 50 Jahren produziert und angewandt wurden. SFAs kommen in Skiwachs zur Anwendung, um sowohl die Reibung als auch die Schmutzhaftung zu reduzieren. In der geringen Anzahl an Publikationen wurden hohe Werte im Schnee und Boden von Skipisten festgestellt. Aufgrund ihrer hohen Flüchtigkeit sind FTOHs in der Atmosphäre omnipräsent. Zugleich können sie durch atmosphärischen Abbau zu PFCAs umgewandelt werden. FTOHs können durch atmosphärischen Langstreckentransport (engl. long range transport, LRAT) entlegene Regionen erreichen und werden daher als mögliche Quelle für PFCAs in entlegenen Gebieten angesehen. PFCAs und PFSAs sind hoch persistent und haben Potential zur Bioakkumulation in der Flora und Fauna. Folglich ist es von großer Bedeutung, das Verhalten von PFCs in der Umwelt zu untersuchen.

In dieser Doktorarbeit wurde die Existenz und Verteilung von FTOHs in Hausstaub untersucht. Mehr als 70 % der Hausstaubproben enthielten 6:2 FTOH, 8:2 FTOH und 10:2 FTOH, wobei 4:2 FTOH in keiner der Proben nachgewiesen werden konnte. Die Gesamtkonzentrationen lagen in einem Bereich von 4.8 bis 734 ng/g. Die FTOH-Gesamtaufnahme betrug 0.1-40.4 ng/Tag für Erwachsene und 1.6-73.4 ng/Tag für Kleinkinder, was zeigt, dass Hausstaub für Kleinkinder ein höheres Gesundheitsrisiko darstellt aufgrund deren Hand-zu-Mund Kontakt. Zudem wurde die höchste auf 8:2-FTOH basierende Perfluorooktanoat-Aufnahme (engl. perfluorooctanoate, PFOA) über Hausstaub auf 0.24 und 0.44 ng/Tag für Erwachsene bzw. Kleinkinder geschätzt.

Um das Vorkommen von FTOHs in aktiv genommenen Proben der alpinen Atmosphäre zu untersuchen, wurde eine Aufreinigungsmethode entwickelt, die auf Silicagel beruht, welches mit 10 % Wasser deaktiviert wurde. Von 2007 bis 2010 wurden Luftmassen von vier potentiellen Quellregionen (NW, NO, S und UND) auf zwei Gipfeln (Sonnblick und Zugspitze) jeweils separat beprobt. 6:2, 8:2 als auch 10:2 FTOH konnten nachgewiesen werden, wobei 8:2 FTOH vorherrschend war. Der Ursprung der Luftmasse war ein wichtiger

Faktor in der Bestimmung der FTOH Werte an der Zugspitze. Luftmassen aus NO (Regionen nordöstlich der Alpen) enthielten die durchschnittlich höchste FTOH-Summenkonzentration (34.8 pg/m^3), gefolgt von Luftmassen aus NW (Regionen nordwestlich der Alpen), S (die Po-Ebene in Italien) und UND (der Atlantik oder die Arktis). Jedoch konnte dieser Trend nicht am Sonnblick bestätigt werden. Zeitliche Durchschnittswerte der FTOH-Summenkonzentration wurden auf 7.4-41.3 pg/m^3 berechnet, was zeigt, dass FTOH-Konzentrationen in der alpinen Atmosphäre niedrig sind und mit 0.1-1.4 ng/m^2/Tag zu PFOA-Depositionflüssen beitragen.

Das Potential der FTOH-Migration ins Grundwasser wurde ebenfalls eingeschätzt. FTOHs konnten in Grundwasser aus Berlin (Deutschland) nachgewiesen werden. Allerdings waren die Unterschiede zwischen Proben und Laborblindwerten nicht signifikant. Die Ergebnisse könnten auf die potentielle Migration von FTOHs ins Grundwasser hindeuten. Allerdings muss dieser Sachverhalt genauer untersucht werden.

Des Weiteren wurden Sedimentbohrkerne des Yangtze-Flusses (China) auf PFSAs und PFCAs untersucht. Unter 12 analysierten Kongeneren, wurde PFOA am häufigsten detektiert, gefolgt von Perfluorooktansulfonat (engl. perfluorooctane sulfonate, PFOS) und Perfluoroundekancarboxylat (engl. perfluoroundecanoate, PFUnDA). Die Summenkonzentrationen variierten von Nichtdetektion bis zu 724.7 pg/g Trockenmasse. Die relative Standardabweichung zwischen den einzelnen Schichten des Tiefenprofils der Sedimentbohrkerne sprach dafür, dass die Konzentrationsunterschiede von PFSAs und PFCAs unter den einzelnen Schichten nicht signifikant waren. Folglich wurden durchschnittliche Konzentrationswerte genutzt, um die Verteilung der Analyten entlang des Yangtze-Flusses nachzuverfolgen. Im Hauptstrom des Yangtze-Flusses war die Gesamtkonzentration in WZ (Wanzhou) am höchsten, verringerte sich um 40 % bei YY (Yunyang), erhöhte sich um 23 % bei FJ (Fengjie) und blieb vergleichbar bei BD (Badong), GJB (Guojiaba) und MP (Maoping).

PFSAs und PFCAs sind zudem in der Flora und Fauna des Yangtze-Flusses untersucht worden. Langkettige PFSAs und PFCAs wurden in Fischproben detektiert. PFOS war die dominierende Substanz mit Konzentrationen im nicht-detektierbaren Bereich bis 11.9 ng/g, gefolgt von PFUnDA.

Schließlich wurde eine Methode für die Detektion von SFAs mittels GC-PCI-MS

entwickelt. Die $[M\text{-}H]^+$- und $[MH\text{-}HF]^+$-Fragmente wurden für die Quantifizierung beziehungsweise Qualifizierung genutzt. In Skiwachs-Produkten wurden keine SFAs detektiert, deshalb sind lediglich Kongenere (F_6H_{16}, F_8H_{16}, $F_{10}H_{16}$, $F_{12}H_{16}$, $F_{12}H_{16}$ene und $F_{12}H_{14}$) in aktiv gesammelten Luftproben untersucht worden, für die auch Standardlösungen verfügbar waren. SFAs sind nur in geringfügigen Konzentrationen bis zu 10.7 pg/m^3 in Luft detektiert worden.

Statements

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List of Abbreviations and Acronyms

4:2 FTOH	4:2 fluorotelomer alcohol
6:2 FTOH	6:2 fluorotelomer alcohol
8:2 FTOH	8:2 fluorotelomer alcohol
10:2 FTOH	10:2 fluorotelomer alcohol
12:2 FTOH	12:2 fluorotelomer alcohol
9:2 FA	9:2 fluorinated alcohol
A_2O	anaerobic/anoxic/oxic
BD	Badong
DC	Dachang
DCM	dichloromethane
dw	dry weight
ECF	electrochemical fluorination
EFSA	European Food Safety Authority
FJ	Fengjie
FTOH	fluorotelomer alcohol
GJB	Guojiaba
GSH	glutathione
GY	Gaoyang
HLB	hydrophilic-lipophilic-balanced
HPG	hypothalamic-pituitary-gonadal
HRL	health risk limit
IS	internal standard
LRAT	long range atmospheric transport
ML-FTOH	mass labeled FTOH
MPFOA	mass labeled perfluorooctanoate
MPFOS	mass labeled perfluorooctane sulfonate
MP	Maoping
MTBE	methyl-tert butyl ether
NCI	negative chemical ionization

PCI	positive chemical ionization
PFCA	perfluorinated carboxylate
PFSA	perfluorinated sulfonate
PFC	per– and polyfluorinated compound
PFBA	perfluorobutanoate
PFPeA	perfluoropentanoate
PFHxA	perfluorohexanoate
PFHpA	perfluoroheptanoate
PFOA	perfluorooctanoate
PFNA	perfluorononanoate
PFDA	perfluorodecanoate
PFUnDA	perfluoroundecanoate
PFDoDA	perfluorododecanoate
PFTriDA	perfluorotridecanoate
PFBS	perfluorobutane sulfonate
PFHxS	perfluorohexane sulfonate
PFHpS	perfluoroheptane sulfonate
PFOS	perfluorooctane sulfonate
PFDS	perfluorodecane sulfonate
PFOSA	perfluorooctanesulfonamide
PPARα	peroxisome proliferator-activated receptor-alpha
PUF	polyurethane foam
PYK	Pingyikou
QM	Quma
RSD	relative standard deviation
SFA	semifluorinated alkane
SFAene	semifluorinated alkene
S_w	aqueous solubility
SFW	synthetic field water
SJ	Shuangjiang

SL	Shuanglong
TBA	tetrabutylammonium hydrogen sulfate
TDI	tolerable daily intake
TGR	Three Gorges Reservoir
USEPA	United States Environmental Protection Agency
WAX	weak anion exchange
WWTP	waste water treatment plant
WJW	Wujiawan
WS	Wushan
WZ	Wanzhou
XK	Xiakou
XX	Xiangxi
YY	Yunyang

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1 Introduction

1.1 Per– and polyfluorinated compounds

Perfluorinated compounds are the compounds which all of the H atoms bounded to C atoms have been substituted with F atoms, except those H atoms whose substitution would modify the nature of any functional groups present (Buck et al., 2011). Polyfluorinated compounds are the compounds which all hydrogen atoms bounded to at least one (but not all) C atom have been substituted with F atoms, which lead to the molecules containing the perfluoroalkyl moiety C_nF_{2n+1}– (Buck et al., 2011). C_nF_{2n+1}– is hydrophobic and oleophobic. The C–F bond is very strong making the perfluoroalkyl group C_nF_{2n+1}– resist biotic and abiotic degradation. Polyfluorinated compounds have the potential to be transformed into perfluorinated compounds.

Per– and polyfluorinated compounds (PFCs) investigated in this work are fluorotelomer alcohols (FTOHs), perfluoroalkyl acids including perfluorinated carboxylates (PFCAs), perfluorinated sulfonates (PFSAs), and semifluorinated alkanes (SFAs). They are anthropogenic compounds, and generally have been produced and applied over 50 years. The ubiquitous distribution of FTOHs, PFCAs and PFSAs in the environment combined with their potential of causing adverse effects on human and biota (Ahrens et al., 2011a; Buhrke et al., 2013; Haug et al., 2011; Jogsten et al., 2012; Kunacheva et al., 2011; Liu et al., 2010a; Plassmann et al., 2011; Reistad et al., 2013; Rosen et al., 2013; Shivakoti et al., 2010; Xiao et al., 2012; Yu et al., 2009) impels scientists to conduct many studies on these and other fluorinated compounds. However, there are still many gaps remaining in our knowledge about their sources, environmental transport and fate, the exposure pathways and toxicology.

The properties, sources, distributions and transport in the environment, human exposure and toxicology of target analytes (FTOHs, PFCAs, PFSAs and SFAs) from recent publications are presented in following sections.

1.2 Fluorotelomer alcohols

1.2.1 Properties

FTOHs are produced via telomerization started with perfluoroalkyl iodide, like

pentafluoroethyl iodide (C_2F_5I). The straight-chained products have an even number of carbon atoms (Knepper and Lange, 2011). The designation of 'X:Y' is used to name FTOHs, like 6:2 FTOH ($C_6F_{13}CH_2CH_2OH$). X is the number of perfluorinated C atoms and Y is the number of the non-fluorinated C atoms (Buck et al., 2011). The FTOH products are normally a mixture containing 8-14 carbon congeners with 8:2 FTOH being the dominant one (Knepper and Lange, 2011). However, 6:2 FTOH, 8:2 FTOH and 10:2 FTOH are the congeners that have been detected intensively in the environment (Ahrens et al., 2011a; Haug et al., 2011; Jahnke et al., 2007a, 2007b, 2007c; Jogsten et al., 2012; Shoeib et al., 2011). The main physicochemical properties of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH and 10:2 FTOH are listed in Table 1.

1.2.2 Sources and transport in the environment

FTOHs are major raw materials for production of fluorotelomer acrylates and fluorotelomer methacrylates, which are used to manufacture fluorotelomer-based polymers (Rao and Baker, 1994). They have been widely applied in the surfactant and surface protection products for repelling water and oil, such as paper coatings, food packaging, lubricants, and so on. FTOHs exist as unreacted and unbound residues in these products (Dinglasan-Panlilio and Mabury, 2006; Fiedler et al., 2010), and could be released into the environment during the production, transport, use and disposal of such product. For example, 16 - 97 ng of 6:2 FTOH and 25 - 204 ng of 8:2 FTOH were released to the atmosphere when non-stick pans were in use initially (Sinclair et al., 2007).

FTOHs have been investigated in indoor environments. They are prominent in the air due to their high volatility; however, they have also been detected in the house dust. Studies have been conducted in Europe, North America and Asia. FTOH concentrations in indoor air are compiled in Table 2. 8:2 FTOH was the dominant compound, with concentrations in the range of 0.36 - 2.5×10^8 pg/m^3 (Table 2). FTOH concentrations varied substantially among sampling sites. Generally, FTOH levels in indoor environments where wax technicians work were the highest, followed by the shops selling furniture, outdoor sport equipment, etc., and residential houses and normal working offices.

Table 1 Main physicochemical properties of FTOHs.

	T (K)	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	Reference
Aqueous solubility (S_w, mg/L)	296	9.74×10^{2}	18.8	1.94×10^{-1}	2.24×10^{-1}	Liu and Lee, 2005, 2007
Vapor pressure (Log P, Pa)	298.15	3.0 [a]	2.87 [a]	2.39 [a]	2.13 [a]	Stock et al., 2004
		3.0 [b]	2.85 [b]	2.41 [b]	2.16 [b]	Stock et al., 2004
K_{AW} (m^3/m^3)	318.15	3.0×10^{-2} [c]	2.8×10^{-2} [c]	3.8 [c]	-	Goss et al., 2006
Henry's law constant (Pa m^3 mol^{-1})	338.15	4.89×10^{2} [d]	6.71×10^{2} [d]	6.5×10^{2} [d]	-	Lei et al., 2004
$\log K_{OW}$	-	3.30 [e]	4.54 [e]	5.58 [e]	6.63 [e]	Carmosini and Lee, 2008
$\log K_{OA}$	283.15	5.02 [f]	5.39 [f]	6.05 [f]	6.27 [f]	Thuens et al., 2008
$\log K_{OC}$	295	0.933 [g]	2.43 [g]	4.13 [g]	6.20 [g]	Liu and Lee, 2005, 2007

[a] values obtained with a boiling point method.

[b] calculated values.

[c] values obtained by a static headspace measurement.

[d] measured with headspace GC.

[e] values obtained with an equilibration method.

[f] values obtained with a generator column method.

[g] values obtained with a cosolvent system.

Various factors, like room characteristics, building characteristics and housekeeping practice, etc. have been examined whether they have an effect on the FTOH concentrations in indoor environment (Haug et al., 2011). The result showed that the age of the residence, ventilation condition and the existence of synthetic rug would influence the indoor FTOH concentrations (Haug et al., 2011). Floor waxes and paragliders have also been considered as the potential sources for FTOHs in indoor environments (Jahnke et al., 2007c; Shoeib et al., 2011).

The investigations of FTOHs in house dust are very scarce. Table 3 lists the FTOH concentrations in the house dust from available publications. The highest FTOH levels in house dust were reported by Shoeib et al. (2011) in Canada, and the lowest FTOH levels was found in Spain (Jogsten et al., 2012). The variations might be attributed to the various FTOH-contained products used in different countries.

In addition to indoor air and house dust, FTOHs have also been investigated in outdoor atmosphere. The atmospheric lifetimes of FTOHs have been estimated approximately to be 20 days (Ellis et al., 2003). Thus, they can undergo long range atmospheric transport (LRAT) and reach to remote/mountainous regions. Air samples have been collected at the Atlantic Ocean (Shoeib et al., 2010) and the Arctic (Ahrens et al., 2011a; Shoeib et al., 2006), to explore the occurrences of FTOHs in remote areas. Table 4 presents the FTOH concentrations in outdoor air. Generally, 8:2 FTOH was the dominant compound. FTOHs were the highest in the urban city, followed by the rural areas and remote regions, like the Arctic and the Atlantic Ocean. Many studies observed that air masses from densely populated and industrialized areas contained elevated FTOH levels whereas air masses from the Atlantic or the Arctic have low FTOH levels (Barber et al., 2007; Dreyer et al., 2009a, 2009b; Jahnke et al., 2007a; 2007b).

Table 2 FTOH concentrations (Min-Max, pg/m^3) in indoor air.

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	Reference
Households in Norway	0.7-38	63-9414	921-25323	377-28898	-	Haug et al., 2011
Living and storage rooms in northern Norway	<15.8-618	16.0-9831	3151-11109	1231-5901	-	Huber et al., 2011
Offices in Tromsø, Norway	n.d.	177-1090	421-33900	898-57700	-	Jahnke et al., 2007c
Homes and offices in Germany	n.d.-1200	100-6000	1100-17400	100-5700	200-3900	Langer et al., 2010
Shops (furniture etc.) in Germany	n.d.-200	1300-33000	3000-209000	900-54000	400-19000	
Catalonia, Spain	-	3.0-47	7.5-170	<0.6-47	-	Jogsten et al., 2012
Homes in Canada	-	n.d.-22890	660-16080	220-8160	-	Shoeib et al., 2011
Homes in Ottawa, Canada	-	982-2330	2060-4790	1270-2160	-	Shoeib et al., 2008
Offices in USA	-	n.d.-11000	283-70600	138-12600	-	Fraser et al., 2012
Labs and offices in Singapore	n.d.	158-836	1487-10458	459-3312	-	Wu and Chang, 2012
South Korea	-	-	2317-52032	972-43346	-	Kim et al., 2012
Respiratory zone of ski wax technicians	-	<1300-2.4×10^6	8.3×10^5-2.5×10^8	1900-2.0×10^6	-	Nilsson et al., 2010

n.d.: not detected; -: not analyzed.

Table 3 FTOH concentrations (Min-Max, ng/g) in house dust.

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	Reference
Homes in Canada	-	n.d.-4830	9.0-4670	5.7-2950	Shoeib et al., 2011
Homes and daycare centers in USA	-	n.d.-804	n.d.-1660	n.d.-883	Strynar and Lindstrom, 2008
Catalonia, Spain	-	0.008-0.060	n.d.-1.3	n.d.-0.39	Jogsten et al., 2012
Households in Germany	n.d.	n.d.-246	2.4-256	1.0-232	Xu et al., 2013

n.d.: not detected; -: not analyzed.

4:2 FTOH has not been investigated as intensively as 6:2, 8:2 and 10:2 FTOH, which could be attributed to the lack of proper air sampling methods. The high volatility and low affinity of 4:2 FTOH to the sampling medium (PUF or XAD) led to the high possibility of breakthrough. The detected concentration of 4:2 FTOH may also be of high uncertainty due to the very low recovery during the sample preparation.

Moreover, the investigations of FTOHs in other environmental matrices are very scarce. There is one publication reporting the FTOH concentrations in soils receiving activated sludge near Decatur, Alabama, USA (Yoo et al., 2010). 10:2 FTOH was found to be the dominant compound, with the concentrations in the range of <5.6-166 ng/g (Yoo et al., 2010). One other publication documented the FTOHs in precipitations and surface water in an urban area of Japan (Mahmoud et al., 2009). The mean concentrations of 8:2 FTOH and 10:2 FTOH were 1.97 and 0.82 ng/L in precipitations, and 1.08 and 1.92 ng/L in the river water, respectively (Mahmoud et al., 2009).

Table 4 FTOH concentrations (mean concentrations or Min-Max, pg/m^3) in outdoor atmosphere.

		4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	Reference
Hamburg,	G	29-32	55-56	106-110	28-29	-	
Germany	P	n.d.	n.d.	<1.0	<0.7	-	Jahnke et al.,
Waldhof,	G	7.2-11	28-29	81-88	27-29	-	2007a
Germany	P	n.d.	n.d.	<1.0	<0.7	-	
GKSS,	G	0.1	23	50	21	16	
Germany	P	n.d.	n.d.	n.d.	0.1	0.1	Dreyer et al.,
Barsbüttel,	G	0.3	22	62	21	13	2009a
Germany	P	n.d.	n.d.	n.d.	0.1	0.1	
Hazelrigg,	G	56.5	81	102	75	-	
UK	P	0.7	<1.1	<1.1	<1.1	-	
Manchester,	G	3	187	237	65	-	
UK	P	2.1	1.8	5.8	2.7	-	Barber et al.,
Kjeller,	G	<0.1	11.7	34.4	17.2	-	2007
Norway	P	<0.3	<0.1	<0.27	<0.4	-	
Mac Head,	G	1.4	4.95	11.3	7.8	<25	
Ireland	P	<2.7	<0.2	<1.9	<0.5	<6.3	
Japan	G	-	n.d.-768	<32-2466	<17-113	-	Oono et al., 2008
Japan	G	2.29-71.9	2.37-42.6	59.4-808	11.5-198	7.48-112	
India	G	2.21-235	<MDL-15.3	19.4-135	9.67-84.5	5.92-41.2	Li et al., 2011
China	G	n.d.-78.2	n.d.-292	14.4-498	6.45-285	3.32-98.7	
Atlantic transfer cruise ANTXXIII-1[a]	G	-	n.d.-174	2.0-190	0.8-48	-	Jahnke et al., 2007b

Bermuda	G	-	1.85-4.90	7.39-24.5	7.31-10.4	-	Shoeib et al., 2010
	P	-	n.d.	n.d.-7.15	n.d.-2.95	-	
Sable	G	-	0.33-10.7	0.79-35.3	0.23-14.4	-	
	P	-	n.d.	n.d.-7.5	n.d.-2.83	-	
North Atlantic and Canadian Archipelago	G+P	-	n.d.-6.0 [b]	5.8-26 [b]	1.9-17 [b]	-	Shoeib et al., 2006
Atlantic and Southern Ocean	G	n.d.	n.d.-165	1.8-130	1.9-53	n.d.-35	Dreyer et al., 2009b

[a] between Bremerhaven, Germany and Capetown, Republic of South Africa.

[b] values were the sum of gaseous phase and particle phase.

n.d.: not detected; -: not analyzed.

MDL: the method detection limit.

G: FTOHs in gaseous.

P: particulate-bound FTOHs.

1.2.3 Transformations

FTOHs can be degraded to PFCAs via the atmospheric oxidation (Andersen et al., 2005; Ellis et al., 2004) or biological degradation (Dinglasan-Panlilio et al., 2004; Liu et al., 2010a, 2010b; Wang et al., 2009; Zhao et al., 2013a, 2013b), and thus are considered as the precursors of PFCAs.

Smog chamber experiments have been conducted to check the end products of atmospheric degradation of FTOHs. PFCAs (perfluorononanoate (PFNA), perfluorooctanoate (PFOA), perfluoroheptanoate (PFHpA), etc.) were formed in the Cl atom oxidation of FTOHs in air (Ellis et al., 2004). The formation of PFCAs was sensitive to the concentration of NO_x, and low level of NO_x was in favor of PFCAs' formation (Andersen et al., 2005).

Gauthier and Mabury (2005) studied the photo degradation of 8:2 FTOH in aqueous

hydrogen peroxide solutions, synthetic field water (SFW) systems, and Lake Ontario water samples. PFOA was formed and the hydroxyl radical was the main degradation agent.

The aerobic degradation of FTOHs have been investigated in the mixed bacterial culture, soil, river sediment and activated sludge (Dinglasan-Panlilio et al., 2004; Liu et al., 2010a, 2010b; Wang et al., 2009; Zhao et al., 2013a, 2013b). The main products were perfluorohexanoate (PFHxA), perfluoropentanoate (PFPeA), and x-3 acids ($F(CF_2)_xCH_2CH_2COOH$, x = n-1, n = 6 or 8), which suggested the two pathways of FTOH microbial degradation; the pathway I was to formation of x:2 ketone (main metabolite, $F(CF_2)_xC(O)CH_3$; x = n-1, n = 6 or 8), x:2 sFTOH ($F(CF_2)_xCH(OH)CH_3$), and PFCAs, and the pathways II led to the production of x:3 polyfluorinated acid ($F(CF_2)_xCH_2CH_2COOH$) and minor short-chain PFCAs (Kim et al., 2012; Liu et al., 2010a). However, differences were observed in the transformation yields in various cultures, such as 22.4% of 5-3 acids formed in sediment in comparison to 14% in activated sludge (Zhao et al., 2013a, 2013b). The variations in the yields of products might be attributed to the different strains, enzymes and carbon sources (Kim et al., 2012; Liu et al., 2010b).

Only one investigation was focused on the anaerobic biotransformation of 6:2 and 8:2 FTOH. The experiment was conducted with digested sludge under methanogenic conditions (Zhang et al., 2013). The main products were x:2 FTCA ($F(CF_2)_xCH_2COOH$, x = 6 and 8), x:2 FTUCA ($F(CF_2)_{x-1}CF=CHCOOH$, x = 6 and 8), and (x-1):3 acid. The result showed the anaerobic degradation in the environment was not likely a major source of PFCAs (Zhang et al., 2013).

The biotransformation of FTOHs in fish and rat was also investigated. PFOA were formed in the rainbow trout exposed to 8:2 FTOH via dietary (Brandsma et al., 2011), through the path of 8:2 FTUCA > 7:3 ß-keto acid > (7:2 ketone) > PFOA in the rainbow trout (Butt et al., 2010). PFOA and PFHxA were detected in the rat orally dosed of 8:2 FTOH (Fasano et al., 2006), however, the pathways were not determined (Martin et al., 2005).

1.2.4 Human exposure to FTOHs

The systemic availability of 8:2 FTOH following dermal exposure was negligible (Fasano et al., 2006). Evaluation of human exposure to FTOHs has been focused on inhalation and

dust ingestion. The intake of FTOHs via dust ingestion has been reported in Canada (Shoeib et al., 2011), USA (Strynar and Lindstrom, 2008), and Spain (Jogsten et al., 2012). For example, the intakes of FTOHs via dust ingestion were 0.1 - 330 ng/d for adults and 2.2 - 1200 ng/d for children in Vancouver, Canada (Shoeib et al., 2011). The intake of FTOHs via inhalation has been estimated in Korea (Kim et al., 2012), Spain (Jogsten et al., 2012), Germany (Langer et al., 2010), and Canada (Shoeib et al., 2011). For instance, the intakes of FTOHs via inhalation were 13 - 1425 ng/d for adults, and 8.4 - 926 ng/d for children in Vancouver, Canada (Shoeib et al., 2011). The results showed that inhalation was more important for adults, while house dust was a more important medium for children to be evaluated, since they ingest much dust through hand-to-mouth activities. Toddlers ingest 60 mg dust per day (US EPA, 2011) in comparison to adults ingesting 4.16 mg dust per day (US EPA, 1997).

1.2.5 Effects on biota

8:2 FTOH could induce cerebellar granule cell death at relative low concentration with EC_{50} of 15 ± 4.2 μM (Reistad et al., 2013). The LC_{50} for 4:2, 6:2, and 8:2 FTOH were observed to be 0.66 ± 0.20, 3.7 ± 0.54, and 1.4 ± 0.37 mM in isolated rat hepatocytes (Martin et al., 2009). Exposure to 8:2 FTOH caused the depletion of glutathione (GSH), increased protein carbonylation and lipid peroxidation, and these cytotoxicity were attributed to the aldehyde intermediates and GSH-reactive α/β-unsaturated acid metabolites (Martin et al., 2009).

8:2 FTOH has shown the effects to inhibit steroidogenesis by disrupting the cAMP signaling cascade in the human adrenocortical carcinoma cell line (H295R) (Liu et al., 2010a).

Estrogenic effect of FTOHs has been examined intensively in adult zebrafish (Liu et al., 2009, 2010b), and male medaka (*Orzias latipes*) (Ishibashi et al., 2008). It has also been screened by *in vitro* assays, like yeast two-hybrid assay (Ishibashi et al., 2007), E-screen assays, cell cycle dynamics of MCF-7 breast cancer cells, and gene expression of estrogen-responsive genes (Maras et al., 2006). FTOHs may disturb the sex hormone biosynthesis (Liu et al., 2010b). The mechanism could be attributed to the alteration of gene

expression in hypothalamic-pituitary-gonadal (HPG) axis and liver (Ishibashi et al., 2008; Liu et al., 2009).

Additionally, one publication investigated the genotoxicity of FTOHs and they showed no genotoxicity with the *umu* test (Oda et al., 2007).

1.3 Perfluorinated carboxylates and perfluorianted sulfonates

1.3.1 Properties

PFCAs and PFSAs are produced by two methods. One is electrochemical fluorination (ECF) with the main reaction of octanesulfonyl fluoride ($C_8H_{17}SO_2F$) for PFOS or 1-heptanecarbonyl fluoride for PFOA, and anhydrous hydrogen fluoride. The products are always a mixture of liner and branched isomers (Kissa, 2001). The other is telomerization process, yielding only linear chemicals. They have been used widely as water-, oil- and stain repellant in the food contact papers, fire-fighting foams, waxes and upholsteries, etc. (Kissa, 2001). Normally, they are persistent in the environment and resist to biological and chemical degradation. The physicochemical properties related with their environmental behavior are listed in Table 5. The partitioning coefficients are dependent on the chain length. For example, for $\log K_{OC}$ values, 0.5-0.6 log units have been recommended for the change of per PF_2– group (Zareitalabad et al., 2013).

1.3.2 Occurrences of PFCAs and PFSAs in the environment

Approximately 80% of PFCAs and PFSAs have been released into the environment directly via fluoropolymer manufacture and application (Zareitalabad et al., 2013). Degradation of precursors (FTOHs and perfluorooctanesulfonamide (PFOSA), etc.) in the environment is also a source of PFCAs and PFSAs. They have been ubiquitously distributed in various environmental compartments, such as surface water, groundwater, sediment, wastewater treatment plant effluent, and sewage, etc.

The studies of PFSAs and PFCAs in house dust have been conducted in North America, Europe and Asia, and the concentrations of PFSAs and PFCAs are presented in Table 6. The main target compounds were PFCAs (C_7-C_9) and perfluorooctane sulfonate (PFOS). PFOS

and PFOA were the dominant compounds, with mean concentrations in the range of 4.86 - 444 ng/g. The concentrations and patterns varied among sampling homes, which may be related with the different PFSAs and PFCAs based products used in the houses, and the amount of the upholstery, etc. For example, perfluorododecanoate (PFDoDA) concentrations were significantly related with the rug used in the living room and PFSA levels were significantly correlated with the age of the residence (Haug et al., 2011).

The PFSAs and PFCAs would eventually enter into the waste water treatment plants (WWTPs), and then partition to the sludge or reach to the natural water bodies. The concentrations of PFSAs and PFCAs in influent, effluent, and sludge in WWTPs from recent years' work are listed in Table 7. The main target compounds in these studies were PFCAs (C_8-C_{12}) and PFSAs (C_6 and C_8). There is few data about perfluorobutanoate (PFBA), PFPeA, perfluorotridecanoate (PFTriDA), perfluorobutane sulfonate (PFBS), perfluoroheptane sulfonate (PFHpS) and perfluorodecane sulfonate (PFDS). High concentrations of PFSAs and PFCAs in WWTPs were observed to be related with the industrial activities (Kunacheva et al., 2011; Shivakoti et al., 2010; Xiao et al., 2012; Yu et al., 2009). PFOS and PFOA concentrations were higher in the WWTP receiving high proportion of industrial wastewater (Yu et al., 2009). WWTP was not effective to remove the PFSAs and PFCAs in wastewater, and WWTP effluent was the main source of aquatic environments for these compounds. For instance, WWTP effluent has observed to be the main contributor of PFSAs and PFCAs in the Tsurumi River in non-rainy days (Zushi et al., 2008). The increase of PFOA and PFOS concentrations in effluent was observed in reports of Chen et al. (2012), Kunacheva et al. (2011), Loganathan et al. (2007), Yu et al. (2009) and Zhang et al. (2013), indicating that the breakdown of precursors may be occurred in the WWTP systems, especially in the anaerobic/anoxic/oxic (A_2O) treatment technology (Chen et al., 2012). On the other hand, the decrease of PFSAs in the WWTP effluent was also observed due to high affinity to sludge for PFSAs in comparison to PFCAs (Chen et al., 2012).

Table 5 Main physicochemical properties of selected PFCAs and PFSAs.

	Solubility, mg/L	Vapor pressure, Log P, Pa 422 K	pKa	K_{AW}, 298.15K	$logK_{OW}$ 298.15K	$logK_{OA}$ 298.15K	$logK_{OC}$
PFBA	4.47×10^{2}	5.08	0.394	-	-0.52	-	-
PFPeA	1.2×10^{2}	-	0.569	-	0.09	-	-
PFHxA	29.5	-	0.840	9.1×10^{-4}	0.70	6.4	-
PFHpA	6.61	4.59	-	2.2×10^{-3}	1.31	6.6	-
PFOA	1.74	4.35	2.8, 3.8, 0	4.3×10^{-3}	1.92	6.8	2.11
PFNA	1.8×10^{-1}	4.18	2.575	9.3×10^{-3}	2.57	7.01	2.50
PFDA	2.8×10^{-2}	3.97	2.606	1.6×10^{-2}	2.90	7.24	2.92
PFUnDA	1.5×10^{-3}	3.65	3.128	3.0×10^{-2}	-	7.44	3.47
PFDoDA	7.59×10^{-5}	3.47	-	8.7×10^{-2}	-	7.65	-
PFTriDA	2.51×10^{-6}	-	-	-	-	-	-
PFHxS	7.59	-	-	-	-	-	-
PFOS	2.1×10^{-1}	-	-	4.0×10^{-3}	2.45	7.8	2.68
PFDS	-	-	-	-	-	-	3.66
References	Bhhatarai et al., 2010	Kaiser et al., 2005; Steele et al., 2002a, 2002b; Washburn et al., 2005	Burn et al., 2008; Brace et al., 1962; Moroi et al., 2001; Rayne et al., 2009	Arp et al., 2006	Jing et al., 2009	Arp et al., 2006	Higgins and Luthy, 2006; Zareitalabad et al., 2013

-: not reported.

Table 6 PFCA and PFSA concentrations in house dust (mean concentrations, ng/g).

	Homes, Norway		Homes, Canada		Homes and offices Sweden		Homes, USA		Homes, Japan		Homes, Belgium	Homes, China
PFBA	-	12.5	-	-	-	-	-	-	-	-	-	-
PFPeA	3.9	-	-	-	-	-	-	-	-	-	-	-
PFHxA	33	10.1	-	-	-	-	117	-	1.21	-	-	-
PFHpA	10	9.2	-	168	-	-	109	17	6.2	-	-	14.0
PFOA	20	38.8	106	97	54	70	296	44	42.3	384	10.1	205
PFNA	29	7	-	26	-	-	22.1	12	738	-	-	3.43
PFDA	4.1	7.5	-	8.4	-	-	15.5	-	17.1	-	-	3.63
PFUnDA	-	96.8	-	7.8	-	-	30.4	-	394	-	-	0.85
PFDoDA	22	0.8		6.3	-	-	18.0	-	8.4	-	-	0.90
PFTriDA	8.8	-	-	7.3	-	-	-	-	155	-	-	-
PFBS	1.3	1.1	-	-	-	-	41.7	1.8	-	-	-	-
PFHxS	8.4	1.4	392	-	-	-	874	16	-	-	-	0.17
PFHpS	0.29	-	-	-	-	-	-	47	-	-	-	-
PFOS	11	9.1	444	280	39	110	761	-	-	195	5.1	4.86
PFDS	3.5	-	-	-	-	-	-	-	-	-	-	0.2
Reference	Haug et al., 2011	Huber et al., 2011	Kubwabo, et al., 2005	Shoeib et al., 2011	Bjoerklund et al., 2009		Strynar and Lindstrom, 2008	Knobeloch et al., 2012	Liu et al., 2011	Moriwaki et al., 2003	D'Hollander et al., 2010	Zhang et al., 2010

-: not analysed.

Table 7 PFCA and PFSA concentrations in the influent (mean concentrations or Min-Max, ng/L), effluent (mean concentrations or Min-Max, ng/L), and sludge (mean concentrations or Min-Max, ng/g).

Reference	Location	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS
Influent										
Loganathan et al., 2007	USA	-	-	97.2	4.1	0.64	0.85	<0.5	4.3	10.5
Yu et al., 2009	Singapore	-	-	31.9	-	-	-	-	-	13.8
		-	-	198.5	-	-	-	-	-	208.4
Sun et al., 2011	China	15.7-33	3.14-17.9	26.2-71.1	n.d.-4.53	n.d.-2.59	<LOQ	<LOQ	8.06-22.3	2.88-12.8
Kunacheva et al., 2011	Thailand	0.1-70.0	0.8-32.2	6.6-142.1	15.3-174.5	1.2-63.1	3.1-81.9	0.5-10.0	25.8-31.7	381.3-465
Chen et al., 2012	China	-	-	2.6-6.6×10^4	-	-	-	-	-	1.8-176.0
Zhang et al., 2013	China	-	-	1.5-90.6	0.05-4.8	0.05-2.7	0.05-1.9	0.05-1.1	-	0.05-32.1
Effluent										
Loganathan et al., 2007	USA	-	-	152	5.5	3.2	<0.5	<0.5	5.5	16
Yu et al., 2009	Singapore	-	-	51	-	-	-	-	-	11.8
		-	-	319.1	-	-	-	-	-	237.9
Sun et al., 2011	China	10.7-11	1.6-24.2	18.4-41.1	n.d.	n.d.-1.36	<LOQ	<LOQ	n.d.-4.32	-
Kunacheva et al., 2011	Thailand	1.0-84.9	1.8-43.5	16.9-149	21.4-353.2	1.8-81.4	3.8-157.6	n.d.-7.6	28.8-50.4	296.2-553

Chen et al., 2012	China	-	-	2.8-1.6×10^5	-	-	-	-	-	1.1-74.8
Zhang et al., 2013	China	-	-	n.d.-106.6	n.d.-7.4	n.d.-8.3	n.d.-2.8	n.d.-0.9	-	n.d.-67.3
Sludge										
Loganathan et al., 2007	USA	-	-	65.8	<2.5	23	6.8	8.6	<2.5	64
Yu et al., 2009	Singapore	-	-	22	-	-	-	-	-	32.2
		-	-	34.8	-	-	-	-	-	330.7
Kunacheva et al., 2011	Thailand	0.3-99.9	1.6-52.6	11.3-136	5.1-512.8	3.8-327.7	45.2-78.2	n.d.-310.6	36.6-157.7	396.9-553
Yan et al., 2012	China	n.d.-100	n.d.-119	23.2-298	n.d.-20.1	1.57-54.7	0.703-133	n.d.-9.23	n.d.-173	27.6-173
Sindiku et al., 2013	Nigeria	<LOQ-246 [a]	<LOQ-14 [a]	18.9-416 [a]	<LOQ-129 [a]	<LOQ-596 [a]	<LOQ-161 [a]	<LOQ-283 [a]	<LOQ-42 [a]	101-540 [a]
Chen et al., 2012	China	-	-	0.5-158.0	-	-	-	-	-	0.5-19.8
Zhang et al., 2013	China	-	-	0.6-6.7	0-6.8	0-8.8	0.6-14	0.5-8.3	-	0.8-22.5

-: not analyzed. n.d.: not detected.

LOQ: limit of quatification.

[a]: concentrations in unit of pg/g.

Table 8 presents the concentrations of PFSAs and PFCAs in water and sediment. Concentrations were in the range of several to hundreds ng per liter in water and several ng per g in sediment. Short-chain PFSAs (C_4 and C_6) and PFCAs (C_4-C_7) have been included in these works. Short chain PFCAs and PFSAs have been used as the substitutes for PFOS and PFOA. Significant high levels of PFBS and PFBA were detected in surface water near a fluorochemical manufacture plants (Zhou et al., 2013), implying that large amount of short chain PFSAs and PFCAs may be introduced into the environment. The investigation of PFTriDA, PFHpS and PFDS were scarce, and their concentrations were low in available publications (Benskin et al., 2012; Clara et al., 2009).

In addition to WWTPs, industries, like e-waste recycling sites and fluorochemical manufactures, are a potential source of PFSAs and PFCAs in rivers or lakes (Naile et al., 2013; Shi et al., 2012; Zhou et al., 2013). Short-chain PFCAs and PFSAs are prone to exist in water phase, while long-chain PFCAs and PFSAs are tend to partition to sediment (Ahrens et al., 2011b; Becker et al., 2008; Zhou et al., 2013). The reported $\log K_d$ (L/kg) was 0.04-1.83 for PFOA (Ahrens et al., 2011b; Zhang et al., 2012) and 0.53-2.9 for PFOS (Ahrens et al., 2011b; Zhang et al., 2012). The electrostatic sorption to ferric oxide minerals and affinity to organic carbon contribute to the sorption of PFSAs and PFCAs to sediment (Ferrey et al., 2012; Zhao et al., 2012; Zhang et al., 2012). In addition, salinity and cation concentrations would also affect the partitioning of PFCAs and PFSAs between water and sediment (Ahrens et al., 2011b).

PFCAs and PFSAs in oceans were 1-2 orders of magnitude lower than those in rivers and lakes (Table 8). High PFSAs and PFOA were found near the European continent. The melting of snow and ice could also be a source of PFCAs and PFSAs in the oceans (Zhao et al., 2012; Zhang et al., 2012).

Groundwater is a potential contaminated compartment by PFCAs and PFSAs. 47000 μg/L of PFOA and 3000 μg/L of PFOS were detected in groundwater from a former disposal site in Minnesota (Ferrey et al., 2012). PFOA and PFOS were also observed to be 120 and 105 ug/L in groundwater in Cottage Grove, MN (Rumsby et al., 2009).

Table 8 PFCAs and PFSAs in aquatic ecosystems: water (Min-Max, ng/L) and sediment (Min-Max, ng/g dw).

Reference	Location	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS
Water													
Kim et al., 2013	Vietnam	<1.5-9.9	<1.3-3.9	<0.8-5.1	<2.5-3.7	<1.4-35	<1.2-100	<1.5-5.1	<0.5-5.2	-	2.1-16	0.59-5.9	0.18-2.7
Zhang et al., 2012	Dianchi Lake, China	-	-	-	-	1.7-15.1	-	-	-	-	-	-	n.d.-35
Wang et al.,2013	Hanjiang River, China	-	-	-	-	n.d.-256	n.d.-73.6	n.d.-94.9	n.d.-76.7	2.48-33.3	-	-	n.d.-88.9
Shi et al., 2012	Baiyangdian Lake, China	-	n.d.	-	0.22-2.7	1.7-39.3	0.40-1.4	0.13-0.6	n.d.	-	0.2-0.6	n.d.-0.13	0.1-1.5
Naile et al., 2013	west coast, Korea	-	-	-	<1.0-110	0.54-31	<0.2-5.9	<0.2-9.3	0.22-1.3	-	<0.2-16	<0.2-8.7	0.35-47
Hong et al., 2013	Yongsan River Estuary, South Korea	0.8-4.3	0.4-5.7	0.81-6.9	1.6-110	1.3-10	0.45-3.2	0.17-2.4	0.32-1.4	0.1-0.92	1.0-8.6	0.83-16	0.57-68
	Nakdong River Estuary, South Korea	1.1-9.5	0.7-8.4	2.4-17	3.3-34	8.9-28	2.5-12	1.1-9.6	0.75-5.2	0.24-2.8	1.3-15	0.83-17	2.5-66
Benskin et al., 2012	Eastern Atlantic Ocean	-	-	-	-	62-229[a]	-	-	-	-	-	-	-
	Norwegian Sea	-	-	-	-	10-350[a]	-	-	-	-	-	-	-
	the Arctic	-	-	-	-	11-145[a]	-	-	-	-	-	-	-

	Western Atlantic Ocean	-	-	-	-	31-1153 [a]	-	-	-	-	-	-	-
Zhao et al., 2012	the Altantic Ocean	-	n.d.-77 [a]	<5.7-88 [a]	-	<4.0-209 [a]	<3.0-100 [a]	n.d.-37 [a]	n.d.-39 [a]	n.d.-27 [a]	<1.6-45 [a]	n.d.-39 [a]	<10-116 [a]
Zhou et al., 2013	Tangxun Lake, China	1820-6280	26.4-254	27.8-462	23.8-478	70.5-1390	2.28-7.2	0.24-4.1	<0.08	<0.16	2240-4520	286-578	73.4-1650
	Danube River, Austria	-	-	<5.2	<2.1	17-19	n.d.	n.d.	n.d.	n.d.	-	-	<4.5
Clara et al., 2009	Schwechat River, Austria	-	-	n.d.-9.1	n.d.-3.2	<1.1-5.1	<1.3	<1.2	n.d.	n.d.	-	-	<5.1-35
	Liesing River, Austria	-	-	n.d.-5.9	<2.1-3.0	6-13	<1.3	<1.2	n.d.	n.d.	-	-	11-22
Sediment													
Zhang et al., 2012	Dianchi Lake, China	-	-	-	-	0.07-0.8	-	-	-	-	-	-	n.d.-0.71
Shi et al., 2012	Baiyangdian Lake, China	-	n.d.	-	n.d.	n.d.-0.30	n.d.-0.12	0.037-0.22	n.d.-0.20	-	n.d.	n.d.	0.06-0.64
Naile et al., 2013	west coast, Korea	-	-	-	-	<0.2-2.4	-	-	-	-	<0.2-16	<0.2-8.7	<0.2-5.8
Hong et al., 2013	Yongsan River Estuary, South Korea	7.0-110 [b]	6.4-130 [b]	11-80 [b]	14-280 [b]	1.7-34 [b]	0.48-40 [b]	1.1-20 [b]	2.1-28 [b]	0.93-16 [b]	n.d.-42 [b]	n.d.-127 [b]	13-360 [b]

	Nakdong River Estuary, South Korea	6.4-67 [b]	n.d.-85[b]	7.7-75 [b]	n.d.-170[b]	5.7-85[b]	4.4-88 [b]	6.0-59[b]	3.1-36[b]	0.78-9.6[b]	n.d.-210[b]	2.3-160 [b]	n.d.-350 [b]
Zhou et al., 2013	Tangxun Lake, China	5.3-61	<0.54	<0.31	<0.2-1.4	0.48-6.3	<0.28	0.14-0.4	<0.4-3.27	<0.8-18.4	21.1-114	0.89-13.2	10.9-632
Becker et al., 2008	Rote Main, Germany	-	-	-	-	<LOQ-0.17	-	-	-	-	-	-	<LOQ-0.42
	Lake Constance, Austria	-	-	0.76-1.3	0.48-1.0	0.2-0.82	0.17-0.4	<0.20	0.21-0.41	0.10-0.17	-	-	<0.94
Clara et al., 2009	Alpine lakes, Austria	-	-	0.27-1.7	0.39-1.3	<0.13-0.34	n.d.-0.53	n.d.-0.36	n.d.-0.8	n.d.-0.37	-	-	n.d.
	Danube riverbank, Austria	-	-	0.19-4.6	0.09-5.1	0.65-2.8	n.d.-0.69	n.d.-0.72	n.d.-0.84	n.d.-0.45	-	-	n.d.-0.9

-: not analyzed.

LOQ: limit of quatification.

n.d.: not detected.

[a] : concentrations in unit of pg/L.

[b] : concentrations in unit of pg/g dw.

The potential of bioaccumulation of PFCAs and PFSAs have been explored in various organisms with different trophic levels (Loi et al., 2011; Martin et al., 2004; Naile et al., 2013; Paiano et al., 2013; Shi et al., 2010, 2012; Wang et al., 2013; Zhou et al., 2013). Organisms with pelagic and benthic food source had different accumulation profiles (Martin et al., 2004; Shi et al., 2012). The significant high PFCAs and PFSAs concentrations in *Diporeia* with low trophic levels may be related with its benthic food source (Martin et al., 2004). The accumulation profiles were observed to be different between males and females, and between different ages (Wang et al., 2013). Biomagnifications of PFOS, PFDA, PFUnDA, PFDoDA and PFTriDA were observed (Loi et al., 2011; Martin et al., 2004; Zhou et al., 2013), while the biomagnifications of PFBS, PFHxS, PFOA and PFBA were not observed (Martin et al., 2004; Zhou et al., 2013).

1.3.3 Human exposure to PFCAs and PFSAs and their detection in humans

The ubiquity of PFSAs and PFCAs in the environment leads to the unavoidable intake of these contaminants by humans. The exposure to PFOS and PFOA has been intensively explored (Ericson et al., 2008; Fromme et al., 2009; Trudel et al., 2008; Vestergren and Cousins, 2009; Zhang et al., 2010). The main exposure media are drinking water, diet, air, house dust and consumer articles (Ericson et al., 2008; Fromme et al., 2009; Trudel et al., 2008; Vestergren and Cousins, 2009; Zhang et al., 2010). The estimated average daily intakes of PFOS and PFOA for adults in western countries were 1.6 $ng/kg_{body\ weight}$ and 2.9 $ng/kg_{body\ weight}$, respectively (Fromme et al., 2009). The estimated maximum daily intakes of PFOS and PFOA for adults in China were 0.3 $ng/kg_{body\ weight}$ and 10 $ng/kg_{body\ weight}$, respectively (Zhang et al., 2010).

For the population of general background exposure, diet intake was the main pathway for human exposure (Fromme et al., 2009; Trudel et al., 2008; Vestergren and Cousins, 2009), constituting of more than 60% of total intake (Vestergren and Cousins, 2009). When population exposed to contaminated drinking water, the intake via drinking water become the dominant pathway, constituting of more than 70% of total intake (Vestergren and Cousins, 2009). When the evaluation was restricted to indoor environments, inhalation was the dominant pathway for adults (Shoeib et al., 2011), while dust ingestion was relative important

for toddlers (Bjoerklund et al., 2009; D'Hollander et al., 2010; Shoeib et al., 2011).

The tolerable daily intake (TDI) values proposed by the European Food Safety Authority (EFSA) for PFOS and PFOA are 150 and 1500 ng/kg/d, respectively (EFSA, 2008). Though the total intakes of PFOS and PFOA were far lower than the TDI values (Fromme et al., 2009; Zhang et al., 2010), the accumulation of PFOS and PFOA in humans has been observed (Guo et al., 2011; Hemat et al., 2010; Kärrman et al., 2007).

Table 9 lists the concentrations of PFSAs and PFCAs in humans from recent publications, like blood and milk. The main target PFSAs and PFCAs were PFHxA, PFOA, PFNA, PFDA, PFHxS and PFOS. Concentrations of PFSAs and PFCAs in blood were higher than those in milk (Kärrman et al., 2007; Kim et al., 2011). PFOA and PFOS concentrations in blood of male were significantly higher than those of female (Guo et al., 2011; Hemat et al., 2010). However, this trend was not observed in blood samples from children younger than 13 years (Schecter et al., 2012). The results about the dependence of PFSAs and PFCAs concentrations on ages were also divergent; the significant differences between ages were not observed in study of Guo et al. (2011), while they were found in studies of Roosens et al. (2010) and Schecter et al. (2012).

1.3.4 Effects on biota

The toxicology of PFCAs and PFSAs has been screened and investigated in cell lines and animal models. PFOA and PFOS are chemicals tested in most studies. Particularly, these compounds have been found to have developmental toxicity, estrogenic effects, reproductive toxicity, developmental toxicity and hepatotoxicity.

Activation of the peroxisome proliferator-activated receptor-alpha (PPARα) has been proposed to be related with the tumor in liver caused by some chemicals (Lau et al., 2007). PFCAs were reported to activate PPARα (Buhrke et al., 2013; Rosen et al., 2013), inducing hepatomegaly (Rosen et al., 2013), and PFOA was observed to be the most agonist (Buhrke et al., 2013). Sub-acute (10 days) and moderate-dose (3 ± 0.7 mg/kg body weight/day) of PFOA exposure induced the acute liver damage caused by concanavalin A (Con A) (Qazi et al., 2013).

Table 9 PFCAs and PFSAs in human milk and blood (Min-Max, ng/mL).

References	Sample	Location	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS
Kärrman et al., 2010	human liver (adult)	Spain	-	<0.77-1.05 [b]	0.42-1.4 [b]	0.48-2.1 [b]	0.73-2.62 [b]	-	-	0.08-1.6 [b]	9.67-52 [b]
Kim et al., 2011	human milk	South Korea	<4.45 [a]	<43-77 [a]	<8.8 [a]	<18 [a]	<24 [a]	<13 [a]	<1.11 [a]	0.83-16 [a]	32-130 [a]
Kubwabo et al., 2013	human milk	Canada	n.d.	n.d.-0.52	n.d.	n.d.	-	-	-	n.d.	n.d.
Roosens et al., 2010	human milk	Belgium	-	<0.3-3.5	-	-	-	-	-	-	<0.4-28.2
Kärrman et al., 2010	human milk	Spain	-	n.d.	n.d.	n.d.	n.d.	-	-	0.02-0.11	0.07-0.22
Kärrman et al., 2007	human milk	Sweden	-	<0.209-0.492	<0.005-0.02	<0.008	<0.005	-	-	0.031-0.172	0.06-0.47
So et al., 2006	human milk	China	<10 [a]	47-210 [a]	7.3-62 [a]	3.8-11 [a]	7.6-56 [a]	-	<5.0 [a]	4.1-100 [a]	45-360 [a]
Schecter et al., 2012	human serum (children)	USA	-	n.d.-13.5	n.d.-55.8	n.d.-2.1	-	-	-	n.d.-31.2	n.d.-93.3
Kim et al., 2011	maternal serum	South Korea	<0.26	0.86-3.2	0.43-1.3	0.19-0.79	0.90-2.4	<0.50	<0.1	0.43-1.4	3.3-9.4
Guo et al., 2011	human blood	China	n.d.-2.23	0.33-7.98	0.09-3.95	n.d.-1.54	n.d.-3.11	n.d.-0.27	-	0.05-6.82	0.43-59.1
Roosens et al., 2010	human serum (adolescent)	Belgium	-	1.8-3.8	-	-	-	-	-	-	34.9-64.4
	human serum (adult)	Belgium	-	1.4-3.4	-	-	-	-	-	-	9.1-17.1
Hemat et al., 2010	human serum	Afghanistan	-	<0.5-1.5	-	-	-	-	-	<0.5-3.0	0.2-11.8

Kärrman et al., 2007	maternal serum	Sweden	-	2.4-5.3	0.43-2.5	0.27-1.8	0.2-1.5	-	-	1.8-11.8	8.2-48.0
Ehresman et al., 2007	human serum	USA	-	n.d.-7320	-	-	-	-	n.d.-24	n.d.-84	14-880
	EDTA plasma	USA	-	n.d.-7440	-	-	-	-	n.d.-31	n.d.-72	12-870
	EDTA whole blood	USA	-	n.d.-3730	-	-	-	-	n.d.-11	n.d.-32	n.d.-449
	Heparin plasma	USA	-	n.d.-7420	-	-	-	-	n.d.-32	n.d.-69	13-915
	Heparin whole blood	USA	-	n.d.-3670	-	-	-	-	n.d.-14	n.d.-36	n.d.-450
Roosens et al., 2010	cord blood	Belgium	-	n.d.-9.5	-	-	-	-	-	-	0.8-15.8
Kim et al., 2011	umbilical cord serum	South Korea	<0.13	0.50-2.7	0.20-0.77	0.06-0.24	0.25-0.86	<0.25	<0.05	0.23-1.1	0.69-3.6

-: not analyzed; n.d.: not detected.

[a] : concentrations in unit of ng/L.

[b] : concentrations in unit of ng/g wet weight.

PFOA has endocrine-related effects. PFOA was found to increase the expression of hhex, esr1 and pax, and interfere with hormone receptor ER and TR in zebrafish embryo (Du et al., 2013). The increase of E2, decrease of the T and the alteration in the expression of major steroidogenic genes and regulator SF-1 caused by PFOA was observed in H295 (Du et al., 2013). PFOA and PFOS were weak agonists of estrogen receptor (ER), behaving similarly like estradiol and forming hydrogen bonds with Arg394 (Gao et al., 2013).

PFOA and PFOS would increase ROS formation and reduce cell viability (Reistad et al., 2013). Long-term exposure to PFOA with low levels may induce excessive generation of reactive oxygen species in algal cells, causing oxidative damage to cells (Xu et al., 2013).

PFHxS exposure during a vulnerable period of brain development was found to induce persistent aberrations in spontaneous behavior and cognitive function of adult mice (Viberg et al., 2013). PFOA and PFOS exposure decreased the egg size in rotifer Brachionus calyciflorus, and 28-day exposure reduced the population density (Zhang et al., 2013).

In addition to laboratory toxic observations, epidemiological studies also give some hints whether PFCAs and PFSAs pose toxicities on humans.

Epidemiological studies obtained opposite results about the effects on semen quality. Serum PFOS concentrations were not observed to be significantly related with semen quality (Joensen et al., 2013), while in the report of Toft et al. (2012), serum PFOS concentrations were negatively associated with morphology, suggesting adverse effects of PFOS on semen quality. *In utero* exposure to PFOA may influence the adult human male semen quality and reproductive hormone level, like decreasing the sperm concentration and total sperm count and increasing the luteinizing hormone (Vested et al., 2013).

PFOA exposure was not observed with stillbirth, pregnancy-induced hypertension and indices of fetal growth in an area of West Virginia and Ohio where drinking water was contaminated (Savitz et al., 2013). Fetal and prenatal exposure to PFOS and PFOA was associated with lower birth weight and bod mass index in early infancy (Andersen et al., 2013; Maisonet et al., 2012). However, prenatal exposure to PFOS and PFOA was not found to have appreciable influence on children’s anthropometry at age of 7 (Andersen et al., 2013).

Due to the potential toxic effects on humans, the health risk limits (HRLs) for PFOA and PFOS in drinking water were suggested to be 0.3 μg/L by Minnesota Department of Health

(Ferrey et al., 2012). The values recommended by the United States Environmental Protection Agency (USEPA) were 0.4 and 0.2 μg/L for PFOA and PFOS, respectively (Ferrey et al., 2012).

1.4 Semifluorinated alkanes

1.4.1 Properties

SFAs are highly fluorinated anthropogenic chemicals. They are diblock molecules with general formula of $F(CF_2)_n(CH_2)_mH$ (shortly F_nH_m), in which two mutually immiscible moieties, namely the hydrocarbon segment and the perfluorocarbon segment are bound covalently (Broniatowski and Dynarowicz-Latka, 2008). They are manufactured through addition of perfluoroalkyl iodides to alkenes followed by reductive dehalogenation with zinc powder (Napoli, 1996). Semifluorinated alkenes (SFAenes) with the general formula of $F(CF_2)_nCH=CH(CH_2)_{m-2}H$ (shortly $F_nH_m$ene) are byproducts in the production of SFAs (Napoli, 1996). SFAs have been used in the ophthalmology for unfolding a retina or for permanent tamponade (Meinert and Roy, 2000), in blood-substitutes as oxygen-carrier (Meinert and Knoblich, 1993), in pulmonary drug delivery as excipient (Tsagogiorgas et al., 2010), and in ski wax to reduce friction and repel dirty, enhancing glide (Napoli, 1996).

For SFAs, there are no experiment data about physicochemical properties concerning the environment transport and fate. Plassmann et al. (2010) first reported the physicochemical properties deriving from the SPARC, EpiWin, ADME and ppLFERs. SFAs are characterized by low vapor pressure (except for short-chain SFAs), extremely low water solubility, high Henry's law constants and high log K_{OW} values (>8.4) (Plassmann et al., 2010). However, these parameter values may be of high uncertainty, since different software always produces various values deviating from experimental values extensively (Arp et al., 2006).

1.4.2 Sources and occurrences in the environment

SFAs with chain lengths of n = 6-16 and m = 14, 16, 18 and corresponding SFAenes have been detected in fluorinated ski waxes (Plassmann and Berger, 2010). They would be abraded from the ski base through skiing activities and released into the environment. Plassmann and

Berger (2010) first reported the environmental occurrences of SFAs in a small cross-country skiing track (Säfsen, Sweden) with concentrations being up to 1.3 μg/L in snow and 47 pg/g in soil.

The investigations of SFAs in the environment are very scarce and limited to the skiing field. SFAs were found at 4.5 to 3240 μg/m^2 in snow, decreasing with the increasing distance from the start of the ski course (Plassmann et al., 2011). SFA levels in soil were from 1.2 to 296 μg/m^2 (Plassmann et al., 2011). The SFAs pattern was observed to shift to a higher proportion of longer chain SFAs in soil when compared to the profiles in snow, indicating the volatilization of shorter chain SFAs from snow or soil (Plassmann et al., 2011).

The fate of SFAs during snowmelt was studied by Plassmann et al. (2011). The SFAs bound to particles or snow grain surfaces would transfer and accumulate in the soil surface during snowmelt (Plassmann et al., 2011).

1.5 Objectives

PFCs, including FTOHs, PFCAs, PFSAs and SFAs, are of high concern to the environment and humans. Although our knowledge about their sources, environmental transport and fate, human exposure and bioeffects has been increasing, there are still many remaining gaps. In this thesis, FTOHs, PFCAs, PFSAs and SFAs were investigated in different environmental matrices as follows.

1. Due to the high volatility, FTOHs are mainly investigated in the gas phase. The high concentrations of FTOHs in indoor air and the strong ability of house dust to adsorb organic compounds make house dust an important medium for evaluating human exposure to FTOHs in indoor environment. However, the studies of FTOHs in house dust are scarce. Hence, FTOHs were measured in house dust collected in Bavaria, Germany, and the FTOH intakes via dust ingestion by adult and toddler were estimated respectively. In addition, the indirect intake of PFOA via the biotransformation of 8:2 FTOH was also evaluated.

2. FTOHs can undergo long range atmospheric transport (LRAT) and reach to remote/mountainous regions. They have been detected in the atmosphere over the Atlantic Ocean, the Arctic, Canadian Rocky mountains and Mount Bachelor, Oregon. The Alps is situated in the center of Europe and the semi-volatile organic pollutants in the Alpine air are

normally imported via the atmosphere. However, there are no studies investigating the occurrences and temporal trends of airborne FTOHs in the Alpine atmosphere. In this thesis, the FTOHs in the alpine atmosphere were analyzed, and the potential source regions and the seasonal variations were discussed. In particular, FTOH-derived PFOA depositions at sampling sites were estimated.

3. FTOHs have been detected in precipitation, surface water and soil. Do they have a potential of migration to groundwater? The preliminary experiment was performed to investigate the FTOHs in groundwater collected in Berlin, Germany.

4. The Yangtze River is the longest River in Asia, on which the Three Gorges Dam, the largest dam in China, is located. The changes in aquatic environment related with the construction of the Three Gorges Dam are sediment accumulation in front of the dam, and pollutants released from flooded urban, industrial and agricultural areas, etc. What's the effect of this Yangtze-Hydro Project on the occurrences and distributions of PFCAs and PFSAs in the Yangtze River? PFCAs and PFSAs were analyzed in sediment cores collected from WZ to MP (in front of the dam). Their variations with depth in sediment cores and the profiles along the Yangtze River were explored.

5. It is of importance to investigate that whether and to what extent PFCAs and PFSAs accumulate in biota in the Yangtze River. The preliminary experiment was performed to investigate PFCAs and PFSAs in fishes and shrimps collected from the Yangtze River.

6. The limited numbers of previous study has only shown high levels of SFAs in snow and soil from skiing tracks. It is of high importance to investigate that whether and to what extent SFAs accumulate in other environmental compartments, such as atmosphere. A method for detection of SFAs on GC-MS was developed. Further, the SFAs were screened in some ski wax products. Finally, the occurrences and distributions of SFAs in atmosphere at Alpine summits were investigated.

2 Material and Methods

2.1 Chemicals and reagents

Native and mass labeled standards used in the method development and chemical analysis are presented in Table 10.

Table 10 Native and mass labeled standards used in method development and chemical analysis.

Compound	Purity (%)	Company
Fluorotelomer alcohols		
4:2 FTOH	97	Fluorochem, Old Glossop, UK
6:2 FTOH	97	Fluorochem, Old Glossop, UK
8:2 FTOH	97	Fluorochem, Old Glossop, UK
10:2 FTOH	97	Fluorochem, Old Glossop, UK
$^{13}C_2{}^2H_2$ 4:2 FTOH	98	Wellington, Laboratories Guelph, Ontario, Canada
$^{13}C_2{}^2H_2$ 6:2 FTOH	98	Wellington, Laboratories Guelph, Ontario, Canada
$^{13}C_2{}^2H_2$ 8:2 FTOH	98	Wellington, Laboratories Guelph, Ontario, Canada
$^{13}C_2{}^2H_2$ 10:2 FTOH	98	Wellington, Laboratories Guelph, Ontario, Canada
9:2 FA	98	Fluorochem, Old Glossop, UK
Perfluorinated sulfonates		
PFBS	98	Wellington, Laboratories Guelph, Ontario, Canada
PFHxS	98	Wellington, Laboratories Guelph, Ontario, Canada
PFOS	98	Wellington, Laboratories Guelph, Ontario, Canada
PFDS	98	Wellington, Laboratories Guelph, Ontario, Canada
$^{13}C_4$ PFOS	98	Wellington, Laboratories Guelph, Ontario, Canada
Perfluorinated carboxylates		
PFBA	98	Wellington, Laboratories Guelph, Ontario, Canada
PFPeA	98	Wellington, Laboratories Guelph, Ontario, Canada
PFHxA	98	Wellington, Laboratories Guelph, Ontario, Canada
PFHpA	98	Wellington, Laboratories Guelph, Ontario, Canada
PFOA	98	Wellington, Laboratories Guelph, Ontario, Canada
PFNA	98	Wellington, Laboratories Guelph, Ontario, Canada
PFDA	98	Wellington, Laboratories Guelph, Ontario, Canada
PFUnDA	98	Wellington, Laboratories Guelph, Ontario, Canada

PFDoDA	98	Wellington, Laboratories Guelph, Ontario, Canada
PFTriDA	98	Wellington, Laboratories Guelph, Ontario, Canada
$^{13}C_4$ PFOA	98	Wellington, Laboratories Guelph, Ontario, Canada
Semifluorinated alkanes		
F_6H_8	n.s.	ABCR, Karlsruhe, Germany
F_6H_{14}	n.s.	ABCR, Karlsruhe, Germany
F_6H_{16}	> 95	Custom-synthesized by Synthon-Lab Ltd., St. Petersburg, Russia
F_8H_{10}	n.s	ABCR, Karlsruhe, Germany
F_8H_{16}	n.s.	ABCR, Karlsruhe, Germany
$F_{10}H_2$	97	Apollo Scientific, Stockport, England
$F_{10}H_{16}$	> 95	Custom-synthesized by Synthon-Lab Ltd., St. Petersburg, Russia
$F_{12}H_{14}$	> 95	Custom-synthesized by Synthon-Lab Ltd., St. Petersburg, Russia
$F_{12}H_{16}$	> 95	Custom-synthesized by Synthon-Lab Ltd., St. Petersburg, Russia
Semifluorinated alkenes		
$F_{12}H_{16}$ene	> 95	Custom-synthesized by Synthon-Lab Ltd., St. Petersburg, Russia

n.s. unspecified purity.

Acetone, methanol, cyclohexane, dichloromethane (DCM), pentane, hexane and methyl-tert butyl ether (MTBE) (all picograde quality) were purchased from LGC-Standards, Wesel, Germany. Tetrabutylammonium hydrogen sulfate (TBA), ammonium acetate, ammonium hydroxide (NH_4OH), sodium carbonate and sodium bicarbonate were purchased from Alfa Aesar, Ward Hill, MA, USA. Water was prepared by a Milli-Q Advantage A10 system (Millipore, USA).

Envi-Carb (250 mg) cartridges were purchased from Sigma-Aldrich, Seelze, Germany. Silica gel (grade 60) was purchased from Wesel Germany. HLB (6 cc, 150 mg) and WAX (6 cc, 150 mg) were purchased from Waters Co. (Made in Ireland).

2.2 Quality assurance/Quality control

To avoid contamination, polytetrafluoroethylene (PTFE) materials were not used during the sample preparation. Glass ware was first rinsed with toluene and acetone, then washed in laboratory dish washer, and baked at 450 ℃ for 8 h before use. To analyze the PFCAs and PFSAs in the sediment and biota samples, the disposable polypropylene centrifuge tubes (50 mL and 10 mL) were used. At least one procedure blank was prepared and analyzed in each batch. For analytes with no blank contamination observed, method detection limits (MDLs) were defined as the same as the instrument limit of detection (LOD) with a value corresponding to a signal-to-noise ratio of 3 (S/N = 3). The limit of quantification (LOQ) was a value corresponding to a S/N ratio of 10. Where blank contamination was detected, MDLs were estimated as the mean blank values plus three times of standard deviation (MDL = mean blank value + 3 SD) and method quantification limits (MQLs) were estimated as the mean blank values plus ten times of standard deviation (MQL = mean blank value + 10 SD). The details of QA/QC for different experiments, like calibration standards, blank values and recoveries, etc. were presented in corresponding sections.

2.3 Statistical analysis

The SPSS 16.0 software was used for statistical analysis. Values below the LOD/MDL were set as LOD/sqrt(2) or MDL/sqrt(2) in the calculation. Shapiro-Wilk test was used to check whether the data set was normally distributed. Spearman Rank correlation was applied to investigate bivariate relationships when the data set was not normally distributed. ANOVA and T test were performed on normally distributed data. A significance level of $p = 0.05$ was applied.

2.4 FTOHs in the house dust

2.4.1 Analysis of FTOHs in the house dust

Dust samples were collected from residences in Bavaria (Munich and nearby suburban and rural areas), Germany during 2008-2009. A total of 31 samples were taken using vacuum cleaners. Samples were sieved, transferred to clean bottles and stored in freezer at -20 ℃ until

analysis.

Sample preparation for FTOHs was done as follows. 400 mg dust was extracted in a 30 mL glass centrifuge tube with the mixture of acetone/MTBE (volume ratio 1/1). 20 mL of the mixture was used for the first extraction. Prior to extraction, 10 μL of a solution containing mass-labeled FTOHs (10 ng/μL) was spiked. Tubes were then placed in an ultrasonic bath for 10 min, centrifuged at 4000 g for 5 min (Heraeus Multifuge 3SR+ centrifuge, Thermo) and the supernatant was collected. Samples were extracted with 10 mL acetone/MTBE for two more times. Supernatants were combined and transferred to a glass column filled with anhydrous sodium sulfate to remove any moisture. The extract was concentrated to 0.5 mL and loaded on an Envi-Carb (250 mg) cartridge conditioned with 5.0 mL MTBE. FTOHs were eluted with 3.5 mL MTBE. The final eluate was evaporated with a stream of N_2 to 0.1 mL and transferred into a GC-vial. 10 μL (10 ng/μL) internal standard 9:2 FA was added before GC-MS analysis.

Table 11 Parameters for measurement of FTOHs on GC-MS

Analytes	Molecular weight	Target ion (m/z)
4:2 FTOH	264	265
6:2 FTOH	364	365
8:2 FTOH	464	465
10:2 FTOH	564	565
9:2 FA (IS)	514	515
4:2 ML-FTOH	268	269
6:2 ML-FTOH	368	369
8:2 ML-FTOH	468	469
10:2 ML-FTOH	568	569

FTOHs were measured using a HP 5890 Series II gas chromatograph (Agilent Technologies, Waldbronn, Germany) coupled with a Finnegan Mat SSQ 7000 mass selective detector (Thermo Scientific, Germany). The GC was equipped with a 5 m Rxi guard column (0.53 mm inner diameter, Restek, Bad Homburg, Germany) followed by a 60 m VMS column (0.25 mm inner diameter, 1.4 μm film thickness, Agilent Technologies). 1 μL sample was

injected in splitless mode at 220 ℃. The oven temperature program was as follows: initial temperature 45 ℃, held for 5 min, 15 ℃/min to 70 ℃, 10 ℃/min to 120 ℃ held for 2 min, 25 ℃/min to 220 ℃ held for 15 min. The carrier gas was helium. The MS system was operated in positive chemical ionization (PCI) mode, and methane was used as reagent gas. Selected-ion monitoring (SIM) was applied for data acquisition. The target ions for each native and mass labeled FTOH (ML-FTOH) are displayed in Table 11.

2.4.2 QA/QC

The isotope dilution method was applied to quantify FTOHs. Before sample extraction, 100 ng of ML-FTOHs were spiked. Calibration standards contained fixed amounts of ML-FTOHs and 9:2 FA (1 ng/μL respectively), and variable amounts of native FTOHs, with the range from 5 to 500 pg/μL. Calibrations were run with each batch of 6 samples measured. The LODs of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were 1.6, 1.6, 2.4 and 0.6 ng/g, respectively. At least one blank sample was prepared and analyzed with each batch of 5 dust samples. Only in one blank sample 6:2 FTOH (2.7 ng/g) was detected, therefore only 6:2 FTOH concentrations in dust samples of this batch were blank corrected by subtracting the blank value from the sample value. The mean recoveries of mass-labeled 4:2, 6:2, 8:2 and 10:2 ML-FTOH were 37%, 54%, 62% and 98%, respectively.

2.4.3 Estimation of human exposure to FTOHs via house dust

On the basis of measured FTOH concentrations in house dust samples, the direct exposure to FTOHs via dust ingestion for adults and toddlers was estimated (eq 1) (Shoeib et al., 2011).

$$R_{i,A} = C_A \times E_{dust} \times \eta / 1000 \quad (1)$$

Where $R_{i,A}$ was the estimated daily exposure to analyte (A) through dust ingestion in indoor environments (ng/d). C_A was the concentration of analyte (A) in house dust (ng/g). E_{dust} was the dust ingestion rate (mg/d). η was the absorption efficiency of analyte intake, which was assumed as 100%. Daily human exposure to FTOHs was roughly estimated for four different scenarios as follows: I) median concentrations and mean dust ingestion rates (E_{dust}, 4.16 and 60 mg/d for adults and toddlers respectively (US EPA, 1997; US EPA, 2011)) were used,

representing the mean scenario. II) median concentrations and high dust ingestion rates (E_{dust}, 55 and 100 mg/d for adults and toddlers respectively (US EPA, 1997; US EPA, 2011)) were used. III) maximum concentrations and mean E_{dust} were used. IV) maximum concentrations and high E_{dust} were used, representing the worst scenario.

2.4.4 Estimation of human exposure to 8:2 FTOH-based PFOA via house dust

The 8:2 FTOH-based PFOA intake was calculated as the product of the intake of 8:2 FTOH by human body and the biotransformation factor of 8:2 FTOH to PFOA. The biotransformation factor of 8:2 FTOH to PFOA showed high variability among different studies due to different interspecies and experimental design. To reduce the bias, the biotransformation factors of 0.0002 and 0.017 were adopted in the present study (Martin et al., 2005; Nabb et al., 2007; Vestergren et al., 2008).

2.5 FTOHs in the Alpine atmosphere

2.5.1 Optimization of clean-up methods for FTOHs

From the measurement of FTOHs in house dust, the samples cleaned by Envi-Carb cartridges (250 mg) often caused the peak-tailing. In this section, the clean-up method using silica gel was optimized. The tested clean-up methods were presented in Table 12. Self-made silica cartridges were conditioned by 10 mL of hexane, and 25 ng of ML-FTOHs was spiked in 0.5 mL of hexane, which was used as sample loading onto a self-made silica cartridge. FTOHs are volatile, and in order to determine whether a low recovery of FTOH obtained was caused by the ineffective elution or loss during solvent evaporation, a solvent control with the same volume as elution solvent which contained 25 ng of ML-FTOHs was used, and evaporated and measured with eluates.

Table 12 Tested clean-up methods using silica gel (500 mg) for FTOHs.

	Method 1	**Method 2**	**Method 3**	**Method 4**	**Method 5**	**Method 6**
Silica gel	heated at 550 ℃	not heated	heated at 550 ℃ deactivated with 4% H_2O	heated at 550 ℃ deactivated with 10% H_2O	heated at 550 ℃ deactivated with 10% H_2O	heated at 550 ℃ deactivated with 10% H_2O
Washing	6 mL hexane	6 mL pentane	6 mL pentane	6 mL pentane	6 mL pentane	6 mL pentane
Elution-1	5 mL DCM	2 mL DCM	2 mL DCM	4 mL DCM	5 mL 15% DCM in pentane	5 mL 50% DCM in pentane
Elution-2	3 mL DCM	3 mL DCM	3 mL DCM	4 mL DCM	5 mL 15% DCM in pentane	5 mL 50% DCM in pentane
Elution-3	2 mL DCM	3 mL DCM	3 mL DCM	4 mL DCM	5 mL 15% DCM in pentane	5 mL 50% DCM in pentane

2.5.2 Sampling

Active air sampling device was the same as described in a publication of Offenthaler et al. (2009). On the basis of hourly trajectory prediction, air flows arriving from three predefined source regions and one undefined origin were sampled separately by four XAD cartridges. The three potential source regions were 1) areas in the Northwest of Alps (denoted by NW), including Germany, Great Britain, Belgium and the Netherlands, 2) areas in the Northeast of the Alps (denoted by NE), including the Czech Republic, Slovakia and Poland, and 3) the Po basin in Italy (denoted by S) (Offenthaler et al., 2009). The undefined origin (denoted by UND) indicated the air mass having residence time of less than two days over a particular region prior to sampling site (Offenthaler et al., 2009). The details about the trajectory

prediction and the distributions of air mass origin were in the MONARPOP technical report (Offenthaler et al., 2009). Low volume samplers (flow rate: 3 m^3/h; Digital Enviro-Sense, Hegnau, Swizerland) were comprised of a glass fiber filter (GF8, Ø = 45 mm) and XAD-2 resin (50 g).

Samples were collected at two weather stations in the Alps: Zugspitze (Germany, 10 °59 ´E, 47 °25 ´N, 2650 m above sea level) and Sonnblick (Austria, 12 °58 ´E, 47 °03 ´N, 3100 m above sea level) as displayed in Figure 1. The Sonnblick is in the 'Hohe Tauern' range in the Austrian Alps. It is considered as a high alpine background station owing to non-existence of local contamination sources (Jabbar et al., 2012; Kasper et al., 1998). The Zugspitze is the highest peak of the Wetterstein Mountains in the German Alps, which is on the border between Germany and Austria (Jabbar et al., 2012). The sampling schedule and sampling air volume were listed in the Table 13.

Figure 1 The locations of the sampling sites (Zugspitze and Sonnblick).

Table 13 Sampling schedule and air volumes (m^3, at 0 ℃ and 101.325 KPa) for each cartridge corresponding to a certain air flow.

Sampling site	Sampling period	Start	End	Air volume				
				NW	NE	S	UND	Sum
Zugspitze	1	06.20.2007	10.04.2007	257 [a]	131	648	581	1618
	2	02.01.2008	04.02.2008	0 [a]	168 [a]	0 [b]	33 [b]	202
	3	04.02.2008	07.29.2008	217	191	615	132	1155
	4	11.05.2008	03.11.2009	1043	428	1273	542	3286
	5	06.17.2009	10.08.2009	993	316	1125	588	3023
	6	10.08.2009	01.18.2010	527	205	887	987	2606
	7	01.18.2010	04.20.2010	671	410	784	1069	2934
	8	04.20.2010	07.26.2010	729	433	899	275[a]	2335
Sonnblick	1	06.20.2007	09.28.2007	556	289	652	188 [b]	1684
	2	09.28.2007	01.17.2008	629 [a]	221 [a]	712	662	2224
	3	01.17.2008	03.20.2008	474	68	393	436	1370
	4	03.20.2008	07.24.2008	983	618 [a]	1447	578	3625
	5	07.24.2008	11.10.2008	1158	474 [a]	758	683	3072
	6	11.10.2008	03.06.2009	1067	737	908 [a]	876	3588
	7	03.06.2009	06.29.2009	1620	975	2658	907	6159
	8	06.29.2009	09.25.2009	868	345	1042	471 [a]	2726
	9	09.25.2009	01.15.2010	824	259	1323	1087	3493
	10	01.15.2010	04.19.2010	748	434 [a]	709	1004	2895

[a] samples were not available for this work.

[b] results for these samples were excluded from the analysis.

2.5.3 Analysis of FTOHs in the Alpine active air samples

The XAD-2 cartridges with glass fibers were Soxhlet extracted with hexane/acetone (volume ratio 3/1) for 24 h. The extracts were evaporated to 2 mL, and 1 mL of the extract

was used for FTOHs analysis except for 8 samples collected in the year of 2007, only 0.5 mL of the extract was used. They were kept in frozen at -20 ℃ until analysis. When analyzed, the extracts were first fortified with ML-FTOH standards, then solvent exchanged to cyclohexane, evaporated to 0.5 mL under a gentle flow of N_2, and cleaned by 0.5 g silica gel deactivated with 10% H_2O (silica gel from Wesel Germany, grade 60). FTOHs were eluted with 10 mL pentane/DCM (1/1). Eluates were concentrated to 25 μL. Prior to analysis by GC-MS, internal standard 9:2 FA (25 ng) was added.

FTOHs were measured on the same GC-MS system with the house dust samples, but with a different analysis column. The GC was equipped with a 5 m Rxi guard column (0.53 mm inner diameter, Restek, Bad Homburg, Germany) followed by a 30 m SUPELCOWAX (0.25 inner diameter, 0.25 μm film thickness, Supelco, Bellefonte, PA). 1 μL of sample was injected in splitless mode at 250 ℃. The oven temperature program was as follows: initial temperature 50 ℃, held for 1 min, 3 ℃/min to 80 ℃, 10 ℃/min to 140 ℃ held for 4 min, 20 ℃/min to 260 ℃ held for 15 min.

2.5.4 Breakthrough experiment

Tests of breakthrough of all FTOHs in the active air sampling system were carried out indoor where FTOHs were detected, Helmholtz Center Munich. For these breakthrough experiments, the filter unit with a glass fiber filter (GF8, Ø=45 mm), the first cartridge with 50 g XAD-2 (equivalent to a normal sample) and the second cartridge with 50 g XAD-2 (collecting analytes that have a breakthrough) were connected in line. The room temperature was in the range of 22-24 ℃. The sampling air volume was 1026 m^3 after 13 d with an approximate flow rate of 3.3 m^3/h. The filter, first cartridge and second cartridge were extracted separately in order to see the fraction of FTOHs among these three parts. One field blank, a cartridge with 50 g XAD-2, was shipped to the sampling room and shipped back to the lab. The field blank and one procedure blank were extracted and cleaned parallel.

2.5.5 Estimation of FTOH-derived PFOA in the depositions

A rough estimation was conducted to calculate the deposition fluxes of FTOH-derived PFOA. 8:2 and 10:2 FTOH were included in the estimation. They were assumed to be

completely in the gaseous phase (Barber et al., 2007; Dreyer et al., 2009a; Jahnke et al., 2007a) and degraded to PFOA with a conversion rate of 3% (Wania, 2007).

Since the presence of PFO (dissociated PFOA) in the atmosphere is negligible (Armitage et al., 2006), only PFOA was assumed in the atmosphere. PFO was taken into consideration in the calculations of wet depositions. The partition coefficient between air and water (K_{AW}) was the COSMOtherm predicted value, and the partition coefficient between octanol and air (K_{OA}) was the New Sparc predicted value (Arp et al., 2006). Temperature dependences were taken into account according to the method used in the Globo-POP model (Wania, 2007; Wania and Mackay, 2000). The partition coefficient between atmospheric particulate phase and gaseous phase (K_P) was estimated with the method selected by Webster et al. (2010). The fraction of PFOA on particles (Φ) was estimated with the method in Pankow (1987). The average PM_{10} value (5 μg/m^3) for sampling periods at Zugspitze was used as the concentration of atmospheric total suspended particle. Wet/dry particle deposition and wet/dry gaseous deposition were included in the estimation (Schenker et al., 2008).

Wet particle deposition

$$F_{wp} = \mathrm{W} \times \mathrm{C_A} \times \phi \times r / 1000 \quad (2)$$

F_{wp}, C_A, r and W were the flux of PFOA by wet particle deposition (ng/m^2/d), FTOH-derived PFOA concentrations in the atmosphere (pg/m^3), water or water equivalent precipitation rate (m/d) and washout ratio (dimensionless) respectively. Barton et al. (2007) calculated the washout ratios in the range of 1.1×10^5 to 5×10^5. The washout ratio was assumed to be the same for snow and rain, and set to be 2.5×10^5.

Wet gaseous deposition

$$F_{wg} = (1-\phi) \times \mathrm{C_A} \times r / K_{aw}^{eff} / 1000 \quad (3)$$

Where F_{wg}, C_A and K_{aw}^{eff} were the flux of PFOA by wet gaseous deposition (ng/m^2/d) and air-water partitioning coefficient for PFO(A) (protonated PFOA and dissociated PFO).

$K_{aw}^{eff} = K_{aw}^{\circ}/(1+10^{pH-pKa})$ (Barton et al., 2007)

K_{aw}° was the air-water partitioning coefficient for protonated PFOA. pH was 5, the pH value of bulk rain/snow in the Alps (Hiltbrunner et al., 2005). pKa was 3.8, the value for protonated PFOA (Burns et al., 2008).

Dry particle deposition

$$F_{dp} = V_d \times C_A \times \phi \times 3600 \times 24/1000 \quad (4)$$

Where F_{dp} and V_d were the flux of PFOA by dry particle deposition (ng/m^2/d), and deposition velocity (m/s), respectively. V_d was set as 0.003 m/s (Schenker et al., 2008).

Dry gaseous deposition

$$F_{dg} = V_g \times C_A \times (1-\phi) \times 3600 \times 24/1000 \quad (5)$$

Where F_{dg} and V_g were the flux of PFOA by dry gaseous deposition (ng/m^2/d), and deposition velocity (m/s), respectively. V_g was set as 0.0003 m/s (Schenker et al., 2008).

2.5.6 Calculations of time-averaged FTOH concentrations and breakthrough rates

The air volume reported in this work was converted to the equivalent volume under the standard state (0 ℃, 101.325 kPa). The breakthrough rate was calculated as the ratio of the amount of FTOHs retained by the back cartridge to that by the master cartridge and back cartridge. Time-averaged air concentrations of FTOHs at Zugspitze and Sonnblick for each sampling period was estimated by weighing the concentration of each source region with its relative incidence using equation (6) (Offenthaler et al., 2009).

$$C_{AVE} = \frac{C_{NW}V_{NW} + C_{NE}V_{NE} + C_S V_S + C_{UND}V_{UND}}{V_{NW} + V_{NE} + V_S + V_{UND}} \quad (6)$$

C_{AVE} was the time-averaged concentration of analyte (pg/m^3), C_i (i = NW, NE, S and UND) was the concentration of the analyte in air mass corresponding to a certain trajectory (pg/m^3), and V_i (i = NW, NE, S and UND) was the air sampling volume (m^3).

2.5.7 QA/QC

The isotope dilution method was applied to quantify FTOHs as described in the section of **2.4.2**. In each batch, one procedure blank was prepared and analyzed. 6:2 FTOH were not detected in procedure blanks. The concentrations of 8:2 and 10:2 FTOH observed in some blanks were less than 10% of the sample values in the same batch. The LODs for 6:2, 8:2 and 10:2 FTOH were 0.8, 0.3 and 0.2 pg/m^3, respectively. The MDLs for 8:2 and 10:2 FTOH were 1.0 and 0.5 pg/m^3, respectively. Field blanks were taken at both sites for each sampling period and treated in the same way as samples. 8:2 and 10:2 FTOH detected in some field blanks were comparable with those found in procedure blanks, showing that the contamination of field blanks was not due to the sampling or sample handling. FTOH concentrations reported in this study were corrected by procedure blanks.

The mean recoveries (standard deviations) of mass-labeled 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were 55 ± 11%, 67 ± 9% and 80 ± 15%, respectively. Two blanks were performed with the ML-FTOHs being spiked before the Soxhlet extraction, to evaluate the FTOH losses during the whole procedure, including the extraction and the first solvent evaporation. The mean recoveries of mass-labeled 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were 35%, 55% and 98%, respectively. The recoveries of 6:2 FTOH in the whole procedure were slightly lower than those obtained in the real sample preparation, which may lead to the underestimation of atmospheric concentrations of 6:2 FTOH.

2.6 PFCAs and PFSAs in the sediment from the Yangtze River

2.6.1 Sampling

The sampling area of this study was the upstream of the Yangtze River, including the Three Gorges Reservoir (TGR). The information of the sampling sites is listed in Table 14. The sampling locations are presented in Figure 2.

The sediment samples were taken as described in Chen et al. (2012) with some modifications. In June, 2010, sediment cores were collected using a stainless gravity sediment core sampler (100 cm length and 25 cm i.d.). These cores were sliced into 10 cm fractions with a spatula and then dried in a freezing dryer at 0 ℃. Dried samples were ground,

homogenized and then wrapped by the alumina foil, and kept at -20 ℃ until analysis. All visible organisms and leaves were removed with a stainless steel forceps.

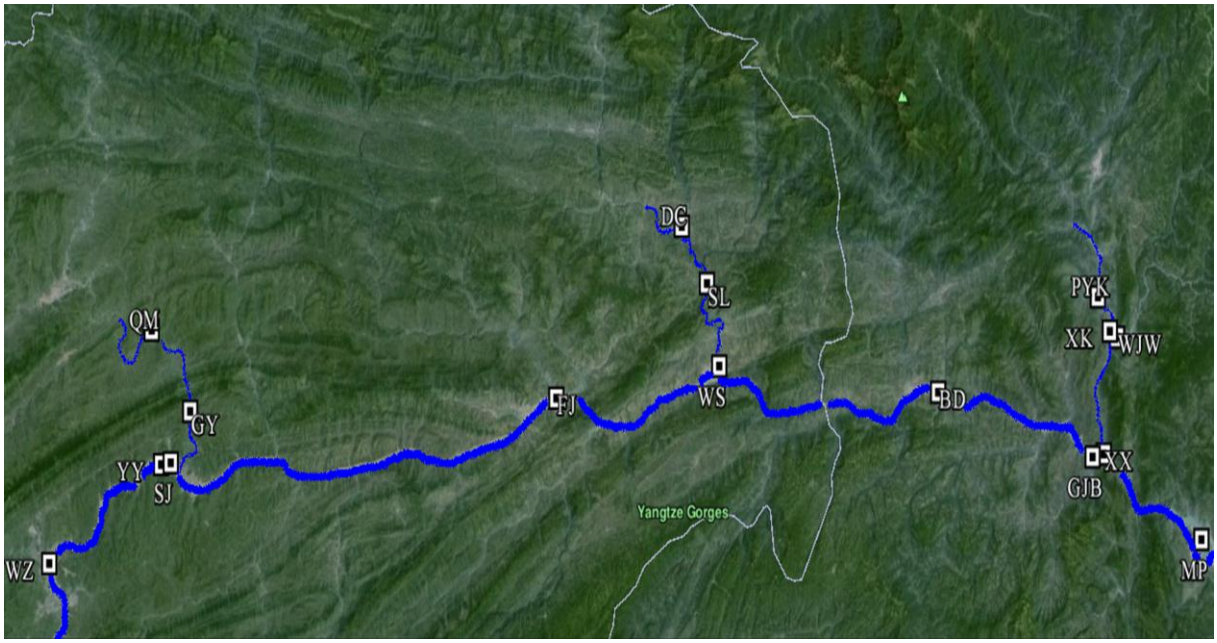

Figure 2 The locations of sampling sites on the main stream and three anabranches.

2.6.2 Analysis of PFCAs and PFSAs in the sediment

The analytes included C_4, C_6, C_8 and C_{10} PFSAs and C_6-C_{13} PFCAs. 5 g of sediment sample was extracted with 10 mL methanol for three times. Before extraction, 5 ng of internal standards ($^{13}C_4$PFOS and $^{13}C_4$PFOA) was spiked and then equilibrated for 30 min. The first and third extractions were performed by sonication for 20 min, and the second extraction was conducted by shaking the slurry for 20 min. After the shaking or sonication, mixtures were centrifuged at 3000 rpm for 8 min, and the supernants were combined and concentrated to 0.5 mL under a gentle flow of N_2. The concentrated extracts were diluted with 50 mL Milli-Q water and loaded onto the HLB cartridges conditioned with 7 mL of methanol and 7 mL of water. The cartridge was washed with 5 mL of 20% methanol in Milli-Q water and was allowed to run dry. Finally, the analytes were eluted with 10 mL methanol. The eluate was then reduced to 200 μL under a gentle stream of N_2, centrifuged at 10000 rpm for 10 min, and transferred to an HPLC vial for measurement.

Table 14 Descriptions of sampling locations.

Sampling sites	Full name	Sampling date	Latitude N	Longitude E	Remark	Weather
WZ	Wanzhou	14.06.2010	30°48.831'	108°23.538'	Main stream of Yangtze River	Sunny
YY	Yunyang	13.06.2010	30°56.929'	108°38.598'		Cloudy
FJ	Fengjie	12.06.2010	31°2.594'	109°32.047'		Shower
BD	Badong	09.06.2010	31°2.994'	110°23.500'		Cloudy
GJB	Guojiaba	09.06.2010	30°57.690'	110°44.380'		Cloudy
MP	Maoping	07.06.2010	30°50.924'	110°59.164'		Rainy
QM	Quma	13.06.2010	31°7.664'	108°37.253'	Xiaojiang River (anabranch)	Cloudy
GY	Gaoyang	13.06.2010	31°1.231'	108°42.542'		Cloudy
SJ	Shuangjiang	13.06.2010	30°57.084'	108°39.913'		Cloudy
DC	Dachang	11.06.2010	31°16.286'	109°48.926'	Daning River (anabranch)	Cloudy
SL	Shuanglong	11.06.2010	31°11.738'	109°52.331'		Cloudy
WS	Wushan	10.06.2010	31°5.172'	109°53.961'		Sunny
PYK	Pingyikou	08.06.2010	31°10.465'	110°45.196'	Xiangxihe River (anabranch)	Cloudy
XK	Xiakou	08.06.2010	31°7.719'	110°46.766'		Cloudy
XX	Xiangxi	08.06.2010	30°57.908'	110°45.734'		Cloudy
WJW	Wujiawan	08.06.2010	31°7.23'	110°47.718'		Cloudy

The PFSA and PFCA concentrations in the sediment samples were analyzed using a high performance liquid chromatograph (HPLC, Alliance 2695 model system, Waters, Milford, MA) interfaced with a tandem mass spectrometer (MS/MS, Quattro Premier XE, Micromass, Manchester, UK) operated in the electrospray negative ion mode. Analytes separation was accomplished with a Dionex Acclaim 120 C18 analytical column (5 μm, 4.6 mm i.d. × 150 mm length, Dionex, Sunnyvale, CA, USA) operated at 25 ℃. The flow rate was 1 mL/min. The gradient started with 72% A (100% methanol) and 28% B (10 mM ammonium acetate), then increased to 95% A and 5% B at 4 min, held for 3 min, returned to initial condition at 7 min, and finally held until 10 min. The parameters of mass spectrometer were as follows: source temperature (110 ℃), desolvation temperature (450 ℃), dwell time (50 ms),

desolvation gas (1000 L/h), and cone gas (50 L/h). Chromatograms were recorded in the MRM mode, and two transitions for each analyte were monitored (Table 15).

Table 15 Monitoring transitions, cone voltages and collision energy for the analytes and internal standards.

Compound	Parent	Daughter	Cone (V)	Collision (eV)	LOD (pg/g)	LOQ (pg/g)
MPFOS	502.8	**80**, 99	40	**40**, 38	-	-
MPFOA	416.8	**372**, 169	20	**10**, 20	-	-
PFBS	299	**80**, 99.1	40	**25**, 28	1.5	4.9
PFHxS	398.8	**80**, 99.1	40	**40**, 35	1.8	6.1
PFOS	498.8	**80**, 99.1	40	**40**, 38	5.2	17.4
PFDS	598.8	**80**, 99.1	40	**40**, 35	2.3	7.7
PFHxA	313	**269**, 119	17	**10**, 20	3.3	11.0
PFHpA	363	**319**, 169	15	**10**, 18	3.3	11.0
PFOA	412.8	**369**, 169	20	**10**, 20	3.1	10.4
PFNA	463	**419**, 219	10	**12**, 20	4.0	13.3
PFDA	512.8	**469**, 269	14	**11**, 16	4.4	14.8
PFUnDA	563	**519**, 169	15	**13**, 25	0.6	2.1
PFDoDA	613	**569**, 169	20	**14**, 25	0.1	0.5
PFTriDA	663	**619**, 119	25	**13**, 35	9.6	31.9

Note: the daughter ions in bold were used for the quantification.

2.6.3 QA/QC

Procedure blanks were prepared with every 10 sediment samples. Solvent blanks were run every 6 samples to check for carryover and background contamination. No PFCAs and PFSAs were found in all blanks. Calibration standards contained fixed amounts of MPFOA and MPFOS (5 ng/mL) and variable amounts of native PFCAs and PFSAs, with the range from

0.2 to 15 ng/mL. 7 calibration standards were run every day, and 1 calibration standard with 1 ng/mL of native compounds was run every 10 samples to check for the deviation of the calibration curve. The LODs and LOQs are listed in Table 15.

The recoveries of the PFCAs and PFSAs were examined by spiking of 5 ng and 10 ng of native standards into 5 g of the sediment. The matrix spike recoveries for all analytes varied between 71% and 118%, with a mean standard deviation (SD) of 6.9%.

2.7 SFAs in ski wax products

2.7.1 Development of instrumental analysis method for SFAs

5 ng/μL of standard solution for single compound ($F_{10}H_2$, F_6H_8, F_6H_{14}, F_6H_{16}, F_8H_{10}, F_8H_{16}, $F_{10}H_{16}$, $F_{12}H_{14}$, $F_{12}H_{16}$ and $F_{12}H_{16}$ene) was used in the method development. The method was developed on HP 5890 Series II gas chromatograph (Agilent Technologies, Waldbronn, Germany), coupled to a Finnegan Mat SSQ 7000 mass selective detector (Thermo Scientific, Germany). The GC was equipped with a 5 m Rxi guard column (0.53 mm inner diameter, Restek, Bad Homburg, Germany) followed by a 30 m Rxi-XLB (0.25 inner diameter, 0.50 μm film thickness, Agilent Technology). The carrier gas was helium and methane was used as reagent gas. 1 μL of standard was injected and analyzed in PCI and NCI modes with various temperature programs. The injector temperature was set at 280 ℃, and the transfer line was set at 300 ℃. The ion source temperature was set at 150 and 200 ℃, respectively. Full scan was used to observe the fragmentation of the analytes and to determine the quantifier and qualifier, and SIM was adopted to optimize the temperature program and mass spectrometry parameters.

2.7.2 Analysis of SFAs in ski wax products

SFAs were analyzed in 7 different ski wax products, which were assigned as 1#, 2#, 3#, 4#, 5#, 6# and 7#. The ski wax sample was prepared as the method described in Plassmann and Berger (2010). Samples were analyzed in PCI mode, and monitored with full scan and SIM scan, respectively.

2.8 SFAs in the Alpine atmosphere

2.8.1 Optimization of clean-up methods for SFAs

In order to incorporate the SFAs into the clean-up method of FTOHs, silica gel (deactivated by 10% distilled water) was chosen for the clean-up of SFAs in active air samples. On the basis of clean-up method developed by Plassmann and Berger (2010), cyclohexane was used for elution. 0.5 mL cyclohexane spiked with 10 ng of standard mixture was loaded onto the self-made cartridges, and SFAs were eluted according to the procedures presented in Table 16.

Table 16 A tested clean-up method for SFAs.

	Method
	500 mg Silica gel (deactivated with 10% H_2O)
Condition	10 mL cyclohexane
Sample loading	0.5 mL cyclohexane
Elution-1	3 mL cyclohexane
Elution-2	3 mL cyclohexane
Elution-3	3 mL cyclohexane

2.8.2 Sampling

Active air sampling was the same as mentioned in the section of **2.5.2**. The sampling periods and air volumes are displayed in Table 13 in the section of **2.5.2**.

2.8.3 Analysis of SFAs in the Alpine active air samples

1 mL of sample extract was used for the analysis of SFAs. Before clean-up, extracts were solvent exchanged to cyclohexane and evaporated to 0.5 mL under a gentle flow of N_2. Active air samples were cleaned by 0.5 g silica gel deactivated with 10% H_2O (silica gel from Wesel Germany, grade 60). 0.5 mL sample was loaded on the silica cartridge, SFAs were eluted with

5 mL cyclohexane. Elutes were concentrated to 25 µL with a gentle flow of nitrogen and volumetric standard F_8H_{10} (25 µL, 0.6 ng/µL) was added, prior to analysis by GC-MS.

2 µL of sample was injected in splitless mode. The oven temperature started at 50 ℃ for 3 min, then elevated to 150 ℃ at a rate of 25 ℃ min^{-1}, further to 225 ℃ at 15 ℃ min^{-1} and held for 3 min, finally elevated to 320 ℃ at 25 ℃ min^{-1} and kept at 320 ℃ for 10 min. The temperatures of injector, transfer line and ion source were set at 280 ℃, 300 ℃ and 150 ℃ respectively. The MS system was operated in PCI mode. SIM mode was applied for data collection. Both the molecular ion $[M-H]^+$ and the fragmentation of $[MH-HF]^+$ were monitored for each analyte, as quantifier and qualifier, respectively.

2.8.4 QA/QC

The quantification was done similar with Plassmann and Berger (2010). Calibration standards contained fixed amounts of F_8H_{10} (0.6 ng/µL respectively), and variable amounts of SFAs (F_6H_{16}, $F_{12}F_{14}$, F_8H_{16}, $F_{10}H_{16}$ and $F_{12}H_{16}$) and $F_{12}H_{16}$ene, with the range of 10 pg/µL to 500 pg/µL were measured to produce a 5-point calibration curve. Peak height was used in calibration curve and sample quantification. LODs and LOQs were in the range of 0.003 - 0.021 pg/m^3 and 0.10 - 0.7 pg/m^3, respectively. The mean recoveries of F_6H_{16}, $F_{12}F_{14}$, F_8H_{16}, $F_{10}H_{16}$ and $F_{12}H_{16}$ and $F_{12}H_{16}$ene were 85%, 92%, 85%, 93%, 75% and 62%, respectively in the real sample preparation, while they were 78%, 96%, 85%, 97%, 70% and 56%, respectively by spiking of 10 ng and 1 ng of SFAs on the XAD-2 cartridges treated with the full procedure, including Soxhlet extraction and the first solvent evaporation. The result indicated that the losses of SFAs during the Soxhlet extraction and the first solvent evaporation were not significant.

2.9 FTOHs in groundwater from Berlin

As a preliminary test, 10% of the sample extract was used to analyze FTOHs. The extracts were spiked with ML-FTOH standards (25 ng of each), solvent exchanged to hexane, then cleaned-up by silica gel (10% deactivated), and analyzed with GC-PCI-MS as described in the section of **2.5.3**.

2.10 PFCAs and PFSAs in fish samples from the Yangtze River

2.10.1 Information of fish samples

Fish samples were collected from three sites along the Yangtze River (XX, WZ and WS). The information of the fish samples is listed in Table 17. The mixture of fish muscle and skin was analyzed for Abbottina rivularis, Cyprinus carpio, Grass carp, Channa argus, Crucian carp, Cyprinus carpio and black carp. Whole bodies of Hemicculter Leuciclus (n=3), Pseudorasbora para (n=2) and Macrobrachim nipponense (n=4) were pooled respectively for analysis. Samples were first dried in a freezing dryer at 0 ℃, and then ground, homogenized, wrapped by alumina foil, and kept at -20 ℃ until analysis.

Table 17 The information of the fish samples.

Number	Species	Sampling site
1	Abbottina rivularis (fish)	XX
2	Macrobrachim nipponense (shrimp)	XX
3	Cyprinus carpio (fish)	XX
4	Cyprinus carpio (fish)	XX
5	Hemicculter Leuciclus (fish)	XX
6	Pseudorasbora para (fish)	XX
7	Grass carp (fish)	WZ
8	Channa argus (fish)	WZ
9	Crucian carp (fish)	WS
10	Cyprinus carpio (fish)	WS
11	black carp (fish)	WZ

2.10.2 Analysis of PFCAs and PFSAs in fish samples

Approximately 0.4 g of sample was added into a 15 mL screw-capped polypropylene tube. 2 mL Milli-Q water was added and thoroughly mixed. 5 ng of MPFOA and MPFOS was spiked and equilibrated for 30 min. 1 mL of 0.5 M tetrabutylammonium hydrogen sulfate (TBA) and 2 mL of 0.25 M Na_2CO_3/$NaHCO_3$ (pH 10) solution were added and thoroughly

mixed using a vortex shaker. Then, 5 mL of MTBE were added, mixed and extracted for 20 min with a platform shaker at a speed of 250 rpm. The suspension was centrifuged for 15 min at 3000 rpm and the organic phase was transferred into a new 15 mL screw-capped polypropylene tube. The residual was extracted with 5 mL MTBE for two more times. The supernatants (14 mL totally) were combined and then evaporated to 1 mL under a gentle stream of N_2. The concentrates were solvent exchanged to methanol, evaporated to about 0.5 mL, diluted with 15 mL Milli-Q water and then cleaned by WAX cartridges. WAX cartridge was conditioned with 4 mL methanol containing 0.1% NH_4OH, 4 mL methanol and 4 mL Milli-Q water. The diluted sample was load onto a cartridge, and the cartridge was washed with 4 mL ammonium acetate buffer (pH 4), 10 mL Milli-Q water and 4 mL methanol. Analytes were eluted by 4 mL methanol containing 0.1% NH_4OH. The eluates were concentrated to 1 mL under a gentle flow of N_2, transferred to 1.5 mL polypropylene centrifuge tubes and stored at -20 ℃ overnight. The 1 mL concentrated eluates were centrifuged for 10 min at 10000 rpm, and the supernatants were transferred to HPLC vials for analysis. The instrumental analysis was the same as described in the section of **2.6.2**.

2.10.3 QA/QC

All PFSAs and PFCAs were not detected in procedure blanks. Carryover was checked by injection of pure methanol every 6 samples, and no carryover was noticed. The recoveries of the PFCAs and PFSAs were tested by spiking of 5 ng and 10 ng of native PFCA and PFSA standards into 0.4 g of fish. The mean matrix spike recoveries are presented in Table 18. The LODs were from 0.01 ng/g of PFHpA to 0.5 ng/g of PFBS. The LOQs were from 0.03 ng/g of PFHpA to 1.5 ng/g of PFBS.

Table 18 The mean matrix spike recoveries of PFCAs and PFSAs.

	5 ng	10 ng
PFBS	139	132
PFHxS	141	140
PFOS	87	88
PFDS	80	69
PFBA	101	99
PFPeA	140	146
PFHxA	119	135
PFHpA	105	117
PFOA	108	109
PFNA	33	314
PFDA	104	160
PFUnDA	55	56
PFDoDA	72	73
PFTriDA	31	23

3 Results and Discussion

3.1 FTOHs in house dust

3.1.1 Concentrations and distributions

Table 19 shows the FTOH concentrations in the house dust samples. The total concentrations varied from 4.8 to 734 ng/g. More than 70% of the house dust samples contained 6:2 FTOH. In addition, 8:2 FTOH, 10:2 FTOH were detected in all samples, whereas 4:2 FTOH was not detected in any of the samples. The non-detection of 4:2 FTOH could be attributed to its low abundance in dust and/or its high volatility. Figure 3 shows that 8:2 FTOH is the dominant compound in 93% of the dust samples. The predominance of 8:2 FTOH in house dust was also reported in studies of Shoeib et al. (2011) and Strynar and Lindstrom (2008). 8:2 FTOH had the highest median concentration (13.1 ng/g), followed by 10:2 FTOH (6.6 ng/g) and 6:2 FTOH (3.7 ng/g). Levels of FTOHs measured in house dust in our study are at least 10 times higher than those observed in homes in Spain (Jogsten et al., 2012), but approximately 10 times lower than those determined in 152 Vancouver homes in Canada (Shoeib et al., 2011) and in homes and daycare centers in USA (Strynar and Lindstrom, 2008).

Table 19 FTOH concentrations (ng/g) in house dust samples from German households (n = 31).

	Mean	SD[a]	Min	10th percentile	Median	90th percentile	Max	% below LOD
4:2 FTOH	-	-	-	-	-	-	-	100
6:2 FTOH	19.4	52.2	<LOD	1.1	3.7	30.4	246	23
8:2 FTOH	29.5	53.5	2.4	5.3	13.1	43.8	256	0
10:2 FTOH	17.5	42.0	1.0	2.6	6.6	23.2	232	0
Σ FTOH [b]	66.4	145	4.8	8.4	26	87	734	-

[a] Standard deviation.

[b] Total concentration of FTOH.

LOD: limit of detection.

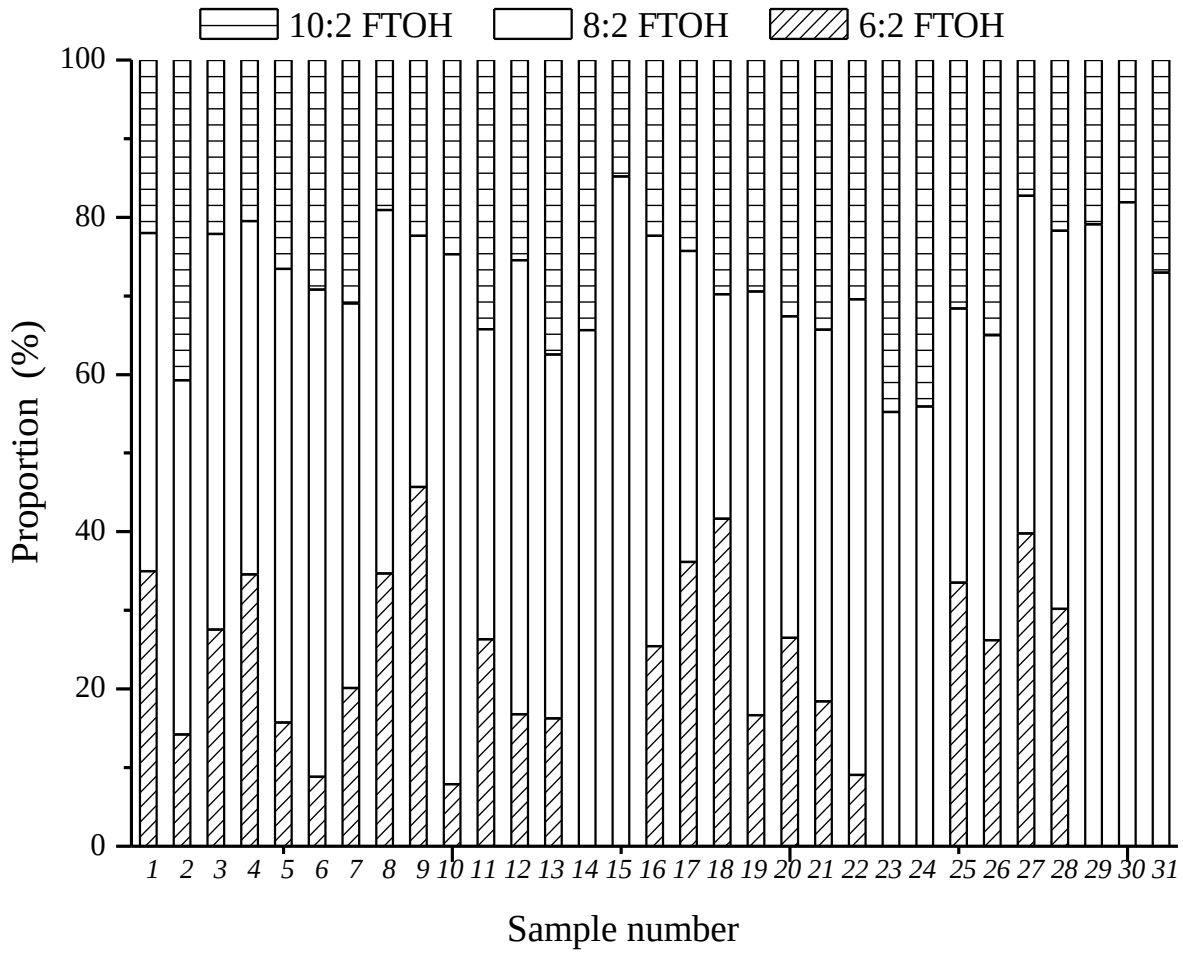

Figure 3 FTOH patterns of house dust samples.

The variation in FTOH concentrations among house dust from different areas might be attributed to geographic and temporal differences in source strength among indoor environments, such as application of different FTOH-containing products, the amount of furniture and surface-impregnation-treatment applied on the furniture. A high variation in concentrations of PFCs was found between studies in Japan (Liu et al., 2011) and Canada (Shoeib et al., 2011) in spite of the same dust size, comparable sampling and extraction methods used, implying that different source strength is the most critical factor to explain the difference in FTOH concentrations in house dust samples.

3.1.2 Bivariate correlations

Spearman Rank Correlation was used to explore bivariate relationships between FTOHs frequently detected in dust samples. 6:2, 8:2 and 10:2 FTOH were significantly correlated

with each other (Table 20), indicating the presence of common sources in the indoor environment for these compounds. Previous works pointed out that 8:2 FTOH and 10:2 FTOH were contained in clothes lint (Shoeib et al., 2011), and 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were present in impregnating agents and lubricants (Fiedler et al., 2010).

Table 20 Spearman Rank Correlations between FTOHs in dust samples.

	8:2 FTOH	10:2 FTOH
6:2 FTOH	0.417 [a]	0.496 [b]
8:2 FTOH		0.868 [b]

[a] Correlation was significant at the 0.05 level (two tailed).

[b] Correlation was significant at the 0.01 level (two tailed).

3.1.3 Human exposure to FTOHs and 8:2 FTOH-based PFOA

Most people spend a large of their time indoors, which makes house dust a potential exposure medium when addressing risks in indoor environments. Table 21 presents that the total FTOH intake is 0.1 - 40.4 ng/d for adults, and 1.6 - 73.4 ng/d for toddlers. This result showed the FTOH intake by toddlers was 2 - 10 times higher than that by adults, indicating that house dust imposes more potential health risk on toddlers due to the hand-to-mouth contact. The FTOH ingestion rate is 0.1 ng/d for adults and 1.6 ng/d for toddlers in the mean scenario (Scenario I). The intake of FTOHs via dust in the present work is lower than that reported in Canada (Shoeib et al., 2011) and USA (Strynar and Lindstrom, 2008), and higher than what was observed in Spain (Jogsten et al., 2012). Moreover, FTOH intake via dust ingestion is lower than that from the use of household consumer products (Fiedler et al., 2010). The intake of FTOHs via dust ingestion should not be neglected in spite that inhalation is the dominant pathway for human exposure to FTOHs in indoor environments (Jogsten et al., 2012; Shoeib et al., 2011). In particular, when compared to FTOH intake via inhalation of 542 ng/d for adults and 352 ng/d for toddlers (in the scenario when maximum concentrations were used) (Shoeib et al., 2011), FTOH intake via dust ingestion in current study represents nearly 8% of the FTOH intake by inhalation for adults and 21% for toddlers.

PFCAs have been intensively detected in human blood (Calafat et al., 2007; Hemat et al.,

2010; Kim et al., 2011). Though it is still debated, whether precursors play a significant role in human exposure to PFCAs, there is evidence that FTOHs could be metabolized to PFCAs in experimental animals or cells (Fasano et al., 2006; Martin et al., 2005; Nabb et al, 2007). Since the POSF production was phased out around the year 2000 by 3M Company, the continued PFOA exposure might be attributed to the biotransformation of precursors originating from fluorotelomer-based commercial products or residuals in the human body (Calafat et al., 2007).

Table 21 PFC intakes via dust ingestion for adults and toddlers (ng/d).

	Compound	Scenario I (mean scenario)	Scenario II	Scenario III	Scenario IV (worst scenario)
Adults	FTOH	0.1	1.4	3.1	40.4
	PFOA (8:2 FTOH-based)	<0.001[a]	<0.001[a]	<0.001[a]	0.003[a]
		0.008[b]	0.012[b]	0.018[b]	0.24[b]
	ΣPFC[c]	0.1	1.4	3.1	40.6
Toddlers	FTOH	1.6	2.6	44.0	73.4
	PFOA (8:2 FTOH-based)	<0.001[a]	<0.001[a]	0.003[a]	0.005[a]
		0.013[b]	0.022[b]	0.26[b]	0.44[b]
	ΣPFC[c]	1.6	2.6	44.3	73.8

[a] biotransformation factor of 0.0002 was used in the calculation.

[b] biotransformation factor of 0.017 was used in the calculation.

[c] intake of PFOA via the biotransformation of 8:2 FTOH with a factor of 0.017 was included.

PFOA intake via the biotransformation of 8:2 FTOH is summarized in Table 21. The 8:2 FTOH-based PFOA ingestion rate via house dust was 0.013 ng/d for toddlers and 0.008 ng/d for adults in the mean scenario when a biotransformation factor of 0.017 was applied.

To our knowledge, the intake of 8:2 FTOH-based PFOA mainly correlates with the biotransformation efficiency of 8:2 FTOH metabolized to PFOA and 8:2 FTOH intake by human body via certain exposure route. In this work, only dust ingestion was investigated.

The contribution of 8:2 FTOH to PFOA intake might be high if inhalation, a main exposure pathway for FTOHs, was included. It was reported that the 8:2 FTOH biotransformation to PFOA was found to be critical to PFOA intake for ski wax technicians and very high 8:2 FTOH concentrations (in the range of 830 - 255000 ng/m^3) in the breathing zone air led to elevated PFOA concentrations in their blood compared to general population (Nilsson et al., 2010). Moreover, PFOA concentrations in human serum were significantly correlated with FTOH concentrations in air when 8:2 FTOH concentrations were much lower than those reported in Nilsson et al. (2010) (Fraser et al., 2012).

3.2 FTOHs in Alpine atmosphere

3.2.1 Clean-up method for FTOHs

The FTOHs were not detected in loading and washing fractions, and the total recoveries of FTOHs for each method are presented in Table 22. The recoveries of FTOHs in controls were in the range of 86 - 91%. Therefore, the low recoveries of FTOHs obtained in Method 1 - 6 were due to the ineffective elution, especially for 4:2 FTOH.

Method 1 and Method 2 were used to test the effect of heating of silica gel on the FTOH recoveries. There were no large differences between the recoveries obtained by these two methods. Therefore, heated silica gel was used in the following method development to decrease the potential blank contamination introduced by silica gel. In order to increase the recovery of 4:2 and 6:2 FTOH, silica gel was deactivated with distilled water. When it was deactivated with 10% of distilled water, the recovery of 4:2 FTOH was increased from 37% to 52%. In Method 5 and Method 6, we tried to use less polar solvent (mixture of pentane and DCM instead of DCM) for elution to elute fewer impurities.

Finally, Method 6 was established for clean-up. 0.5 g silica gel deactivated with 10% distilled water was used, and 6 mL of pentane was used for washing followed by 10 mL of pentane and DCM (1/1) for elution.

Table 22 The total recoveries of FTOHs for each method (%).

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH
Method 1	29 ± 4	36 ± 5	52 ± 6	61 ± 5
Method 2	32 ± 2	46 ± 5	61 ± 8	66 ± 10
Method 3	37 ± 3	52 ± 2	73 ± 2	78 ± 4
Method 4	52 ± 2	60 ± 3	67 ± 5	74 ± 9
Method 5	5 mL of 15% dichloromethane in pentane was used for elution for 6 times (30 mL totally), and FTOHs can't be eluted.			
Method 6	45 ± 2	58 ± 5	67 ± 3	70 ± 4

3.2.2 Summary of the FTOH concentrations in air masses from different trajectories

33 air samples from Sonnblick and 28 samples from Zugspitze were collected during 06.2007-07.2010 and analyzed for 6:2, 8:2 and 10:2 FTOH. Due to the malfunction of the sampling device, one sample from Sonnblick during July to September in 2007 and two samples from Zugspitze during February to April in 2008 were excluded from the calculation. Breakthrough was observed in the breakthrough experiment with breakthrough rates of 18%, 11% and 5% for 6:2, 8:2 and 10:2 FTOH, respectively. The breakthrough of FTOHs in the field sampling was expected to be insignificant due to the low temperature at the Sonnblick and Zugspitze sites, and small sampling air volumes (>85% of the sampling volume was less than 1000 m^3). For two samples from Sonnblick with large sampling volumes (1620 m^3 and 2685 m^3), the concentrations of 6:2 FTOH might be underestimated.

In our study, the filter and cartridge were extracted by Soxhlet extraction together, and the concentrations presented here were the sum of gaseous and particle-bound FTOHs, although FTOHs were predominantly in the gas phase rather than the particle-bound phase (Barber et al., 2007; Dreyer et al., 2009a; Jahnke et al., 2007a). At Sonnblick, the frequencies of detection above the MDLs/LODs for 6:2, 8:2 and 10:2 FTOH were 81%, 94% and 94%, respectively. At Zugspitze, all samples contained 8:2 and 10:2 FTOH whereas in 81% of the samples 6:2 FTOH was determined. FTOHs were not detected mainly in the samples collected during July-September in 2007, which might be caused by the low fraction of the extract used

in the analysis. 25% of the extract was analyzed for samples from July-September in 2007 in comparison to 50% for others. The high detection indicated the extensive occurrences of FTOHs in the Alpine atmospheric environment. The total FTOH concentrations ranged from 3.4 to 109 pg/m^3 in air flows from four potential source regions at Zugspitze and from non-detection to 36.1 pg/m^3 at Sonnblick. 8:2 FTOH was found to be the dominant compound, constituting 41% - 72% of the total FTOHs at both sites, which is consistent with the observation in European air masses (Barber et al., 2007; Dreyer et al., 2009a), Asian air mass (Oono et al., 2008) and the Arctic air mass (Shoeib et al., 2006). 6:2, 8:2 and 10:2 FTOH were significantly correlated with each other at the Zugspitze and Sonnblick sites (p<0.05), indicating the common source for FTOHs.

3.2.3 FTOH variations among air masses from four trajectories

Air masses arriving from NW, NE, S and UND were sampled separately. Figure 4 gives an overview of the distribution of FTOH concentrations in the air masses from four potential source regions (NW, NE, S and UND). At Zugspitze, FTOH concentrations of two samples from NE appeared to be significantly high (20.3 pg/m^3 of 6:2 FTOH, 62.0 - 72.4 pg/m^3 of 8:2 FTOH and 26.7 - 28.5 pg/m^3 of 10:2 FTOH) compared to other samples. So, median concentrations were used to track the FTOH variations among NW, NE, S and UND. Air mass from NE led to the highest median ΣFTOH concentration (34.8 pg/m^3), followed by NW, S and UND. For individual compound, medians of NE were 4.8 pg/m^3 for 6:2 FTOH, 22.9 pg/m^3 for 8:2 FTOH, and 6.8 pg/m^3 for 10:2 FTOH, which were 2-17 times higher than those of UND. At Sonnblick, the highest median of ΣFTOH was observed in the air masses from NW (Figure 4) with the concentration of 12.3 pg/m^3. FTOH levels are far lower than those reported in the corresponding potential source regions, such as 55-980 pg/m^3 in Barsbüttel, Germany (Dreyer et al., 2010), 527 pg/m^3 in Manchester, UK (Barber et al., 2007), 194 pg/m^3 in Hamburg and of 146 pg/m^3 in Waldhof, Germany (Jahnke et al., 2007b), indicating the reduction in FTOH levels when going through long range atmospheric transport (LRAT). The reduction might be due to the forest filter effect of the Alps (Nizzetto et al., 2006).

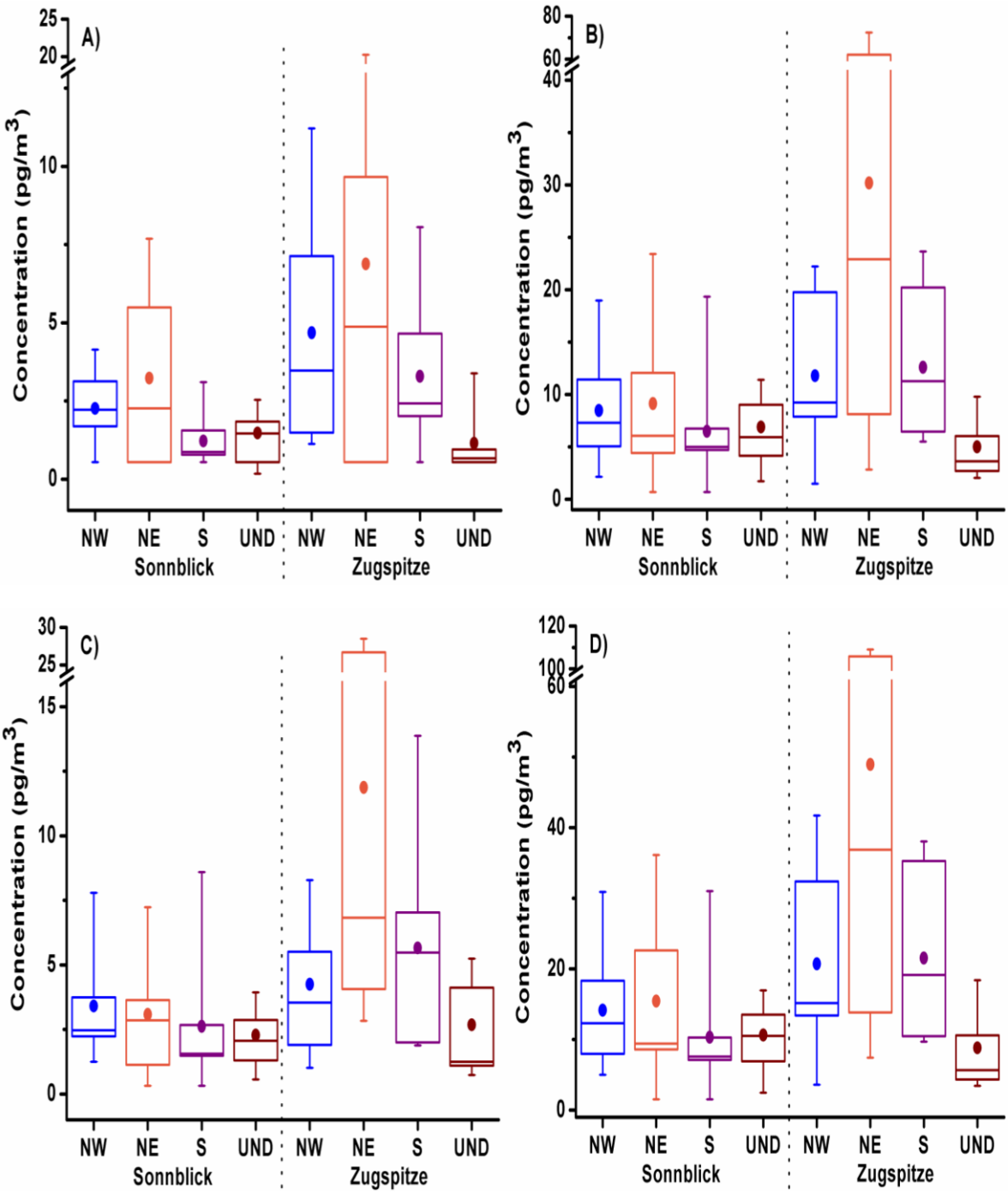

Figure 4 FTOH concentrations in air masses originated from NW, NE, S and UND at Sonnblick and Zugspitze. A) 6:2 FTOH, B) 8:2 FTOH, C) 10:2 FTOH and D) total concentration of three FTOHs (ΣFTOH). Box-whisker plot: whiskers at minimum and maximum, box at P25 and P75 with line at P50 (median), and with dot (●) at mean value.

At the Zugspitze site, the variable median values of FTOH among NW, NE, S and UND indicated that air mass origin was an important factor influencing the levels of atmospheric FTOH. High population, industrialized areas and fluoropolymer manufactures in sectors of

NW and NE, such as UK, France, Belgium, Germany, Netherland and Poland (NoMiracle, 2007) might result in the elevated FTOH levels in corresponding air flows. It was not surprised that air mass from UND showed the lowest FTOH concentrations, since UND was high speed air masses from the Atlantic or the Arctic, or great heights (Offenthaler et al., 2009). On the whole, our observation of elevated FTOH levels in air masses from densely populated and industrialized areas and low FTOH levels in air masses from the Atlantic or the Arctic is in agreement with the reports by Jahnke et al. (2007b) and Dreyer et al. (2009b). However, at Sonnblick, the variabilities of FTOHs in the air masses from four different sectors (NW, NE, S and UND) were not so pronounced compared to the Zugspitze site. The results might imply that other than air mass origin, there are unknown forces also playing a critical role in the FTOH concentrations. For the majority of analytes, arithmetic concentration means and median values were slightly higher at the Zugspitze site than the Sonnblick site although there was no significant differences (t-test, $p>0.05$).

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3.2.4 Seasonal variations

Concentrations of FTOHs in the air masses from NE, NW, S and UND varied a lot over the sampling period (Figure 5 and 6). No obvious seasonal tendency was observed partly due to the interrupted time course. At Zugspitze, take air mass from NE as an example, the highest FTOH concentrations were generally observed in periods of April-July in 2008 and November, 2008-March, 2009 with levels of 20.4 - 72.2 pg/m^3 for three individuals (Figure 5). The significant high FTOH levels in these two periods compared to others might be due to the temporal pulsing sources. At Sonnblick, also take NE as an example, the highest FTOH levels were generally found in period of January-March in 2008 with values of 5.5 - 23.4 pg/m^3 for three individuals, and the lowest FTOH concentrations was detected in period of June-September, 2009 with levels of 0.6 - 4.1 pg/m^3 (Figure 6).

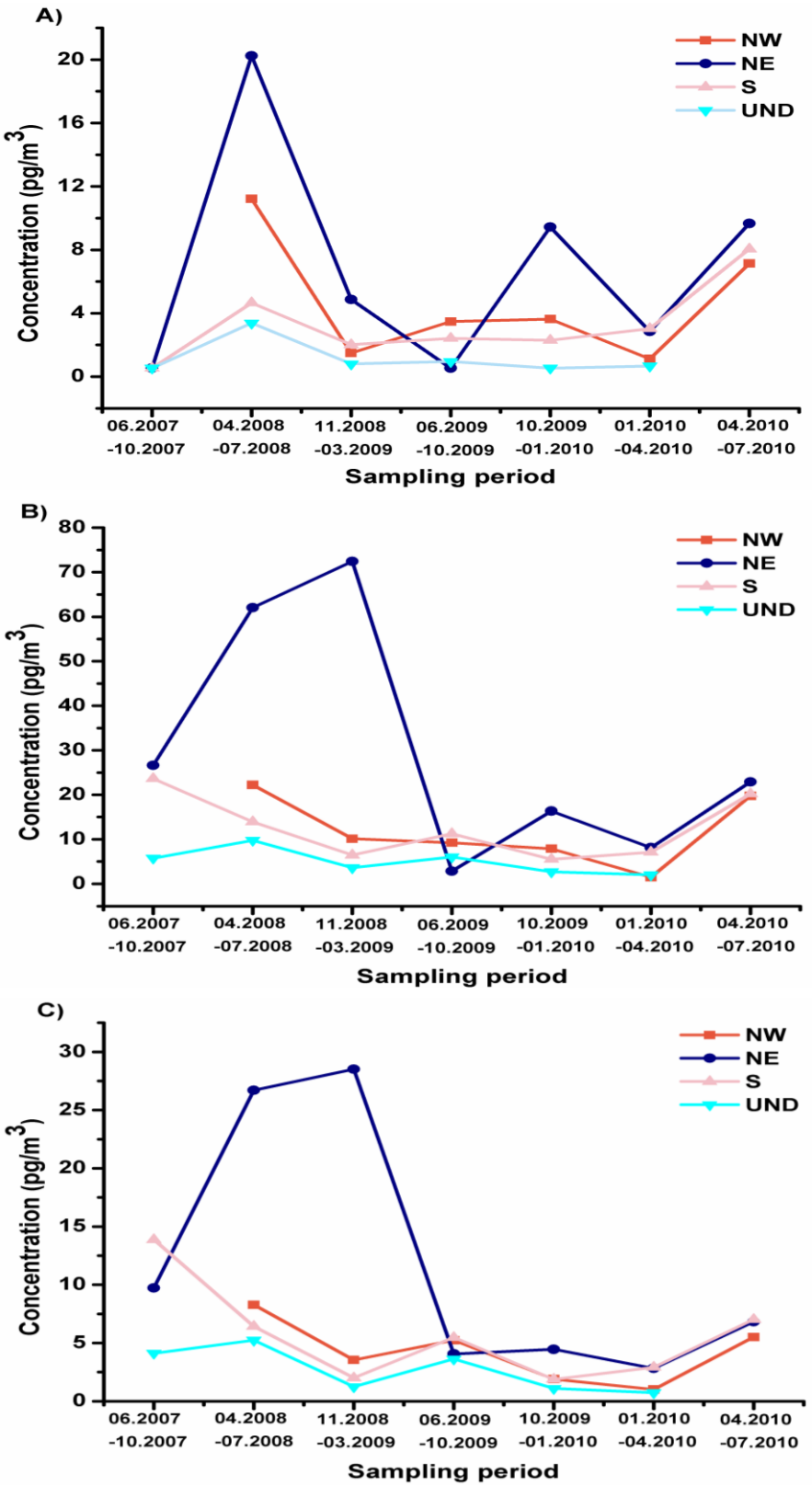


Figure 5 FTOH concentrations in air masses from NE, NW, S and UND over the whole sampling period at the Zugspitze site. A) 6:2 FTOH, B) 8:2 FTOH, and C) 10:2 FTOH.

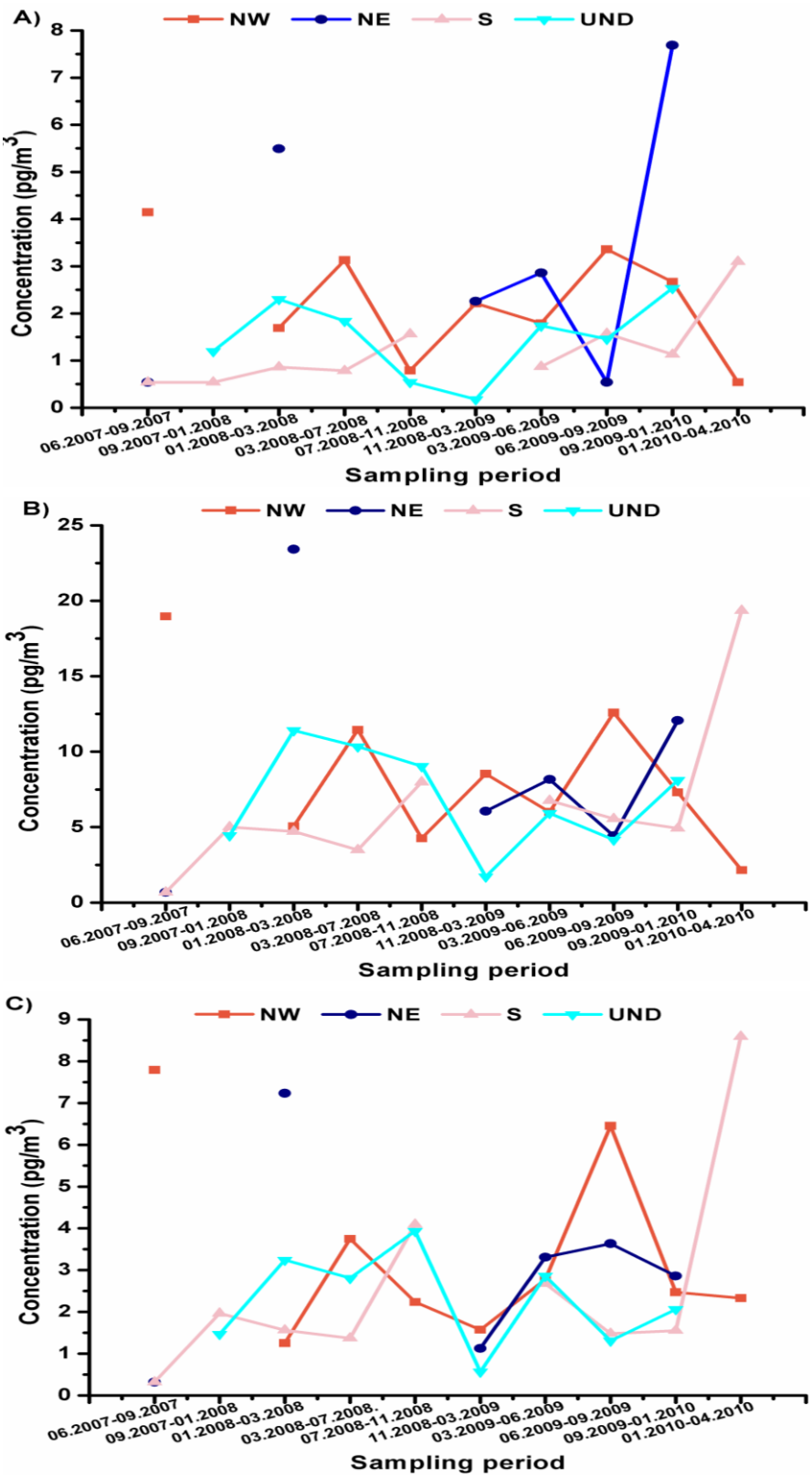


Figure 6 FTOH concentrations in air masses from NE, NW, S and UND over the whole sampling period at the Sonnblick site. A) 6:2 FTOH, B) 8:2 FTOH, and C) 10:2 FTOH. Note: course was interrupted where the data was not available.

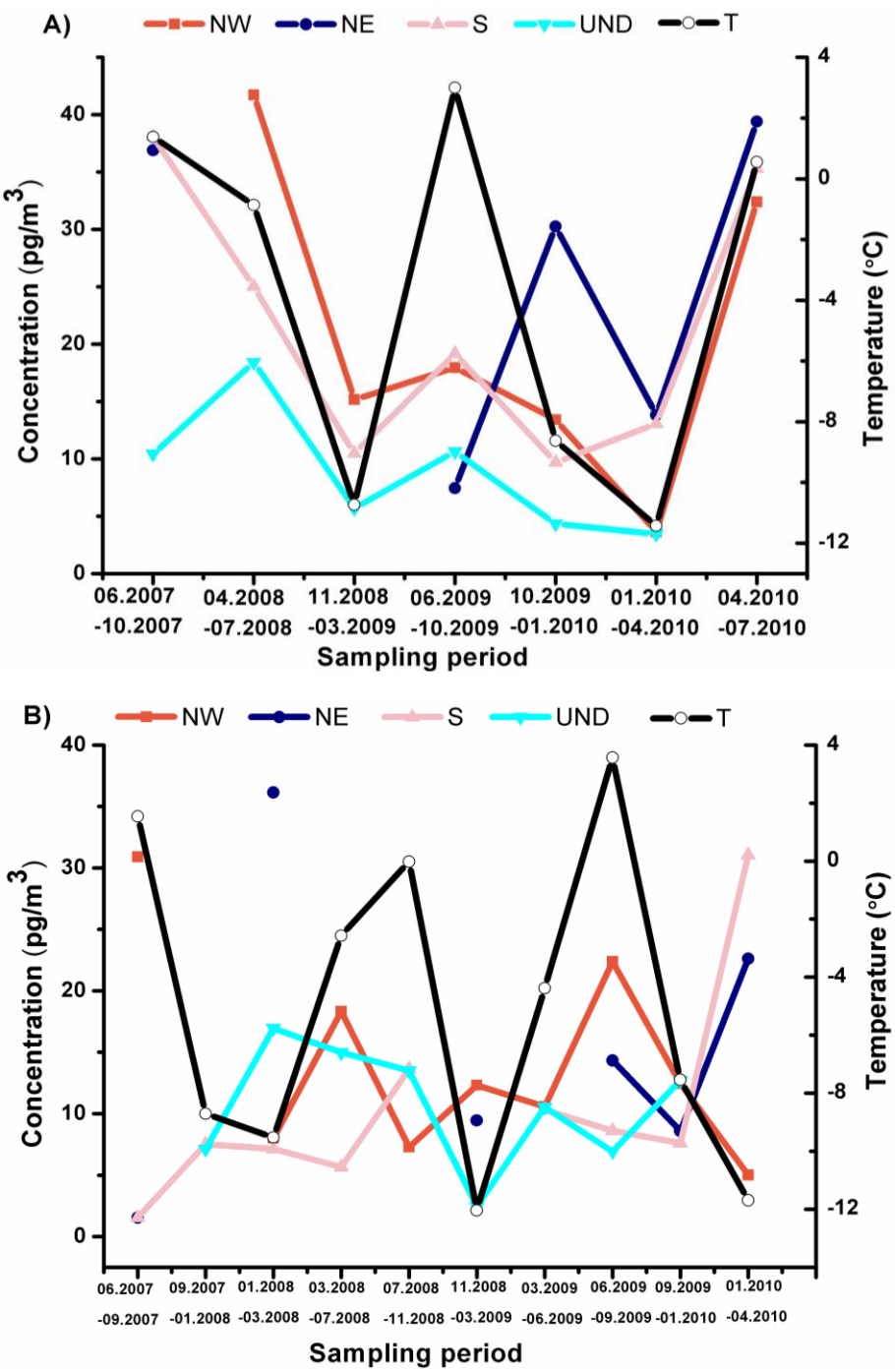


Figure 7 Relationships of ΣFTOH concentrations and temperature. A) Courses of ΣFTOH concentrations and temperature over the whole sampling period at Zugspitze. B) Courses of ΣFTOH concentrations and temperature over the whole sampling period at Sonnblick. Note: course was interrupted where the data was not available.

Figure 7 shows the time courses of ΣFTOH and site temperature. Correlation analysis was carried out to investigate the possible relationship between them. At Zugspitze and Sonnblick sites, no significant relationships were found between ΣFTOH and the temperature (Spearman

Rank correlation, p>0.05). The result is consistent with the finding of Piekarz et al (2007). Wania et al. (1998) modeled the relations between site temperatures and atmospheric concentrations of volatile organic compounds, and pointed out that the independence of air concentrations on site temperatures was an indicative of that air concentrations were controlled by long range atmospheric transport. Therefore, the absence of any dependence of FTOHs in air masses originated from NW, NE, S and UND on the site temperatures implied that long range atmospheric transport governed the concentrations of FTOH in the Alpine atmosphere. The diffusive emissions of FTOHs from the vicinity of the sampling sites should have negligible effects on the FTOH concentrations.

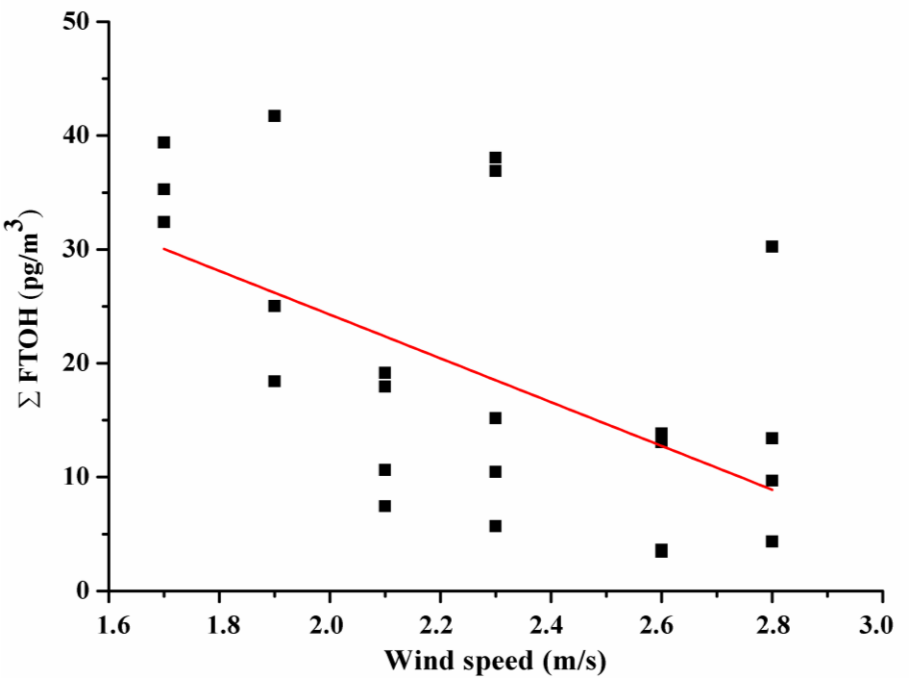


Figure 8 The relationship of ΣFTOH concentrations and wind speed for samples from Zugspitze. Note that two high concentration events were excluded from this consideration.

Other meteorological parameters if available were investigated to explain the seasonal FTOH variations. At Zugspitze, ΣFTOH was significantly negatively correlated with the wind speed (Figure 8, Spearmann correlation, $p < 0.05$, R = -0.6), which implied that high wind speed representing the short residence time of the air parcel at the potential source regimes led to the low FTOH concentrations. The residence time was also used to assign the potential source regions of (semi)volatile pollutants at the receptor site; Piekarz et al. (2007) calculated

the SRIF (source region impact factor) values, the percentage of time that an air parcel spent in a particular source region before arriving at sampling site, and China with a SRIF value greater than 40% was considered as a source region for Ftenes (fluorotelomer olefins) in the Okinawa atmosphere, Japan.

3.2.5 Time-averaged FTOH concentrations in the Alpine atmosphere

The time-averaged FTOH concentrations were used to evaluate the FTOH levels in the Alpine atmosphere. They were calculated only for periods when data of four trajectories were all available. As shown in Table 23, the ΣFTOH is 7.5 - 41.3 pg/m^3 during 2008-2010 at Zugspitze and 9.7 - 12.0 pg/m^3 during 2008-2009 at Sonnblick, demonstrating the low FTOH levels in the Alpine atmosphere. In the summer of 2007, air samples were collected at background sites over the northeast Atlantic Ocean and the ΣFTOH varied from 16.6 to 50 pg/m^3 in Bermuda, and from 1.4 to 70.7 pg/m^3 in Sable Island (Shoeib et al., 2010). In the summer of 2005, air samples were taken in a cruise over the North Atlantic Ocean and Canadian Archipelago, and 5.8 - 26 pg/m^3 of 8:2 FTOH, 1.9 - 17 pg/m^3 of 10:2 FTOH and non-detection - 6.0 pg/m^3 of 6:2 FTOH were observed (Shoeib et al., 2006). Ahrens et al. (2011a) determined FTOHs in the air samples collected during a ship cruise crossing the Canadian Arctic, and ΣFTOH was 20 - 138 pg/m^3. ΣFTOH was reported to be <1.2 - 32 pg/m^3 at Mount Bachelor, Oregon in 2004 (Piekarz et al., 2007). Overall, FTOH concentrations in the Alpine atmosphere are similar to the ranges observed at sites over the Atlantic Ocean, the Arctic and remote mountainous areas.

3.2.6 FTOH-derived PFOA deposition

PFOA was detected in the deposition samples with the deposition rate of 3.3 - 6.2 ng/m^2/d at Zugspitze and of non-detection - 7.0 ng/m^2/d at Sonnblick (Fiedler, 2010). In order to investigate the contributions of airborne FTOHs to the PFOA depositions, the deposition fluxes of PFOA derived from 8:2 and 10:2 FTOH were roughly estimated. The calculated deposition fluxes of 8:2 and 10:2 FTOH-derived PFOA depositions were 0.1 - 1.4 ng/m^2/d (Table 23). The FTOH-derived PFCA deposition flux was predicted to be 154 kg/a in the Artic (Wania, 2007), corresponding to 0.02 ng/m^2/d when the surface area of the Arctic north was

assumed to be 26.4 million km^2 (Schenker et al., 2008). Schenker et al. (2008) modeled the FTOHs globally transport from the emission areas (mainly in the Europe and North America) to the Arctic, and predicted the FTOH-derived PFOA precipitation deposition rates were 0.01 - 0.03 $ng/m^2/d$. The PFOA deposition fluxes from FTOHs in the Alpine area in this work are at least one order of magnitude higher than those in the Artic.

Table 23 Average atmospheric FTOH concentrations (pg/m^3) and FTOH-derived PFOA depositions ($ng/m^2/d$) at Zugspitze and Sonnblick.

	6:2 FTOH	8:2 FTOH	10:2 FTOH	ΣFTOH	FTOH-derived PFOA deposition
Zugspitze					
04.2008 – 07.2008	8.3	23.0	10.0	41.3	1.1
11.2008 – 03.2009	2.0	15.8	5.8	23.6	1.4
06.2009 – 10.2009	2.3	8.7	4.9	15.9	0.4
10.2009 – 01.2010	2.5	5.8	1.8	10.1	0.2
01.2010 – 04.2010	1.7	4.1	1.7	7.5	0.2
Sonnblick					
01.2008 – 03.2008	1.8	7.9	2.3	12.0	0.1
03.2009 – 06.2009	1.6	6.7	2.8	11.1	0.3
09.2009 – 01.2010	2.1	5.8	1.8	9.7	0.4

Further, the contribution of airborne FTOHs to the PFOA deposition was estimated based on the total PFOA deposition flux from Fiedler's study (Fielder, 2010). The FTOH-derived PFOA accounted for 17% of the total PFOA in the deposition sample collected at Zugspitze during the period of April-July in 2008. Schenker et al. (2008) predicted the FTOH-derived PFOA deposition fluxes were 7 - 18% of the total PFOA depositions in the Arctic. Yarwood et al. (2007) found that the 1 - 2% of the PFCAs in the North America rainfall was attributed to the FTOH emissions. Our assessment is consistent with the finding of Schenker et al. (2008) and a little higher than the observation of Yarwood et al. (2007). The variability of FTOH-derived PFOA deposition fluxes in different areas were possibly due to the various

conversion rates of FTOH to PFOA and partitioning coefficients used in the estimation, such as K_{AW} and the rain/snow pH, etc. (Schenker et al., 2008; Wania, 2007). Further investigations should be conducted to investigate the occurrences and levels of PFOA in the Alpine environment, and to elucidate the role of precursors in the environmental distributions of PFOA. In addition to FTOHs, other precursors, such as fluorotelomer olefins (Nakayama et al., 2007), should also be included.

3.3 PFCAs and PFSAs in sediment from the Yangtze River

3.3.1 Summary of the concentrations of PFCAs and PFSAs in sediment samples

Sediment cores were collected from 17 sites along the upstream of the Yangtze River, covering the distance span of 249 km. Totally, 111 sediment samples were analyzed for PFBS, PFHxS, PFOS, PFDS, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA. PFBS, PFHxS, PFDS, PFHxA, PFHpA, and PFDoDA were not detected in all samples. The summary of the PFCA and PFSA concentrations are listed in Table 24. PFOA was the compound with the highest detection rate, followed by PFOS and PFUnDA. The ΣPFCs ranged from non-detection to 724.7 pg/g dw. Generally, PFOA was the dominant compound, followed by PFOS. The PFOA and PFOS constituted up to 96 % of the total PFCs. The PFCA and PFSA concentrations in sediment from the Yangtze River are comparable to those observed in Baiyangdian Lake, China (Shi et al., 2012), Rote Main, Germany (Becker et al., 2008), Alpine lakes, Austria (Clara et al., 2009), and lower than those detected in Tangxun Lake, China (Zhou et al., 2013), Yongsan River and Nakdong River, Korea (Hong et al., 2013). The correlation analysis indicated that PFOS, PFOA, PFNA, PFDA, PFUnDA and PFTriDA detected in sediment cores had common sources (Table 25).

Table 24 The descriptive statistics of the PFCA and PFSA concentrations in sediment samples (pg/g dw).

	Detection rate (%)	Min	Max	P25	P50	P75
PFOS	78	3.7	240.6	45.8	80.5	110.8
PFOA	96	2.2	492.0	44.9	107.7	159.0
PFNA	39	2.8	107.3	2.8	2.8	26.8
PFDA	68	3.1	99.6	3.1	28.1	46.1
PFUnDA	77	0.4	214.3	17.6	34.4	52.2
PFTriDA	11	6.8	66.0	6.8	6.8	6.8
ΣPFCAs	-	15.3	708.7	131.8	211.9	278.0
ΣPFCs	-	19.0	724.7	184.5	302.2	389.6

ΣPFCAs: sum of the concentrations of PFOA, PFDA, PFUnDA and PFTriDA.

ΣPFCs: sum of the concentrations of PFOA, PFDA, PFUnDA, PFTriDA and PFOS.

When values were lower than LOD, value of LOD/sqrt(2) was used in the calculations.

Table 25 Spearman Rank Correlations between PFCAs and PFSAs in sediment samples (Bold text indicates significant correlations).

	PFOA	PFNA	PFDA	PFUnDA	PFTriDA
PFOS	**0.51**[b]	**0.36**[b]	**0.52**[b]	**0.27**[b]	**0.26**[a]
PFOA		**0.38**[b]	**0.33**[b]	**0.22**[a]	0.27
PFNA			**0.42**[b]	**0.27**[a]	0.35
PFDA				**0.3**[b]	**0.49**[b]
PFUnDA					**0.29**[b]

[a] Correlation was significant at the 0.05 level (two tailed).

[b] Correlation was significant at the 0.01 level (two tailed).

3.3.2 Variations of PFCAs and PFSAs with depth in sediment cores

The PFCA and PFSA concentrations varied with depth in each sediment core. However, no obvious trend was observed. Relative standard deviation (RSD) was used to describe the

variations of PFC levels with depth. Generally, as indicated by RSD values (Table 26), the differences in analyte concentrations among layers were not significant except for some compounds, like PFNA and PFUnDA. The high RSD values of PFNA and PFUnDA were partly caused by the low detection rates. The insignificant differences in PFC concentrations in sediment cores might be related with the hydro dynamically-disturbed sedimentation process due to the regulations of TGR. Therefore, the average concentration values were used to track the distribution of PFCs along the Yangtze River.

Table 26 The descriptive statistics of RSD (%) for PFCA and PFSA concentrations in all sediment cores.

	PFOS	PFOA	PFNA	PFDA	PFUnDA	PFTriDA	ΣPFCs
Min	8	15	0	0	12	0	19
P10	11.2	22.2	0	6.4	42.8	0	20.8
P25	29	30.5	31	34	61	0	24.5
P50	55	45	105	54	88	0	38
P75	109	62.5	144	96.5	120.5	64.5	57.5
P90	131.4	75.6	168	115.8	184.4	94.8	62.6
Max	177	86	177	166	220	147	63

3.3.3 Distributions of PFCAs and PFSAs along the Yangtze River

The profiles of PFSA and PFCA concentrations are presented in Figure 9. The highest mean ΣPFC was found at WZ with a value of 477.7 pg/g dw. In the main stream of the Yangtze River, the total concentrations of PFC were the highest at WZ, then decreased by 40% towards YY, then increased by 23% at FJ, and stayed comparable at BD, GJB and MP. The high PFC concentrations at WZ might be attributed to the high population in Wanzhou city (the second biggest city in Chongqing), intensive industries and the input of the Tianxian Lake receiving the effluent of wastewater treatment plant (WWTP). WWTPs and industries were found to be a source of PFSAs and PFCAs in rivers or lakes (Kim et al., 2013; Naile et al., 2013; Shi et al., 2012; Zhou et al., 2013). The decrease in PFC concentrations at YY may be due to the dilution effect caused by the anabranch of Xiaojiang River, which flows into the

Yangtze River at YY with an annual flow of 3.4 billion cubic meters. When comparing the PFC concentrations in three anabranches (Xiaojiang River, Daning River and Xiangxi River), a common trend was observed; the PFC concentrations were high at the headstream (QM, DC and PYK), and getting lower in the middle stream of each river (GY, SL and XK), and then becoming the highest in the downstream which is close to the main stream of the Yangtze River (SJ, WS and XX). The concentrations observed at SJ were comparable to those at YY, and concentrations at WS and XX were comparable to those at GJB, BD and FJ. The observation implied the mixing effect of the anabranches and Yangtze River at the junctions.

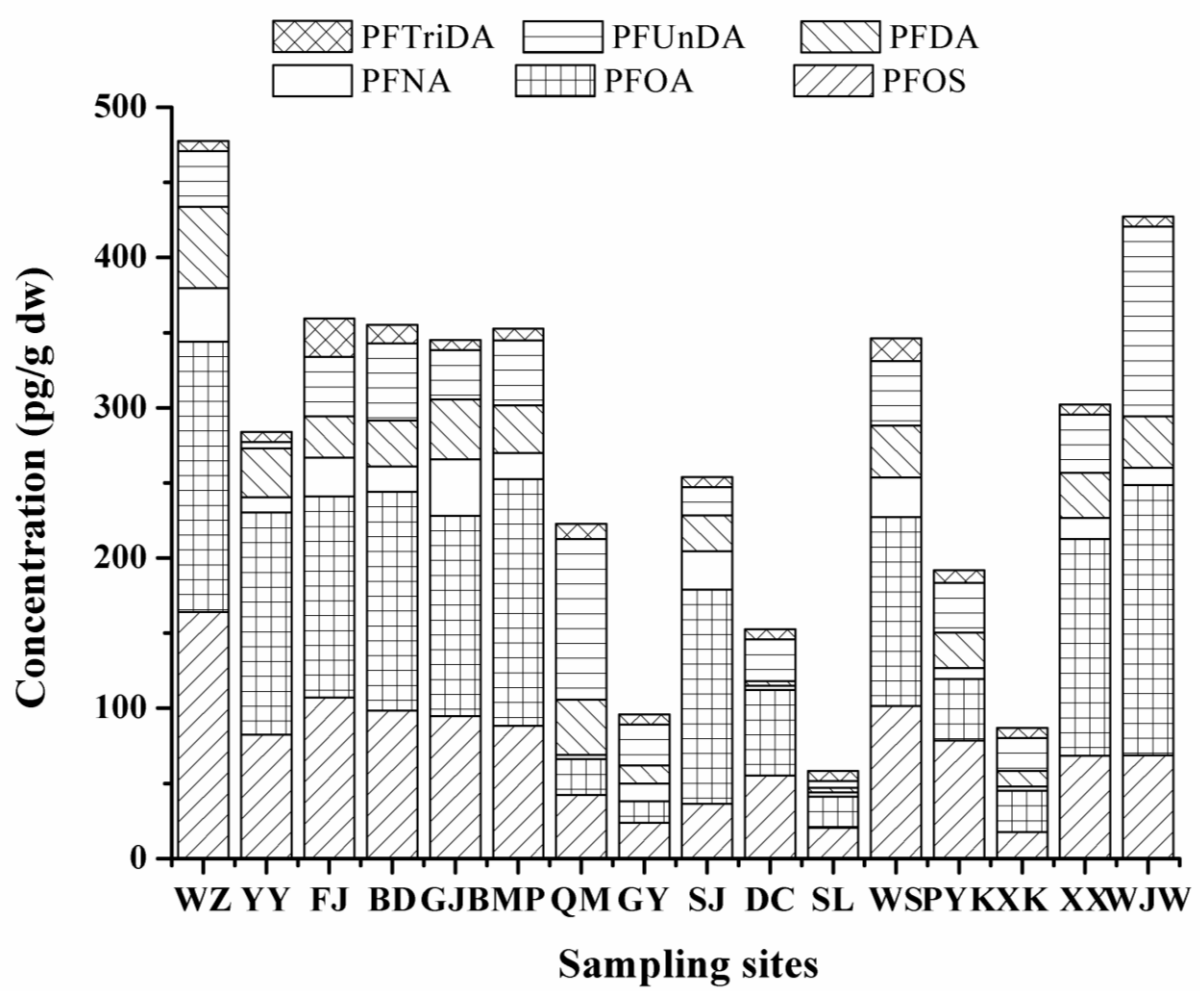


Figure 9 Distributions of PFCAs and PFSAs along the Yangtze River.

3.4 SFAs in the ski wax products

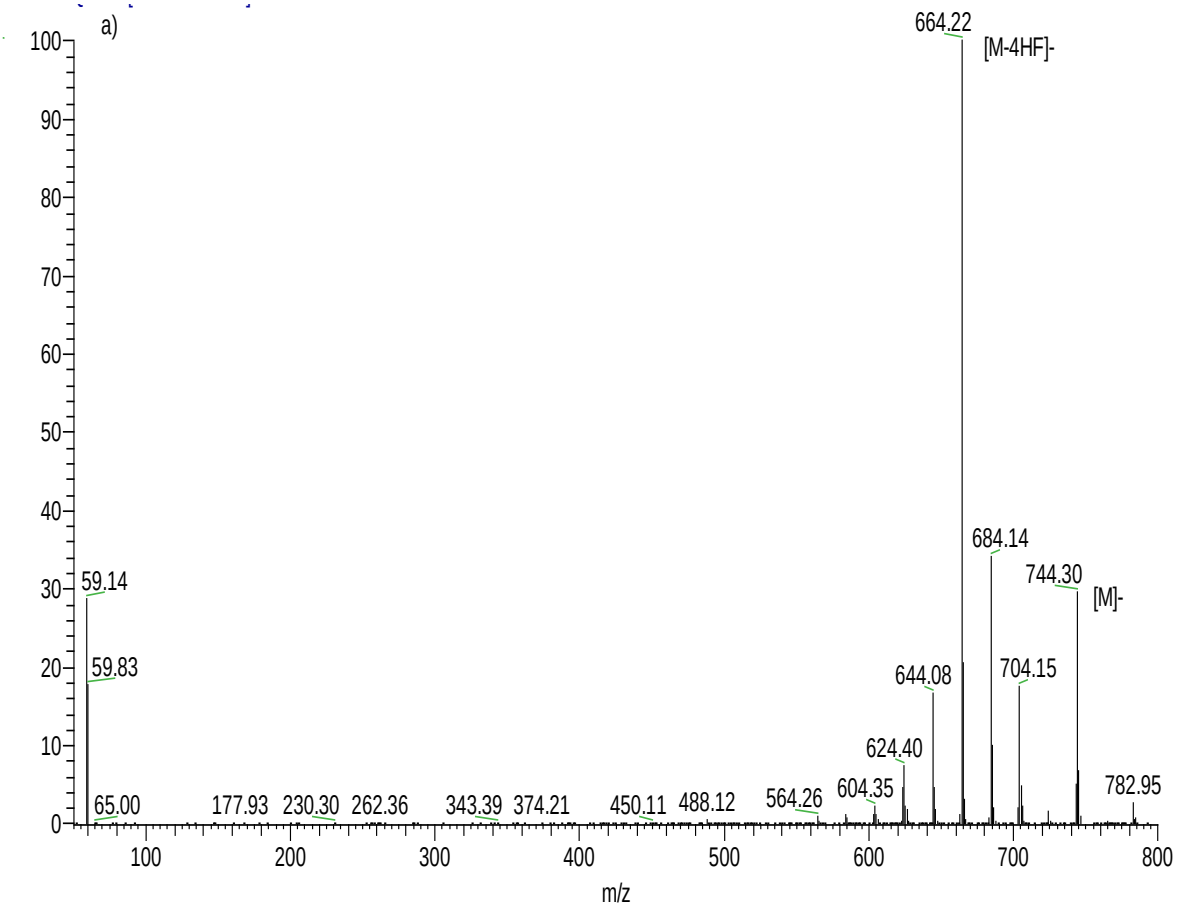
3.4.1 Method development of SFAs analysis on GC-MS

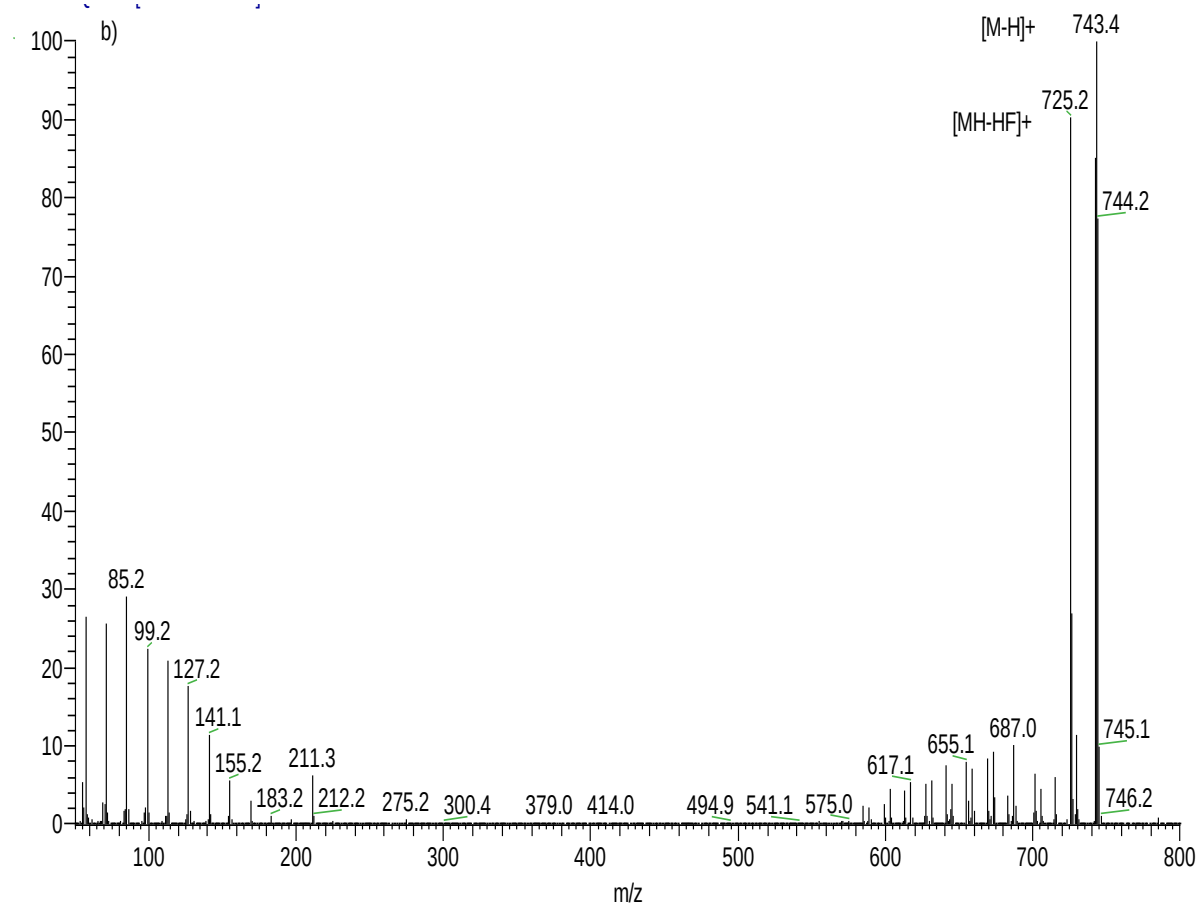
Figure 10a shows the mass spectrum of $F_{10}H_{16}$ in NCI mode. The fragmentations in NCI

were the same as reported by Plassmann and Berger (2010) for SFAs, but there was some difference in the distribution pattern. The intensity ratio of $[M]^-/[M-4HF]^-$ was 0.6% for $F_{10}H_{16}$ when the ion source temperature was set at 200 ℃. It was increased to 35% when the ion source temperature was 150 ℃, but the intensity was decreased. Compared to the results of Plassmann and Berger (2010), more fragments and less molecular ions were obtained in this thesis. This was probably attributed to the different reagent gases used. Ammonium was used in Plassmann and Berger (2010), and ammonium CI was less energetic than methane CI used in our work.

Figure 10b shows the mass spectrum of $F_{10}H_{16}$ in PCI mode. Two main fragments were observed. One was the $[M-H]^+$ resulted from the hydride abstraction reaction. For the other fragmentation, it was about 19 mass units lower than the molecular weight. Fragments of $[M-F]^+$ and $[M-HF]^+$ were detected for some fluorohydrocarbons in EI mode (Santoro and Piccardi, 1973), but these were not observed for SFAs in EI mode (Plassmann and Berger, 2010). Due to the high bond energy of C–F and less energetic of CI in comparison to EI, the other fragmentation was assigned as $[MH-HF]^+$ rather than $[M-F]^+$. Moreover, fragments of $[MH-HF]^+$ and $[M-H]^+$ were seen for cyclohexyl fluoride in methane PCI (Jardine and Fenselau, 1976). A pseudo-six-membered ring via fluorine-hydrogen bonding was suggested to be formed for SFAs in EI mode (Napoli et al., 1993). In the low mass-to-charge range, hydrocarbon fragments were detected.

Figure 10c shows the fragmentation of $F_{12}H_{16}$ene in NCI. It was comparable with those of SFAs. The $[M-H]^+$ was the dominant fragment independent of the fluorinated chain length or hydrocarbon chain length except for $F_{10}H_2$. For $F_{10}H_2$, molecular ion was not observed, and the two main fragments were $[MH-2HF]^+$ and $[MH-HF]^+$. When the ion source temperature was increased to 200 ℃, more hydrocarbon fragments in the low mass-to-charge range and less fragments of $[MH-HF]^+$ and $[M-H]^+$ were seen.


a)
664.22
[M-4HF]-
684.14
744.30
[M]-
59.14
59.83
644.08
704.15
624.40
604.35
782.95
65.00
177.93
230.30
262.36
343.39
374.21
450.11
488.12
564.26
m/z


b)
[M-H]+
743.4
725.2
[MH-HF]+
744.2
85.2
99.2
127.2
141.1
155.2
211.3
183.2
212.2
275.2
300.4
379.0
414.0
494.9
541.1
575.0
617.1
655.1
687.0
745.1
746.2
m/z

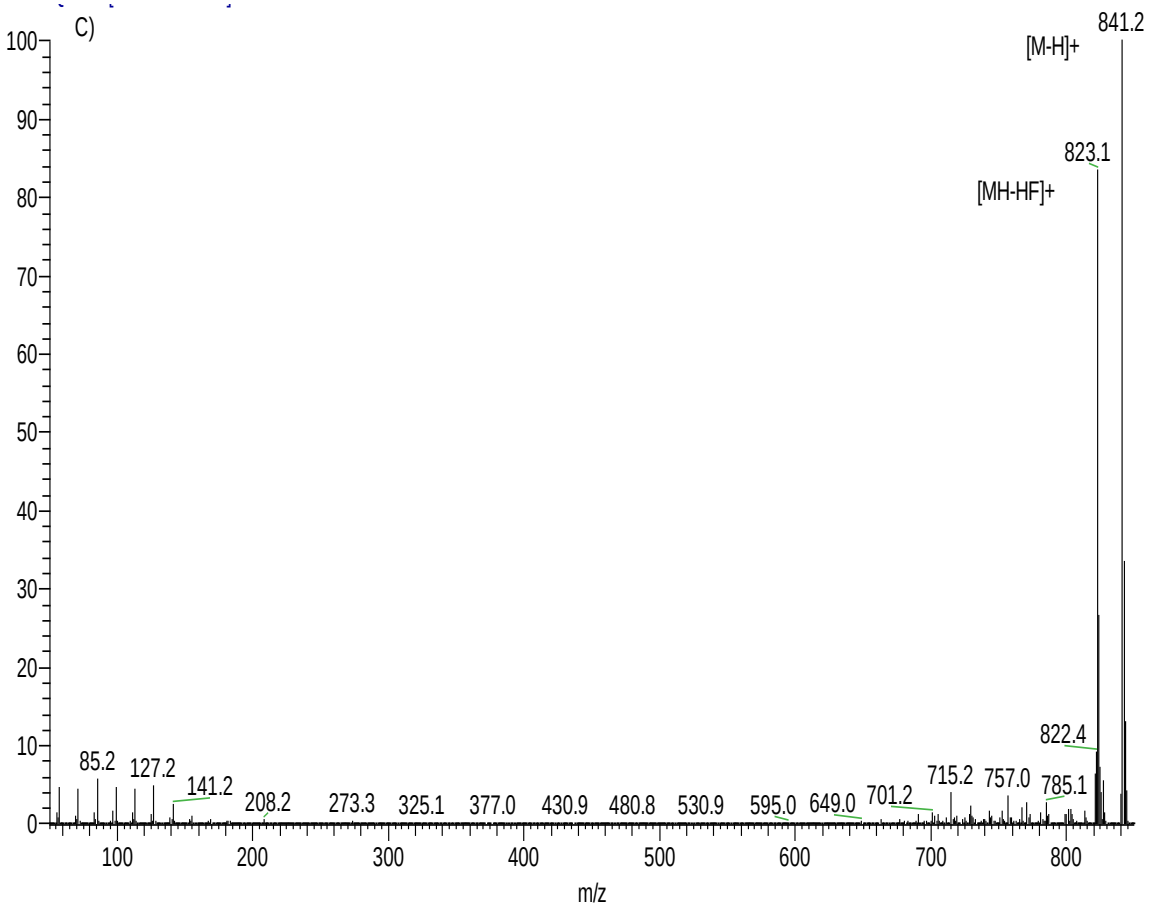


Figure 10 Mass spectrums at 150 ℃ of ion source temperature. a) NCI for $F_{10}H_{16}$, b) PCI for $F_{10}H_{16}$, c) PCI for $F_{12}H_{16}$ene.

Due to the lack of isotope-labeled SFA and SFAene standards and probably low concentrations of SFAs and SFAenes in environmental matrices, it is important to monitor at least two fragments to identify the analytes. Compared to the methane NCI, there was higher relative abundance of main fragments in methane PCI giving more reliable results. Therefore, methane PCI at ion source temperature of 150 ℃ was used in the quantitative analysis. The quantifier and qualifier of each analyte are listed in Table 27. The instrumental limit of detection in methane PCI mode (Table 28) was comparable to ammonium NCI (Plassmann and Berger, 2010). Figure 11 shows the chromatogram of SFA standard at 200 pg/mL.

Table 27 Qualifiers and quantifiers used in the analysis of SFAs.

Compound	Molecular weight	Qualifier $[MH\text{-}HF]^+$	Quantifier $[M\text{-}H]^+$
$F_{10}H_2$	548	509 [b]	529 [a]
F_6H_8	432	413	431
F_8H_{10}	560	541	559
F_6H_{14}	516	497	515
F_6H_{16}	544	525	543
F_8H_{16}	644	625	643
$F_{10}H_{16}$	744	725	743
$F_{12}H_{16}$	844	825	843
$F_{12}H_{14}$	816	797	815
$F_{12}H_{16}$ene	842	823	841

[a]: quantifier was $[MH\text{-}HF]^+$.

[b]: qualifier was $[MH\text{-}2HF]^+$.

Table 28 Instrumental LODs and linearity of SFAs and SFAenes in methane PCI.

	$F_{10}H_2$	F_6H_8	F_6H_{14}	F_6H_{16}	$F_{12}F_{14}$	F_8H_{16}	$F_{10}H_{16}$	$F_{12}H_{16}$	$F_{12}H_{16}$ene
LOD/pg	16	18	15	13	5	11	6	2.7	5.1
LOQ/pg	53	60	50	45	17	37	20	9.3	17
Linear range/ ng	0.01 - 9								

3.4.2 SFAs in ski wax products

SFAs were not detected in all ski wax products. In full scan mode, the peaks for normal paraffin were observed. Compared to the results of Plassmannn and Berger (2010), the observation in this thesis indicated that the application of SFAs in ski wax products were significantly variable. Only SFAs with standard solutions (F_6H_{16}, $F_{12}H_{14}$, F_8H_{16}, $F_{10}H_{16}$, $F_{12}H_{16}$ and $F_{12}H_{16}$ene) were analyzed in air in the following works.

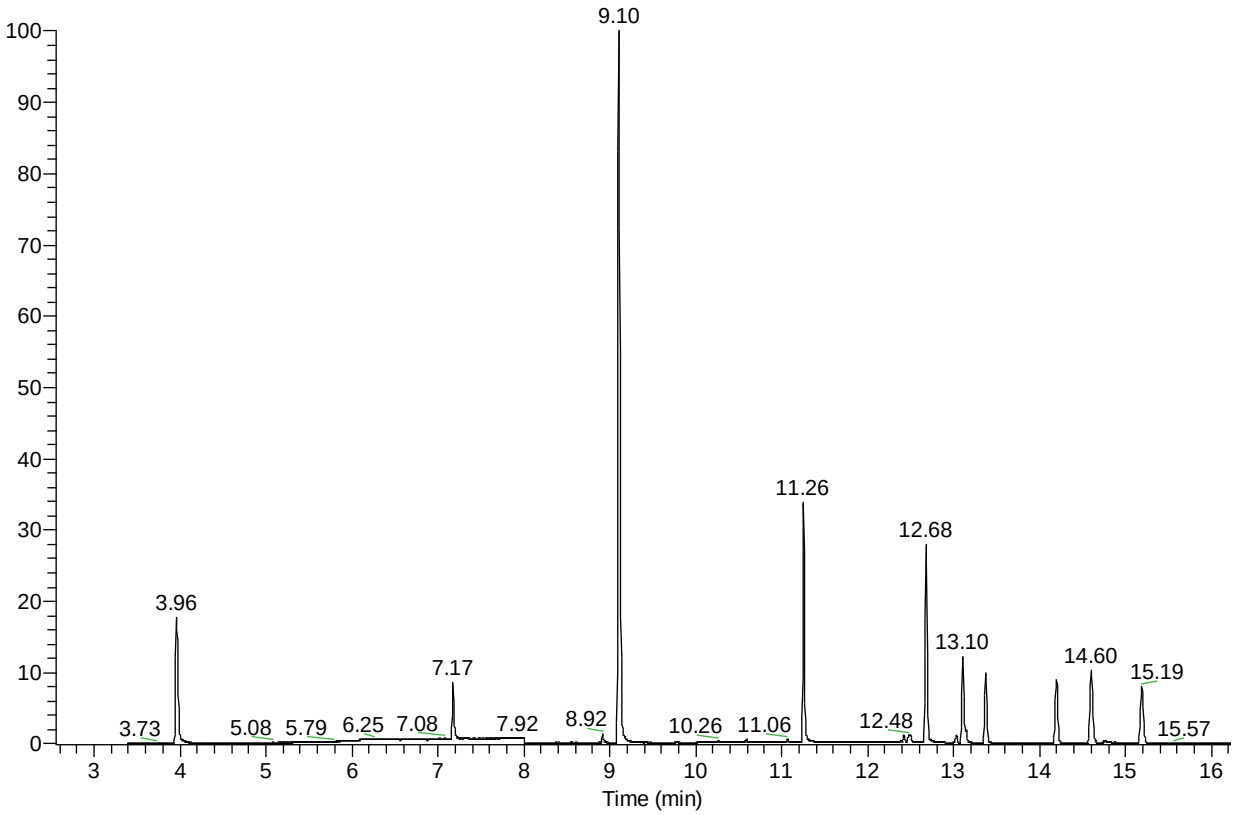


Figure 11 The chromatogram of SFAs (200 pg/mL) in the SIM mode. ($F_{10}H_2$ at 3.96 min, F_6H_8 at 7.18 min, F_8H_{10} at 9.11 min, F_6H_{14} at 11.26 min, F_6H_{16} at 12.68 min, $F_{12}H_{14}$ at 13.10 min, F_8H_{16} at 13.38 min, $F_{10}H_{16}$ at 14.21 min, $F_{12}H_{16}$ene at 14.61 min and $F_{12}H_{16}$ at 15.19 min).

3.5 SFAs in the active air samples

3.5.1 Development of clean-up method for SFAs

SFAs were not detected in loading fraction. 60-95% of SFAs were eluted by first fraction of cyclohexane (Table 29). The low recovery of $F_{10}H_2$ might be attributed to its high volatility.

Therefore, the clean-up method was established as follows. Active air samples were cleaned by 0.5 g silica gel deactivated with 10% H_2O. 0.5 mL sample was loaded on the silica cartridge, SFAs and SFAenes were eluted with 5 mL cyclohexane.

Table 29 Recoveries of SFAs.

	Elution-1	Elution-2	Elution-3
$F_{10}H_2$	13 ± 4	0.3 ± 0.1	n.d.
F_6H_8	75 ± 7	1.2 ± 0.6	n.d.
F_6H_{14}	79 ± 7	1.2 ± 0.4	n.d.
F_6H_{16}	88 ± 5	1.1 ± 0.3	n.d.
$F_{12}F_{14}$	94 ± 6	1.0 ± 0.4	n.d.
F_8H_{16}	80 ± 6	1.1 ± 0.4	n.d.
$F_{10}H_{16}$	76 ± 6	1.1 ± 0.4	n.d.
$F_{12}H_{16}$ene	63 ± 8	1.1 ± 0.4	n.d.
$F_{12}H_{16}$	71 ± 4	1.1 ± 0.4	n.d.

3.5.2 SFA concentrations in Alpine air

The sampling system was tested for polycyclic aromatic hydrocarbons (PAHs), and no breakthrough was observed. The $\log K_{OA}$ values of PAHs range from 5.1 for naphthalene to 11.9 for Benzo[k]fluoranthene (Mackay et al., 2006). The $\log K_{OA}$ values of SFAs ranging from 9.2 for F_6H_{16} to 9.9 for $F_{12}H_{16}$ are in the range of those for PAHs (Plassmann et al., 2010). Therefore, no breakthrough in field sampling was assumed for SFAs.

25 active air samples from four different air trajectories collected during 2007.06 to 2010.04 were analyzed to investigate ranges of SFAs and SFAenes at Zugspitze. The ΣSFA ranged from 0.78 to 10.70 pg/m^3 (Table 30). SFAs were sparsely detected in the air and the frequencies of detection above the LODs were less than 30% for most analytes. The most frequent detected compound was $F_{10}H_{16}$, $F_{12}H_{14}$ and F_8H_{16}.

28 active air samples from four trajectories were collected from 2007.06 to 2010.04 at Sonnblick. The ΣSFA in the active air samples from Sonnblick ranged from 0.073 to 3.1 pg/m^3 (Table 31). SFAs were sparsely detected in the air with the frequencies of detection above the LODs less than 30% for most analytes.

Table 30 SFA concentrations in air at Zugspitze (n=25, pg/m^3).

	% above LOD	Min	10th percentile	Median	90th percentile	Max
F_6H_{16}	0	0.018	0.018	0.018	0.018	0.018
$F_{12}H_{14}$	28	0.069	0.069	0.069	0.39	0.47
F_8H_{16}	28	0.16	0.16	0.16	0.47	0.71
$F_{10}H_{16}$	42	0.099	0.099	0.099	4.26	6.90
$F_{12}H_{16}$ene	0	0.005	0.005	0.005	0.005	0.005
$F_{12}H_{16}$	14	0.15	0.15	0.15	1.39	3.26
SUM	-	0.78	0.78	1.06	6.75	10.70

Note: values below LOD was set as LOD/sqrt(2).

Table 31 SFA concentrations in air at Sonnblick (n=28, pg/m^3).

	% above LOD	Min	10th percentile	Median	90th percentile	Max
F_6H_{16}	21	0.018	0.018	0.018	0.44	0.54
$F_{12}H_{14}$	32	0.014	0.023	0.023	0.26	0.56
F_8H_{16}	18	0.006	0.006	0.006	0.09	0.41
$F_{10}H_{16}$	25	0.007	0.007	0.007	0.08	0.55
$F_{12}H_{16}$ene	32	0.005	0.005	0.005	0.33	0.42
$F_{12}H_{16}$	29	0.014	0.014	0.014	0.15	0.61
SUM	-	0.073	0.073	0.11	0.43	3.10

Note: values below LOD was set as LOD/sqrt(2).

SFAs in the environment are originated from the ski wax, which is applied on the ski board. They are released into the environment via the abrasion from the ski board during the skiing activity. SFAs were predicted to be sorbed to the snow grain surface and consequently released to the underlying (soil) surface after snowmelt (Plassmann et al., 2010). Therefore, the snow and soil were the main source pools for the SFAs in other environmental compartments, like air, especially in the non-skiing season.

This was the first study to measure SFAs present in ski waxes in the ambient air of mountainous skiing area and there was no available air concentration data to be compared to. However, the magnititude of SFA concentrations in air were far lower than this in snow and soil. SFAs were at ng/L level in snow and at μg/m^2 level in soil (Plassmann et al., 2011). As indicated by the difference of inventories between soil and snow, SFAs would be, to some extent, partitioned into the air in real environment, especially for F_6H_{16}, F_8H_{16} and $F_{10}H_{16}$ (Plassmann et al., 2011). The detection of SFAs in the ambient air in our work supported this observation. The low vapor pressure of SFAs (1.1×10^{-4} – 8.7×10^{-7}) (Plassmann et al., 2010) combined with the extremely low SFA levels might imply that the occurrence of SFAs in the atmosphere was due to the particle-based SFAs blew away from the snow or soil surface since particles and aerosols were collected by glass fibers in our active air samplers and treated together with XAD-2. Additionally, compared to the study of Plassmann and Berger (2010), the non-detection of SFAs in ski wax products in this work (result in the section of **3.4.2**) indicted that the SFA levels varied significantly among these products, which could lead to the variations of SFA concentrations in snow and soil pools. The extreme low SFA levels might also attributed to the low SFAs levels in snow and soil in skiing tracks at Zugspitze and Sonnblick. This needs further investigations.

3.6 FTOHs in groundwater from Berlin

The test result is presented in Table 32.The recoveries of ML-FTOHs were from 31% to 84%. 6:2, 8:2 and 10:2 FTOH were detected in groundwater samples. However, the differences in absolute amount between samples and procedure blank were not significant. The study of FTOHs in groundwater was not continued. The more proportion of the extracts should be used for the analysis if the investigation would be conducted in future. Moreover, the sampling efficiency, the extent of aqueous FTOHs retained by XAD-2, and the breakthrough water volume should be tested.

Table 32 FTOHs in tested groundwater samples (absolute amount, pg).

Sample	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH
Procedure blank	n.d.	n.d.	158.8 (<LOQ)	175.7 (<LOQ)
Aqueous	n.d	123.9	216.4	283.0
Filter (particles)	n.d	176.6	241.9	218.7

n.d. : not detected.

LOQ: limit of quantification (185 pg).

3.7 PFCAs and PFSAs in fish samples from the Yangtze River

Short-chain PFSAs (C4 and C6) and PFCAs (C4-C7) were not detected in fish samples, which is in agreement with other studies (Martin et al., 2004; Zhou et al., 2013). PFDS, PFNA and PFDA were also not detected, which may be due to their low concentrations in the Yangtze River. The concentrations of PFSAs and PFCAs are listed in Table 33. PFOS was the dominant compound with concentrations in the range of non-detection to 11.9 ng/g, followed by PFUnDA.

This preliminary experiment showed the bioaccumulation of long chain PFSAs and PFCAs in biota from the Yangtze River. The fishes analyzed are food sources for local population. Intensive studies should be performed to investigate the accumulation of PFSAs and PFCAs in various biota from the Yangtze River and to evaluate the human exposure to these compounds via consumption of fishes and shrimps, etc.

The extraction and clean-up method should be optimized further. PFSAs and PFCAs were not analyzed in Abbottina rivularis, Hemicculter Leuciclus and Pseudorasbora para due to the blockage of the cartridges probably caused by high content of lipids and proteins in sample extracts. Recoveries of PFNA, PFDA, PFUnDA, PFDoDA and PFTriDA were not satisfactory for quantification, which would introduce high uncertainty into results. Although ion-pair extraction with TBA combined with the clean-up by WAX was widely applied in biota samples, it was not suitable for some fish and shrimp samples in this thesis. Other methods, like alkali-assisted extraction, or clean-up with Envi Carb or florisil (Vestergren et al., 2012) could be tested to decrease the matrix effect and improve the recoveries.

Table 33 Concentrations of PFSAs and PFCAs in biota samples from the Yangtze River (ng/g).

Species	PFOS	PFOA	PFUnDA	PFDoDA	PFTriDA
Cyprinus carpio	n.d.	0.5	1.0	n.d.	0.3
black carp	4.9	n.d.	0.8	n.d.	n.d.
Crucian carp	3.3	n.d.	1.0	n.d.	n.d.
Cyprinus carpio	6.2	n.d.	0.7	n.d.	n.d.
Cyprinus carpio	n.d.	n.d.	n.d.	n.d.	n.d.
Macrobrachim nipponense	11.9	n.d.	1.2	0.5	0.2
Grass carp	4.0	n.d.	1.0	n.d.	n.d.
Channa argus	n.d.	0.2	n.d.	n.d.	n.d.

n.d. : not detected.

4 Conclusions

In this thesis, FTOHs were investigated in the house dust, and 8:2 FTOH was the dominant compound. On the basis of FTOH concentrations in house dust, the FTOH intakes via dust ingestion were evaluated for humans. The results showed that the FTOH ingestion via indoor dust was generally low, and only under a worst scenario high intakes should be expected for toddlers. In general, dust ingestion is a minor pathway, but for some subgroups, house dust is an important exposure medium for FTOHs. These findings provide crucial insight regarding human exposure to FTOHs via dust ingestion.

A clean-up method using silica gel deactivated with 10% H_2O was developed for FTOHs, and FTOHs were eluted with the mixture of pentane and DCM (1/1). This method was applied in the active air samples and groundwater samples. The GC performance was stable during the measurement of these samples.

FTOHs were investigated in the Alpine atmosphere. The result indicated that air mass origin was an important factor determining the atmospheric FTOH levels at Zugspitze. Air mass arriving from densely populated and industrialized area contained elevated FTOHs. Wind speed was observed to have a negative effect on the FTOH levels in air masses. ΣFTOH was 7.5 - 41.3 pg/m^3 with 8:2 FTOH being the dominant compound, showing low FTOH concentrations in the Alpine atmospheric environment. FTOH-derived PFOA deposition was estimated to be 0.1 - 1.4 ng/m^2/d. Further investigations should be conducted to investigate the occurrences and levels of PFOA in the Alpine environment, and to elucidate the role of precursors in the distributions of PFOA.

FTOHs could be detected in groundwater collected in Berlin, Germany, implying that FTOHs have a potential of migration to groundwater. However, the differences in absolute amount between samples and procedure blank were not significant. More proportion of the extracts should be used for the analysis if the investigation would be conducted in future. Moreover, the sampling efficiency, the extent of aqueous FTOHs retained by XAD-2, and the breakthrough water volume should be tested.

PFSAs and PFCAs were investigated in sediment cores from the Yangtze River. The total concentrations ranged from non-detection to 724.7 pg/g, showing low contamination of PFSAs and PFCAs in the upstream of the Yangtze River. The differences in analyte

concentrations from different layers were not significant, which may be related with the hydro dynamically-disturbed sedimentation process due to the regulations of TGR. The distribution profiles along the Yangtze River showed that densely populated and industrialized area, such as WZ area, was a potential source of PFSAs and PFCAs.

PFSAs and PFCAs were also investigated in biota from the Yangtze River. Long-chain PFSAs and PFCAs were detected in biota samples. Although ion-pair extraction with TBA combined with clean-up by WAX was widely applied in biota samples, it was not suitable for some shrimp and fish samples in this thesis due to the high interference of matrices. The reason might be the high content of lipid or protein in these samples. Further method optimization should be conducted.

A method for the detection of SFAs on GC-PCI-MS was developed, and the sensitivity was comparable to the published GC-NCI-MS method. Two main fragments were observed, which were assigned as $[M-H]^+$ and $[MH-HF]^+$. They were used as quantifier and qualifier in the measurement. No SFAs were detected in tested ski wax products, indicating large variations in SFAs used in ski wax products. Therefore, only SFA congeners (F_6H_{16}, F_8H_{16}, $F_{10}H_{16}$, $F_{12}H_{16}$, $F_{12}H_{16}$ene and $F_{12}H_{14}$) with available standard solutions were investigated in active air samples from two Alpine summits. A clean-up method using silica gel deactivated with 10% H_2O was optimized for SFAs in air samples, which realized the simultaneous analysis of SFAs and FTOHs. SFAs were sparsely detected in air with concentrations up to 10.7 pg/m^3. The low vapor pressures of SFAs combined with the extremely low SFA levels observed might imply that the occurrence of SFAs in the atmosphere was due to the particle-based SFAs blew away from the snow or soil surface since particles and aerosols were retained by glass fibers in our active air samplers and treated together with XAD-2.

5 References

Ahrens, L., Shoeib, M., Vento, S.D., Codling, G., Halsall, C. Polyfluoroalkyl compounds in the Canadian Arctic atmosphere. Environ. Chem. 2011a, 8, 399-406.

Ahrens, L., Yeung, L.W.Y., Taniyasu, S., Lam, P.K.S., Yamashita, N. Partitioning of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (PFOSA) between water and sediment. Chemosphere 2011b, 85, 731-737.

Andersen, C.S., Fei, C., Gamborg, M., Nohr, E.A., Sorensen, T.A., Olsen, J. Prenatal exposures to perfluorinated chemicals and anthropometry at 7 years of age. Am. J. Epidemiol. 2013, 178, 921-927.

Andersen, S.M.P., Nielsen, O.J., Hurley, M.D., Ball, J.C., Wallington, T.J., Ellis, D.A., Martin, J.W., Mabury, S.A. Atmospheric chemistry of 4:2 fluorotelomer alcohol (n-$C_4F_9CH_2CH_2OH$): products and mechanism of Cl atom initiated oxidation in the presence of NO_x. J. Phys. Chem. A 2005, 109, 1849-1856.

Armitage, J., Cousins, I.T., Buck, R.C., Prevedouros, K., Russell, M.H. Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. Environ. Sci. Technol. 2006, 40, 6969-6975.

Arp, H.P.H., Niederer, C., Goss, K. Predicting the partitioning behavior of various highly fluorinated compounds. Environ. Sci. Technol. 2006, 40, 7298-7304.

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

Barton, C.A., Kaiser, M.A., Russell, M.H. Partitioning and removal of perfluorooctanoate during rain events: the importance of physical-chemical properties. J. Environ. Monit. 2007, 9, 839-846.

Becker, A.M., Gerstmann, S., Frank, H. Perfluorooctanoic acid and perfluorooctane sulfonate in the sediment of the Roter Main river, Bayreuth, Germany. Environ. Pollut. 2008, 156, 818-820.

Benskin, J.P., Ahren, L., Muir, D.C.G., Scott, B.F., Spencer, C., Rosenberg, B., Tomy, G., Kylin, H., Lohmann, R., Martion, J.W. Manufacturing origin of perfluorooctanoate (PFOA) in Altantic Canadian Arctic seawater. Environ. Sci. Technol. 2012, 46, 677-685.

Bhhatarai, B., Gramatica, P. Prediction of aqueous solubility, vapor pressure and critical micelle concentration for aquatic partitioning of perfluorinated chemicals. Environ. Sci. Technol. 2010, 45, 8120-8128.

Bjoerklund, J.A., Thuresson, K., De Wit, C.A. Perfluoroalkyl compounds (PFCs) in indoor dust: concentrations, human exposure estimates, and sources. Environ. Sci. Technol. 2009, 43, 2276-2281.

Brace, N.O. Long chain alkanoic and alkenoic acids with perfluoroalkyl terminal segments. J. Org. Chem. 1962, 27, 4491-4498.

Brandsma, S.H., Smithwick, M., Solomon, K., Small, J., de Boer, J., Muir, D.C.G. Dietary exposure of rainbow trout to 8:2 and 10:2 fluorotelomer alcohols and perfluorooctane sulfonamide: uptake, transformation and elimination. Chemosphere 2011, 82, 253-258.

Broniatowski, M., Dynarowicz-Latka, P. Semifluorinated alkanes-primitive surfactants of fascinating properties. Adv. Colloid Interface Sci. 2008, 138, 63-83.

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., Voogt, P.D., Jensen, A.A., Kannan, K., Mabury, S.A., van Leeuwen, P.J. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integrated Environ. Assess. Manag. 2011, 7, 513-541.

Buhrke, T., Kibellus, A., Lampen, A. *In vitro* toxicological characterization of perfluorinated carboxylic acids with different carbon chain lengths. Toxicol. Lett. 2013, 218, 97-104.

Burns, D.C., Ellis, D.A., Li, H., McMurdo, C.J., Webster, E. Experimental pKa determination for perfluorooctanoic acid (PFOA) and the potential impact of pKa concentration dependence on laboratory-measured partitioning phenomena and environmental modeling. Environ. Sci. Technol. 2008, 42, 9283-9288.

Butt, C.M., Muir, D.C.G., Mabury, S.A. Elucidating the pathways of poly- and perfluorinated acid formation in rainbow trout. Environ. Sci. Technol. 2010, 44, 4973-4980.

Calafat, A.M., Wong, L.Y., Kuklenyik, Z., Reidy, J.A., Needham, L.L. Polyfluoroalkyl chemicals in the U.S. population: data from the National Health and Nutrition Examination Survey (NHANES) 2003-2004 and comparisons with NHANES 1999-2000. Environ. Health. Persp. 2007, 115, 1596-1602.

Carmosini, N., Lee, L.S. Partitioning of fluorotelomer alcohols to octanol and different

sources of dissolved organic carbon. Environ. Sci. Technol. 2008, 42, 6559-6565.

Chen, H., Zhang, C., Han, J., Yu, Y., Zhang, P. PFOS and PFOA in influents, effluents, and biosolids of Chinese wastewater treatment plants and effluent-receiving marine environments. Environ. Pollut. 2012, 173, 26-31.

Chen, L., Bi, Y., Zhu, K., Hu, Z., Zhao, W., Henkelmann, B., Bernhöft, S., Temoka, C., Schramm, K.-W. Contamination status of dioxins in sediment cores from the Three Gorges Dam area, China. Environ. Sci. Pollut. Res. 2012, 20, 4268-4277.

Clara, M., Gans, O., Weiss, S., Sanz-Escribano, D., Scharf, S., Scheffknecht, C. Perfluorinated alkylates substances in the aquatic environment: an Austrian case study. Water Res. 2009, 43, 4760-4768.

D'Hollander, W., Roosens, L., Covaci, A., Cornelis, C., Reynders, H., Campenhout, K.V., de Voogt, P., Bervoets, L. Brominated flame retardants and perfluorinated compounds in indoor dust from homes and offices in Flanders, Belgium. Chemosphere 2010, 81, 478-487.

Dinglasan-Panlilio, M.J.A., Mabury, S.A. Significant residual fluorinated alcohols present in various fluorinated materials. Environ. Sci. Technol. 2006, 40, 1447-1453.

Dinglasan-Panlilio, M.J.A., Ye, Y., Edwards, E.A., Mabury, S.A. Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. Environ. Sci. Technol. 2004, 38, 2857-2864.

Dreyer, A., Shoeib, M., Fiedler, S., Barber, J., Harner, T., Schramm, K.-W., Jones, K.C., Ebinghaus, R. Field intercomparison on the determination of volatile and semivolatile polyfluorinated compounds in air. Environ. Chem. 2010, 7, 350-358.

Dreyer, A., Matthias, V., Temme, C., and Ebinghaus, R. Annual time series of air concentrations of polyfluorinated compounds. Environ. Sci. Technol. 2009a, 43, 4029-4039.

Dreyer, A., Weinberg, I., Temme, C., Ebinghaus, R. Polyfluorinated compounds in the atmosphere of the Atlantic and Southern Oceans: Evidence for a Global Distribution. Environ. Sci. Technol. 2009b, 43, 6507-6514.

Du, G., Huang, H., Hu, J., Qin, Y., Wu, D., Song, L., Xia, Y., Wang, X. Endocrine-related effects of perfluorooctanoic acid (PFOA) in zebrafish, H295R steroidogenesis and

receptor reporter gene assays. Chemosphere 2013, 91, 1099-1106.

EFSA (European Food Safety Authority). Opinion of the scientific panel on contaminants in the food chain on perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts (EFSA-Q-2004-163), European Food Safety Authority, Parma, 2008.

Ehresman, D.J., Froehlich, J.W., Olsen, G.W., Chang, S.C., Butenhoff, J.L. Comparison of human whole blood, plasma and serum matrices for the determination of perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA), and other fluorochemicals. Environ. Res. 2007, 103, 176-184.

Ellis, D.A., Martin, J.W., De Silva, A.O., Mabury, S.A., Hurley, M.D., Andersen, S.M.P., Wallington, T.J. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. Environ. Sci. Technol. 2004, 38, 3316-3321.

Ellis, D.A., Martin, J.W., Mabury, S.A. Atmospheric lifetime of fluorotelomer alcohols. Environ. Sci. Technol. 2003, 37, 3816-3820.

Ericson, I., Nadal, M., van Bavel, B., Lindstroem, G., Domingo, J.L. Levels of perfluorochemicals in water samples from Catalonia, Spain: is drinking water a significant contribution to human exposure? Environ. Sci. Pollut. Res. 2008, 15, 614-619.

Fasano, W.J., Carpenter, S.C., Gannon, S.A., Snow, T.A., Stadler, J.C., Kennedy, G.L., Buck, R.C., Korzeniowski, S.H., Hinderliter, P.M., Kemper, R.A. Absorption, distribution, metabolism, and elimination of 8-2 fluorotelomer alcohol in the rat. Toxicol. Sci. 2006, 91, 341-355.

Ferrey, M.L., Wilson, J.T., Adair C., Su, C.M., Fine, D.D., Liu, X.Y., Washington, J.W. Behavior and fate of PFOA and PFOS in sandy aquifer sediment. Ground Water Monit. R. 2012, 32, 63-71.

Fiedler, S., Pfister, G., Schramm, K.-W. Poly- and perfluorinated compounds in household consumer products. Toxicol. Environ. Chem. 2010, 92, 1801-1811.

Fiedler, S.A. Method development and determination of anthropogenic poly- and perfluorinated compounds in air, water, soil, house dust and several consumer products. Ph.D Dissertation, Technische Universität München, Munich, 2010.

Fraser, A.J., Webster, T.F., Watkins, D.J., Nelson, J.W., Stapleton, H.M., Calafat, A.M., Kato, K., Shoeib, M., Vieira, V.M., McClean, M.D. Polyfluorinated compounds in serum linked

to indoor air in office Environments. Environ. Sci. Technol. 2012, 46, 1209-1215.

Fromme, H., Tittlemier, S.A., Voelkel, W., Wilhelm, M., Twardella, D. Perfluorinated compounds - exposure assessment for the general population in western countries. Int. J. Hyg. Environ. Health. 2009, 212, 239-270.

Gao, Y., Li, X., Guo, L.H. Assessment of estrogenic activity of perfluoroalkyl acids based on ligand-induced conformation state of human estrogen receptor. Environ. Sci. Technol. 2013, 47, 634-641.

Gauthier, S.A., Mabury, S.A. Aqueous photolysis of 8:2 fluorotelomer alcohol. Environ. Toxicol. Chem. 2005, 24, 1837-1846.

Goss, K., Bronner, G., Harner, T., Hertel, M., Schmidt, T.C. The partition behavior of fluorotelomer alcohols and olefins. Environ. Sci. Technol. 2006, 40, 3572-3577.

Guo, F., Zhong, Y., Wang, Y., Li, J., Zhang, J., Liu, J., Zhao, Y., Wu, Y. Perfluorinated compounds in human blood around Bohai Sea, China. Chemosphere 2011, 85, 156-162.

Haug, L.S., Huber, S., Schlabach, M., Becher, G., Thomsen, C. Investigation on per- and polyfluorinated compounds in paired samples of house dust and indoor air from Norwegian homes. Environ. Sci. Technol. 2011, 45, 7991-7998.

Hemat, H., Wilhelm, M., Voelkel, W., Mosch, C., Fromme, H., Wittsiepe, J. Low serum levels of perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and perfluorohexane sulfonate (PFHxS) in children and adults from Afghanistan. Sci. Total Environ. 2010, 408, 3493-3495.

Higgins, C.P., Luthy, R.G. Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. 2006, 40, 7251-7256.

Hiltbrunner, E., Schwikowski, M., Körner, C. Inorganic nitrogen storage in alpine snow pack in the Central Alps (Switzerland). Atmos. Environ. 2005, 39, 2249-2259.

Hong, S., Khim, J.S., Park, J., Kim, M., Kim, W.K., Jung, J., Hyum, S., Kim, J.G., Lee, H., Choi, H.J., Codling, G., Giesy, J.P. In situ fate and partitioning of waterborne perfluoroalkyl acids (PFAAs) in the Youngsan and Nakdong River Estuaries of South Korea. Sci. Total Environ. 2013, 445-446, 136-145.

Huber, S., Haug, L.S., Schlabach, M. Per- and polyfluorinated compounds in house dust and indoor air from northern Norway - a pilot study. Chemosphere 2011, 84, 1686-1693.

Ishibashi, H., Yamauchi, R., Matsuoka, M., Kim, J.-W., Hirano, M., Yamaguchi, A., Tominaga, N., Arizono, K. Fluorotelomer alcohols induce hepatic vitellogenin through activation of the estrogen receptor in male medaka (*Orzias latipes*). Chemosphere 2008, 71, 1853-1859.

Ishibashi, H., Ishida, H., Matsuoka, M., Tominaga, N., Arizono, K. Estrogenic effects of fluorotelomer alcohols for human estrogen receptor isoforms α and β *in vitro*. Biol. Pharm. Bull. 2007, 30, 1358-1359.

Jabbar, T., Steier, P., Wallner, G., Priller, A., Kandler, N., Kaiser, A. Iodine isotopes (^{127}I and ^{129}I) in aerosols at high altitude Alp stations. Environ. Sci. Technol. 2012, 46, 8637-8644.

Jahnke, A., Ahrens, L., Ebinghaus, R., Berger, U., Barber, J.L., Temme, C. An improved method for the analysis of the volatile polyfluorinated alkyl substances in environmental air samples. Anal. Bioanal. Chem. 2007a, 387, 965-975.

Jahnke, A., Berger, U., Ebinghaus, R., Temme, C. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Afica (53 °N-33 °S). Environ. Sci. Technol. 2007b, 41, 3055-3061.

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

Jardine, I., Fenselau, C. Proton localization in chemical ionization fragmentation. J. Am. Chem. Soc. 1976, 98, 5086-5088.

Jing, P., Rodgers, P.J., Amemiya, S. High lipophilicity of perfluoroalkyl carboxylate and sulfonate: implications for their membrane permeability. J. Am. Chem. Soc. 2009, 131, 2290-2296.

Joensen, U.N., Veyrand, B., Antignac, J.P., Jensen, M.B., Petersen, J.H., Marchand, P., Skakkebaek, N.E., Andersson, A.M., Bizec, B.L., Jorgensen, N. PFOS (perflurorooctane sulfonate) in serum is negatively associated with testosterone levels, but not with semen quality, in healthy men. Hum. Reprod. 2013, 28, 599-608.

Jogsten, I.E., Nadal, M., van Bavel, B., Lindström, G., Domingo, J.L. Per- and polyfluorinated compounds (PFCs) in house dust and indoor air in Catalonia, Spain: implications for human exposure. Environ. Int. 2012, 39, 172-180.

Kaiser, M.A., Larsen, B.S., Kao, C.P.C., Buck, R.C. Vapor pressure of perfluorooctanoic, -nonanoic, -undecanoic, and dodecanoic acids. J. Chem. Eng. Data, 2005, 50, 1841-1843.

Kasper, A., Puxbaum, H., Brantner, B., Paleczek, S. Scavenging efficiency of lead and sulfate in sulfate in supercooled clouds at Sonnblick, 3106 m a.s.l., Austria. Atmos. Environ. 1998, 32, 3967-3974.

Kärrman, A., Domingo, J.L., Llebaria, X., Nadal, M., Bigas, E., van Bavel, B., Lindstroem, G. Biomonitoring perfluorinated compounds in Catalonia, Spain: concentrations and trends in human liver and milk samples. Environ. Sci. Pollut. Res. 2010, 17, 750-758.

Kärrman, A., Ericson, I., van Bavel, B., Darnerud, P.O., Aune, M., Glynn, A., Lignell, S., Lindstroem, G. Exposure of perfluorinated chemicals through lactation: levels of matched human milk and serum and a temporal trend, 1996-2004, in Sweden. Environ. Health Persp. 2007, 115, 226-230.

Kim, J.W., Tue, N.M., Isobe, T., Misaki, K., Takahashi, S., Viet, P.H., Tanabe, S. Contamination by perfluorinated compounds in water near waste recycling and disposal sites in Vietnam. Environ Monit. Assess. 2013, 185, 2909-2919.

Kim, M.H., Wang, N., McDonald, T., Chu, K.-H. Biodefluorination and biotransformation of fluorotelomer alcohols by two alkane-degrading *Pseudomonas* Strains. Biotechnol. Bioeng. 2012, 109, 3041-3048.

Kim, S.K., Shoeib, M., Kim, K.S., Park, J.E. Indoor and ourdoor poly- and perfluoroalkyl substances (PFASs) in Korea determined by passive air sampler. Environ. Pollut. 2012, 162, 144-150.

Kim, S.K., Lee, K.T., Kang, C.S., Tao, L., Kannan, K., Kim, K.R., Kim, C.K., Lee, J.S., Park, P.S., Yoo, Y.W., Ha, J.Y., Shin, Y.S., Lee, J.H. Distribution of perfluorochemicals between sera and milk from the same mothers and implications for prenatal and postnatal exposures. Environ. Pollut. 2011, 159, 169-174.

Kissa, E. Fluorinated surfactants and repellents. 2nd ed. Marcel Dekker: New York, 2001.

Knepper, T.P., Lange, F.T. The handbook of environmental chemistry. Polyfluorinated chemicals and transformation products. New York, 2011, 26-28.

Knobeloch, L., Imm, P., Anderson, H. Perfluoroalkyl chemicals in vacuum cleaner dust from 39 Wisconsin homes. Chemosphere 2012, 88, 779-783.

Kubwabo, C., Kosarac, I., Lalonde, K. Determination of selected perfluorinated compounds and polyfluoroalkyl phosphate surfactants in human milk. Chemosphere 2013, 91, 771-777.

Kubwabo, C., Stewart, B., Zhu, J., Marro, L. Occurence of perfluorosulfonates and other perfluorochemicals in dust from selected homes in the city of Ottawa, Canada. J. Environ. Monit. 2005, 7, 1074-1078.

Kunacheva, C., Tanaka, S., Fujii, S., Boontanon, S.K., Musirat, C., Wongwattana, T., Shivakoti, B.R. Mass flows of perfluorinated compounds (PFCs) in central wastewater treatment plants of industrial zones in Thailand. Chemosphere 2011, 83, 737-744.

Langer, V., Dreyer, A., Ebinghaus, R. Polyfluorinated compounds in residential and nonresidential indoor air. Environ. Sci. Technol. 2010, 44, 8075-8081.

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

Lei, Y.D., Wania, F., Mather, D., Mabury, S.A. Determination of vapor pressures, octanol-air, and water-air partition coefficients for polyfluorinated sulfonamide, sulfonmidoethanols, and telomere alcohols. J. Chem. Eng. Data. 2004, 49, 1013-1022.

Li, J., Del Vento, S., Schuster, J., Zhang, G., Chakraborty, P., Kobara, Y., Jones, K.C. Perfluorinated compounds in the Asian Atmosphere. Environ. Sci. Technol. 2011, 45, 7241-7248.

Liu, W., Chen, S., Harada, K.H., Koizumi, A. Analysis of perfluoroalkyl carboxylates in vacuum cleaner dust samples in Japan. Chemosphere 2011, 85, 1734-1741.

Liu, J.X., Wang, N., Szostek, B., Buck, R.C., Panciroli, P.K., Folsom, P.W., Sulecki, L.M., Bellin, C.A. 6-2 fluorotelomer alcohol aerobic biodegradation in soil and mixed bacterial culture. Chemosphere 2010a, 78, 437-444.

Liu, J.X., Wang, N., Buck, R.C., Wolstenholme, B.W., Folsom, P.W., Sulecki, L.M., Bellin, C.A. Aerobic biodegradation of [^{14}C] 6:2 fluorotelomer alcohol in a flow-through soil incubation system. Chemosphere 2010b, 80, 716-723.

Liu, C., Zhang, X., Chang, H., Jones, P., Wiseman, S., Naile, J., Hecker, M., Giesy, J.P., Zhou, B.S. Effects of fluorotelomer alcohol 8:2 FTOH on steroidogenesis in H295R cells: targeting the cAMP signaling cascade. Toxicol. Appl. Pharm. 2010a, 247, 222-228.

Liu, C., Deng, J., Yu, L., Ramesh, M., Zhou, B.S. Endocrine disruption and reproductive impairment in zebrafish by exposure to 8:2 fluorotelomer alcohol. Aquat. Toxicol. 2010b, 96, 70-76.

Liu, C., Yu, L., Deng, J., Lam, P.K.S., Wu, R.S.S., Zhou, B.S. Waterborne exposure to fluorotelomer alcohol 6:2 FTOH alters plasma sex hoemone and gene trandcription in the hypothalamic-pituitary-gonadal (HPG) axis of zebrafish. Aquat. Toxicol. 2009, 93, 131-137.

Liu, J., Lee, L.S. Effect of fluorotelomer alcohol chain length on aqueous solubility and sorption by soils. Environ. Sci. Technol. 2007, 41, 5357-5362.

Liu, J., Lee, L.S. Solubility and sorption by soils of 8:2 fluorotelomer alcohol in water and cosolvent systems. Environ. Sci. Technol. 2005, 39, 7535-7540.

Loganathan, B.G., Sajwan, K.S., Sinclair, E., Kurmar, K.S., Kannan, K. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. Water Res. 2007, 41, 4611-4620.

Loi, E.I.H., Yeung, L.W.Y., Taniyasu, S., Lam, P.K.S., Kannan, K., Yamashita, N. Trophic magnification of poly- and perfluorinated compounds in a subtropical food web. Environ. Sci. Technol. 2011, 45, 5506-5513.

Mackay, D., Shiu, W.Y., Ma, K.-C., Lee, S.C. Physical-chemical properties and environmental fate for organic chemicals (2nd ed.). Introduction and hydrocarbons (Volume I). Boca Raton, FL, 2006, 620-841.

Mahmoud, M.A.M., Kärrman, A., Oono, S., Harada, K.H., Koizumi, A. Polyfluorinated telomers in precipitation and surface water in an urban area of Japan. Chemosphere 2009, 74, 467-472.

Maisonet, M., Terrell, M.L., McGeehin, M.A., Christensen, K.Y., Holmes, A., Calafat, A.M., Marcus, M. Maternal concentrations of polyfluoroalkyl compounds during pregnancy and fetal and postnatal growth in British girls. Environ. Health Persp. 2012, 120, 1432-1437.

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

Martin, J.W., Chan, K., Mabury, S.A., O'Brien, P.J. Bioactivation of fluorotelomer alcohols in

isolated rat hepatocytes. Chem.-Biol. Interact. 2009, 177, 196-203.

Martin, J.W., Mabury, S.A., O'Brien, P.J. Metabolic products and pathways of fluorotelomer alcohols in isolated rat hepatocytes. Chem.-Biol. Interact. 2005, 155, 165-180.

Martin, J.W., Whittle, D.M., Muir, D.C.G., Mabury, S.A. Perfluoroalkyl contaminants in a food web from Lake Ontario. Environ. Sci. Technol. 2004, 38, 5379-5385.

Meinert, H., Roy, T. Semifluorinated alkanes - A new class of compounds with outstanding properties for use in ophthalmology. Eur. J. Ophthalmol. 2000, 10, 189-197.

Meinert, H., Knoblich, A. The use of semifluorinated alkanes in blood-substitutes. Biomater. Artif. Cells Immobilization Biotechnol. 1993, 21, 583-595.

Moriwaki, H., Takata, Y., Arakawa, R. Concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acis (PFOA) in vacuum cleaner dust collected in Japanese homes. J. Environ. Monit. 2003, 5, 753-757.

Moroi, Y., Yano, H., Shibata, O., Yonemitsu, T. Determination of acidity constants of perfluoroalkanoic acids. Bull. Chem. Soc. Japan 2001, 74, 667-672.

Nabb, D.L., Szostek, B., Himmelstein, M.W., Mawn, M.P., Gargas, M.L., Sweemey, L.M., Stadler, J.C., Buck, R.C., Fasano, W.J. In vitro metabolism of 8-2 fluorotelomer alcohol: interspecies comparisons and metabolic pathway refinement. Toxicol. Sci. 2007, 100, 333-344.

Naile, J.E., Khim, J.S., Hong, S., Park, J., Kwon, B.-O., Ryu, J.S., Hwang, J.H., Jones, P.D., Giesy, J.P. Distributions and bioconcentration characteristics of perfluorinated compounds in environmental samples collected from the west coast Korea. Chemosphere 2013, 90, 387-394.

Nakayama, T., Takahashi, K., Toft, A., Andersen, M.P.S., Nielsen, O.J., Waterland, R.L., Buck, R.C., Hurley, M.D., Wallington, T.J. Atmospheric chemistry of $CF_3CH=CH_2$ and $C_4F_9CH=CH_2$: gas-phase reactions with Cl atoms and OH radicals. J. Phys. Chem. A 2007, 111, 909-915.

Napoli, M. Diblock and triblock semifluorinated n-alkanes: preparations, structural aspects and applications. J. Fluorine Chem. 1996, 79, 59-69.

Napoli, M., Krotz, L., Conte, L. Mass spectrometric studies on some $F(CF_2)_n(CH_2)_mH$ semifluorinated alkanes. Rapid Commun. Mass Sp. 1993, 7, 1012-1016.

Nilsson, H., Kärrman, A., Rotander, A., van Bavel, B., Lindström, G., Westberg, H. Inhalation exposure to fluorotelomer alcohols yield perfluorocarboxylates in human blood? Environ. Sci. Technol. 2010, 44, 7717-7722.

Nizzetto, L., Cassani, C., Guardo, A.D. Deposition of PCBs in mountains: the forest filter effect of different forest ecosystem types. Ecotox. Environ. Safe 2006, 63, 75-83.

NoMiracle: Report on the large-scale, predicted fate and exposure of perfluorooctanoic acid including evaluation against monitoring data; D.2.4.8; Stockholm University: Sweden, 2007; http://nomiracle.jrc.ec.europa.eu/webapp/ViewPublicDeliverables.aspx (accessed in May, 2013).

Oda, Y., Nakayama, S., Harada, K.H., Koizumi, A. Negative results of *umu* genotoxicity test of fluorotelomer alcohols and perfluorinated alkyl acids. Environ. Health Prev. Med. 2007, 12, 217-219.

Offenthaler, I., Bassan, R., Belis, C., Garo-Stach, I., Ganz, S., Iozza, S., Jakobi, G., Kaiser, A., Kirchner, M., Knoth, W., Kräuchi, N., Levy, W., Moche, W., Nurmi-Legat, J., Raccanelli, S., Schramm, K.-W., Schröder, P., Sedivy, I., Simoncic, P., Staudinger, M., Thanner, G., Uhl, M., Vilhar, U., Weiss, P. Monarpop Technical Report, Federal Ministry of Agriculture, Forestry, Environment and Water Management: Wien, Austria, 2009.

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

Paiano, V., Generoso, C., Mandich, A., Traversi, I., Palmiotto, M., Bagati, R., Colombo, A., Davoli, E., Fanelli, R., Fattore, E. Persistent organic pollutants in sea bass (*Dicentrarchus labrax L.*) in two fish farms in the Mediterranean Sea. Chemosphere 2013, 93, 338-343.

Pankow, J. F. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. Atmos. Environ. 1987, 21, 2275-2283.

Piekarz, A.M., Primbs, T., Field, J.A., Barofsky, D.F., Simonich, S. Semivolatile fluorinated organic compounds in Asian and Western U.S. air masses. Environ. Sci. Technol. 2007, 41, 8248-8255.

Plassmann, M.M., Denninger, A., Berger, U. Environmental occurrence and fate of semifluorinated n-alkanes in snow and soil samples from a ski area. Chemosphere 2011, 85, 1458-1463.

Plassmann, M.M., Meyer, T., Lei, Y.D., Wania, F., Mclachlan, M.S., Berger, U. Theoretical and experimental simulation of the fate of semifluorinated n-alkanes during snowmelt. Environ. Sci. Technol. 2010, 44, 6692-6697.

Plassmann, M.M., Berger, U. Trace analytical methods for semifluorinated n-alkanes in snow, soil, and air. Anal. Chem. 2010, 82, 4551-4557.

Qazi, M.R., Hassan, M., Nelson, B.D., DePierre, J.W., Abedi-Valugerdi, M. Sub-acute, moderate-dose, but not short-term, low-dose dietary pre-exposure of mice to perfluorooctanoate aggravates concanavalin A induce hepatitis. Toxicol. Lett. 2013, 219, 1-7.

Rao, N.S., Baker, B.E. Textile finishes and fluorosurfactants. In: Banks, R.E., Smart, B.E., Tatlow, J.C. Organofluorine chemistry: Principles and commercial applications. New York, Plenum. 1994, 321-338.

Rayne, S., Forest, K. Theoretical studies on the pKa values of perfluoroalkyl carboxylic acids: Non-helicl conformation acidity constants for n-perfluorooctanoic acid (n-PFOA). Nature Proc. 2009. http://precedings.nature.com/documents/3837/version/2.

Reistad, T., Fonnum, F., Mariussen, E. Perfluoroalkylated compounds induce cell death and formation of reactive oxygen species in cultures cerebellar granule cells. Toxicol. Lett. 2013, 218, 56-60.

Roosens, L., D'Hollander, W., Bervoets, L., Reynders, H., Van Campenhout, K., Corelis, C., Van Den Heuve, R., Koppen, G., Covaci, A. Brominated flame retardants and perfluorinated chemicals, two groups of persistent contaminants in Belgian human blood and milk. Environ. Pollut. 2010, 158, 2546-2552.

Rosen, M.B., Das, K.P., Wood, C.R., Wolf, C.J., Abbott, B.D., Lau, C. Evaluation of perfluoroalkyl acid activity using primary mouse and human hepatocytes. Toxicology, 2013, 308, 129-137.

Rumsby, P.C., McLaughlin, C.L., Hall, T. Perfluorooctane sulfonate and perfluorooctanoic acid in drinking and environmental waters. Philos. T. Roy. Soc. A 2009, 367, 4119-4136.

Santoro, E., Piccardi, P. Mass sperta of some partially fluorinated aliphatic compounds. Org. Mass Spectrom. 1973, 7, 123-131.

Savitz, D.A., Stein, C.R., Elston, B., Wellenius, G.A., Bartel, S.M., Shin, H.-M., Vieira, V.M.,

Fletcher, T. Relationship of perfluorooctanoic acid exposure to pregnancy outcome based on birth records in the Mid-Ohio valley. Environ. Health Persp. 2013, 120, 1201-1207.

Schecter, A., Malik-Bass, N., Calafat, A.M., Kato, K., Colacino, J.A., Gent, T.L., Hynan, L.S., Harris, T.R., Malla, S., Birnbaum, L. Polyfluoroalkyl compounds in Texas chidren from birth through 12 years of age. Environ. Health Persp. 2012, 120, 590-594.

Schenker, U., Scheringer, M., Macleod, M., Martin, J.W., Cousins, I.T., Hungerbühler, K. Contribution of volatile precursor substances to the flux of perfluorooctanoate to the Arctic. Environ. Sci. Technol. 2008, 42, 3710-3716.

Shi, Y., Pan, Y., Wang, J., Cai, Y. Distribution of perfluorinated compounds in water, sediment, biota and floating plants in Baiyangdian Lake, China. J. Environ. Monit. 2012, 14, 636-638.

Shi, Y., Pan, S., Yang, R., Wang, Y., Cai, Y. Occurrence of perfluorinated compounds in fish from Qinghai-Tibetan Plateau. Environ. Int. 2010, 36, 46-50.

Shivakoti, B.R., Tanaka, S., Fujii, S., Kunacheva, C., Boontanon, S.K., Musirat, C., Seneviratne, S.T.M.L.D., Tanaka, H. Occurrences and behavior of perfluorinated compounds (PFCs) in several wastewater treatment plants (WWTPs) in Japan and Thailand. J. Environ. Monit. 2010, 12, 1255-1264.

Shoeib, M., Harner, T., Webster, G.M., Lee, S.C. Indoor sources of poly- and perfluorinated compounds (PFCs) in Vancouver, Canada: implications for human exposure. Environ. Sci. Technol. 2011, 45, 7999-8005.

Shoeib, M., Vlahos, P., Harner, T., Peters, A., Graustein, M., Narayan, J. Survey of polyfluorinated chemicals (PFCs) in the atmosphere over the northeast Atlantic Ocean. Atmos. Environ. 2010, 44, 2887-2893.

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

Shoeib, M., Harner, T., Vlahos, P. Perfluorinated chemicals in the arctic atmosphere. Environ. Sci. Technol. 2006, 40, 7577-7583.

Sinclair, E., Kim, K.S., Akinleye, H.B., Kannan, K. Quantitation of gas-phase perfluoroalkyl surfactants and fluorotelomer alcohols released from nonstick cookware and microwave

popcorn bags. Environ. Sci. Technol. 2007, 41, 1180-1185.

Sindiku, O., Orata, F., Weber, R., Osibanjo, O. Per- and polyfluoroalkyl substances in selected sewage sludge in Nigeria. Chemosphere 2013, 92, 329-335.

So, M.K., Yamashita, N., Taniyasu, S., Jiang, Q.T., Giesy, J.P., Chen, K., Lam, P.K.S. Health risks in infants associated with exposure to perfluorinated compounds in human breast milk from Zhoushan, China. Environ. Sci. Techinol. 2006, 40, 2924-2929.

Steele, W.V., Chirico, R.D., Knipmeyer, S.E., Nguyen, A. Vapor pressure, heat capacity, and density along the saturation line: measurements for benzenamine, butylbenzene, sec-butylbenzene, tert-butylbenzene, 2,2-dimethylbutanoic acid, tridecafluoroheptanoic acid, 2-butyl-2-ethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, and 1-chloro-2-propanol. J. Chem. Eng. Data 2002a, 47, 648-666.

Steele, W.V., Chirico, R.D., Knipmeyer, S.E., Nguyen, A. Measurements of vapor pressure, heat capacity, and density along the saturation line for cyclopropane carboxylic acid, N,N-diethylethanolamine, 2,3-dihydrofuran, 5-hexen-2-one, perfluorobutanoic acid, and 2-phenylpropionaldehude. J. Chem. Eng. Data 2002b, 47, 715-724.

Stock, N.L., Ellis, D.A., Deleebeeck, L., Muir, D.C.G., Mabury, S.A. Vapor pressures of fluorinated telomere alcohols: limitations of estimation methods. Environ. Sci. Technol. 2004, 38, 1693-1699.

Strynar M.J., Lindstrom, A.B. Perfluorinated compounds in house dust from Ohio and North Carolina, USA. Environ. Sci. Technol. 2008, 42, 3751-3756.

Sun, H.W., Li, A., Zhang, T., Zhang, X., He, N., Song, Q., Zhao, L., Sun, L., Sun, T. Perfluorinated compounds in surface waters and WWTPs in Shenyang, China: mass flows and source analysis. Water Res. 2011, 45, 4483-4490.

Thuens, S., Dreyer, A., Sturm, R., Temme, C., Ebinghaus, R. Determination of the octanol-air partition coefficient (K_{OA}) of fluorotelomer alcohols. J. Chem. Eng. Data 2008, 53, 223-227.

Toft, G., Joensson, B.A.G., Lindh, C.H., Giwercman, A., Spano, M., Heederik, D., Lenters, V., Vermeulen, R., Rylander, L., Pedersen, H.S., Ludwocki, J.K., Zviezdai, V., Bonde, J.P. Exposure to perfluorinated compounds and human semen quality in arctic and European populations. Hum. Reprod. 2012, 27, 2532-2540.

Trudel, D., Horowitz, L., Wormuth, M., Scheringer, M., Cousins, I.T., Hungerbuehler, K. Estimating consumer exposure to PFOS and PFOA. Risk Anal. 2008, 28, 251-269.

Tsagogiorgas, C., Krebs, J., Pukelsheim, M., Beck, G., Yard, B., Theisinger, B., Quintel, M., Luecke, T. Semifluorinated alkanes-a bew class of excipients suitable for pulmonary drug delivery. Eur. J. Pharm. Biopharm. 2010, 76, 75-82.

US EPA. Exposure Factors Handbook. EPA/600/R-09/052F. National Center for Environmental Assessment: Washington DC; 2011.

US EPA. Exposure Factors Handbook. EPA/600/P-95/002. National Center for Environmental Assessment: Washington DC; 1997.

Vested, A., Ramlau-Hansen, C.H., Olsen, S.F., Bonde, J.P., Kristensen, S.L., Halldorsson, T.I., Becher, G., Haug, L.S., Ernst, E.H., Toft, G. Associations of *in utero* exposure to perfluorinated alkyl acids with human semen quality and reproductive hormones in adult men. Environ. Health Persp. 2013, 121, 453-458.

Vestergren, R., Ullah, S., Cousins, I.T., Berger, U. A matrix effect-free method for reliable quantification of perfluoroalkyl carboxylic acids and perfluoroalkane sulfonic acids at low parts per trillion levels in dietary samples. J. Chromtogr. A 2012, 1237, 64-71.

Vestergren, R., Cousins, I.T. Tracking the pathways of human exposure to perfluorocarboxylates. Environ. Sci. Technol. 2009, 43, 5565-5575.

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

Viberg, H., Lee, I., Eriksson, P. Adult dose-dependent behavioral and cognitive disturbances after a single neonatal PFHxS dose. Toxicology 2013, 304, 185-191.

Wania, F.A. global mass balance analysis of the source of perfluorocarboxylic acids in the Arctic ocean. Environ. Sci. Technol. 2007, 41, 4529-4535.

Wania, F., Mackay, D. The global distribution mode - A non-steady multicompartment mass balabce model of the fate of persistent organic pollutanys in the global environment (version 1.0); 2000. http://www.utsc.utoronto.ca/~wania/reports/GloboPOP.pdf

Wania, F., Haugen, J.E., Lei, Y.D., Mackay, D. Temperature dependence of atmospheric concentrations of semivolatile organic compounds. Environ. Sci. Technol. 1998, 32,

1013-1021.

Wang, B., Cao, M., Zhu, H., Chen, J., Wang, L., Liu, G., Gu, X., Lu, X. Distribution of perlfuorinated compounds in surface water from Hanjiang River in Wuhan, China. Chemosphere 2013, 93, 468-473.

Wang, J., Zhang, Y., Zhang, F., Yeung, L.W.Y., Taniyasu, S., Yamazaki, E., Wang, R., Lam, P.K.S., Yamashita, N., Dai, J. Age- and gender-related accumulation of perfluoroalkyl substances in captive Chinese alligators (*Alligator sinensis*). Environ. Pollut. 2013, 179, 61-67.

Wang, N., Szostek, B., Buck, R.C., Folsom, P.W., Sulecki, L.M., Gannon, J.T. 8-2 fluorotelomer alcohol aerobic soil biodegradation: pathways, metabolites, and metabolite yields. Chemosphere 2009, 75, 1089-1096.

Washburn, S.T., Bingman, T.S., Braithwaite, S.K., Buck, R.C., Buxton, L.W., Clewell, H.J., Haroun, L.A., Kester, J.E., Rickkard, R.W., Shipp, A.M. Exposure assessment and risk characterization for perfluorooctanoate in selected consumer articles. Environ. Sci. Technol. 2005, 39, 3904-3910.

Webster, E., Ellis, D.A., Reid, L.K. Modeling the environmental fate of perfluorooctanoic acid and perfluorooctanoate: an investigation of the role of individual species partitioning. Environ. Toxicol. Chem. 2010, 29, 1466-1475.

Wu, Y.X., Chang, V.W.C. Development of analysis of volatile polyfluorinated alkyl substances in indoor air using thermal desorption-gas chromatography-mass spectrometry. J. Chromatogr. A 2012, 1238, 114-120.

Xiao, F., Halbach, T.R., Simcik, M.F., Gulliver, J.S. Input characterization of perfluoroalkyl substances in wastewater treatment plants: source discrimination by exploratory data analysis. Water Res. 2012, 46, 3101-3109.

Xu, D., Li, C., Chen, H., Shao, B. Celluar response of freshwater green algae to perfluorooctanoic acid toxicity. Ecotox. Environ. Safe 2013, 88, 103-107.

Xu, Z.L., Fiedler, S., Pfister, G., Henkelmann, B., Mosch, C., Völkel, W., Fromme, H., Schramm, K.-W. Human exposure to fluorotelomer alcohols, perfluorooctane sulfonate and perfluorooctanoate via house dust in Bavaria, Germany. Sci. Total Environ. 2013, 443, 485-490.

Yan, H., Zhang, C.J., Zhou, Q., Chen, L., Meng, X.Z. Short- and long-chain perfluorinated acids in sewage sludge from Shanghai, China. Chemosphere 2012, 88, 1300-1305.

Yarwood, G., Kemball-Cook, S., Waterland, R.L., Korzeniowski, S.H., Buck, R.C., Russell, M. H., Washburn, S.T. High-resolution atmospheric modeling of fluorotelomer alcohols and perfluorocarboxylic acids in the North American Troposphere. Environ. Sci. Technol. 2007, 41, 5756-5762.

Yu, J., Hu, J., Tanaka, S., Fujii, S. Perfluorooctane sullfonate (PFOS) and perfluorooctanoic acid (PFOA) in sewage treatment plants. Water Res. 2009, 43, 2399-2408.

Yoo, H., Washington, J.W., Ellington, J.J., Jenkins, T.M., Neill, M.P. Concentrations, distribution, and persistence of fluorotelomer alcohols in sludge-applied soils near Decatur, Alabama, USA. Environ. Sci. Technol. 2010, 44, 8397-8402.

Zareitalabad, P., Siemens, J., Hamer, M., Amelung, W. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater - a review on concentrations and distribution coefficients. Chemosphere 2013, 91, 725-732.

Zhang, S., Szostek, B., McCausland, P.K., Wolstenholme, B.W., Lu, X., Wang, N., Buck, R.C. 6:2 and 8:2 fluorotelomer alcohol anaerobic biotransformation in digester sludge from a WWTP under methanogenic conditions. Environ. Sci. Technol. 2013, 47, 4227-4235.

Zhang, L., Niu, J., Li, Y., Wang, Y., Sun, D. Evaluating the sub-lethal toxicity of PFOS and PFOA using rotifer *Brachionus calyciflorus*. Environ. Pollut. 2013, 180, 34-40.

Zhang, W., Zhang, Y., Taniyasu, S., Yeung, L.W.Y., Lam, P.K.S., Wang, J., Li, X., Yamashita, N., Dai, J. Distribution and fate of perfluoroalkyl substances in municipal wastewater treatment plants in economically developed areas of China. Environ. Pollut. 2013, 176, 10-17.

Zhang, Y., Meng, W., Guo, C.S., Xu, J., Yu, T., Fan, W.H., Li, L. Determination and partitioning behavior of perfluoroalkylcarboxylic acids and perfluorooctanesulfonate in water and sediment from Dianchi Lake, China, 2012. Chemosphere 2012, 88, 1292-1299.

Zhang, T., Sun, H.W., Wu, Q., Zhang, X.Z., Yun, S.H., Kannan, K. Perfluorochemicals in meat, eggs, and indoor dust in China: assessment of sources and pathways of human exposure to perfluorochemicals. Environ. Sci. Technol. 2010, 44, 3572-3579.

Zhao, L.J., Folsom, P.W., Wolsrenholme, B.W., Sun, H., Wang, N., Buck, R.C. 6:2

Fluorotelomer alcohol biotransformation in an aerobic river sediment system. Chemosphere 2013a, 90, 203-209.

Zhao, L.J., McCauslan, P.C., Folsom, P.W., Wolsrenholme, B.W., Sun, H., Wang, N., Buck, R.C. 6:2 Fluorotelomer alcohol biotransformation in activated sludge from two domestic wastewater treatment plants. Chemosphere 2013b, 92, 464-470.

Zhao, Z., Xie, Z., Moeller, A., Sturn, R., Tang, J., Zhang, G., Ebinghaus, R. Distribution and long-range transport of polyfluoroalkyl substances in the Arctic Atlantic Ocean and Antarctic coast. Environ. Pollut. 2012, 170, 71-77.

Zhou, Z., Liang, Y., Shi, Y., Xu, L., Cai, Y. Occurrence and transport of perfluoroalkyl acids (PFAAs), including short-chain PFAAs in Tangxun Lake, China. Environ. Sci. Technol. 2013, 47, 9249-9257.

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

6 Appendix

List of publications:

1. **Zhenlan Xu**, Stefan Fiedler, Gerd Pfister, Bernhard Henkelmann, Christine Mosch, Wolfgang Völkel, Hermann Fromme, Karl-Werner Schramm. Human exposure to fluorotelomer alcohols, perfluorooctane sulfonate and perfluorooctanoate via house dust in Bavaria, Germany. **Science of the Total Environment**, 2013, 443, 485-490.

List of posters:

1. **Zhenlan Xu**, Bernhard Henkelmann, Karl-Werner Schramm. The occurrences of fluorotelomer alcohols in the Alpine atmosphere: sources, transport, temporal trends. Dioxin 2013, Daegu, South Korea.
2. **Zhenlan Xu**, Bernhard Henkelmann, Karl-Werner Schramm. Human exposure to fluorotelomer alcohols via house dust in Bavaria, Germany'. Urban Environmental Pollution, 2012, Amsterdam, The Netherlands.