Per- and Polyfluoroalkyl Substances in the Environment
–
Shifting toward Fluorinated Alternatives?

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List of Publications

Parts of this thesis have been published in peer and non-peer reviewed journals:

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Franziska Heydebreck, Jianhui Tang, Zhiyong Xie, Ralf Ebinghaus
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Franziska Heydebreck, Jianhui Tang, Zhiyong Xie, Ralf Ebinghaus
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Franziska Heydebreck, Jianhui Tang, Zhiyong Xie, Ralf Ebinghaus
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Vorkommen und Verbreitung von perfluorierten Alkylsubstanzen (PFASs) in europäischen und chinesischen Fluss-Ästuar Systemen
Franziska Heydebreck, Jianhui Tang, Zhiyong Xie, Ralf Ebinghaus
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Abstract

With the increasing number of studies and publications revealing the hazardous properties of per- and polyfluoroalkyl substances (PFASs), there has been a growing concern about the use of PFASs, especially of long-chain compounds, in western countries. Consequently, the production of PFASs and PFASs-based products has been shifted toward countries in Asia as well as toward so-called fluorinated alternatives that have putatively more favorable toxicological and environmental attributes. However, the structural similarity suggests that the fluorinated alternatives are, likewise, persistent chemicals having the potential to accumulate in the environment. This thesis addresses the occurrence and distribution of legacy PFASs and fluorinated alternatives in riverine and coastal areas of Germany, the Netherlands, and China. By presenting first data on the widespread occurrence of fluorinated alternatives in surface waters, the thesis seeks to answer whether the recently identified fluorinated alternatives 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3,-heptafluoropropoxy)-propanoic acid (HFPO-DA) and 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxypropoxy)-propanoic acid (DONA) replace their predecessor substance perfluorooctanoic acid (PFOA) as emerging contaminants in the environment of the areas studied. Additionally, environmental samples from two selected potential sources in the textile and chemical industry were analyzed to gain knowledge about the origins of fluorinated alternatives in the environment. In particular, the textile industry is under pressure to substitute PFOA with alternative chemicals.

Therefore, surface water samples were collected during ship as well as land-based sampling campaigns from the rivers Rhine, Elbe, Weser, Ems, and Xiaoqing as well as the Rhine-Meuse delta, the German Bight, the German coast of the Baltic Sea, the Laizhou Bay, the North Sea, and the Norwegian Sea. Moreover, effluent water from the chemical and textile industry was taken, and air and dust were sampled at a textile manufacturing site and analyzed for PFASs for the first time. Water samples were extracted via solid phase extraction using a polymeric weak anion-exchange material, whereas air and dust samples were extracted via Soxhlet extraction. In the samples, in general, a large set of PFASs, including well-studied compounds, such as PFOA, and less-studied substances, such as perfluoroalkyl phosphinic acids (PFPiAs), were analyzed. Ionic PFASs were quantified via LC-MS/MS, neutral compounds via GC-MS.

The results revealed significant differences in the concentrations and the substance pattern of PFASs found in the study areas. While long-chain legacy PFASs were the main compounds observed in environmental samples from China, the fluorinated alternatives, especially HFPO-DA, were widely spread in river basins and the coastal environment of Germany and the Netherlands. High surface water concentrations of HFPO-DA of up to 91.4 ng/L were detected in the Rhine-Meuse delta, probably attributable to the local fluoropolymer manufacturing industry. Furthermore, HFPO-DA was detected in all samples along the coastlines of the North Sea and the Baltic Sea. In the North Sea, its concentrations were either higher than or similar to those of its predecessor substance PFOA, reflecting the strong impact of this point source in the Rhine-Meuse delta on the pollution burden of the North Sea. In addition, the alternative compound DONA was detected in the River Rhine and in effluent samples from a chemical park in Leverkusen. Its emissions probably originated from downstream users using or processing

fluoropolymers that contain DONA as residue or impurity. The exposure of the environment to fluorinated alternatives highlights the necessity to evaluate these compounds regarding hazardous properties and the potential for long-range transport.

Although the environmentally relevant properties of PFOA have led to an increasing use and, apparently, emission of fluorinated alternatives in Europe, the worldwide demand for fluorine-containing polymer products still results in high emissions of PFOA and perfluorodecanoic acid (PFDA) or their precursors, fluorotelomer alcohols, at industrial sites in China. Therefore, the Chinese samples showed concentrations that were several orders of magnitude higher than those from Germany. In Germany, direct emissions of long-chain legacy PFASs from industrial point sources were not observed. Nevertheless, PFOA is still widely dispersed in all analyzed European surface waters, demonstrating that, even if direct emissions of PFOA have declined, the compound may still be emitted via diffuse sources. In conclusion, the results suggest that activities to restrain PFASs within manufacturing sites and to recycle them during production and use, as well as a proper "end-of-life" treatment of PFASs-containing products and wastes are vital to prevent PFAS emissions into the environment.

Zusammenfassung

Die stetig steigende Anzahl an Studien und Veröffentlichungen, die die umweltbelastenden Eigenschaften von per- und polyfluorierten Alkylverbindungen (PFASs) offenlegen, haben dazu geführt, dass die Verwendung von PFASs, vor allem von langkettigen Verbindungen, zunehmend Besorgnis in der westlichen Welt erregt. Als Folge wurde die Produktion von PFASs und PFASs-basierten Produkten nach Asien ausgelagert. Zudem wird vermehrt auf strukturähnliche fluorierte Alternativsubstanzen, die vermeintlich vorteilhaftere Umwelteigenschaften besitzen, gesetzt. Allerdings impliziert die Strukturähnlichkeit, dass die fluorierten Alternativsubstanzen ebenso persistente Chemikalien sind, die das Potenzial besitzen sich in der Umwelt anzureichern. Die vorliegende Arbeit beschäftigt sich mit dem Vorkommen und der Verteilung von „klassischen" PFASs und fluorierten Alternativsubstanzen in Flüssen und Küstengewässern Deutschlands, der Niederlande und Chinas. Durch die erstmalige Beobachtung des weitverbreiteten Auftretens von fluorierten Alternativsubstanzen in Oberflächengewässern, wird der Frage nachgegangen, ob die fluorierten Alternativsubstanzen 2,3,3,3-Tetrafluor-2-(1,1,2,2,3,3,3,-heptafluorpropoxy)-propansäure (HFPO-DA) und 2,2,3-Trifluor-3-(1,1,2,2,3,3-hexafluor-3-trifluormethoxypropoxy)-propansäure (DONA) ihre Vorgängersubstanz Perfluoroctansäure (PFOA) in den untersuchten Gebieten als Umweltkontaminanten ablösen. Zusätzlich sollen Quellen für einen Eintrag dieser Alternativstoffe identifiziert werden, indem Proben, die der chemischen Industrie und der Textilindustrie entstammen, untersucht werden. Vor allem die Textilindustrie ist einem stetigen Druck ausgesetzt PFOA mit alternativen Chemikalien zu ersetzen.

Zur Beantwortung der wissenschaftlichen Fragestellung wurden Wasserproben aus den Flüssen Rhein, Elbe, Weser, Ems und Xiaoqing sowie dem Rhein-Maas-Delta, der Deutschen Bucht, der deutschen Ostseeküste, der Laizhou Bucht, der Nordsee und dem Europäischen Nordmeer entnommen. Zusätzlich wurden Abwasserproben aus der chemischen Industrie und der Textilindustrie untersucht und, darüber hinaus, zum ersten Mal Luft- und Staubproben, die während der Produktion von Textilien genommen worden waren, auf PFASs analysiert. Die Wasserproben wurden mittels Festphasenextraktion an einem schwachen Anionenaustauscher aufgearbeitet. Die Luft- und Staubproben wurden in einer Soxhlet-Apparatur extrahiert. Im Allgemeinen wurden die Proben auf eine Vielzahl von PFASs hin untersucht, darunter bereits gut bekannte Substanzen wie PFOA und bislang seltener untersuchte Substanzgruppen wie die perfluorierten Phosphinsäuren (PFPiAs). Nachweis und Bestimmung von ionischen PFASs erfolgte mittels LC-MS/MS, wohingegen neutrale Substanzen mittels GC-MS analysiert wurden.

Die Ergebnisse zeigen deutliche Unterschiede in der Schadstoffbelastung und im Verteilungsmuster zwischen den Untersuchungsgebieten. Während die langkettigen „klassischen" PFASs in den Umweltproben aus China dominierten, kamen die fluorierten Alternativsubstanzen, vor allem HFPO-DA, weit verbreitet in Flussgebieten und der küstennahen Umgebung Deutschlands und der Niederlande vor. Hohe Konzentrationen an HFPO-DA von bis zu 91.4 ng/L wurden in Wasserproben aus dem Rhein-Maas-Delta detektiert, die vermutlich auf die dort ansässige Fluorpolymerindustrie zurückzuführen sind. Des Weiteren wurde HFPO-DA in allen Proben entlang der Küstenlinien von Nord- und Ostsee nachgewiesen. In der Nordsee

waren die HFPO-DA Konzentrationen entweder höher oder ähnlich denen der Vorgängersubstanz PFOA, was den starken Einfluss der direkten industriellen Emissionsquellen im Rhein-Maas-Delta auf die Schadstoffbelastung in der Nordsee widerspiegeln könnte. Die Alternativsubstanz DONA wurde im Rhein und in Abwasserproben eines Chemieparks in Leverkusen nachgewiesen. Da DONA im Chemiepark vermutlich nicht hergestellt wird, wäre es denkbar, dass nachgeschaltete Anwender, also Unternehmen, die Fluorpolymere verwenden oder weiterverarbeiten, für das Vorkommen von DONA im Rhein verantwortlich sind. Die Umweltexposition gegenüber den fluorierten Alternativsubstanzen zeigt die Notwendigkeit diese Chemikalien bezüglich ihrer besorgniserregenden Eigenschaften und ihres Potenzials zum Langstreckentransport zu bewerten.

Obwohl die Kenntnisse über die umweltrelevanten Eigenschaften von PFOA zu einem Anstieg der Nutzung von fluorierten Alternativsubstanzen und deren Emissionen in Europa führen, sorgt die weltweite Nachfrage nach fluorbasierten Polymeren weiterhin für hohe Emissionen von PFOA und Perfluordecansäure (PFDA) sowie den entsprechenden Fluortelomeralkoholen, an Industriestandorten in China. Dies zeigt sich daran, dass die chinesischen Proben um mehrere Größenordnungen höhere Konzentrationen aufwiesen als die Proben aus Deutschland. In Deutschland wurden keine direkten industriellen Emissionsquellen für die langkettigen „klassischen" PFASs beobachtet. Dennoch ist PFOA in allen europäischen Oberflächengewässern weit verbreitet. Dies veranschaulicht, dass diese Chemikalie immer noch indirekt emittiert wird, selbst wenn die direkten Emissionen für PFOA zurückgegangen sind. Schlussendlich legen die Ergebnisse nahe, dass sowohl Maßnahmen um PFASs innerhalb von Industriestandorten zurückzuhalten und während der Produktion und Verwendung zu recyceln als auch eine fachgerechte Entsorgung von PFASs-basierten Produkten essentiell sind um zu verhindern, dass PFASs in die Umwelt gelangen.

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Contents

List of Abbreviations

AFFF	aqueous film-forming foams
CE	collision energy
CXP	collision cell exit potential
DMRM	dynamic multiple reaction monitoring
DONA	2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxypropoxy)-propanoic acid
DP	declustering potential
ECHA	European Chemicals Agency
ECF	electrochemical fluorination
EU	European Union
F-53B	2-[(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyl)oxy]-1,1,2,2-tetrafluoroethanesulfonic acid
FASAs	N-alkyl perfluoroalkane sulfonamides
FASEs	N-alkyl perfluoroalkane sulfonamidoethanols
FP	focusing potential
FTACs	fluorotelomer acrylates
FTMACs	fluorotelomer methacrylates
FTOHs	fluorotelomer alcohols
FTUCAs	fluorotelomer unsaturated carboxylic acids
GC-MS	gas chromatography-mass spectrometry
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
IDLs	instrumental detection limits
IQLs	instrumental quantification limits
ISO	International Organization for Standardization
LANUV	Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen
LC-MS/MS	liquid chromatography-mass spectrometry/mass spectrometry
LfU	Bavarian Environmental Protection Office
MDL	method detection limit
MQL	method quantification limit
n.d.	not detected
O/W	oil-in-water
PAPs	fluorotelomer phosphates
PBT	persistent, bioaccumulative, and toxic
PCI	positive chemical ionization
PFAAs	perfluoroalkyl acids
PFASs	per- and polyfluoroalkyl substances
PFCAs	perfluoroalkyl carboxylic acids
PFECAs	per- and polyfluoroalkyl ether carboxylic acids
PFPAs	perfluoroalkyl phosphonic acids
PFPIAs	perfluoroalkyl phosphinic acids
PFSAs	perfluoroalkane sulfonic acids
pK_a	acid dissociation constant

POPs	persistent organic pollutants
POSF	perfluorooctane sulfonyl fluorid
PPARα	proliferator-activated receptor alpha
psi	pound-force per square inch
psig	pound-force per square inch gauge
psu	practical salinity units
PTFE	polytetrafluoroethylene
REACH	Registration, Evaluation, Authorization, and Restriction of Chemicals
SIM	selected ion monitoring
SPE	solid phase extraction
UBA	Umweltbundesamt
USEPA	United States Environmental Protection Agency
vPvB	very persistent and very bioaccumulative
WWTP	wastewater treatment plant

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1 Introduction

It is widely accepted that chemical pollution has adverse implications for the environment and ecosystems. In 2009, it was proposed that chemical pollution is as a planetary boundary, meaning that it can delimitate the resilience of ecosystems and humanity.[1,2] To date, only a small number of chemicals have been banned or restricted under the Stockholm Convention, a global treaty designed to protect the environment and human health from persistent organic pollutants (POPs).[3] One of these chemicals is perfluorooctane sulfonic acid (PFOS),[4] which belongs to the class of per- and polyfluoroalkyl substances (PFASs).

PFASs are chemicals of anthropogenic origin that have been the subject of research for nearly two decades. Since 1950, PFASs have been widely used in numerous industrial and consumer applications due to their beneficial chemical properties, such as the amphiphilic character and the stability of the C-F bond. However, their chemical nature also entails considerable environmental problems. Perfluoroalkyl substances are persistent chemicals and have the potential to be transported over long ranges, with the result that they can be found ubiquitously in the environment, in wildlife, and in humans.[5-8] The increasing number of studies revealing their environmentally harmful behavior have resulted in a serious concern about the use of PFASs, especially of compounds with long carbon chains. For example, perfluorooctanoic acid (PFOA) and the long-chain C_{11} to C_{14} perfluoroalkyl carboxylic acids (PFCAs) have been listed in the candidate list of substances of very high concern by the European Chemicals Agency.[9] Consequently, the production of PFASs has been shifted toward less regulated countries in Asia as well as toward the so-called fluorinated alternatives thought to have more favorable toxicological and environmental attributes.[10-13] Fluorinated alternatives are all types of compounds that are structurally similar to the legacy and well-studied PFASs. They are, for example, salts of per- and polyfluoroalkyl ether carboxylic acids (PFECAs) thus differing only from their predecessor substances by, e.g. ether linkages (cf. Figure 2-2). The structural similarity suggests that the fluorinated alternatives are, likewise, persistent chemicals that have the potential to accumulate in the environment.

So far, studies have focused mainly on the occurrence of PFCAs and perfluoroalkane sulfonic acids (PFSAs), or their precursor compounds, in the environment. However, it has been reported that PFCAs and PFSAs account only for a smaller fraction of organofluorine compounds in environmental samples.[14,15] This highlights the importance of quantifying the less-studied PFASs, especially the recently identified fluorinated alternatives, in environmental samples. Furthermore, knowledge about their sources in the environment is vital to describe pathways of human and environmental exposures as a basis for regulatory measures.

2 General Information on Per- and Polyfluoroalkyl Substances

2.1 Terminology, Classification, and Properties

Per- and polyfluoroalkyl substances (PFASs) are defined as aliphatic substances that contain the perfluoroalkyl moiety $C_nF_{2n+1}^{-}$.[16] The difference between perfluoroalkyl and polyfluoroalkyl substances is exemplified in Figure 2-1. Perfluoroalkyl substances are denoted by a functional group and a carbon chain, on which all hydrogen atoms have been replaced by fluorine atoms, whereas polyfluoroalkyl substances contain at least one fully fluorinated carbon atom within the alkyl chain.

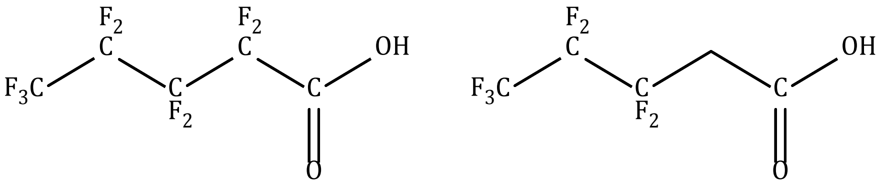
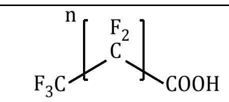
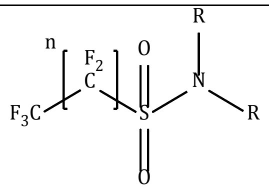
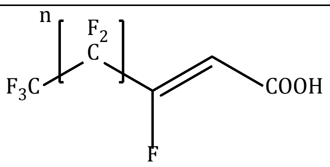
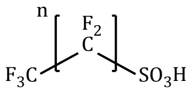
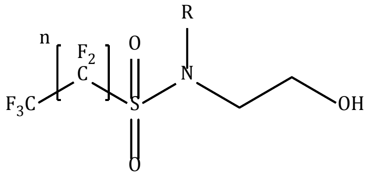
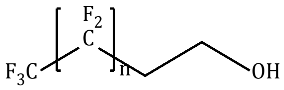
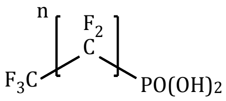
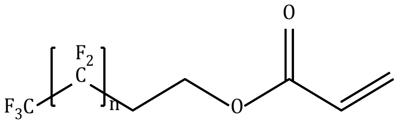
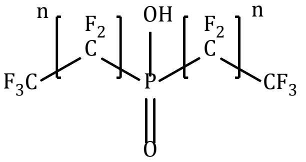
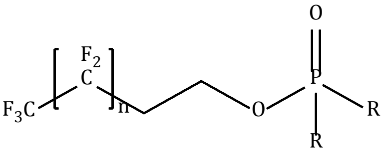
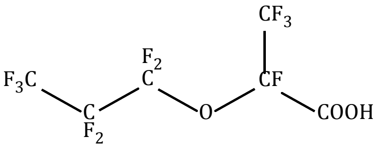
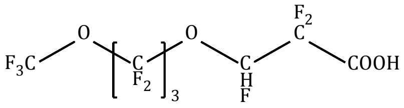


Figure 2-1. Chemical structure of perfluoropentanoic acid (left) and 3,3,4,4,5,5,5-heptafluoropentanoic acid (right).

As illustrated in Table 2-1, PFASs are divided into numerous subgroups depending on the nature of the functional group.

Table 2-1. Classification of study-relevant non-polymeric per- and polyfluoroalkyl substances (PFASs) according to Buck et al.[16]

Perfluoroalkyl substances		**Polyfluoroalkyl substances**
perfluoroalkyl acids (PFAAs)	perfluoroalkane sulfonamido substances	fluorotelomer substances
 perfluoroalkyl carboxylic acids (PFCAs)	 *N*-alkyl perfluoroalkane sulfonamides (FASAs) R = H; CH_3; CH_3-CH_3	 fluorotelomer unsaturated carboxylic acids (n:2 FTUCAs)
 perfluoroalkane sulfonic acids (PFSAs)	 *N*-alkyl perfluoroalkane sulfonamidoethanols (FASEs) R = CH_3; CH_3-CH_3	 fluorotelomer alcohols (n:2 FTOHs)
 perfluoroalkyl phosphonic acids (PFPAs)		 fluorotelomer acrylates (n:2 FTACs)
 perfluoroalkyl phosphinic acids (PFPiAs)		 fluorotelomer phosphates (PAPs) R = OH; O-CH_2-CH_2-C_nF_{2n+1}-
 HFPO-DA perfluoroalkyl ether carboxylic acids (PFECAs)		 DONA polyfluoroalkyl ether carboxylic acids (PFECAs)

The high electronegativity of fluorine (χ=4) induces a strongly polarized carbon-fluorine bond, with a partial positive charge on the carbon ($C^{\delta+}$) and a partial negative charge on the fluorine ($F^{\delta-}$).[17,18] Consequently, the C-F bond is the strongest C-X bond with a bond dissociation energy of 105.4 kcal/mol.[19] For understanding the transport mechanisms and the fate of PFASs in the environment, knowledge of the aqueous solubility and the vapor pressure is essential. For example, perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) may be present in the protonated form or as the dissociated anion depending on the acid dissociation constant pK_a and the pH of the environmental medium. In general, the presence of the strong electron-withdrawing fluorine is associated with an increase in acidity of PFASs compared with their corresponding hydrocarbons.[17] However, reliable pK_as are still under scientific review for numerous PFASs and values between -0.2 and 3.8 have been proposed for perfluorooctanoic acid (PFOA).[20] The protonated and anionic forms have different physicochemical properties. The anionic form has a negligible vapor pressure and a high water-solubility, whereas the protonated form has an appreciable vapor pressure, leading to a higher air-water partition coefficient K_{AW}.[21,22] Under environmentally relevant conditions, where the pH is typically ≥5, almost all PFCA and PFSA molecules are expected to occur as anions.[21,23] Thus, these compounds are preferably present in water bodies and aerosols and mainly undergo environmental transport via ocean currents or particle-bound via air. Fluorotelomer alcohols (FTOHs), on the other hand, have a higher rate of volatilization and, therefore, mainly exist in the gas phase.[24]

Another important physical property is the amphiphilic nature induced by the fluorinated carbon chain (hydrophobic tail) and the functional group (hydrophilic head). In aqueous systems, PFAS molecules accumulate on the water-air interface, with the hydrophobic tail oriented toward air and the hydrophilic head toward water. The work, W_{min}, needed to transport molecules from the interior of a liquid to the surface by a unit area, ΔA, is called the surface tension, γ. The larger the cohesive energy between molecules, the more work is required.[25] The intermolecular interactions between fluorinated carbon chains are weak because of the low polarizability of fluorine, resulting in a low cohesive energy.[17] Consequently, less work is required to transport a PFAS molecule to the water surface, i.e. to remove the hydrophobic part of a PFAS molecule from water, than a water molecule, resulting in a decrease of the surface tension of aqueous systems.[25] The longer the fluorinated carbon chain, the higher is the surface activity, i.e. the efficiency in surface tension reduction.[17] Depending on the number of perfluorinated carbon atoms, PFASs are divided into long-chain PFASs (≥ seven carbon atoms) and short-chain PFASs (< seven carbon atoms),[16] except for PFSAs, which are already considered as long-chain with a chain length of C_6 and higher.[26]

2.2 Manufacturing and Use

PFASs are chemicals of anthropogenic origin. Direct fluorination of hydrocarbons using elemental fluorine is not feasible for commercial production because of the high reactivity of fluorine.[25] Therefore, other fluorine sources are used in various synthesis pathways. The most common manufacturing processes are (i) electrochemical fluorination (ECF) and (ii) telomerization.[16]

ECF was invented by Simons and coworkers in the middle of the 20th century.[27] Organic compounds are dissolved in anhydrous hydrofluoric acid, with an applied voltage of 5 to 7 V, ensuring complete fluorination without developing elemental fluorine.[25,27] Principally, numerous hydrocarbons can be used as starting substances. However, yields of perfluoroalkyl acids and the nature of undesirable by-products considerably vary depending on the starting material.[25] Due to higher yields compared with the alkanesulfonic acids ($C_nH_{2n+1}SO_2H$) and the carboxylic acids ($C_nH_{2n+1}COOH$), alkanesulfonyl fluorides ($C_nH_{2n+1}SO_2F$) and carboxylic acid fluorides ($C_nH_{2n+1}COF$) are preferably used as starting substances, following the reaction scheme:[25,28]

$$C_nH_{2n+1}COF + (2n+1)F^- \xrightarrow{HF} C_nF_{2n+1}COF + (2n+1)H^+ + (4n+2)e^- \qquad (1)$$

All hydrogen atoms of the molecule are replaced by fluorine on the anode surface, while hydrogen is generated at the cathode. The perfluoroalkane sulfonic acid fluorides ($C_nF_{2n+1}SO_2F$) and perfluoroalkyl carboxylic acid fluorides ($C_nF_{2n+1}COF$) are further hydrolyzed to PFSAs and PFCAs or their salts, respectively:[25]

$$C_nF_{2n+1}COF + 2NaOH \rightarrow C_nF_{2n+1}COONa + NaF + H_2O \qquad (2)$$

Reaction with amines would yield perfluoroalkane sulfonamides (FASAs), which can be further converted to perfluoroalkane sulfonamidoethanols (FASEs).[25]

In the telomerization process, a telogen, most commonly pentafluoroethyl iodide (C_2F_5I), reacts with tetrafluoroethylen (C_2F_4), called taxogen, yielding a mixture of even-carbon-numbered perfluoroalkyl iodides:[25]

$$C_2F_5I + nC_2F_4 \rightarrow C_2F_5(C_2F_4)_nI \qquad (3)$$

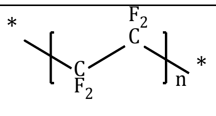
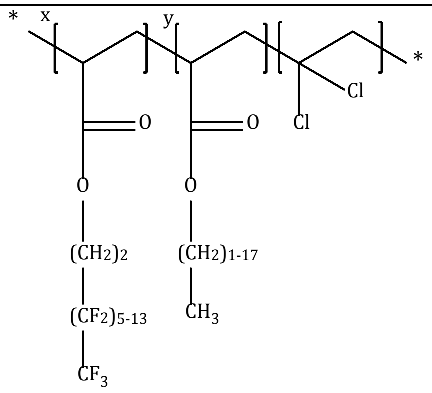
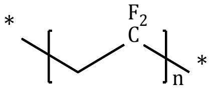
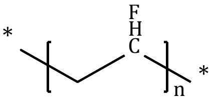
In a second process step, perfluoroalkyl iodides react with ethylene via radical coupling:

$$C_2F_5(C_2F_4)_nI + CH_2CH_2 \rightarrow C_2F_5(C_2F_4)_nCH_2CH_2I \qquad (4)$$

The resulting perfluoroalkylethyl iodides can be further hydrolyzed to fluorotelomer alcohols (FTOHs), which are intermediates for the manufacturing of numerous fluorinated surfactants, such as fluorotelomer acrylates (FTACs) and fluorotelomer phosphates (PAPs).[16,25]

The stability of the C-F bond, the low surface tension, the high surface activity, the amphiphilic character, and the effectiveness at low concentrations (see Chapter 2.1) have led to a widespread use of PFASs.[17] Most of all, they are used as processing aids for the production of fluoropolymers, such as polytetrafluoroethylene (PTFE) (Table 2-2).

Table 2-2. Classification of polymers that involve the use of PFASs according to Buck et al. and Russell et al.[16,29]

Fluoropolymers	Side-chain fluorinated polymers
 polytetrafluoroethylene (PTFE)	 simplified structure of a fluoroacrylate polymer
 polyvinylidene fluoride (PVDF)	
 polyvinyl fluoride (PVF)	

The polymerization of tetrafluoroethylene is usually conducted as an oil-in-water (O/W) emulsion. PFASs are used to facilitate the polymerization by solubilizing the fluoromonomer and by obtaining a fine particle size distribution of the fluoropolymer.[16,30] The ammonium salts of PFOA and perfluorononanoic acid (PFNA) were traditionally used as processing aids. However, because of environmental concerns, the major historic producers have discontinued the use of PFOA and PFNA, resulting in the application of per- and polyfluoroalkyl ether carboxylic acids (PFECAs) (see Chapter 2.4). The majority of fluoropolymers are sold as solids, with >99% of the fluorosurfactant thermally destroyed during the drying process.[31] Besides, fluoropolymers are sold as aqueous dispersions, which are used for the coating of, for example, metal and fabric surfaces. The fluorosurfactants are further destroyed during the curing of the polymer if high temperatures are applied.

Additionally, PFASs are used for the manufacturing of side-chain fluorinated polymers (Table 2-2). Prevalent raw materials for the manufacturing of side-chain fluorinated polymers that are used for the finishing of textiles are FTACs, fluorotelomer methacrylates (FTMACs), or FASEs.[32] Aqueous dispersions of these polymers typically contain 80% water, 20% polymer, and 0.5% unreacted and unbound residuals, such as FTOHs.[16,29] By lowering the critical surface tension of a given surface, side-chain fluorinated polymers impart water, oil, soil, and stain repellency to, for example, textiles, leather, and papers.[32] The resistance to soil is achieved further by increasing the hardness of a surface, considering that a hard surface has a smaller contact area with soil particles than a soft and deformable one.[32] Fluoromonomers are typically copolymerized with nonfluorinated hydrophobic monomers, such as vinyl monomers, to enhance repellency and durability performances, while reducing the amount of cost-intensive fluorinated repellents at the same time.[25,32] The repellent effectiveness can also be improved by a copolymerization with hydrophilic monomers based on, for example, poly(oxyethylene), resulting in an enhanced soil-release in the presence of aqueous detergents.[25]

The unique properties of PFASs result further in their use as wetting agents in paints, cleaning formulations, pesticides, and aqueous film-forming foams (AFFF).

2.3 Environmental Concerns

PFASs are emitted during their entire life cycle, i.e. during their production, use, and disposal.[33-35] As mentioned in Chapter 2.1, the C-F bond is the strongest C-X bond and is, thus, stable against biotic and abiotic degradation.[36-38] Consequently, perfluoroalkyl substances are persistent chemicals with long half-lives that cannot be determined experimentally. In contrast, polyfluoroalkyl substances may be subject to environmental degradation processes due to their methylene groups.[28] However, degradation studies have shown that polyfluoroalkyl substances, such as FTOHs and FASEs, are transformed ultimately into persistent perfluoroalkyl substances, such as PFCAs and PFSAs.[39-43] Thus, the widespread and longtime use of PFASs in general, and the stable properties of PFCAs and PFSAs in particular, entails that PFASs are being found ubiquitously in the environment, in wildlife, and in humans, even in remote areas where industrial sources are nonexistent.[5-8]

Furthermore, PFOS and several long-chain PFCAs have been identified as (very) bioaccumulative chemicals with the potential for biomagnification.[44-48] In contrast to traditional organohalogen POPs, they do not primarily accumulate in fat tissues because fluorination of saturated aliphatic groups usually decrease the lipophilicity of a molecule.[17] The nonbonding electron pairs are held tightly by the fluorine because of its high electronegativity, resulting in a poor polarizability and a low susceptibility of carbon-fluorine bonds to van der Waals interactions.[19] Instead, PFASs are mainly found in blood, liver, and kidney samples because of a high affinity to associate with probably both proteins, such as serum albumin and liver fatty acid binding protein (L-FABP), and phospholipid membranes.[5,49-53] Precise binding mechanisms are still under discussion. For protein binding, it was proposed that PFAAs behave similarly to endogenous fatty acids, involving hydrophobic and ionic interactions, induced by the PFAAs' amphiphilic nature, as wells as covalent and hydrogen bonds to proteins.[49-51,54,55] The association with phospholipid membranes may be attributed to hydrogen bonds and electrostatic interactions between the hydrophilic headgroups.[56,57]

The interaction of PFAAs with proteins and phospholipid membranes may affect biochemical processes. It is generally believed that a major mode of action of the PFAAs is the ligation and activation of the nuclear reporter protein peroxisome proliferator-activated receptor alpha (PPARα), which is, among others, a regulator of the fatty acid metabolism.[58,59] It has been shown that PFOA and PFOS alter the fatty acid metabolism, causing, among others, a decrease in serum lipids and an increase in liver lipids in rodents.[60-62] In contrast to animal studies, epidemiologic literature reveals a positive correlation between PFOA and blood cholesterol,[63] emphasizing that the susceptibility to PFAAs' toxicity differs among species and sexes and that extrapolating animal data to humans comes along with huge uncertainties. Thus, health effects of PFASs in humans remain controversial and a subject for further research. However, PFAAs can cross the placental barrier, causing an exposure of neonates to these chemicals.[64,65] From the mother's blood, PFAAs can also be transferred to breast milk.[65-67] There is some evidence that PFAAs may be associated with immunosuppressive effects, such as reduced anti-rubella antibodies and increased numbers of episodes of common cold and gastroenteritis, in early childhood.[68] Additionally, elimination half-lives of PFAAs were assumed to be highest in humans and were estimated in the order of a few years for long-chain PFAAs,[69-73] emphasizing the strong bioaccumulation potential and the necessity for studies focusing on health effects after long-time exposure. Renal elimination rates for PFAAs tend to decrease with increasing number of carbon atoms,[73-75] resulting in a lower bioaccumulation potential for shorter-chain compounds although they are similarly interactive with albumin.[54,76] However, short-chain PFAAs were observed to accumulate at higher concentrations in shoots of *Zea mays* than long-chain PFAAs.[77] The short-chain alternative perfluoro-1-butane-sulfonamide (FBSA) was also recently found to be bioaccumulative in fish in Canada.[78] Additionally, the solubility of PFAAs increases with decreasing chain-length,[79,80] which makes the short-chain PFAAs more mobile in the environment and problematic if, for example, contaminated surface water is used as a drinking water source.[81] Furthermore, a higher amount of short-chain PFASs or the use of other chemicals that are not necessarily environmentally friendlier, such as polydimethylsiloxanes, is necessary to achieve, for example, a comparable level of water repellency in consumer goods.[82]

In the past, studies focused mainly on the environmental and biochemical behavior of long-chain PFAAs in general, and of PFOA and PFOS in particular, because of their historical and widespread use. However, blood concentrations of especially PFOS are decreasing in countries with a historical PFASs production and use because of the phase-out of perfluorooctane sulfonyl fluorid (POSF)-based products (see Chapter 2.4).[83-86] The same trend can be observed in environmental samples.[87-89] Thus, future studies on environmental and biochemical behavior need to focus on chemicals that are increasingly replacing the legacy compounds.

2.4 Regulatory Actions and their Consequences

PFASs have been the subject of research for nearly two decades. The increasing number of studies and publications revealing their persistence, bioaccumulation, long-range transport, and toxic potential has resulted in a growing concern about the use of PFASs, especially of long-chain compounds. However, up to now only PFOS and related substances based on POSF have been restricted under Annex B of the Stockholm Convention, a global treaty designed to protect the environment and human health from POPs.[3,4] Thus, since 2009, the production and use of POSF-based chemicals is restricted to specific exemptions or acceptable purposes where alternatives do not exist yet or are not readily available, such as for metal plating or certain medical devices. Moreover, PFOS is the only compound that was included as a priority pollutant in the European water framework directive (2000/60/EC) and the directive on environmental quality standards (2008/105/EC).[90,91] Both directives were established to set strategies against the pollution of European waters.

In 2006, a voluntary agreement between the United States Environmental Protection Agency (USEPA) and the eight major global fluoropolymer and fluorotelomer manufacturers was established to 1) reduce emissions and product content of PFOA and related chemicals, i.e. PFOA salts and precursors, by 95% by 2010 and 2) eliminate these chemicals by 2015.[92] In early 2016, the USEPA announced that all participating companies have met the goals of the agreement.[92] In the European Union (EU), PFOA, PFNA, and their ammonium or sodium salts or both are listed in the Candidate List of substances of very high concern according to the European REACH

(Registration, Evaluation, Authorization, and Restriction of Chemicals) regulation because of their persistent, bioaccumulative, and toxic (PBT) properties and their toxicity for reproduction.[9,93] The long-chain C_{11} to C_{14} PFCAs are likewise listed in the Candidate List because of their very persistent and very bioaccumulative (vPvB) behavior, though. A proposal to list PFDA for its suspected PBT properties is currently under review by the European Chemicals Agency (ECHA).[94] The inclusion in the Candidate List is the first step of an authorization procedure, i.e. to list a chemical in the Authorization List (Annex XIV) of the REACH regulation and, consequently, to grant authorization before its use. PFOA and PFOA-related substances have recently been proposed for the inclusion in Annex XIV by the European Commission after a 2-years authorization procedure.[95] Since 2015, there is, moreover, an ongoing proposal to include PFOA and PFOA-related compounds in the annex of the Stockholm Convention.[96] Besides, several downstream users became aware of the environmental concerns of PFASs and are planning to substitute long-chain PFAAs with “short-chain chemistry”, environmental friendlier chemicals or naturally water-resistant materials in the textile industry, aiming to stop the emission of PFOA and PFOS into the environment by the end of 2020.[97,98] The most important fluoropolymer manufacturers have developed their own alternative processing aids, PFASs containing ether linkages and branches (Figure 2-2),[12,16] but information on their properties, production volumes, uses, and environmental behavior is limited.[99] However, HFPO-DA and DONA were detected in surface waters downstream of known industrial discharges of fluorochemical or fluoropolymer production facilities in the Cape Fear and Alz Rivers, respectively,[100-102] demonstrating that the fluorinated alternatives have the potential to spread beyond production sites as well. For replacing PFOS in the metal plating industry, salts of, for example, 6:2 fluorotelomer sulfonic acid are applied.[12] Besides, perfluoroalkyl ether sulfonic acids have been used in China since the late 1970s and are, consequently, “alternatives” overlooked by the scientific community so far.[12,103] F-53B (2-[(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyl)oxy]-1,1,2,2-tetrafluoroethanesulfonic acid) and its predecessor substance PFOS were found at similar concentrations in surface water close to a chrome plating facility.[103]

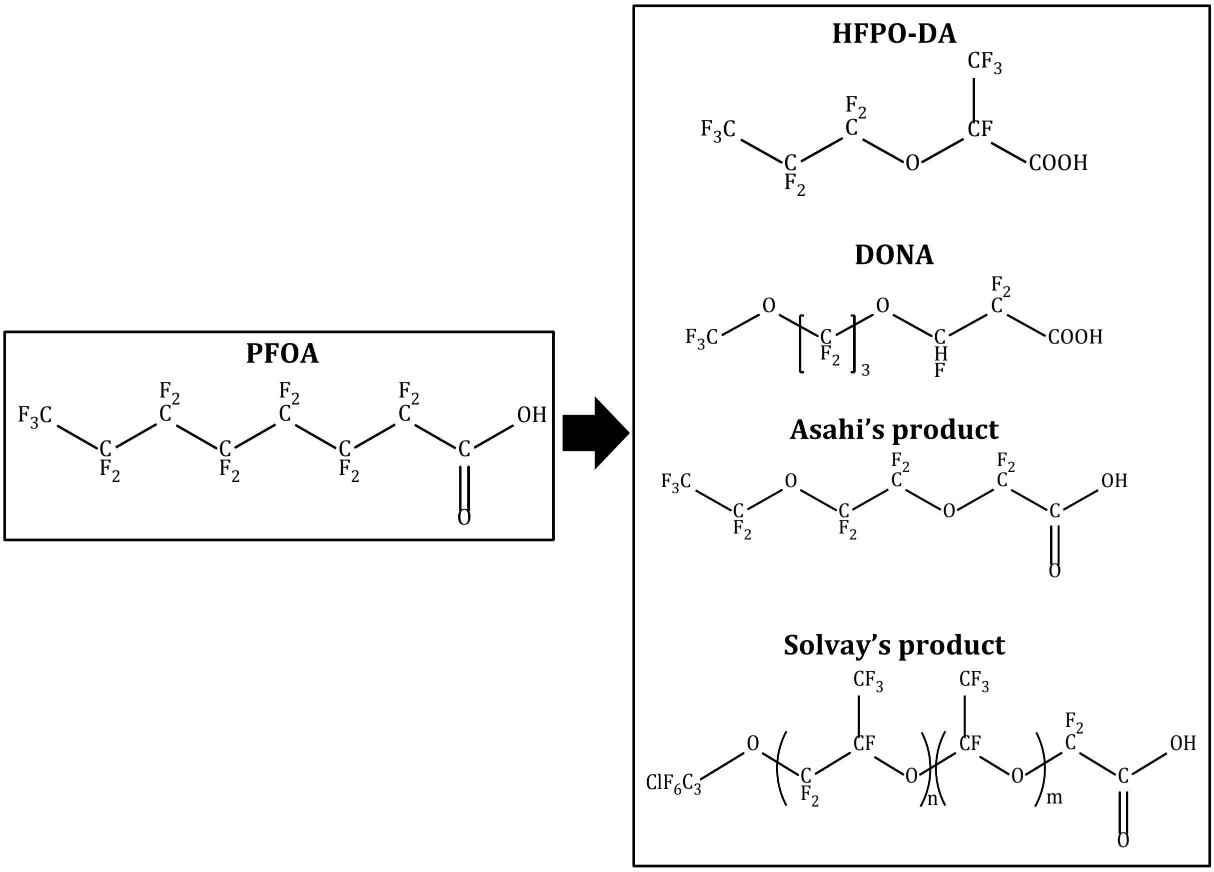


Figure 2-2. PFOA alternative compounds (adapted from Wang et al.)[12]

As another consequence of the increasingly stringent regulations in Europe and the increasing awareness of the environmental concerns in developed western countries, the production of long-chain PFASs and fluoropolymers has been outsourced to less regulated countries in Asia, such as the People's Republic of China. In contrast to developed countries in the EU and North America, the industrial development in China has rapidly expanded primarily over the past decade. The fast economic growth has also led to an increasing demand for fluoropolymers and PFASs-based chemicals. Furthermore, a large portion of PFAAs or fluoropolymer products produced in China is exported to downstream users in other countries, including companies that joined the USEPA agreement on the voluntary phase-out of PFOA, indicating that the global demand for fluoropolymers is currently very strong and possibly not compatible with the ambitious aims of a PFOA phase out.[104]

3 Point of Departure and Research Objectives

When starting this doctoral research, it was found in several studies that legacy per- and polyfluoroalkyl substances, i.e. PFCAs and PFSAs, account only for a smaller fraction of organofluorine compounds in environmental samples.[14,15] The so-called fluorinated alternatives and other per- and polyfluoroalkyl substances, such as perfluoroalkyl phosphonic acids (PFPAs), have just been identified, emphasizing the need to study these emerging compounds in the environment to assess their relevance.[12,105,106] Furthermore, knowledge of the origins of PFASs in general, and fluorinated alternatives in particular, was still limited and data gaps were identified, including the emission volumes of PFASs other than from fluoropolymer production facilities.[107]

In light of this, the objectives of this doctoral research were as follows:

(i) to investigate whether the fluorinated alternatives HFPO-DA and DONA as well as other less-studied PFASs, such as PFPAs, are present in riverine and coastal areas of Germany and China and, if so, to locate the sources of their releases. By comparing the concentrations of the fluorinated alternatives with those of their predecessor substance PFOA, the historically developed differences in pollution levels and distribution patterns of PFASs between Germany and China should become apparent. Furthermore, it should be investigated whether such alternatives have, like PFOA, the potential for long-range transport.

(ii) to investigate whether textile production in China can be a significant point source of PFASs in the environment and, if so, whether previous efforts to substitute “long-chain chemistry” at a textile manufacturing site reflect the pattern of the compounds emitted. Furthermore, exposure of the textile workers to PFASs should be estimated and compared with exposure scenarios from other environments.

The thesis comprises an introduction to and background information about per- and polyfluoroalkyl substances (Chapters 1-2), and the point of departure and research objectives of the thesis (Chapter 3). Results are presented and discussed in Chapters 4-5. Chapter 4, in general, deals with the occurrence and distribution of per- and polyfluoroalkyl substances in European and Chinese surface waters. Chapters 4.1-4.3 present first data on the widespread occurrence of the fluorinated alternative HFPO-DA in surface waters. These chapters were published in an international peer-reviewed journal (cf. Chapter *List of Publications*). Chapters 4.4-4.8 address questions that arose during the research process for Chapters 4.1-4.3. They act as independent “add-on studies” that complement the content-related questions in Chapters 4.1-4.3, but are not published in these. Chapter 5 presents first data on emissions of per- and polyfluoroalkyl substances in a textile manufacturing plant in China via various environmental media. The chapter also addresses the relevance of their emissions for the exposure of the workers at the textile manufacturing site. This chapter, too, was published in an international peer-reviewed journal (cf. Chapter *List of Publications*). Chapter 7 gives a summary of the materials and methods used. Overall conclusions and future perspectives are presented in Chapter 8. The Chapters A-D give supplemental information for Chapters 4-7.

4 Alternative and Legacy Perfluoroalkyl Substances: Differences between European and Chinese River/Estuary Systems (Paper 1)

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Abstract

The production and use of long-chain perfluoroalkyl substances (PFASs) must comply with national and international regulations. Driven by increasingly stringent regulations, their production has been outsourced to less regulated countries in Asia. In addition, the fluoropolymer industry started to use fluorinated alternatives, such as 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid (HFPO-DA). Between August 2013 and September 2014, we investigated the occurrence and distribution of HFPO-DA and legacy PFASs in surface waters of the following river/estuary systems: the Elbe and Rhine Rivers in Germany, the Rhine-Meuse delta in the Netherlands, and the Xiaoqing River in China. Distinct differences were revealed among the study areas; notably: the Chinese samples were highly polluted by an industrial point source discharging mainly perfluorooctanoic acid (PFOA). This particular point source resulted in concentrations more than 6000 times higher than an industrial point source observed in the Scheur River, where HFPO-DA was the dominant compound with a concentration of 91.4 ng/L. Moreover, HFPO-DA was detected in all samples along the coastline of the North Sea, indicating that the compound may be transported from the Rhine-Meuse-delta into the German Bight via the water current. To the best of our knowledge, the fluorinated alternative, HFPO-DA, was detected for the first time in surface waters of Germany and China.

4.1 Introduction

Perfluoroalkyl substances (PFASs), chemicals of anthropogenic origin, have been the subject of research for nearly two decades. Based on their chemical structures, the substances are divided into long-chain PFASs (≥seven carbon atoms) and short-chain PFASs (<seven carbon atoms).[16] Long-chain PFASs are of great concern because they are highly persistent, bioaccumulative, toxic, and ubiquitous in the environment.[108] Their production and use have been restricted to comply with national and international regulations. In 2009, perfluorooctane sulfonic acid (PFOS) and related substances based on perfluorooctane sulfonyl fluoride (POSF) were included in the Stockholm Convention, a global treaty designed to protect the environment and human health from persistent organic pollutants (POPs).[3] Additionally, the long-chain C11 to C14 perfluoroalkyl carboxylic acids (PFCAs), as well as perfluorooctanoic acid (PFOA) and its salt ammonium pentadecafluorooctanoate (APFO), were listed in the Candidate List of substances of very high concern by the European Chemicals Agency.[9] There has been, since October 2014, an ongoing proposal to ban the production, use and placement on the market of PFOA, its salts, and PFOA-related substances in the European Union.[109] As a consequence of these regulations, the production of long-chain PFASs has shifted toward less regulated countries in Asia as well as toward non regulated short-chain PFASs.[110,111] The short-chain PFASs, such as perfluorobutanesulfonic acid (PFBS), are allegedly less toxic and bioaccumulative than the long-chain PFASs, but they are still resistant to environmental degradation.[112] Additionally, their solubility increases as the number of carbon atoms decreases,[79] which makes the substances more mobile and problematic if contaminated surface water is used as a drinking water source.[81] Furthermore, a higher amount of short-chain PFASs is necessary to achieve a comparative level of water and oil repellency. Thus, the fluoropolymer industry has attempted to develop fluorinated substances with more favorable toxicological and environmental attributes.[10,11] Information on structural properties, production volumes, uses, and environmental and biological effects of those alternatives is limited. Some fluorinated alternatives have been identified recently including 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid (HFPO-DA, $C_6HF_{11}O_3$).[12,101] It is the dimer acid of hexafluoropropylene oxide (HFPO) that is used as a monomer or monomer precursor in the synthesis of organofluorine products.[113] The chemical structure is characterized by a carboxylic group that is attached to a perfluoroether chain (Figure A-1). The ammonium salt of HFPO-DA, namely GenX, is known as an APFO or PFOA alternative that has been produced as a processing aid for fluoropolymer resin manufacturing since 2010.[114] The substance has been registered under REACH — a regulation for the registration, evaluation, authorization, and restriction of chemicals in the European Union — with an annual production volume of 10 to 100 tons.[115] The producer developed an exposure control strategy to prevent the substance from spreading beyond the production site.[114] However, GenX is chemically stable and would be persistent if released into the environment. [114,115] Thus it is debatable whether this chemical is a suitable alternative for PFOA. Preliminary results have shown that HFPO-DA and other structurally similar compounds are present in river water downstream of a known historical fluorochemical manufacturer effluent in North Carolina, USA.[101] Other fluorinated alternatives, such as DONA

and F-53B, have been detected in the Alz River[100] or in wastewater from the chrome plating industry.[103] However, for quantification of fluorinated alternatives in environmental samples, analytical standards are mandatory.

Within the scope of this study, HFPO-DA was the only available analytical standard. Thus, the purpose of our study was to investigate whether the fluorinated alternative HFPO-DA is present in riverine and coastal areas of Germany and China and, if so, to locate the sources of its release. By comparing the concentrations of HFPO-DA in the study areas with those of the predecessor substance PFOA and the short-chain PFASs, which were primarily used as alternatives, the differences in pollution levels and distribution patterns of PFASs between Germany and China should become apparent. In addition, a discussion regarding the possible causes behind the different results is warranted.

4.2 Materials and Methods

4.2.1 Sampling Sites

The areas of study were the Lower Rhine River, including its branch streams Waal, Old Meuse, Hollands Diep, Scheur, and Ijssel; the Elbe River; the coastal region of the North Sea, including the estuaries of the Weser and Ems Rivers; and the Xiaoqing River, including Laizhou Bay in the province of Shandong, China (Figure 4-1). All sampling areas were located in industrialized regions. Major urban districts, such as Leverkusen, Hamburg, and Bremen in Germany, Rotterdam in the Netherlands, as well as Jinan, Zibo, and Dongying in China, are located in the river catchment areas. The Rhine River is Germany's longest river, at a total length of 1238 km.[116] It is an important waterway in Europe, connecting large industrial inland complexes with the port of Rotterdam, one of the biggest logistics hubs worldwide. The Rhine River splits downstream of the Dutch-German border forming the Rhine-Meuse delta before discharging into the North Sea. The Elbe River is the third largest river in Central Europe, with a length of approximately 1090 km.[117] The population density is high along the German portion of the river, especially in the estuary — Hamburg had 2382 inhabitants km-2 in 2011[118] — and numerous industrial activities are also located along the river. Both the Rhine and the Elbe catchment areas have a long history of industrialization and have been the seat of chemical, pharmaceutical, paper, and leather-processing industries since the 19th century.[117,119]

In contrast, in the People's Republic of China, the industrial development has rapidly expanded over the last decade. The fast economic growth has led to an increasing demand for the production and use of PFASs and related chemicals. The Xiaoqing River is an artificial river channel that is 233 km long. Once an important waterway, its use has been terminated due to decreased water flow and heavy pollution from domestic sewage and industrial wastewater. The Xiaoqing River receives wastewater from several major cities in which petrochemical, marine chemical, electronic, iron, and steel industries are located. It is, moreover, an important location for the fluoropolymer industry, with manufacturing sites for fluorinated refrigerants and polytetrafluoroethylene (PTFE) reaching production capacities from hundreds to thousands of tons per year.[120] The Xiaoqing River, thus, became one of the most polluted rivers in China,[121] in which high PFOA levels of up to 76.9 ng/g in sediments[122] and 4.5 µg/L in surface water[120] were detected. The river discharges into Laizhou Bay, which is a part of the southern Bohai Sea and an important fishing region in North China.

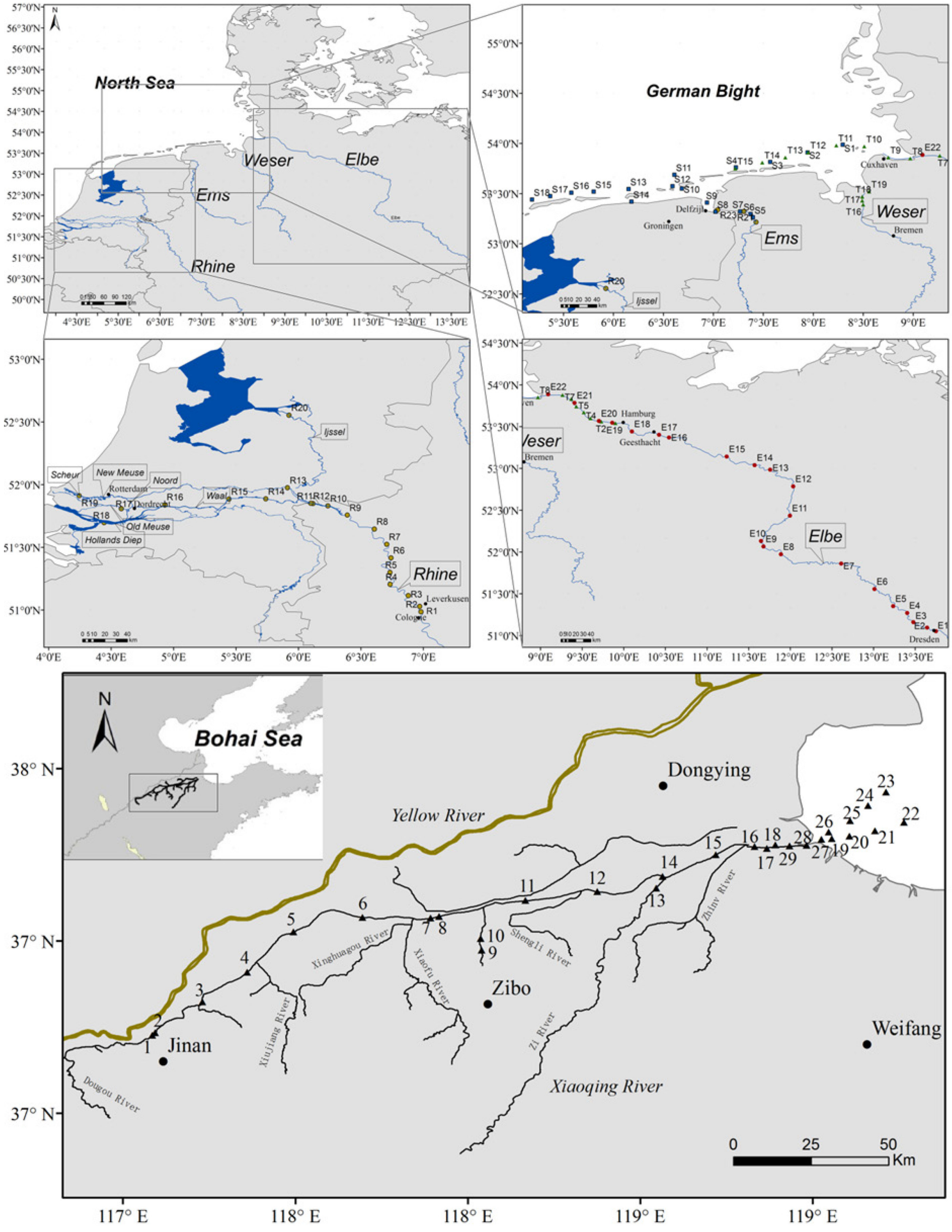

Figure 4-1. Overview of the sampling sites in the Netherlands and Germany (top) and in the People's Republic of China (bottom) (created with the help of Esri ArcGIS 10.2.1.3497 software).

4.2.2 Sample Collection

Five sampling campaigns were performed in Germany, the Netherlands, and the People's Republic of China between August 2013 and September 2014 (Figure 4-1 and Table C-1). One liter of water samples were collected in polypropylene bottles (VWR International) or in polyethylene terephthalate bottles. The samples from the Rhine (August 2013) and Elbe (September 2014) Rivers were cooled during the sampling campaign and filtrated through glass fiber filters (GF/F, Whatman, Ø 47 mm) in the clean laboratory (class 10.000 according to US FED 209D) at the Helmholtz-Zentrum Geesthacht. All glass fiber filters were baked at 450°C for 12 hours before usage. The sampling campaigns in the coastal area of the North Sea (March and August 2014) were carried out on board the R/V Ludwig Prandtl. The filtration of the samples from March 2014 was performed on board, and the samples from August 2014 were frozen to -20°C and filtrated in the clean laboratory. The samples from the Xiaoqing River (April 2014) were cooled during the sampling campaign and filtrated in the laboratory at the Yantai Institute for Coastal Zone Research. In total, 111 samples were analyzed for PFASs as described below.

4.2.3 Chemicals

The following substances were detected during the study: 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3,-heptafluoropropoxy)-propanoic acid (HFPO-DA), perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorooctanesulfonic acid (PFOS), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane-1-sulfonic acid (6:2 FTS), 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonamide (FOSA) (Table A-2). All native and mass-labeled reference standards were purchased from Wellington Laboratories (Guelph, Canada). The following solvents and reagents were used for the sample treatment at Helmholtz-Zentrum Geesthacht, Germany: Methanol (Picograde) and acetone (Picograde) were purchased from LGC Standards (Wesel, Germany). Methanol (LiChroSolv) and ammonia solution 25% (Suprapur) were purchased from Merck (Darmstadt, Germany). Ammonium acetate (LC-MS ultra) was purchased from Sigma Aldrich (Steinheim, Germany). Millipore water was supplied by a Milli-Q Integral 5 (Darmstadt, Germany). In China, purified water was supplied by a Pall Cascada LS system. Methanol and acetone were purchased from Kermel (Tianjin, China) and from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), respectively. Both solvents were distilled before usage.

4.2.4 Sample Extraction

The samples from the coastal area of the North Sea (August 2014) and the Rhine and Elbe Rivers were extracted in a clean laboratory. The samples from the Elbe estuary and German Bight (March 2014) were extracted on board the R/V Ludwig Prandtl, while vacuum drying and elution were performed in the clean laboratory. The samples from the Xiaoqing River were extracted in the laboratory at the Yantai Institute for Coastal Zone Research. For sample extraction, glass funnels and solid phase extraction (SPE) cartridges (Waters Oasis Wax, 150 mg, 6 cm^3, 30 µm particle size) were used. Due to local conditions, the extraction was modified based on the method described by Ahrens et al.[123] The SPE cartridges were cleaned with 10 mL acetone, methanol, and 0.25% ammonium hydroxide in methanol, respectively. The samples were spiked with mass-labeled internal standards before extraction (20 µL, 250 pg/µL). The cartridges were loaded with the samples at approximately 2 mL/min. A volume of 1 L was extracted for a majority of samples. The cartridges were washed with 5 mL Millipore water and then dried using a vacuum pump topped with aluminum foil and then eluted with 10 mL of 0.25% ammonium hydroxide in methanol. The eluates were reduced to 150 µL under a gentle stream of nitrogen (>99.999%) and the mass-labeled [$^{13}C_2$]-PFOA and [$^{13}C_8$]-PFOA were added as injection standards (10 µL, 100 pg/µL). The samples from the Xiaoqing River were treated similarly, but only 400 mL of water were extracted. The dried cartridges were stored at -20°C until elution.

4.2.5 Instrumental Analysis

All samples were analyzed through a HPLC-MS/MS system using a HP 1100 LC system (Agilent Technologies) coupled to an API 3000 mass spectrometer (AB Sciex). Analysis was performed using negative electrospray ionization, with unit resolution in Q1 and Q3. MRM transitions for the target compounds are provided in Table A-2. High performance liquid chromatography was performed using a Synergi 4 µm Fusion-RP-C_{18} column (150x2 mm; Phenomenex) combined with a SecurityGuard cartridge for Fusion-RP HPLC columns (4x2 mm, Phenomenex). The mobile phase consisted of A) water and B) methanol, both added with 10 mmol ammonium acetate. The gradient profile was achieved at a flow rate of 200 µL/min and initiated with an equilibration of 70% A for 10 min, which was decreased to 30% A for 3 min and to 10% A up to 29 min, and then increased to 100% B up to 31 min. 100% B was held for 14 min. The column was heated constantly at 30°C.

4.2.6 Quality Assurance and Quality Control

Analytes were quantified using solvent based calibration curves obtaining the relative response of the target analyte to the amount of an appropriate mass-labeled internal standard. No appropriate internal standards were available for PFBS, PFPeA, and PFHpA. For those substances, internal standards with one or two carbon atoms longer or shorter were used. For HFPO-DA, [$^{13}C_3$]-HFPO-DA was only available for the extraction of the samples from the Rhine River. For the other samples, [$^{13}C_2$]-PFHxA was used, as recovery tests without matrix resulted in an accordance of 106 ± 9%. The mean recoveries of the internal standards ranged from 49 ± 20% ([$^{13}C_4$]-PFOA) to 98 ± 70% ([$^{13}C_5$]-PFNA). All calibration graphs were linear and the correlation coefficients were >0.99 for all analytes. The calibration levels ranged from 0 pg/µL to 500 pg/µL (11-point calibration). Higher concentration levels were added for HFPO-DA, PFBA, PFPeA, PFHpA, PFHxA, and PFOA when analyzing the samples from the Xiaoqing River. Some calculated concentrations had to be considered as semiquantitative, particularly for PFOA (Table A-5). These concentrations were extremely high because of a strong point source near sampling site X10, which made a suitable calibration impracticable. Furthermore, diluting the samples was not a feasible option, as the concentration of the internal standards would be too low to be detected. If the calculated values were above the calibration range, then the real values would be even higher. However, the semiquantitative results should have no effect on the discussion of the Xiaoqing River results. The Limit of Detection (LOD) and the Limit of Quantification (LOQ) are defined as the concentration measured by the analytical instrument at a signal-to-noise ratio (S/N) of 3 and 10, respectively. Accordingly, the LOD and LOQ ranged from 0.1 pg (PFOS) to 0.7 pg (PFPeA) and from 0.3 pg (PFOS) to 2.4 pg (PFPeA), respectively. Methanol was regularly injected as an instrumental blank after injecting five samples. As all PTFE consisting parts had been removed or replaced by stainless steel, polyethylene, or polypropylene, the methanol blanks did not register instrumental contamination. At least five procedural blank samples were extracted with the water samples. The blank contaminations distinguished among the sample batches which were extracted at varying times and locations. The method blank concentrations were taken into consideration when calculating sample concentrations. For the analytes present in the method blanks, the Method Detection Limit (MDL) and the Method Quantification Limit (MQL) were calculated with the blank standard deviations multiplied by the variable from the Student's t table at 98% confidence[124] and by a factor of 10, respectively. For the analytes absent in the method blanks, the sample with the lowest concentration was chosen to extrapolate from the calculated S/N at this concentration to a S/N of 3 and 10, respectively. All values, including the LODs, LOQs, MDLs, MQLs, and mean recoveries, are listed in the Tables A-3 and A-4.

4.2.7 Principal Component Analysis

The Kaiser-Meyer-Olkin measure of sampling adequacy (KMO) was calculated using SPSS Statistics 22 software (IBM, Armonk, NY) to determine the appropriateness of the data set for Principal Component Analysis (PCA). The KMO was calculated to be 0.804, suggesting the data set as suitable for PCA.[125] PCA was applied using OriginPro 9.1G software (OriginLab Corporation, Northampton, MA) to compare statistically the PFASs distribution patterns among sampling sites and to identify the factors that mostly influence the sampling sites. Five principle components were retained as they cumulatively contributed to more than 90% of total variation in the data set.[126] Raw data (measured PFASs concentrations) was normalized by subtracting the average concentration of each compound from the individual concentrations and dividing through the standard deviation. Principal Component 1 (PC1), Principal Component 2 (PC2), and Principal Component 3 (PC3) contributed 49.34%, 21.46%, and 12.44% to total variation in the data set, respectively. The score and loading plots for PC1 and PC2 and for PC2 and PC3 are given in the Supporting Information (Figures A-6 and A-7).

4.3 Results and Discussion

4.3.1 Spatial Distribution of PFASs

The spatial distribution of PFASs was investigated in the Lower Rhine and its branch streams (R1 to R23); the Elbe River (E1 to E22); the nearshore zone of the North Sea, including the Elbe estuary, the Lower Weser and the Lower Ems (T1 to T19 and S1 to S18); and the Xiaoqing River, including the Laizhou Bay (X1 to X29) (Figure 4-1). The alternative substance HFPO-DA and 14 legacy perfluoroalkyl substances were detected. PFASs concentrations at all sampling sites are illustrated in Table A-5, and the detection frequencies, as well as the maximum, minimum, mean, and median for the analyte concentrations, are highlighted in Table A-6. To the best of our knowledge, this study is the first to report quantitative measurements of the fluorinated replacement substance HFPO-DA in surface water.

4.3.2 PFASs in the Lower Rhine and its Branch Streams

HFPO-DA, as well as 13 legacy PFASs, were quantified along the Lower Rhine and its branch streams, including the Ems estuary (Figure 4-2).

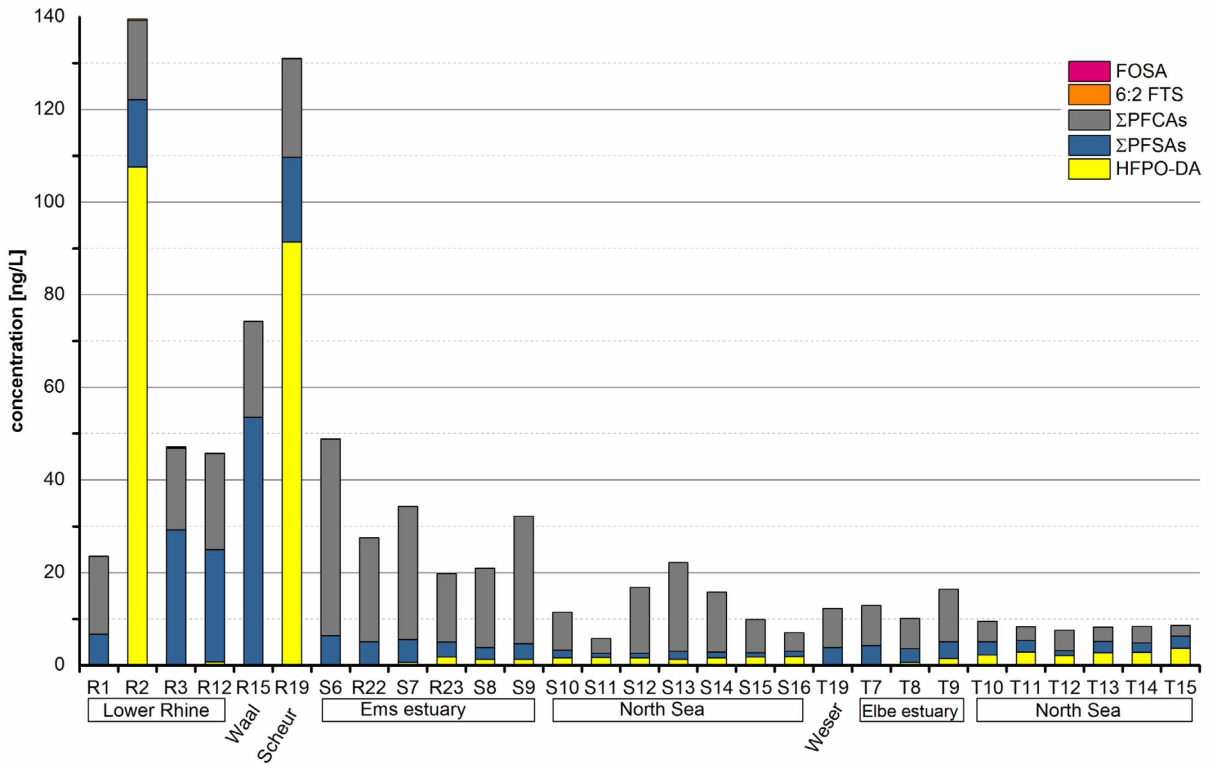

Figure 4-2. PFASs concentrations [ng/L] in selected surface water samples from the Lower Rhine and its branch streams Waal and Scheur (R1-R19, August 2013), from the Ems estuary (S6-S9, August 2014 and R22-R23, August 2013), from the North Sea (S10-S16, August 2014 and T10-T15, March 2014), from the Weser (T19, March 2014), and from the Elbe estuary (T7-T9, March 2014).

The ΣPFASs concentrations ranged from 23.6 ng/L at the city of Cologne (R1) to 140 ng/L at the city of Leverkusen (R2). The pollution burden at station R1 was relatively low; it greatly increased at station R2 where a lot of industrial sites are located. Since 2007, the North-Rhine-Westphalia State Environment Agency (LANUV) has offered to support companies in reducing their discharges of PFASs into the environment.[127] Consequently, total concentrations of PFASs were found to be below the LANUV predefined guideline limit of 1 µg/L. However, the alternative substance HFPO-DA was the dominant compound detected, with a remarkably high concentration of 108 ng/L at sampling site R2 in Leverkusen. It is noteworthy that the concentration of HFPO-DA was approximately three times higher than that of the sum of legacy PFASs. Moreover, HFPO-DA was detected in a relatively low concentration of 0.8 ng/L downstream at station R12, close to the German-Dutch border. Between sampling sites R2 and R12, HFPO-DA was not detected. As HFPO-DA has an estimated low pKa value of 0.06, a high water solubility of 7.1 g/L and a half-life in water of 17280 hours,[128] the detection of HFPO-DA may have resulted from a temporary, discontinuous or accidental discharge of this chemical upstream of sampling site R2. Therefore, it is possible that we measured the maximum concentration of a pollution wave that dropped sharply due to dilution and dispersion processes.[129] As this result stems from a single measurement, it could be that HFPO-DA was observed accidentally.

A second point source of HFPO-DA appears to be located near sampling site R19 in the city of Rozenburg-Rotterdam in the branch stream Scheur, which is a part of the Rhine-Meuse delta. There it was detected at a concentration of 91.4 ng/L, a magnitude comparable to that of sampling site R2 and, similarly, approximately two times greater than that of the sum of legacy PFASs. In 2008, the dominant compound at this sampling site was PFBA at a concentration of 105 ng/L.[130] A possible source of contamination is the Port of Rotterdam with more than 45 chemical plants situated here.[131] The city of Dordrecht may also be a source area, because some fluoropolymer manufacturing industry is located there.[132] HFPO-DA was not detected in the Old Meuse; however, it could have been transported through the Noord and New Meuse Rivers to the Scheur and ultimately into the North Sea, as it was detected at a concentration of 1.8 ng/L at station R23 in the Ems estuary.

The main legacy PFASs were PFBS, PFPeA, and PFOA with average concentrations of 19.5 ± 11.5 ng/L, 5.9 ± 2.1 ng/L and 6.1 ± 1.3 ng/L, respectively. PFBS had higher variations compared with PFPeA and PFOA. The highest PFBS concentration of 50.0 ng/L was detected in the Waal River at station R15. Comparing our results with those from 2008,[130] PFBS pollution was approximately five times lower, most likely due to reducing its discharge into wastewater.[127] Additionally, PFHxS, PFBA, PFHxA, PFHpA, PFNA and PFDA were detected in all samples. PFOS was detected in 74% of the samples, FOSA in 87% of the samples, 6:2 FTS in 26% of the samples, and PFDoDA in one sample.

4.3.3 PFASs in the Elbe River

Fourteen legacy PFASs were quantified along the Elbe River (Figure A-5). PFBS, PFHxS, PFPeA, PFHxA, PFOA, and PFNA were detected in all samples. PFBA and PFUnDA were detected in 91% of the samples. PFDA was detected in 95%, PFHpA in 68%, FOSA in 64%, 6:2 FTS in 59%, PFDoDA in 50%, and PFOS in 36% of the samples. The ΣPFASs concentration ranged from

5.8 ng/L at the city of Dömitz (E15) to 38.8 ng/L at the city of Glückstadt (E21). As expected, levels were lower than those from the Lower Rhine. In general, PFASs pollution in the Elbe River results from diffuse sources rather than from industrial point sources. This hypothesis is statistically supported by the results from PCA. As Figure A-6 illustrates, the sampling sites from the Elbe River are mainly situated on the positive side of PC2, whereas the sampling sites from the Rhine River are dominant on the negative side of PC1. Comparing PC2 with PC3, the separation of the study areas becomes even more obvious (Figure A-7). The compounds PFBS and PFHxS are major contributors to PC3, whereas PFDoDA, PFUnDA, 6:2 FTS, and FOSA are major contributors to PC2, indicating that these compounds, which may come from different sources, are mainly responsible for separating the Elbe River samples from the Rhine River samples.

The dominant compounds in all samples were PFBS, PFPeA, and PFHxA, with average concentrations of 2.8 ± 0.9 ng/L, 3.0 ± 1.8 ng/L, and 3.6 ± 0.9 ng/L, respectively. High ΣPFASs concentrations were detected in samples close to the city of Hamburg and downstream of the city, particularly an increase of PFOS after the barrage in Geesthacht which is located between sampling sites E17 and E18. In 2006, an increase of the PFOS concentration by approximately 190% was detected close to the same location.[123] However, the ΣPFASs concentration of 26.8 ng/L is lower than in 2006 (50.7 ng/L)[123] and similar to 2011 (15 ng/L).[133] Another local source of PFOS pollution appears to be located near sampling site E6, where the highest concentration, 13.1 ng/L, was detected. In 2008, a PFOS concentration of 6.7 µg/L was detected in the same area of the Elbe River.[134] Although the current concentration is much lower than six years ago, the unknown source potentially still exists. PFHpA was not detected between sampling sites E1 and E7, whereas 2.1 ng/L was observed at station E8. This increase in levels could be the result of a nearby chemical plant that produces cleaning agents and other products. The concentration decreased at subsequent stations and increased again after the barrage in Geesthacht (E18). The substance 6:2 FTS was detected in samples mainly from the Upper Elbe and partially from the Middle Elbe. The source may be film-forming fluorinated surfactants used, for example, in aqueous film-forming foams (AFFF). The surfactants are based on perfluoroalkyl betaine, which ultimately could degrade to 6:2 FTS and PFHxA.[127,135]

4.3.4 Transport of PFASs into the North Sea

As mentioned previously, the fluorinated alternative HFPO-DA was detected in the Ems estuary in August 2013 (R23). To locate the source of HFPO-DA pollution and to investigate whether it is equally present in the German Bight, two sampling campaigns were conducted along the German and Dutch coast in March and August 2014. HFPO-DA, as well as 11 legacy PFASs were quantified in the coastal region of the North Sea, including the estuaries of the Elbe, Weser, and Ems Rivers (Figure 4-2). The ΣPFASs concentrations ranged from 4.9 ng/L in the German Bight (S2) to 44.7 ng/L in the Ems River (S6). In general, the ΣPFASs concentrations decreased as seawater dilution increased.

HFPO-DA was detected in all samples along the coastline with average concentrations of 2.3 ± 0.9 ng/L in March and 1.5 ± 0.3 ng/L in August 2014. The substance was not detected in the Elbe, Weser, and Ems Rivers, but was detected in a few samples taken from their estuaries (T8-T9 and S7-S9). These samples had been affected by seawater, as salinity levels were above 9.5 practical salinity units (psu). HFPO-DA was the dominant compound in the samples taken from the German Bight in March 2014 (T10-T15). In the samples from August 2014, the substance was dominant along with PFOA and PFHpA, except in the samples from the Ems estuary. The results confirm that the fluorinated alternative HFPO-DA has not been transported through the Elbe, Weser, and Ems Rivers into the German Bight. We hypothesize that its contamination originates from the Rhine-Meuse-delta and has been transported via the water current[136] along the coastline of the German Bight. A similar assumption has been made to explain higher PFBS concentrations in the German Bight than in the Elbe River in 2009.[123]

The legacy PFASs (PFHxS, PFPeA, PFNA, PFDA, and PFUnDA) were found mainly in the estuaries. Nevertheless, slightly elevated ΣPFASs concentrations were found at sampling sites T9, S9, and between S12 to S14. Results at T9 primarily showed an increase in PFOA, which could be attributed to its proximity to the harbor of Cuxhaven. The sample from site S9 showed mainly an increase in PFHpA and PFOA and was possibly affected by the Ems canal connecting the cities of Groningen and Delfzijl. Generally, a higher average ΣPFASs concentration was observed in the Ems (43.6 ± 1.4 ng/L) than in the Elbe and Weser (13.2 ± 1.4 ng/L and 15.2 ± 2.5 ng/L, respectively). The ΣPFASs concentration in the Elbe estuary was lower in March 2014 than in September 2014, which suggests a possible seasonal influence, also noticed in 2011.[133]

4.3.5 PFASs in the Xiaoqing River

HFPO-DA and 10 legacy PFASs were quantified along the Xiaoqing River (Figure 4-3).

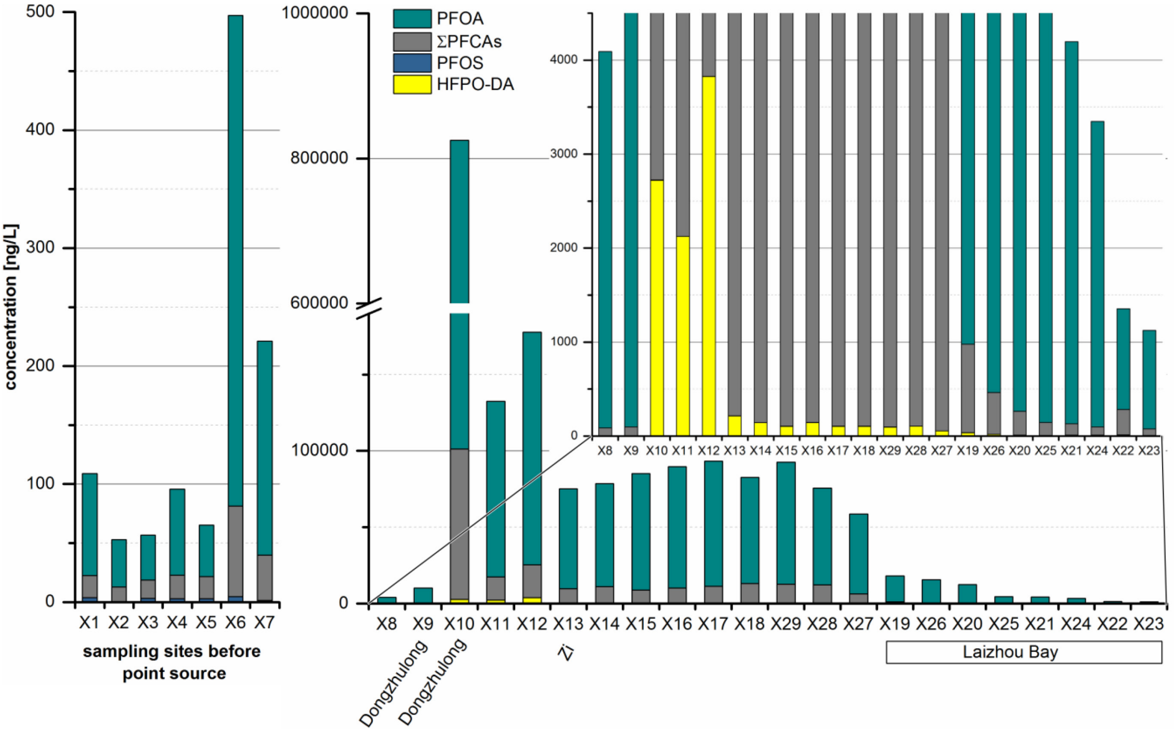

Figure 4-3. PFASs concentrations [ng/L] in surface water along the Xiaoqing River including the tributaries Dongzhulong and Zi, and Laizhou Bay.

The ΣPFASs concentrations ranged from 53.0 ng/L near the city of Jinan (X2) to 825 µg/L in the Dongzhulong River (X10), implying an increase in ΣPFASs concentration by 4 orders of magnitude. The fluorinated alternative HFPO-DA was detected in 76% of the samples with a maximum level of 3.8 µg/L at site X12, which is approximately 36 times higher than the concentration caused by the point source in the Rhine River. Nevertheless, HFPO-DA — and likewise the shorter-chained PFCAs — were a minor component in the Chinese samples compared with the dominant compound PFOA, which made up the highest proportion, 87 ± 9%, in all samples. Interestingly, no short-chain sulfonic acids were detected and PFOS was only observed in low concentrations or below the MDL. A likely explanation for these results is that the sulfonic acids were neither manufactured nor widely applied in industrial processes in this region.[137] Based on the results from PCA, PC1 was characterized by high loadings of HFPO-DA and PFCAs with a chain length of C4 to C10 (Figure A-6). Thus, these compounds mainly contribute to a separation of the Xiaoqing River samples from the European samples, indicating a different source of pollution among the areas of study. Concentration levels of the long-chain carboxylic acids PFDA, PFUnDA, and PFDoDA were similar to those from the Elbe River or below the MDL, indicating that they are less relevant in surface waters of the Xiaoqing River.

The ΣPFASs concentrations between sampling sites X1 and X5 were of a similar level compared to samples from the Rhine River, followed by an eightfold increase at X6, primarily caused by PFOA and PFBA. The ΣPFASs concentration decreased from X6 to X7 and then increased rapidly to X8 by a factor of 19. The sampling sites X7 and X8 are in close proximity; however, the Shengli River flows into the Xiaoqing River between these two sites, indicating that this tributary directly impacts the PFASs pollution of the Xiaoqing River. It is possible that smaller fluoropolymer manufacturing sites which are located in the region of Zouping county are responsible for the increased concentrations from sampling site X6.[120] Along the Xiaoqing River, a high ΣPFASs concentration of 132 µg/L was observed at station X11, which has been attributed to a substantial point source in proximity to sampling site X10 located in the tributary Dongzhulong. PFOA was the dominant compound detected, with a concentration of 724 µg/L, whereas the ΣPFHpA, PFHxA, PFPeA, PFBA, HFPO-DA, PFNA, PFDA, and PFUnDA concentration was 101 µg/L. The percentage of these compounds was only 13%; however, their concentrations were considerably higher compared with the concentrations in the Rhine and Elbe Rivers. The levels from sampling site X10 totaled approximately 6000 times that of sampling site R2 in the Rhine River. The difference between the concentration levels may be due to both higher production volumes and less current technological standards at the wastewater treatment facility. Such high concentrations are almost certainly caused primarily by industrial discharges from fluorochemical or fluoropolymer manufacturing sites. This hypothesis is supported by the fact that, to the best of our knowledge, this area is home to Asia's largest industrial park for fluorine- and silicon-based products, including manufacturing sites for polytetrafluoroethylene (PTFE), tetrafluoroethylene (TFE), and other fluorinated and fluoropolymer fine chemicals with production capacities of several hundred thousand tons per year.[120] In 2011, high concentrations of PFOA were found in human blood samples from Zouping, a neighboring district to Huantai, where the industrial park is located.[138] Our results reveal that the fluoropolymer industry located in the North of Zibo seriously impact the Dongzhulong River, and consequently the Xiaoqing River and the Laizhou Bay, as the following sampling sites are strongly affected by the point source, as described below.

The ΣPFASs concentrations decreased by a factor of six from the sampling sites X10 to X11, followed by a recurring increase at X12. However, PFBA showed a marginally lower concentration at station X12 than at X11. Although the ΣPFASs concentration at station X12 was lower than at station X10, HFPO-DA was the only compound that registered a slightly higher concentration, 3.8 µg/L, than at station X10 (2.7 µg/L). It is possible that the Shengli River contributes to the PFASs pollution of the Xiaoqing River (Figure 4-1). Other tributaries, such as the Zi and Zhinve Rivers, may also impact the PFASs pollution levels of the Xiaoqing River, because the ΣPFASs concentrations increased slightly until sampling site X17. However, it is uncertain what the sources of PFASs are and it could be that these tributaries are likewise directly influenced by the fluoropolymer industry at the Dongzhulong River due to a strongly interconnected waterway network. In 2011, a ΣPFASs concentration of 5.1 µg/L was detected near sampling site X12.[120] Comparing our results with those from 2011, we found an increase in the total concentration by a factor of approximately 35.

From sampling site X17, the concentrations of HFPO-DA decreased to levels similar to the European sampling sites R2 and R19. In general, ΣPFASs concentrations declined steadily towards Laizhou Bay due to dilution with fresh seawater. The concentrations are, however, significantly higher than before the point source input. Because Laizhou Bay is a fishing area and home to numerous macrobenthic species,[121] the impact of the PFASs pollution from the Xiaoqing River can be considered harmful to the aquatic life. However, there are no official limits on the amount of PFASs in surface water. In Germany, for example, it is the task of individual states to establish limits for levels of PFASs in surface water. As mentioned previously, the North-Rhine-

Westphalia State Environment Agency set a guideline limit of 1 µg/L for the sum of 10 PFASs in discharged wastewater.[127] This guideline limit was exceeded in 72% of the Chinese samples. Some German states, such as Bavaria, evaluate their surface waters based on the PNEC (Predicted-No-Effect-Concentration), which represents the concentration of a chemical which has no predicted effect on species in the environment.[139] The PNECaquatic is only available for PFOA (570 µg/L)[140] and PFOS (0.05 µg/L),[139] because necessary toxicity data for the individual PFASs in different aquatic species is limited. The PNECaquatic for PFOA was marginally exceeded in sample X10 from the Dongzhulong River.

4.3.6 Comparison of PFASs Distribution Patterns between European and Chinese River/Estuary Systems

Figure 4-4 illustrates the distribution patterns of PFASs, which was examined on a proportional basis, highlighting the significant differences between the river/estuary systems.

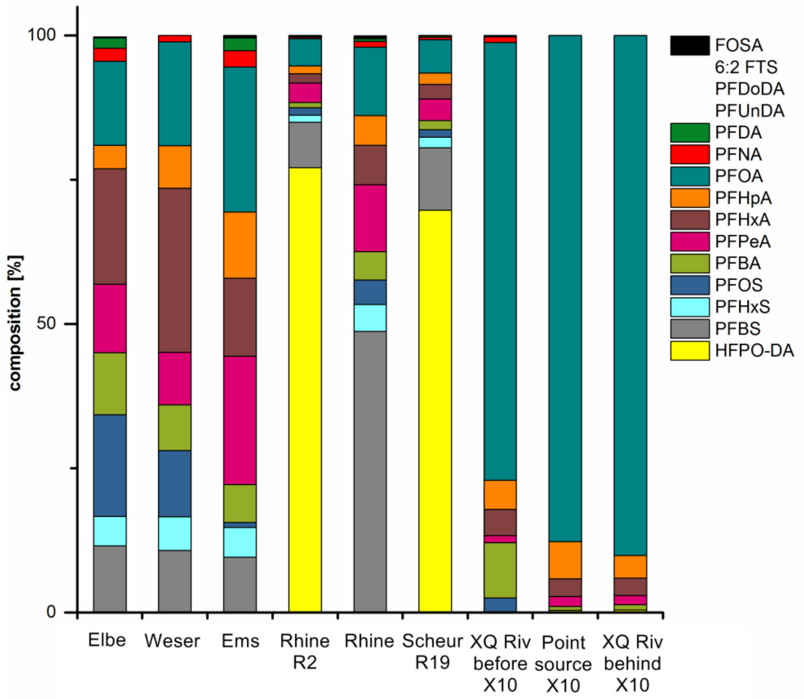

Figure 4-4. Average contribution of individual PFASs to ΣPFASs in the Lower Elbe (T1-T7 and E19-E21), Weser (T16-T19), Ems (S5-S6 and R21-R22), Rhine (R2), Rhine (R3-R13), Scheur (R19), Xiaoqing River before the point source (X1-X7), Dongzhulong near the point source (X10), and in the Xiaoqing River behind the point source (X11-X12 and X14-X29).

Comparing the Elbe, Weser, and Ems Rivers as discharging rivers into the North Sea, the distribution pattern is characterized by a variety of legacy perfluoroalkyl compounds, assuming that the pollution is caused by diffuse sources rather than by point sources. In contrast, we observed two point sources along the Rhine River as well as in the Rhine-Meuse delta, where the fluorinated alternative HFPO-DA was the dominant compound with percentages of 77% and 70%, respectively, and concentrations 16 or 12 times higher than concentrations of its predecessor substance PFOA. In Germany and the Netherlands, we did not observe a current industrial discharge source of PFOA; however, driven by concerns around the use of long-chain and possibly short-chain PFASs, industry seems to respond by using replacement substances like HFPO-DA. Along the Dongzhulong River, we observed a high rate of industrial discharge of PFASs in general and PFOA in particular probably due to both the strong demand for PFASs-based products and the outsourcing of a large part of the fluoropolymer industry to China in response to actual and pending regulations in Europe. The worldwide demand for high-quality PTFE products still results in high emissions of PFOA at fluoropolymer manufacturing sites. However, its replacement substance HFPO-DA was detected in concentrations up to 42 times greater in China than in Germany and the Netherlands. Along the Dongzhulong and Xiaoqing Rivers, we observed an increase in concentrations of 490 and 644 times, respectively. Hence, as HFPO-DA is environmentally persistent and chemically stable, its detection in the aquatic environments of both Europe and China is of concern. Moreover, HFPO-DA has similar physicochemical properties (high water solubility and low pKa) and similar long-range transport potential indicators (characteristic travel distance CTD and overall persistence Pov) to those of PFOA or its dissociated anionic form, indicating that they may have the same ability to be transported from the river/estuary systems and coastal regions to remote areas via ocean currents.[128] In addition, specific target organ toxicity can occur under prolonged or repeated exposure, suggesting a similar mode of toxic action as of PFOA.[115] The structural similarity to PFOA also implies that HFPO-DA cannot be metabolized in biota and may have a similar high affinity to proteins, resulting in a potential for bioaccumulation.[99] However, future studies are necessary to fully understand the fate and behavior of HFPO-DA in the environment.

Acknowledgements

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4.4 Add-on: Study on PAPs, PFPiAS, and PFPAs

Several studies confirm that PFCAs and PFSAs account only for a smaller fraction of organofluorine compounds in environmental and human blood samples.[14,15,141] For example, Miyake et al. showed that 60-90% of the organofluorine fraction in seawater samples cannot be described by PFCAs and PFSAs and, thus, remains unknown.[15] This highlights the importance to identify less-studied PFASs, such as fluorotelomer phosphates (PAPs), perfluoroalkyl phosphinic acids (PFPiAs), and perfluoroalkyl phosphonic acids (PFPAs), in environmental samples. These compound groups are characterized by a phosphate group that can be substituted up to three times with per- or polyfluorocarbon chains (see Table 2-1). They are structurally very similar, especially PFPiAs and PFPAs, compared to PFCAs or PFSAs, indicating that they show similar behaviors in the environment. Furthermore, PFPiAs may be of high environmental concern because of their two fluorinated carbon chains, resulting possibly in a high bioaccumulation potential. PAPs are known as precursor substances of PFCAs and may, consequently, be an important source for their occurrence in the environment.

This add-on study concentrates on the method development for the analysis of 15 PAPs, PFPiAs, and PFPAs in surface water. It includes (i) a description and results of the method development for the instrumental analysis and extraction, (ii) the application to surface water samples and discussion of the results, and (iii) an outlook. The extraction method should be, at best, combine both legacy PFASs and PAPs, PFPiAs, and PFPAs. With the developed method, surface water from the German Bight and from the Xiaoqing River in China should be analyzed to assess whether PAPs, PFPiAs, and PFPAs contribute to the pollution burden and, if so, to what extent compared to the well-known PFCAs and PFSAs.

In a first step, the precursor and product ions of the individual compounds were determined. If two product ions were available, the mass transition which showed the lowest response was chosen as qualifier, whereas the mass transition with the highest response was selected as quantifier. For all mass transitions, the mass spectrometer-specific parameters, i.e. declustering potential, focusing potential, collision energy, and collision cell exit potential, were optimized (see Table 7-4). In a second step, the chromatographic method was developed based on methods described in the literature. The chromatographic separation of monoPAPs and PFPAs was previously described as challenging because of their *pKa* values (2.1-7.0), which are close to the *pH* value of the mobile phase when ammonium acetate is used as an additive. This means that the compounds are doubly negatively charged, leading to a lesser retention on a C_{18} stationary phase.[142,143] Several studies tried to solve this problem by optimizing the LC conditions, including mobile phases and columns.[143-147] In this doctorate, a promising approach according to Ullah et al. was followed.[143] Ullah et al. added an ion-pair reagent, i.e. 1-methylpiperidine, to the mobile phases, with the effect that the negative charges of the phosphonate group are masked and, consequently, the retention on a C_{18} stationary phase is increased. The increased sorption behavior is illustrated in Figure 4-5.

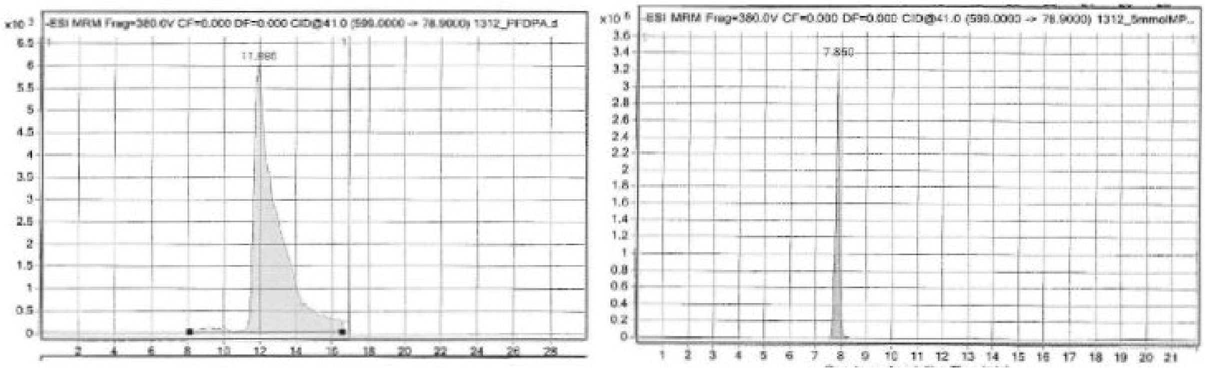

Figure 4-5. PFDPA analyzed with 10 mmol ammonium acetate (left) and 5 mmol 1-methylpiperidine and 2 mmol ammonium acetate (right).

Ullah et al. used 5 mmol 1-methylpiperidine and 2 mmol ammonium acetate in (A) 95% water and 5% methanol and (B) 75% methanol, 20% acetonitrile, and 5% water. Various compositions of the mobile phases and amounts of additives were tested. In general, the use of 5 mmol 1-methylpiperidine and 2 mmol ammonium acetate as additives for the mobile phases showed the highest response for all compounds, especially for the monoPAPs and PFPAs. The chromatographic separation of the analytes was best using (A) 100% water and (B) 100% methanol, both added with 5 mmol NH_4Ac and 5 mmol 1-methylpiperidine. The final LC method is presented in Table 7-7. Figure 4-6 shows a dynamic multiple reaction monitoring (DMRM) chromatogram of the final method. The retention times of the compounds are given in Table 7-4.

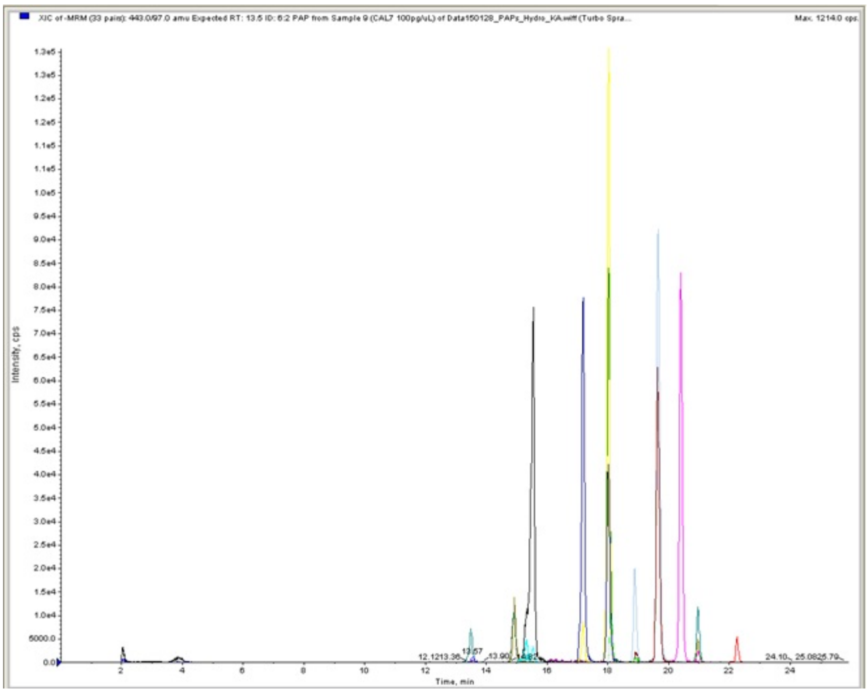

Figure 4-6. Dynamic multiple reaction monitoring (DMRM) chromatogram of the final method analyzing PAPs, PFPiAs, and PFPAs via LC-MS/MS.

In a third step, the turbo ion source parameters, i.e. source temperature, needle voltage and gas flows, were optimized. The final MS/MS method is presented in Table 7-7.

Table 4-1 shows the instrumental precision s_{rel} [%] for PAPs, PFPiAS, and PFPAs on the mass spectrometer API 3000 (Sciex) at different mass levels. The instrumental precision was calculated according to equation (10).

Table 4-1. Instrumental precision s_{rel} [%] for quantifier ions of PAPs, PFPiAs, and PFPAs at m_1=100 pg, m_2=2000 pg, and m_3=5000 pg (N=10).

Substance	$s_{rel,m1}$ [%]	$s_{rel,m2}$ [%]	$s_{rel,m3}$ [%]
6:2-PAP	12.3	20.5	10.8
8:2-PAP	15.1	27.9	18.2
10:2-PAP	8.4	9.6	4.6
6:2-diPAP	5.6	3.7	2.7
8:2-diPAP	7.2	6.2	5.9
10:2-diPAP	7.0	6.2	5.9
6:2-8:2-diPAP	7.5	6.9	5.0
6:2-triPAP	3.8	4.6	3.8
diSAmPAP	7.0	6.5	5.8
6:6-PFPi	2.5	4.0	3.6
6:8-PFPi	2.9	2.8	3.2
8:8-PFPi	7.5	6.5	3.3
PFHxPA	6.8	5.8	4.7
PFOPA	3.8	4.1	3.3
PFDPA	2.5	9.3	5.6

The instrumental precision gets worse approaching the instrumental detection limits. Thus, it is not surprising that $s_{rel,m3}$ were the best for a large part of the compounds. According to the manufacturer, an instrumental precision below 3% can be achieved when injecting the compound diphenhydramine, whereby the amount of this compound was not given by the manufacturer. This could be achieved only sporadically. Most of the compounds can be analyzed with an instrumental precision better than 7%. The mono-PAPs, especially 6:2-PAP and 8:2-PAP, had comparably worse instrumental precisions because of their challenging chromatographic behavior discussed above. Fortunately, ^{13}C-mass labeled internal standards, which compensate random variations during the measurement, were available for both compounds.

The instrumental detection limits (IDLs) and instrumental quantification limits (IQLs) were calculated according to equations (8) and (9), respectively, and are presented in Table 4-2.

Table 4-2. Comparison of instrumental detection limits (IDLs) and instrumental quantification limits (IQLs) between the two developed instrumental methods analyzing PAPs, PFPiAs, and PFPAs (N=10).

Substance	**IDL [pg]**	**IQL [pg]**	**IDL [pg]**	**IQL [pg]**
	with 1-methylpiperidine		without 1-methylpiperidine	
6:2-PAP	0.2	0.6	N.A.	N.A.
8:2-PAP	0.2	0.8	N.A.	N.A.
10:2-PAP	0.4	1.3	N.A.	N.A.
6:2-diPAP	0.1	0.4	0.4	1.0
8:2-diPAP	0.2	0.6	0.3	1.0
10:2-diPAP	1.2	3.9	1.8	5.5
6:2-8:2-diPAP	0.6	1.9	1.5	4.4
6:2-triPAP	0.6	2.2	1.6	4.6
diSAmPAP	0.1	0.4	0.3	1.0
6:6-PFPi	0.04	0.1	0.5	1.3
6:8-PFPi	0.5	1.7	1.3	3.9
8:8-PFPi	1.2	4.1	2.2	6.6
PFHxPA	0.3	1.0	N.A.	N.A.
PFOPA	0.1	0.3	N.A.	N.A.
PFDPA	0.1	0.4	N.A.	N.A.

N.A. Not analyzed because of poor chromatographic performance

Table 4-2 shows that the use of 1-methylpiperidine in the mobile phases generally decreases the IDLs/IQLs of PAPs, PFPiAs, and PFPAs. The IDLs and IQLs ranged from 0.04 to 1.2 pg and from 0.1 to 4.1 pg, respectively, whereas - without 1-methylpiperidine - the IDLs and IQLs ranged from 0.3 to 2.2 pg and from 1.0 to 6.6 pg, respectively. The latter were still in an acceptable range and also similar to the IDLs and IQLs of legacy PFASs.[123] However, six monoPAPs and the PFPAs could not be analyzed with this method because of their very poor chromatographic performance without the addition of 1-methylpiperidine.

For the extraction of PFASs from water samples, solid phase extraction (SPE) is the method of choice. In general, extraction methods vary among laboratories and numerous methods have been developed for the extraction of legacy PFASs from water samples over the last decade. The regional authorities in Germany, for example, are required to extract liquid samples according to DIN 38407-42 (Figure 7-2),[148] whereas, at international level, efforts have been recently made to establish a new ISO method.[149] Most of the methods involve polymeric weak anion exchange-material using various loading rates and washing and elution solutions. Methods using a hydrophilic-lipophilic balanced copolymer were also described as being sufficient. For the extraction of PAPs, PFPiAs, and PFPAs from water samples, an extraction method used for legacy PFASs and described by Ahrens et al. was optimized.[123] The objective was to integrate PAPs, PFPiAs, PFPAs, and legacy PFASs into one extraction method.

Table 4-3 shows the absolute recovery rates [%] of native standards after extracting 1 L surface water from the Elbe River with four different methods adapted from methods existing in the literature for the extraction of legacy PFASs.[123,143] After loading the Oasis® WAX cartridges with the sample at a loading rate of approximately 2.5 mL/min, the cartridges were washed with 5 mL Millipore water and dried for 30 min using vacuum, respectively.

Table 4-3. Absolute recovery rates [%] of native standards (PAPs, PFPiAs, and PFPAs). 1 L surface water from the Elbe River was extracted together with 2.5 ng of native standards, respectively, using various elution solvents for solid phase extraction: (i) Elution with 10 mL 0.25% NH_4OH in MeOH (N=6), (ii) Elution with 10 mL 0.1% NH_4OH in MeOH (N=2), (iii) Elution with 10 mL 0.1% NH_4OH in 80/20 MeOH/ACN (N=2), (iv) Elution with 5 mL MeOH and 5 mL 0.1% NH_4OH in MeOH (N=2).

Substance	**Recovery [%]**	**Recovery [%]**	**Recovery [%]**	**Recovery [%]**
	0.25% NH_4OH in MeOH	0.1% NH_4OH in MeOH	0.1% NH_4OH in 80/20 MeOH/ACN	ACN + 0.1% NH_4OH in MeOH
6:2-PAP	83.7 ± 5.5	88.8	93.6	84.4
8:2-PAP	88.0 ± 3.5	94.0	90.4	86.4
10:2-PAP	N.A.	N.A.	N.A.	N.A.
6:2-diPAP	87.2 ± 3.1	81.2	80.8	80.1
8:2-diPAP	82.8 ± 4.4	80.2	82.4	81.6
10:2-diPAP	81.2 ± 3.3	92.0	82.6	80.5
6:2-8:2-diPAP	81.5 ± 8.4	40.8	47.8	54.7
6:2-triPAP	62.9 ± 7.9	51.3	56.7	61.6
diSAmPAP	50.0 ± 3.9	49.0	53.4	55.9
6:6-PFPi	48.7 ± 5.9	69.3	69.5	74.3
6:8-PFPi	78.7 ± 9.2	51.5	55.7	65.7
8:8-PFPi	72.1 ± 8.2	50.5	55.8	61.5
PFHxPA	81.9 ± 13.1	82.4	77.4	83.2
PFOPA	82.8 ± 4.4	46.0	57.9	66.2
PFDPA	71.4 ± 36.1	41.7	72.0	132.8

N.A. 10:2-PAP showed a poor chromatographic performance in matrix spiked samples and was excluded in subsequent measurements

For most compounds, the four different elution approaches resulted in similar recovery rates, concluding that, in general, all elution solvents were sufficient for the extraction of PAPs, PFPiAs, PFPAs, and legacy PFASs. The method using 0.25% NH_4OH in MeOH as elution solvent showed slightly higher recovery rates for the largest part of compounds. Thus, samples were subsequently extracted and analyzed on PAPs, PFPiAs, PFPAs, and legacy PFASs using 0.25% NH_4OH in MeOH as elution solvent (see Figure 7-1). The method detection limits (MDLs) and method quantification limits (MQLs) were calculated according to equations (8) and (9) and are presented in Table 4-4.

Table 4-4. Method detection limits (MDLs) and method quantification limits (MQLs) of native standards (PAPs, PFPiAs, and PFPAs). 1 L surface water from the Elbe River was extracted together with 2.5 ng of native standards, respectively, and eluted with 10 mL of 0.25% NH_4OH in MeOH (*N*=6).

Substance	MDL [pg/L]	MQL [pg/L]
6:2-PAP	42	141
8:2-PAP	57	189
10:2-PAP	N.A.	N.A.
6:2-diPAP	2	7
8:2-diPAP	1	3
10:2-diPAP	4	14
6:2-8:2-diPAP	3	11
6:2-triPAP	9	31
diSAmPAP	2	5
6:6-PFPi	0.4	1
6:8-PFPi	5	17
8:8-PFPi	3	11
PFHxPA	69	230
PFOPA	58	192
PFDPA	54	180

N.A. 10:2-PAP showed a poor chromatographic performance in matrix spiked samples and was excluded in subsequent measurements

MDLs and MQLs ranged from 0.4 to 69 pg/L and from 1 to 230 pg/L, respectively. MDLs and MQLs of diPAPs, 6:2-triPAP, and PFPiAs were considerably lower than those of legacy PFASs (cf. Chapter A.1) as a result of the use of 1-methylpiperidine in the mobile phases. MonoPAPs and PFPAs had similar MDLs and MQLs compared to that of legacy PFASs, although IDLs and IQLs were as low as those of diPAPs, 6:2-triPAP, and PFPiAs. However, mono-PAPs and PFPAs showed generally poorer chromatographic performances in matrix spiked samples compared with those in calibration standards.

With the optimized method, surface water samples from the Xiaoqing River and the German Bight were extracted and analyzed on PAPs, PFPiAs, PFPAs, and legacy PFASs. The results for legacy PFASs were presented in Chapter 4.3. PAPs, PFPiAs, and PFPAs were not detected in any sample, which may have multiple reasons: (i) They are not relevant in the aqueous phase. DiPAPs and PFPiAs have a high molecular weight because of their two or three hydrophobic fluorinated carbon chains. The estimated log K_{OW} of 6:6-PFPi, for example, is 6.96,[150] demonstrating that this group of compounds may be mainly particle-phase bound. This hypothesis is supported by the fact that Frömel et al. observed diPAPs only in the particulate phase of influent water from an industrial wastewater treatment plant (WWTP) with concentrations up to 7.6 ng/g wet weight, but not in the dissolved phase.[151] However, PFPAs are structurally very similar compared to PFCAs and PFSAs and should be mainly distributed in the aqueous phase. (ii) The MDLs/MQLs are too high. However, MDLs/MQLs are lower or similar compared to that reported in the literature. Loi et al. reported similar MQLs like ours for diPAPs in water (0.01 ng/L) and detected these compounds in surface water near Hong Kong with concentrations ranging from 0.01 to 0.2 ng/L.[152] Assuming that we can find similar concentration levels in our surface water samples, the MDLs/MQLs should be adequate. (iii) The compounds are not emitted in the nearest surrounding of our sampling locations. (iv) PAPs are known to be precursor compounds of fluorotelomer alcohols (FTOHs) and, consequently, of perfluoroalkyl carboxylic acids (PFCAs).[144] Frömel et al. have shown that PAPs are present in the influent but not in the effluent water of WWTPs, concluding that they were biodegraded in the WWTPs.[151] Thus, it is possible that, at least, the PAPs are readily biodegradable in WWTPs, resulting in the release of PFCAs from a WWTP. This hypothesis is supported by the fact that higher PFCA concentrations were found in the effluent of the WWTPs than in the influent.

Concluding, during this doctorate, a method was developed to analyze PAPs, PFPiAs, and PFPAs in surface water with MQLs ranging from 1 to 230 pg/L. The method uses 1-methylpiperidine as additive for the mobile phases, resulting in a better chromatographic separation and lower IQLs for, most of all, monoPAPs and PFPAs. However, the use of 1-methylpiperidine includes a number of disadvantages: (i) Two separate methods are necessary for PAPs, PFPiAs, and PFPAs on the one hand, and legacy PFASs on the other hand. Due to the use of 1-methylpiperidine, the *pH* of the mobile phases increases with the result that the Synergi Fusion-RP-C_{18} column regularly used for analyzing PFCAs and PFSAs is subject to a higher level of wear. To counter this, another column, i.e. Kinetex EVO C_{18}, can be used which allows to work at *pH*s between 1 and 12. Thus, two separate methods are recommended with the result that twice the length of time and more resources are needed. (ii) 1-methylpiperidine shows a very sticky behavior on the mass spectrometer. Frequent cleaning of the ion source and the 1st quadrupole is necessary after every sample batch because the mass spectrometer API3000 is especially prone to turbo pump wear. For the cleaning procedure, the instrument has to be shut down - the more sample batches, the more often. For future analyses, the use of 1-methylpiperidine is not recommended and compounds should be analyzed with a method which includes both legacy PFASs and PAPs, PFPiAs, and PFPAs.

Based on these considerations, a master thesis was supervised where (i) an instrumental method for diPAPs and PFPiAs that can be included in the basic analytical method for legacy PFASs was developed and (ii) a method to extract PAPs and PFPiAs from sediments via ultrasonic was developed.[153] In the future, sediments from the German Bight shall be analyzed on diPAPs and PFPiAs with this novel method, monoPAPs and PFPAs cannot be analyzed with this method though.

4.5 Add-on: Study on the Long-Range Transport of the Fluorinated Alternative Substance HFPO-DA

The transport via the water phase is a major pathway for the global distribution of ionic PFAAs.[154,155] For listing a chemical as a POP under Stockholm Convention, one major criterion is the evidence of long-range transport into remote areas where sources of POPs don't exist. Long-chain PFAAs have been detected in surface water, snow, sediments, and biota, including the food web, from the Arctic for more than 10 years, demonstrating that they reach remote areas and accumulate there.[46,156-161] HFPO-DA has, like its predecessor compound PFOA, a high persistence and water solubility and a low pK_a,[128] indicating that it also has the ability to be transported from river/estuary system to remote areas over long distances. Within the scope of this doctorate, it was possible to analyze five samples, that were up to approximately 1800 km north of the German coastline, from the northern part of the North Sea and the Norwegian Sea (Figure 4-7). The purpose was to investigate whether HFPO-DA has the ability to be transported over longer ranges. Emissions of PFAAs, in general, and PFOA, in particular, to the North Sea can be considered as crucial to the exposure of the Artic to PFAAs because 50-80% of the total PFOA amount in the Arctic is delivered via the Norwegian Coastal Current (Figure 4-8).[155]

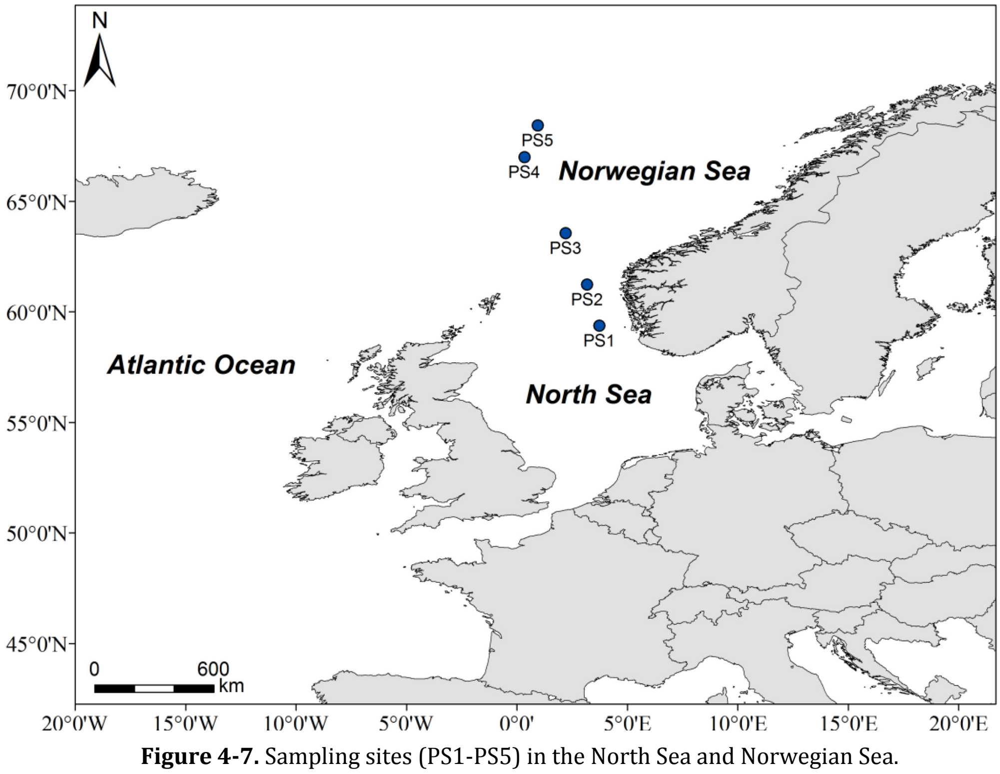

Figure 4-7. Sampling sites (PS1-PS5) in the North Sea and Norwegian Sea.

The sampling campaign was carried out on board of the *R/V Polarstern* during cruise PS85 (ARK-XXVIII/2) in June 2014. One liter water samples were taken via the ship's intake stainless steel seawater pump at approximately 11 m below sea level and collected in polypropylene bottles (VWR International). The samples were cooled during and after the sampling campaign for 10 months and extracted in the clean laboratory (class 10.000 according to US FED 209D) according to Figure 7-1.

Table 4-5 shows the PFAS concentrations [pg/L] in the northern part of the North Sea and the Norwegian Sea.

Table 4-5. PFAS concentrations [pg/L] in the northern part of the North Sea and the Norwegian Sea (cruise PS85 (ARK-XXVIII/2) with the *R/V Polarstern*). Compounds with >9 carbon atoms showed no peaks and are, consequently, classified as not detected (n.d.). Values less than a blank-defined method dectection limit (MDL) are reported as <MDL. Values in brackets are below the method quantification limit (MQL). MDL and the MQL were calculated with the blank standard deviations multiplied by the appropriate variable from Student's t table at 98% confidence and 10, respectively.[124]

No.	HFPO-DA	PFBS	PFHxS	PFOS	PFBA*	PFPeA	PFHxA	PFHpA	PFOA	ΣPFASs
PS1	370	262	68	<MDL	544	<MDL	150	<MDL	<MDL	1394
PS2	500	234	57	<MDL	770	<MDL	120	<MDL	<MDL	1682
PS3	178	101	45	<MDL	518	<MDL	88	<MDL	<MDL	930
PS4	n.d.	n.d.	41	<MDL	498	<MDL	77	<MDL	<MDL	616
PS5	n.d.	(72)	n.d.	<MDL	426	<MDL	16	<MDL	<MDL	514

*Results for PFBA may have to be considered as semi-quantitative because of high recovery rates for $^{13}C_4$-PFBA (128 to 233%) and poor chromatographic performance

The ∑PFASs concentrations decreased as the distance from the coastline increased and ranged from 514 to 1390 pg/L. HFPO-DA was detected in the samples PS1-PS3 with an average concentration of 349 pg/L. Assuming that HFPO-DA emissions from Norway and Great Britain are negligible,[162] HFPO-DA findings in the samples PS1-PS3 indicate that the compound was transported at least approximately 1700 km after its emission. Compared with the concentrations of legacy PFASs, HFPO-DA was the second dominant compound behind PFBA. The concentration of PFOA, HFPO-DA's predecessor compound, was below the MDL in all samples, partly due to the higher MDL of PFOA (134 pg/L) compared with that of HFPO-DA (23 pg/L). The composition profile of PFASs was, in general, similar to that from the German Bight (see Chapter 4.3.4). In 2007, ∑PFASs concentrations along the Norwegian coast were lower ranging from 10 to 550 pg/L.[163] The dominant compounds were PFHxA and PFOA, whereas PFBA was not detected. Shorter-chain compounds, i.e. PFBS, PFHxS and PFBA are, at similar experimental conditions, more present in the water phase than 7 years ago, reflecting the increased use of alternatives instead of longer-chain compounds. In the samples PS4 and PS5, HFPO-DA was not detected, which may be attributed to an increasing spatial dispersion of the compound.[164] HFPO-DA may also be preferably transported to the Arctic Ocean via the Norwegian Coastal Current along the Norwegian coast instead of transported directly northwards because different densities of the East Iceland Current and the North Atlantic Drift Current prevent both water masses from mixing (Figure 4-8).[165,166]

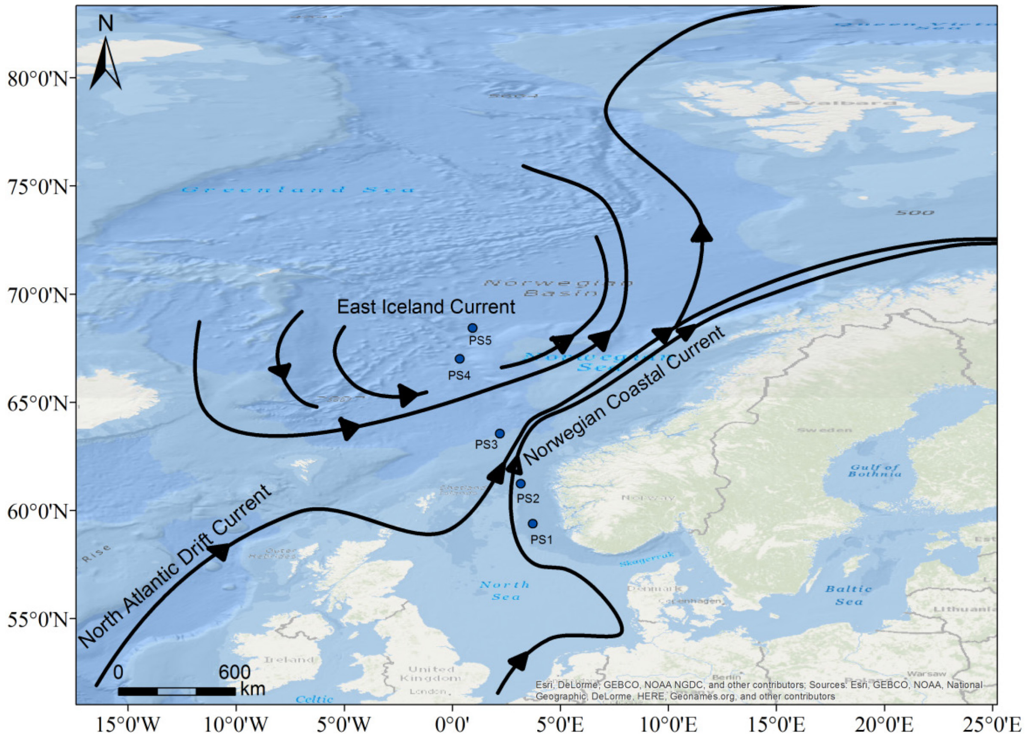

Figure 4-8. Schematic circulation of the Norwegian Coastal Current, the North Atlantic Drift Current, and the East Iceland Current (according to Helland-Hansen and Nansen[167] and Smith et al.[168])

It is believed that pollutants, in general, are transported from the North Sea to the Arctic Ocean on time scales of several years.[169] For example, Buraglio et al. estimated a maximum transport time for ^{129}I of 11 years from the English Channel to the central Arctic.[170] The transfer time of PFOA to the Barents Sea was predicted to be 5 years and is in line with estimates from passive radiotracer studies.[155] Considering the facts that HFPO-DA (i) has similar physicochemical properties like PFOA and (ii) is probably emitted continuously to the North Sea since 2010, it is not unlikely that the compound is already distributed in parts of the Arctic Ocean. However, an increase in pollutant emissions doesn't necessarily result in an increase in pollutant concentrations in the Arctic Ocean because the variability in water mass transport may compensate increasing emissions.[155] Thus, more experiments are needed to assess whether HFPO-DA is further transported to the Arctic Ocean.

4.6 Add-on: Study on the Fluorinated Alternative Substance DONA

Analytical standards are mandatory for an accurate determination and quantification of organic contaminants in environmental samples. Because publications and, thus, the knowledge of alternative compounds, have been arising recently, an analytical standard of HFPO-DA was the only one available for most time of the doctorate. However, for a comprehensive study on the shifting from legacy to alternative per- and polyfluoroalkyl substances and its effects on environmental concentrations, the analysis of environmental samples for other fluorinated alternatives is equally important because almost all fluoropolymer manufacturers have developed their own PFOA alternatives (Figure 2-2).[12] An important producer of fluoropolymers in Germany is the company Dyneon/3M based in the chemical park Gendorf in Bavaria. Since 2008, Dyneon has been using the fluorinated alternative DONA as a processing aid for the fluoropolymer manufacturing (Figure 4-9).[11,171]

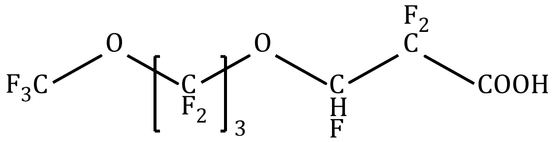

Figure 4-9. Chemical structure of DONA.

The Bavarian Environmental Protection Office (LfU) is in charge of the monitoring of PFASs in the Bavarian environment and, thus, occasionally analyses effluent water from the chemical park Gendorf and surface water from the Alz River for DONA. DONA was monitored in the Alz River downstream of the chemical park's effluent water discharge between 2008 and 2009 and was detected in all surface water samples with concentrations ranging from 0.32 to 6.2 µg/L.[100] The concentration of the predecessor substance PFOA decreased compared with previous years and ranged between 0.03 and 4.3 µg/L.[100]

In cooperation with the LfU, 20 samples from the rivers Rhine, Waal, and Xiaoqing, the Rhine-Meuse delta, and the German Bight were analyzed on the fluorinated alternative DONA. The purpose of this study was to investigate whether the fluorinated alternative DONA is, like HFPO-DA, present in riverine and coastal areas of Germany and China. Dyneon discharges in the Alz River, which flows into the Black Sea via the rivers Inn and Donau. Thus, the Rhine River and the German Bight are not influenced directly by Dyneon's effluent water discharge. However, along the Rhine River and in the Rhine-Meuse delta, at least two huge chemical parks are situated (Figure 4-10). Thus, downstream users that are situated in these chemical parks may use products of Dyneon, possibly resulting in the emission of DONA in these areas. For the Xiaoqing River, it can also not be ruled out that DONA is produced or used by Dyneon/3M or other companies in China.

Figure 4-10 shows the sampling locations analyzed on DONA.

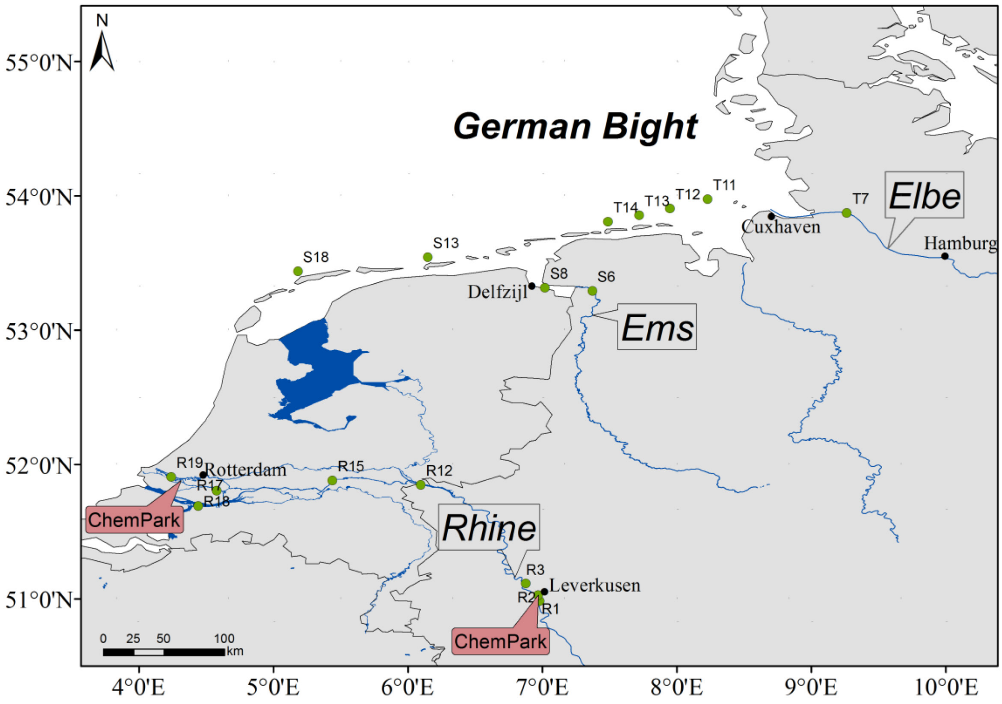

Figure 4-10. Sampling sites analyzed on DONA.

Detailed information on sampling locations, sample collection, and extraction method are given in the Chapters 4.2 and A.1. The LfU extracts water samples according to DIN 38407-42 with recovery rates for DONA of more than 80%.[148,172] The results are usually corrected towards mass-labeled $^{13}C_4$-PFOA as internal standard because of structural similarity, but might be calculated without any correction if concentrations of $^{13}C_4$-PFOA and DONA differ significantly from each other. For consistency and for consideration that the extraction method differed slightly from the DIN 38407-42 method (see Chapter 7.3), concentrations of DONA were corrected with $^{13}C_4$-PFOA and calculated according to equations (1) and (4). The samples were analyzed via a 4000 Q Trap mass spectrometer (AB Sciex) provided at the LfU. Analysis was performed using negative electrospray ionization. MRM transitions and mass-spectrometric parameters are given in Table 4-6.

Table 4-6. Substance-specific mass-spectrometric parameters of DONA and $^{13}C_4$-PFOA for a 4000 Q Trap system and retention times R_t [min].

Compound	MRM transition [m/z]	R_t [min]	DP	CE	CXP
DONA	377>85	6.4	-35	-60	-5
DONA	377>251	6.4	-35	-18	-21
$^{13}C_4$-PFOA	417>169	8.3	-50	-26	-3

DP	declustering potential [V]
CE	collision energy [V]
CXP	collision cell exit potential [V]

High performance liquid chromatography was performed using a Synergi 4 µm Polar-RP-C_{18} column (150x2 mm; Phenomenex). The mobile phases consisted of A) water and B) methanol, both with 0.05% formic acid. The gradient profile was achieved at a flow rate of 250 µL/min and initiated with an equilibration of 72% A for 8 min, which was decreased to 70% A for 5 min, to

15% A up to 14 min, and to 5% A up to 21 min. The method detection limit (MDL) and method quantification limit (MQL) were 16 pg/L and 53 pg/L, respectively.

DONA was only detected at the sampling locations R3 (Lower Rhine) and R15 (Waal River) with concentrations of 79 pg/L and 347 pg/L, respectively (see Table B-3). Because (i) the sampling location R3 is close to and downstream of the chemical park in Leverkusen and (ii) DONA was not detected upstream in the samples R1 and R2, the results indicate that downstream users situated in the chemical park may have used the fluorinated alternative DONA or fluoropolymers that contain residuals or impurities of this processing aid. This hypothesis is supported by the fact that industrial effluent water from the chemical park, which was analyzed later on, was also contaminated with DONA (see Chapter 4.7). The concentration of DONA was in a similar range like that of the legacy long-chain compounds PFNA and PFDA (see Chapter 4.3.2). On the other hand, DONA's predecessor substance PFOA had 1 or 2 order of magnitude higher concentrations than DONA. However, the findings of PFOA along the investigated section of the Rhine River indicate the presence of diffuse sources rather than of point sources. Compared with the findings in the Alz River in the years 2008/2009,[100] the concentrations were 4 orders of magnitude lower in the rivers Rhine and Waal.

DONA is, like legacy PFAAs, not readily biodegradable and can be considered as very persistent according to European REACH regulation.[11,128] The physicochemical properties, such as high water solubility and low *pKa*, of DONA were estimated to be similar to that of its predecessor substance PFOA, indicating the same high mobility in water.[128] Additionally, there is some evidence that DONA is, like PFOA, a PPARα agonist and, thus, causes hepatocellular hypertrophy and reduction in serum cholesterol in male Sprague–Dawley rats.[11] The detection of DONA in the aquatic environment is of concern, but future studies are necessary to fully understand its fate and behavior in the environment. In 2017, the Umweltbundesamt (UBA) will evaluate the ammonium salt of DONA, i.e. ADONA, under the substance evaluation process of the REACH regulation because of suspected PBT/vPvB properties, wide dispersive use, and exposure of the environment.[173] The substance evaluation shall clarify whether the use of DONA poses a risk to human health or the environment.

4.7 Add-on: Study on Effluent Water from a Chemical Park Situated Along the Rhine River

Chapter 4.3.2 described the PFASs pollution in surface water from the Lower Rhine from August 2013. A major finding was the detection of the fluorinated alternative compound HFPO-DA downstream of a chemical park in Leverkusen. HFPO-DA was the dominant compound with a concentration of 108 ng/L. However, the result stemmed from a single measurement and HFPO-DA was detected only at two sampling points downstream of the chemical park, indicating that the detection of HFPO-DA may have resulted from a temporary, discontinuous or accidental discharge. The operating company of the chemical park stated that it was not responsible for the emission of the alternative compound HFPO-DA because the sampling point R2/13-08, although located downstream of the chemical park, was located upstream of the wastewater treatment plant (WWTP) *Bürrig*, where the contaminated industrial effluent water from the chemical park is treated and discharged (Figure 4-11). The other WWTPs (*Y2, X,* and *S*) located upstream of the sampling location R2/13-08 treat allegedly water of non-industrial processes from the chemical park.

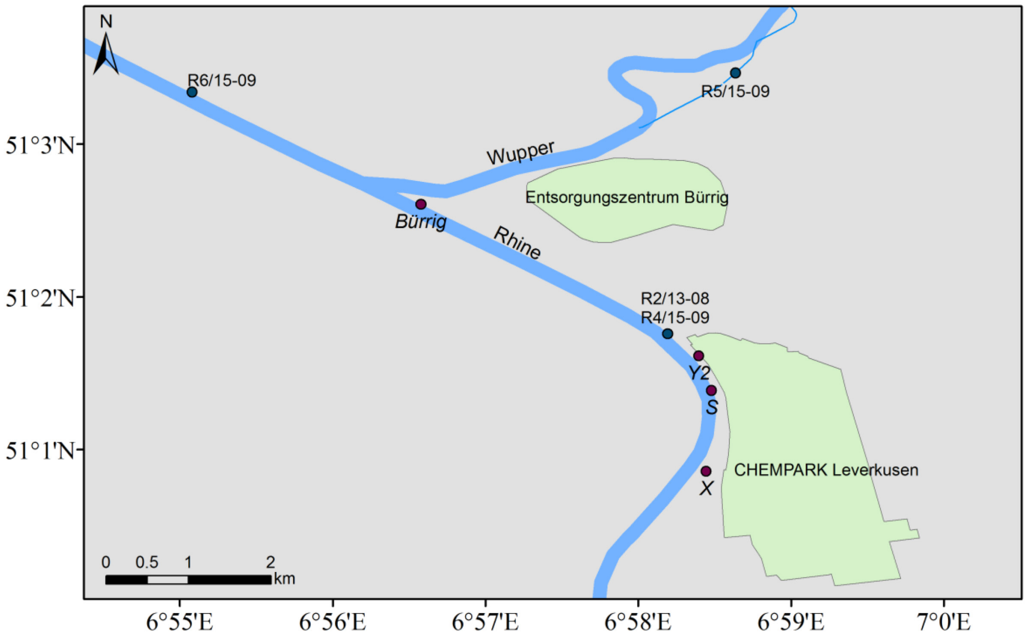

Figure 4-11. Sampling locations in August 2013 (R2/13-08) and September 2015 (R4, R5, R6/15-09) near the WWTPs (X, S, Y2, and Bürrig) of CHEMPARK Leverkusen.

In cooperation with the Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen (LANUV), effluent water from three WWTPs (*Y2, X,* and *Bürrig*) of the chemical park in Leverkusen was analyzed. Effluent water from the WWTP *S* was not analyzed because of a low and irregular discharge. The purpose of this study was to investigate possible recent emissions of HFPO-DA from the chemical park into the Lower Rhine and, if so, to locate the emissions within the chemical park. In addition, surface water from the Lower Rhine was sampled to investigate the recent pollution levels in the Lower Rhine and to compare the concentrations with those from the effluent water and from surface water sampled in the Lower Rhine in August 2013 (Figure 4-12). Furthermore, it was possible to analyze the alternative compound

DONA because the analytical standard became available by the end of the doctorate. Thus, it should be investigated whether DONA is discharged from the chemical park in Leverkusen as supposed in Chapter 4.6.

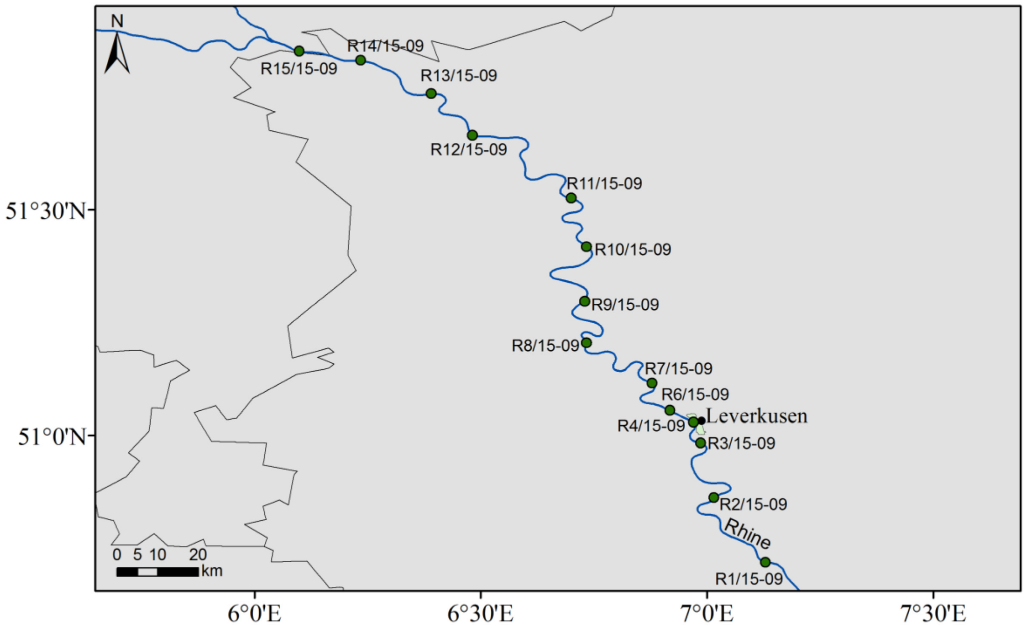

Figure 4-12. Sampling locations along the Lower Rhine in September 2015.

Detailed information on sampling locations and extraction method are given in Table B-4, Figure 7-2, and Figure 7-4. In short, effluent water was sampled in duplicate in 1 L brown wide-neck flasks, whereas surface water from the Lower Rhine was sampled in polypropylene bottles (VWR International), and cooled until extraction. Approximately 0.5 L and 1 L of the effluent water and the river water, respectively, were extracted 3 weeks after sampling. Concentrations were calculated according to equations (1) to (3). MDLs and MQLs ranged from 0.00001 ng/L (DONA) to 0.30 ng/L (PFBA) and from 0.00003 ng/L (DONA) to 1.01 ng/L (PFBA), respectively. The mean recoveries of the internal standards ranged from 35 ± 12% ([$^{13}C_2$]-PFDoDA) to 149 ± 44% ([$^{13}C_4$]-PFBA) (Table D-3).

Table 4-7 shows the PFAS concentrations [ng/L] in effluent water from the chemical park in Leverkusen.

Table 4-7. PFAS concentrations [ng/L] in industrial effluent water from a chemical park in Leverkusen. The results were rounded to three significant figures.

No.	PFBS	PFHxS	PFOS	PFBA*	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	DONA	HFPO-DA	ΣPFAS
Y2-A	1480	3.54	2.73	10.1	3.02	2.89	0.92	2.71	0.08	0.02	1.73	<MDL	1510
Y2-B	1580	3.91	3.38	11.3	3.32	2.60	1.18	3.37	0.11	0.05	1.68	<MDL	1610
X-A	18.6	5.29	1.50	3.70	1.36	1.76	0.41	2.85	n.d.	n.d.	0.06	n.d.	35.5
X-B	16.9	5.03	1.01	2.83	1.56	1.59	0.71	3.08	n.d.	n.d.	0.05	n.d.	32.8
Bürrig A	3180#	6.67	1.26	155	12.9	20.4	6.35	13.7	n.d.	n.d.	3.69	n.d.	3400#
Bürrig B	4030#	8.20	1.77	153	20.4	33.3	7.36	25.5	n.d.	n.d.	4.37	n.d.	4290#

n.d. not detected

\# These values have to be considered as semiquantitative because concentrations calculated for PFBS were above the calibration range

* Results have to be taken with care because of poor chromatography of PFBA

The fluorinated alternative compound HFPO-DA was below the MDL or not detected in the effluent water from the chemical park in Leverkusen. Instead, the PFOA alternative substance DONA was detected in all samples with a concentration of up to 4.37 ng/L. These findings confirm the hypothesis from Chapter 4.6, that DONA was emitted, although probably not produced there, from the chemical park in Leverkusen. The concentrations of DONA were slightly lower than those of its predecessor substance PFOA. The major compound in the effluent samples was PFBS at concentrations ranging from a few ng/L (*X*) to a few µg/L (*Y2* and *Bürrig*). In general, PFASs were mainly emitted via the WWTP *Bürrig* with increased concentrations also observed for C_4 to C_8 PFCAs. However, PFBS was found at high concentrations not only in contaminated industrial effluent water from *Bürrig* but also in allegedly non-industrial process water from *Y2*, demonstrating that WWTP *Bürrig* is not the only point source emitting PFASs into the Rhine River.

Table 4-8 shows PFAS concentrations [ng/L] in surface water of the Lower Rhine from September 2015.

Table 4-8. PFAS concentrations [ng/L] in surface water of the Lower Rhine from September 2015. The results were rounded to three significant figures. Values in brackets were below the MQL.

No.	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	DONA	HFPO-DA	ΣPFASs
R1/15-09	4.67	1.89	1.34	(0.85)	4.59	2.65	1.01	3.09	0.61	0.20	<MDL	0.03	20.9
R2/15-09	4.65	1.82	1.26	1.04	5.32	3.27	0.99	3.55	0.43	0.26	<MDL	0.03	22.6
R3/15-09	3.74	1.61	1.09	1.10	4.92	2.35	0.84	3.30	0.27	0.25	<MDL	n.d.	19.5
R3-A/15-09	6.26	2.63	1.30	(0.96)	5.26	2.67	0.71	3.75	0.41	0.22	<MDL	0.02	24.2
R4/15-09	138	1.89	1.16	2.42	5.34	2.58	0.84	3.27	(0.21)	0.04	0.14	0.02	156
R4-A/15-09	148	1.78	1.03	1.69	5.65	2.81	1.32	5.18	0.25	0.14	0.16	0.04	169
R5/15-09	10.9	1.36	1.70	(0.79)	4.64	2.37	1.08	5.52	0.25	0.20	n.d.	0.05	28.8
R6/15-09	59.8	1.63	1.47	1.51	5.65	2.75	0.90	5.21	(0.16)	0.09	0.05	0.02	79.2
R6-A/15-09	56.9	1.62	1.78	1.59	6.23	4.02	1.12	5.72	0.56	0.23	0.04	0.04	79.9
R7/15-09	40.6	2.27	0.96	1.46	6.58	3.71	0.74	5.63	(0.17)	0.04	0.04	0.02	62.3
R8/15-09	30.5	2.60	0.94	1.28	7.53	3.11	0.94	7.19	n.d.	0.01	0.02	0.01	54.2
R9/15-09	25.9	2.31	0.88	1.19	6.18	3.27	1.04	6.98	0.33	0.04	0.01	0.04	48.2
R10/15-09	16.3	2.01	1.53	1.24	7.37	2.88	0.60	6.59	(0.22)	0.25	<MDL	0.02	39.0
R11/15-09	23.1	2.44	0.76	1.45	8.31	4.02	(0.51)	6.81	(0.20)	0.19	0.0005	0.02	47.9
R12/15-09	16.2	2.84	1.02	1.02	8.52	3.35	0.71	8.25	(0.17)	n.d.	<MDL	0.02	42.0
R13/15-09	20.7	2.34	1.37	2.74	4.25	3.87	1.00	5.36	0.25	0.17	0.0001	0.03	41.8

R14/15-09	18.7	1.72	1.39	1.73	4.01	3.11	1.04	4.07	0.38	0.20	<MDL	0.02	36.2
R15/15-09	14.2	1.36	0.96	1.73	3.25	2.57	0.84	3.39	0.31	0.14	<MDL	0.02	28.6

n.d. not detected

Generally, the concentrations of, especially, PFBS and PFBA were considerably lower in the Rhine River than in the chemical park's effluents *Bürrig* and *Y2* because of dilution. The highest concentrations were observed at sampling location R4/15-09, which is located between WWTP *Y2* and *Bürrig*, with a mean ΣPFASs concentration of 163 ng/L. Interestingly, the concentrations were higher than those at sampling point R6/15-09, which is located downstream of *Bürrig*. Although *Bürrig* emitted a higher amount of PFASs compared with WWTP *Y2*, concentrations in the Rhine River were higher downstream of *Y2* than downstream of *Bürrig*. A possible explanation for this is that the Wupper River flows into the Rhine River downstream of *Bürrig*, resulting in a dilution of the Rhine River's surface water. The Wupper River has an average discharge rate of 17 m^3/s at its mouth.[174] Compared to the results from August 2013 (see Chapter 4.3.2), the short-chain compound PFBS is still the major substance observed in the Lower Rhine with 35.5 ± 42.4 ng/L, followed by PFPeA and PFOA with 5.8 ± 1.5 ng/L and 5.2 ± 1.6 ng/L, respectively. The concentration profile and the substance pattern of the legacy compounds were relatively similar to those from 2013, emphasizing the continuous pollution burden of the Rhine River with PFASs. The fluorinated alternative compounds HFPO-DA and DONA were detected in 94% and 50% of the samples, respectively. Concentrations of HFPO-DA were uniform along the Lower Rhine with a mean of 0.03 ± 0.01 ng/L, demonstrating that there was, contrary to our findings from 2013, a continuous contamination of the Lower Rhine with the PFOA alternative compound HFPO-DA. However, it must be taken into account that MDLs and MQLs of HFPO-DA were lower by 2 orders of magnitude in this study than in that from 2013 because samples were analyzed with the more sensitive mass spectrometer API 4000 (AB Sciex). With the old mass spectrometer (API 3000), HFPO-DA could not be observed in the Rhine River samples from this study. HFPO-DA was detected in surface water samples upstream of the chemical park and not detected in the effluent water of the chemical park, indicating that its contamination probably originated from another source discharging into the River Rhine. In contrast to HFPO-DA, DONA was detected at highest concentration downstream of the chemical park at sampling point R4/15-09 with a mean of 0.15 ng/L. Upstream of the chemical park, DONA concentrations were below the MDL. DONAs surface water concentrations decreased continuously along the River with the minimum concentration (0.1 pg/L) occurring at sampling point R13/15-09. Compared with the concentrations of their predecessor substance PFOA, concentrations of HFPO-DA and DONA were lower by 2 orders of magnitude on average. The concentrations and the substance pattern in the stream Mühlengraben (R5/15-09), which is a branch stream of the Wupper River (Figure 4-11), were comparable to the concentrations in the Lower Rhine. It may be that the chemical park in Leverkusen influenced other surrounding water systems as well. Another possible explanation is that an additional PFAS source discharged upstream into the Wupper River. Between 2008 and 2009, the PFAS concentrations in the Wupper River were generally below the method quantification limit of 10 ng/L, except for PFOS which was detected at 20 ng/L.[127]

4.8 Add-on: Study on PFASs along the German coast of the Baltic Sea

The Baltic Sea is, in contrast to the North Sea, a nearly enclosed brackish water body with an area of 415000 km^2.[175] Water exchange to the North Sea is restricted by the Danish straits with the result that the salinity of the Baltic Sea is low. The low salinity puts stress on many species, that are often poorly adapted to it, and, thus, live at the edge of their physiological tolerance ranges.[176] In addition, water in the Baltic Sea has a long residence time of approximately 30 years and, therefore, it is a widely held view that the Baltic Sea is strongly susceptible to pollution.[175] Thus, species living in the Baltic Sea have not only to deal with natural stress factors, such as low salinity, but also with anthropogenic stress factors, such as temperature increase and chemical pollution, emphasizing the high sensitivity of the Baltic Sea ecosystem.

The purpose of this study was to investigate the PFASs pollution along the German coast of the Baltic Sea and to compare the pollution burden and pattern with that of the German Bight.

Detailed information on sampling locations and extraction method are given in Table B-4 and Figure 7-4. In short, 1 L surface water was sampled in polypropylene bottles (VWR International) and cooled until extraction. Sampling was mainly carried out from piers along the German Baltic Sea coast in March 2016 (Figure 4-13). The salinity increased, in general, from East to West (7.6-18.3 psu), reflecting the increasing proximity to the North Sea. Approximately 1 L was extracted immediately after sampling. Concentrations were calculated according to equations (1) to (3). MDLs and MQLs ranged from 0.000003 ng/L (PFUnDA) to 1.26 ng/L (PFPeA) and from 0.000010 ng/L (PFUnDA) to 3.73 ng/L (PFPeA), respectively. The mean recoveries of the internal standards ranged from 39 ± 6% ([$^{13}C_2$]-PFHxA) to 91 ± 11% ([$^{13}C_2$]-PFDA) (Table D-3).

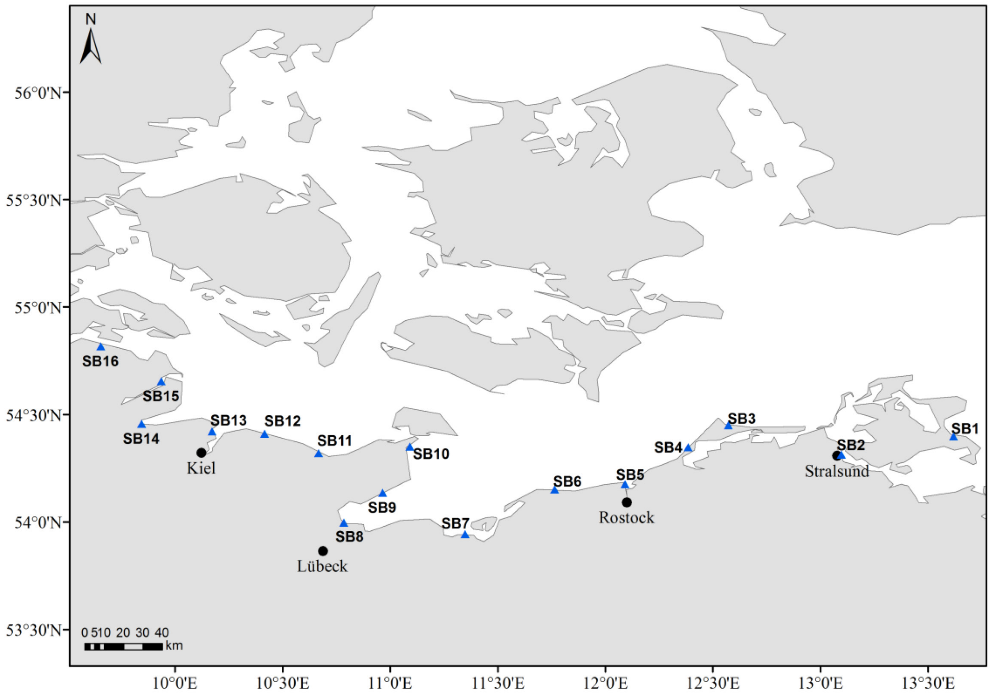

Figure 4-13. Sampling points along the German coast of the Baltic Sea.

Table 4-9 shows the PFAS concentrations [ng/L] in surface water from the German coast of the Baltic Sea.

Table 4-9. PFAS concentrations [ng/L] in surface water along the German coast of the Baltic Sea and in the Schlei River (SB15). Values in brackets are below the MQL. Concentrations of PFBA cannot be calculated because of poor chromatographic performance in the samples. Concentrations of PFPeA were always below the MDL.

No.	PFBS	PFHxS	PFOS	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	HFPO-DA	ΣPFASs
SB1	0.18	0.19	0.06	0.40	0.21	0.34	0.10	(0.01)	0.00004	<MDL	0.11	1.60
SB2	0.12	0.18	<MDL	0.43	0.21	0.32	0.10	(0.02)	0.00246	<MDL	0.10	1.47
SB3	0.17	0.17	<MDL	0.25	0.21	0.30	0.10	<MDL	<MDL	<MDL	0.12	1.34
SB4	0.15	0.19	0.03	0.26	0.27	0.33	0.11	<MDL	0.00027	<MDL	0.13	1.46
SB5	0.16	0.17	0.02	0.24	0.23	0.34	0.10	<MDL	0.00032	<MDL	0.14	1.40
SB6	0.15	0.17	0.02	0.20	0.21	0.32	0.11	<MDL	0.00012	<MDL	0.13	1.32
SB7	0.14	0.14	<MDL	0.24	0.23	0.28	0.07	<MDL	0.00030	<MDL	0.15	1.25
SB8A	0.14	0.16	<MDL	0.25	0.22	0.29	0.08	<MDL	0.00086	<MDL	0.14	1.28
SB8B	0.13	0.15	<MDL	0.26	0.27	0.29	0.08	<MDL	<MDL	<MDL	0.12	1.30
SB8C	0.15	0.18	<MDL	0.26	0.24	0.30	0.08	<MDL	<MDL	<MDL	0.13	1.35
SB9	0.13	0.18	0.03	0.24	0.21	0.32	0.09	<MDL	0.00007	<MDL	0.12	1.33
SB10	0.13	0.17	<MDL	0.25	0.17	0.32	0.09	<MDL	0.00107	<MDL	0.11	1.25
SB11	0.17	0.17	<MDL	0.23	0.23	0.28	0.07	<MDL	<MDL	<MDL	0.18	1.32
SB12	0.16	0.12	<MDL	0.22	0.29	0.29	0.08	<MDL	0.00098	<MDL	0.21	1.37
SB13	0.20	0.31	0.19	0.51	0.40	0.80	0.30	0.03	0.00524	0.00	0.22	2.98
SB14	0.16	0.19	0.16	0.18	0.24	0.42	0.16	(0.01)	0.00150	<MDL	0.18	1.70
SB15	0.24	0.53	0.12	0.34	0.21	0.34	0.11	(0.01)	0.00206	<MDL	0.16	2.06
SB16	0.14	0.14	0.01	0.26	0.24	0.31	0.08	<MDL	<MDL	<MDL	0.14	1.31

In general, the pollution burden among the sampling sites was similar with a mean ∑PFASs concentration of 1.51 ± 0.42 ng/L. Slightly higher concentrations were found in Strande at SB13, possibly reflecting the influence of the Kieler Förde or a nearby marina, where construction works have been carried out during the sampling. Compared with the surface water concentrations from the German Bight, the concentrations from the Baltic Sea were approximately 6 times lower (cf. Chapter 4.3). It was estimated that PFASs pollution in the Baltic Sea originates mainly from diffuse sources, such as atmospheric deposition.[177] In contrast to this, the German Bight suffers from continuous pollution discharges in the Rhine-Meuse delta. However, the results are somewhat surprising as water of the Baltic Sea has a long residence time of approximately 30 years and is, thus, susceptible to pollution.[175] Filipovic et al. showed that the input of PFHxA, PFOA, PFDA, and PFOS to the Baltic Sea exceeds the output, indicating that the concentrations of these compounds are increasing in the Baltic Sea.[177] However, our findings are in accordance with that of Kirchgeorg and Ahrens et al. who observed similar concentrations to ours in the years 2007-2008.[178,179] Thus, no significant increase in PFASs pollution can be observed since the last studies were conducted.

Major compounds detected were PFOA, PFHxA, and PFHpA with mean proportions of 22.8 ± 2.2%, 18.7 ± 3.8%, and 16.3 ± 2.8%, respectively. A major observation in this study is that the fluorinated alternative HFPO-DA was detected in all samples with a mean concentration of 0.14 ± 0.03 ng/L and a mean proportion of 9.7 ± 2.2%.

In general, it is assumed that PFASs pollution in the Baltic Sea originates mainly from diffuse sources and that the contribution of the North Sea inflow is insignificant.[177] However, for PFHxA, the contribution of the North Sea inflow was estimated to account for 49%,[177] suggesting that the contribution is compound-depending. This hypothesis is supported by the fact that HFPO-DA concentrations in the Baltic Sea were a function of salinity, as illustrated in Figure 4-14.

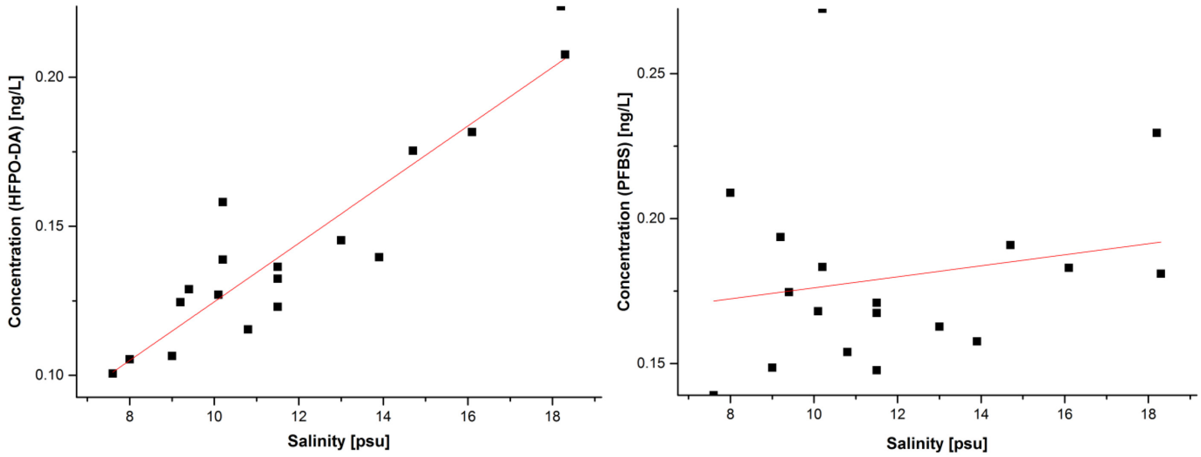

Figure 4-14. Correlation between the salinities [psu] of the samples from the Baltic Sea and the concentrations [ng/L] of HFPO-DA (left) and PFBS (right). The data sets followed normal distribution at a significance level α of 0.05 (Kolmogorov-Smirnov test). Pearson r was 0.92 and 0.19 for HFPO-DA and PFBS, respectively.

HFPO-DA concentrations correlate strongly and positively with the salinity of the Baltic Sea ($r = 0.92$), whereas most legacy PFASs, as exemplified with the compound PFBS, show weak or moderate (positive and negative) or no relationships ($-0.31 < r/r_{SP} < 0.41$). These findings suggest that HFPO-DA pollution and, to a lesser extent, PFHpA pollution ($r = 0.71$), originated from the North Sea and, consequently, from the Rhine-Meuse delta, whereas most legacy compounds were emitted to the Baltic Sea on various ways, such as river run-off. It can be expected that the contribution of the North Sea inflow on HFPO-DA concentrations in the Baltic Sea is, similar to PFHxA, higher compared with river discharges or atmospheric deposition.

5 Emissions of Per- and Polyfluoroalkyl Substances in a Textile Manufacturing Plant in China and Their Relevance for Worker's Exposure (Paper 2)

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Abstract

The manufacturing of high-performance fabrics requires numerous chemical treatment steps that involve the use of per- and polyfluoroalkyl substances (PFASs) to protect apparel against water, stain, and oil penetration. However, air and wastewater emissions of PFASs generated during this manufacturing are a potential threat to both factory workers and the environment. We investigated the occurrence and distribution of PFASs in wastewater, air, airborne particles, and settled dust in a textile manufacturing plant in China. PFOA and PFDA or their precursor compounds 8:2 FTOH and 10:2 FTOH were the dominant compounds in all environmental media tested, revealing that long-chain PFASs were preferably used for the manufacturing of functional garments. Besides, PFASs were detected along the textile manufacturing chain, indicating that they were used as durable water repellents and as surfactants in, for example, coating agents. The workers' exposure to FTOHs via air inhalation was up to 5 orders of magnitude higher than the background exposure of the general western population. To the best of our knowledge, this is the first study providing information regarding the emission of PFASs during the manufacturing of textiles via various environmental media.

5.1 Introduction

A key requirement for outdoor and protective apparel is a resistance to water, stains, and oil. Using per- and polyfluoroalkyl substances (PFASs) seems to be the most efficient method to provide these types of clothing with this functionality. However, concerns about their hazardousness have led to the use and further development of numerous fluorine-free alternatives based on, for example, polyurethane, silicones, and (paraffin) waxes.[180,181] Because the performance of garments treated with these alternatives is not comparable with the performance generated by the fluorochemicals,[180,181] PFASs are still widely used and, therefore, found in various textiles in a typical concentration range of several hundred μg/m^2.[182-184] PFASs may escape during the lifetime and disposal of apparel via wastewater, air, and sewage sludge, potentially threatening both consumers and the environment.[185-187] The manufacturing of high-performance fabrics is potentially an additional source of PFAS emissions because PFASs act as main ingredients in durable water repellent (DWR) finishes.[25] DWRs extend the lifetime of a garment and, by lowering the fiber's surface energy, impart water, oil, soil, and stain repellency to textiles. Their chemical structure is characterized by side-chain fluorinated polymers prevalently based on fluorotelomer acrylates (FTACs), fluorotelomer methacrylates (FTMACs), or perfluoroalkane sulfonamidoethanols (FASEs) (Figure C-1).[32] Aqueous dispersions of these polymers typically contain 80% water, 20% polymer, 0.5% unreacted and unbound residuals, such as fluorotelomer alcohols (FTOHs), and impurities, such as perfluoroalkyl carboxylic acids (PFCAs).[29,188] The exact composition and, thus, the proportion of residuals and impurities vary among the fluorinated polymeric products on the market. For instance, residual fluorinated alcohols have been found in various fluorinated polymers and fluorosurfactants at percentages between 0.04 and 5.9% of the dry weight.[188,189] Residuals and impurities may be released directly from the products into the environment through volatilization. Additionally, the polymers can degrade under environmentally relevant conditions via cleavage of the ester bond of the fluorinated side-chain, resulting in the release of fluorinated alcohols.[190-192] Once in the environment, fluorinated alcohols can break down into PFCAs and perfluoroalkane sulfonic acids (PFSAs).[39-43] PFCAs and PFSAs are environmentally concerning because of their high persistence; potential to bioaccumulate, and thereby possibly biomagnify; and potential to cause toxic effects.[108]

With more than 100000 garment manufacturers and over 10 million people employed in the garment industry, China has rapidly become the world's leading manufacturer and exporter of garment products over the past decade.[193] The textile manufacturing plant with approximately 1800 employees specializes in the weaving, dyeing, and finishing of polyester textiles and produces functional fabrics for numerous national and international brands. Textile wet-processing generally generates numerous air and wastewater emissions of volatile organic compounds and chemical auxiliaries.[194] Thus, textile manufacturing plants, where DWRs containing fluorinated polymers are applied to fabrics, are potential sources of PFASs in the environment. Until now, studies have only focused on the PFCAs load in effluent water and sewage sludge from the textile industry.[195-197]

This paper reports the emissions of PFASs via wastewater, air, airborne particles, and settled dust along the textile manufacturing chain, from the scouring to the quality inspection of the fabric, in a manufacturing plant in China. The results are compared with concentration levels from other environments, in general, and with concentration levels emitted from the fluorochemical and fluoropolymeric industries, in particular. The workers' exposure is roughly estimated and compared with exposure scenarios from other occupational environments, where similarly high PFAS emissions were observed. Wang et al. emphasized that the understanding of the PFCA origins in the environment is still incomplete.[107] The authors identified critical knowledge and data gaps that include the emission volume of PFCAs from other than from fluoropolymer production facilities. Our results may help in closing this knowledge gap.

5.2 Materials and Methods

5.2.1 Sampling Site

The textile manufacturing plant of this study is located in a typical industrial park in the Yangtze River Delta. The Yangtze River is China's longest river, at about 6300 km, and has an average discharge of 23400 m^3/s.[198] It receives large volumes of municipal and industrial wastewater and, consequently, has been dealing with heavy pollution for the last three decades.[199] The plant consists of four independent workshops (W) (Figure 5-1): Workshop K (Weaving), Workshop 1 and 2 (Scouring, Dyeing, Finishing, Drying, Heat Setting, and Quality Inspection), and Workshop 3 (Coating). Textiles for heavyweight garments, such as uniforms and fashion clothes, were produced in workshop 1, whereas lightweight garments, such as sportswear and outdoor clothes, were produced in workshop 2. However, the textiles were produced in the same way by using identical chemicals and amounts in the workshops 1 and 2. Mechanical ventilation in the workshops was provided using continuously operating exhaust fans that emitted untreated exhaust air to the atmosphere while pulling in fresh air on the other side of the workshop.

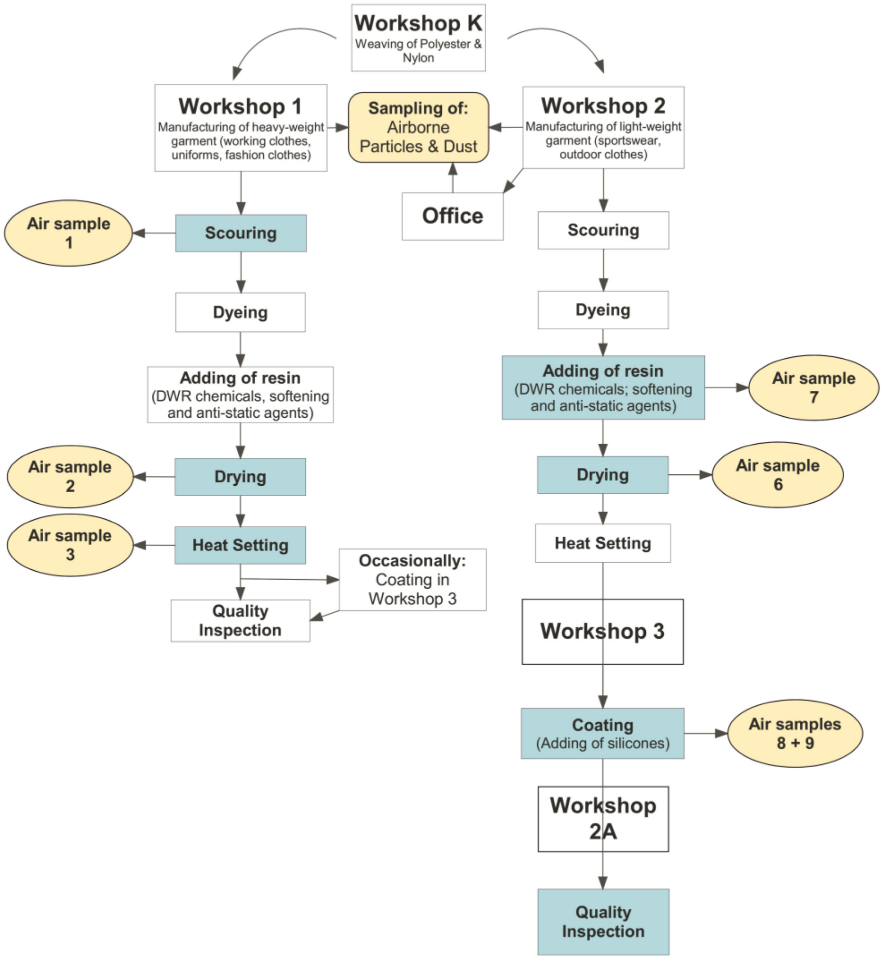

Figure 5-1. Production steps during the manufacturing of textiles, including sampling plan.

5.2.2 Sample Collection

In April 2014, 34 samples consisting of water, air (gas and particle phase), or settled dust were collected in three workshops, involving the following manufacturing steps (Figure 5-1): Scouring (W1), DWR treatment (W2), Drying (W1+W2), Heat Setting (W1), Coating (W3), and Quality Inspection (W2A). One liter each of fresh tap water, effluent water, and Yangtze River surface water was collected in precleaned polyethylene terephthalate bottles and filtered through glass fiber filters (GFFs, Whatman, Ø 47 mm), which were retained for analysis of the particulate phase. The amount of suspended particulate matter (SPM) varied between 25.8 and 68.9 mg (Table C-1). Airborne particles were sampled in duplicate using GFFs (Jiuding High-Tech Filtration, Ø 147 mm) deployed on lockers or production machines, at heights of approximately 1.5 to 2 m, for 17 days. The particle deposition fluxes *F* varied between 12 and 47 mg/(m^2·d) with the minimum occurring in the office and the maximum occurring in the coating workshop (Table C-2). At the end of the sampling campaign, seven GFFs were used to wipe off settled dust from the same lockers or production machines. All GFFs were baked at 450 °C for 12 hours before usage and covered in aluminum foil. The air was sampled using polyurethane foam (PUF) disk passive samplers deployed for 17 days.[200] The PUF disks (14 x 1.35 cm, Tisch Environmental, Cleves, OH) were cleaned before usage with acetone, methanol, and hexane via Soxhlet extraction. The sampler housing was wiped with acetone and methanol before deployment. Procedural blank samples (3 PUF disks and 6 GFFs) were covered in aluminum foil and transported together with the sampling material to the textile manufacturing plant. The particle, dust, and air samples were stored at −20 °C until extraction.

5.2.3 Chemicals

Twelve neutral compounds were monitored: fluorotelomer alcohols (6:2 FTOH, 8:2 FTOH, 10:2 FTOH, and 12:2 FTOH), fluorotelomer acrylates (6:2 FTAC and 8:2 FTAC), perfluoroalkane sulfonamides (MeFBSA, MeFOSA, and EtFOSA), and perfluoroalkane sulfonamidoethanols (MeFBSE, MeFOSE, and EtFOSE). Additionally, 20 ionic PFASs were monitored: perfluoroalkyl carboxylic acids (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA), perfluoroalkane sulfonic acids (PFBS, PFHxS, PFHpS, PFOS, and PFDS), fluorotelomer unsaturated carboxylic acids (6:2 FTUCA, 8:2 FTUCA, and 10:2 FTUCA), and the fluorinated alternative compound HFPO-DA. The full names of the PFAS compounds and all solvents, reagents, and chemical standards are listed in detail in Table C-3.

5.2.4 Sample Extraction and Instrumental Analysis

The extraction of the water samples was modified based on a previous study.[201] In contrast to that study, 500 mg of sorbent was used for the solid phase extraction (SPE, Waters Oasis Wax, 6 cm^3, 60 µm particle size) and an additional cleanup using Envi-Carb (Supelclean ENVI-Carb, 250 mg, 3 cm^3) was deemed necessary for the effluent samples. Particles from the water samples that retained on GFFs were extracted with methanol using an ultrasonic bath (2 x 60 min). The amounts of particles and dust were gravimetrically determined after conditioning at 20 ± 2 °C and 58 ± 2% relative humidity. Air and particle samples were halved to extract both neutral and ionic PFASs. One half was chopped and extracted via Soxhlet extraction using dichloromethane[202,203] and methanol for the neutral and ionic compounds, respectively. Dust samples were extracted with methanol for the ionic PFASs. All samples were extracted for approximately 20 h. The extracts were reduced to 150 µL under a gentle stream of nitrogen (>99.999%) and filtered through 0.2 µm polypropylene filters (Puradisc, GE Healthcare Life Sciences). An additional cleanup using Envi-Carb was applied for some air samples. Before extraction, all samples were spiked with 20 µL of a mass-labeled ionic PFASs solution (500 pg/µL) or with 40 µL of a mass-labeled neutral PFASs solution (250 pg/µL). Before instrumental analysis, mass-labeled [$^{13}C_2$]-PFOA was added as injection standard (10 µL, 100 pg/µL) for HPLC-MS/MS and 9:1 FTOH (10 µL, 100 pg/µL) for GC-MS. The instrumental analyses for ionic and neutral PFASs are described elsewhere.[201-203]

5.2.5 Quality Assurance

Analytes were quantified plotting the ratio of the area of the analyte to the area of the corresponding mass-labeled internal standard on the y-axis and the ratio of the concentration of the analyte to the concentration of the corresponding mass-labeled internal standard on the xaxis. The calibration levels ranged from 0 to 500 pg/µL (11-point calibration). All solvent-based calibration curves were linear with correlation coefficients above 0.99. If analyte concentrations were above the calibration range, the sample solution was diluted by a factor of 5 or 10. No appropriate internal standards were available for PFBS, PFPeA, PFHpA, PFTrDA, PFTeDA, 12:2 FTOH, 6:2 FTAC, 8:2 FTAC, MeFBSA, and MeFBSE. For those substances, internal standards with a similar chemical structure and retention time were used (Table C-3). For 6:2 FTOH, [$^2H_2$,$^{13}C_2$]-8:2 FTOH was used as an internal standard because the signal of the [$^2H_2$,$^{13}C_2$]-6:2 FTOH was overlapped by a matrix peak in some air samples. For the extraction of the dissolved and particulate phase of the water samples, the mean recovery rates of the internal standards ranged from 33 ± 15% ($^{13}C_4$-PFOA) to 79 ± 41% ($^{13}C_4$-PFBA) and from 51 ± 19% ($^{13}C_4$-PFBA) to 79 ± 36% ($^{13}C_2$-6:2 FTUCA), respectively (Table C-4). The mean recoveries for the Soxhlet extraction ranged from 33 ± 15% ([$^{13}C_2$]-PFDA) to 185 ± 60% (d9-EtFOSE). The extraction efficiencies ranged from 43 ± 5% (HFPO-DA) to 92 ± 15% (PFBA). Because ^{13}C-labeled FTUCAs showed low recoveries for the Soxhlet extraction, the results have to be considered as semiquantitative. Procedural blank concentrations were taken into consideration when calculating sample concentrations, method detection limits (MDLs), and method quantification limits (MQLs). MDLs and MQLs are listed in Table C-5.

5.2.6 Statistical Analysis

The Kolmogorov-Smirnov test was used to determine the appropriateness of the data set for Pearson correlation. When the data set followed normal distribution at a significance level α of 0.05, we conducted Pearson correlation. When normal distribution was rejected, we conducted Spearman correlation. A two-tailed test was used to test statistical significance with $p < 0.05$. Cohen's definition was used to classify Pearson r and Spearman r_{SP} as weak (≥0.1), moderate (≥0.3), and large/strong (≥0.5).[204]

5.3 Results and Discussion

5.3.1 Introductory Remarks

Filtration through GFFs may cause underestimation and overestimation of long-chain ($C \geq 9$) PFAS concentrations in the dissolved and particulate phase, respectively, because sorption has been observed on GFFs for several sample matrices (<15% sorption for effluent water).[205,206] PUF disks impregnated with XAD-4 (a styrene-divinylbenzene copolymer) are used preferentially for the trapping of PFASs because of a higher sorption capacity of the medium. However, limited preparation time before the sampling campaign made the impregnation with XAD-4 powder unfeasible. Furthermore, calibration studies, which are necessary to get location-dependent uptake rates and equilibration times, could not be carried out during the ongoing textile production. Therefore, we primarily report the passive sampling data on a mass per sample per day basis. For the calculation of workers' exposure scenarios and for the comparison with data from previous studies, we derived air concentrations, referred to 1 m^3 air, from reported linear uptake rates R and PUF-air partition coefficients $K_{PUF\text{-}A}$ (Table C-6). For neutral PFAS concentrations in air, we only considered the PUF concentrations of 8:2 FTOH and 10:2 FTOH because they totaled 87% of the overall burden and reliable values for $K_{PUF\text{-}A}$ were available.[207] Equilibration times of more than 17 days were expected for the ionic PFASs,[208] as a previous study showed a linear uptake phase for PFSAs over several months.[209] For calculating air concentrations, we used an average gas-phase sampling rate R of 4 m^3/d, according to the Global Atmospheric Passive Sampling (GAPS) network and other studies using the same sampler housing and same sized sampling medium.[200,209-211] However, air concentrations and, thus, the workers' exposure via inhalation have to be considered as rough estimations. The comparability with other studies is reduced because of different sampling techniques and input parameters for the estimation of the workers' exposure. In addition, PUF is able to accumulate both gas-phase and particle-bound pollutants. The sampler chamber principally protects the PUF disks from coarse particle deposition. However, PFASs associated with fine or ultrafine particles may also be collected, leading to overestimated air concentrations especially for ionic PFASs.[200,212-214]

5.3.2 Ionic PFASs in Effluent Water

The most commonly used technique for textile finishing is called Pad-Dry-Cure or Padding, during which the textile is impregnated continuously with the DWR dispersion. The excess liquid is squeezed out through a pair of rollers to guarantee a uniform pickup of the chemicals and the wet textile is cured with heat afterwards. When the excess liquid is removed, it leaves the manufacturing plant as wastewater. Thirteen ionic PFASs were quantified in the effluent from the textile factory's in-house wastewater treatment plant (WWTP) (Figure 5-2, Table C-7).

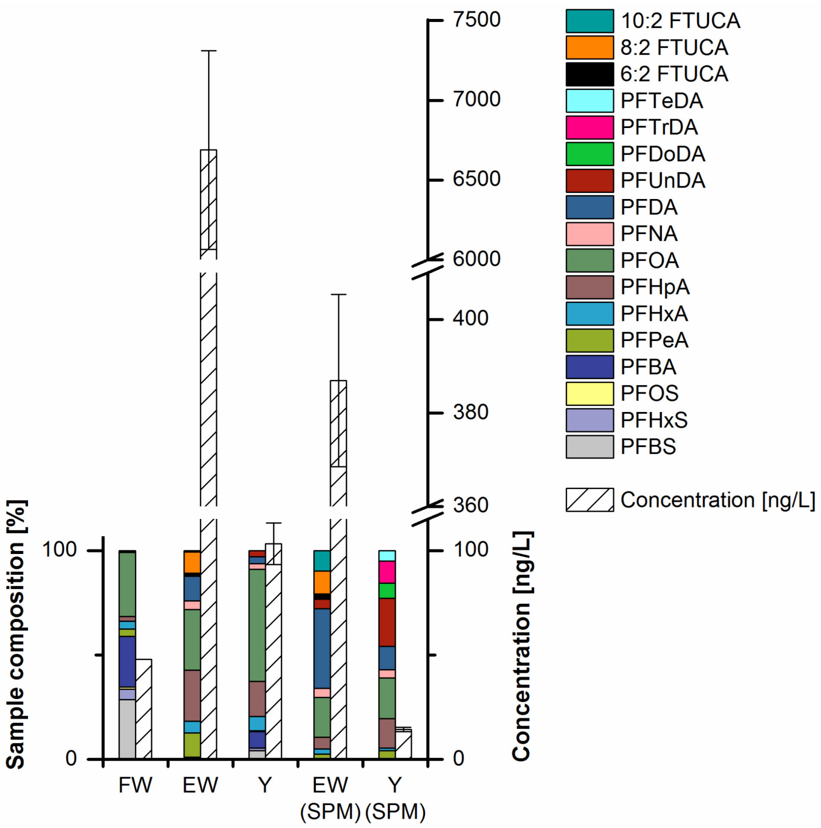

Figure 5-2. Mean concentrations of ionic PFASs [ng/L] in the dissolved phase and particulate phase (SPM) of fresh tap water (FW), effluent water from the textile manufacturing plant (EW), and surface water from the Yangtze River (Y). No particles were observed in the fresh tap water.

PFTrDA and PFTeDA were detected only in the particulate phase, whereas PFBA was detected in the dissolved phase. The concentrations calculated in the fresh tap water were subtracted from the concentrations in the effluent water to take the PFASs input into the manufacturing site into account. The mean ΣPFASs concentration in the effluent's dissolved phase was 6690 ng/L, which was 2 orders of magnitude higher than the mean ΣPFASs concentration of 47.9 ng/L in the fresh tap water. The main compounds in the fresh tap water were PFBS, PFBA, and PFOA. In the effluent water, no short-chain PFSAs were detected and PFOS was only observed in low concentrations or below the MQL. In general, the PFSAs had no impact on the PFASs pollution at the manufacturing site, indicating that they had not been used during the textile manufacturing. PFHpA and PFOA contributed 54% to the overall burden in the effluent water, with mean concentrations of 1640 ng/L and 1950 ng/L, respectively. Additionally, PFPeA, PFDA, and 8:2 FTUCA contributed similarly to the ΣPFASs concentration, approximately 11%. FTUCAs were detected only in the effluent water, indicating that PFCA findings have resulted from the use of textile finishes that are based on FTOHs because FTUCAs are intermediates formed during biotransformation or aerobic biodegradation of FTOHs to PFCAs.[39,215,216] Higher PFCA concentrations were also found in treated effluent samples from a fluorotelomer polymer manufacturing plant compared with those from the influent, demonstrating the relevance of biotransformation during wastewater treatment.[34]

About 95% of the ΣPFASs were distributed in the dissolved phase, whereas 5% were found on suspended particulate matter with a mean ΣPFASs concentration of 372 ng/L. The main compound in the particulate phase was PFDA with a percentage of 38%, followed by PFOA with 19%. Because adsorption to particles increases as carbon chain length increases,[123,217] PFCAs with ≥ 9 carbon atoms showed a greater proportional contribution to the ΣPFASs concentration in the particulate phase than to the ΣPFASs concentration in the dissolved phase. Additionally, the composition ratios of 6:2 FTUCA and 8:2 FTUCA were slightly higher in the particulate phase than they were in the dissolved phase. A similar observation was made for 8:2 FTUCA and other precursors in samples from Tokyo Bay in 2012.[218]

In 2011, an average ΣPFASs concentration of 165 ng/L, which is approximately 40 times lower than our result, was found in wastewater from a textile manufacturing site discharging, likewise, into the Yangtze River Delta.[196] However, this facility from Ningbo used "advanced technology" for its sewage treatment, whereas the effluent from our study was treated only biologically before being analyzed. Similarly to our study, though, PFOA was the dominant compound detected, but with a higher proportional contribution of about 83%. Clara et al. observed smaller PFAS concentrations of 664 ng/L in the effluent of a textile production facility, where yarn had been manufactured, bleached, and dyed, and PFNA contributing 48% to the overall burden.[195]

In the Yangtze River, we found mean ΣPFASs concentrations of 103 ng/L in the dissolved phase and 14.3 ng/L in the particulate phase, with PFOA and PFUnDA as the main compounds, respectively. Before being discharged into the Yangtze River, the in-house biologically treated effluent has been treated in a local WWTP that receives about 70% of its wastewater from the surrounding textile industry. The WWTP is located 1 km upstream from the sampling site in the Yangtze River. However, it is unknown where the effluent has been discharged into the Yangtze River and whether the water samples from the Yangtze River were influenced by the surrounding textile industry. In 2013, mean ΣPFASs concentrations of approximately 30 ng/L, with PFBS, PFHxA, and PFOA as the main compounds, were detected in the dissolved phase close to our sampling site.[199]

5.3.3 PFASs in Air

Neutral PFASs. Neutral PFAS concentrations in air are shown in Table C-8. Twelve compounds were detected with ΣPFASs concentrations ranging from 188 ng/(sample·d) (coating) to 3260 ng/(sample·d) (drying in W1). The high concentrations observed close to the DWR treatment are primarily related to the heat curing process of the wet textile. This is exemplified in the work undertaken by Washington et al., who observed a loss of neutral residuals in fluorotelomer-based polymers (FTPs) by 2 orders of magnitude during the curing at 127°C.[188] The PUF disks were dominated by 8:2 FTOH and 10:2 FTOH, which accounted for 55 ± 7% and 32 ± 10% of total neutral PFASs, respectively. In general, 6:2 FTOH had a smaller contribution with 12 ± 10%, but had a higher contribution at the drying process in workshop 1 with a concentration of 898 ng/(sample·d). A similar pattern was observed in three commercial FTP dispersions, where the ratios of residual FTOHs were averagely 3:61:36 (C6:C8:C10), indicating that the DWR solution used for the textile finishing had a residual composition comparable to that of the FTP dispersions.[29,188] Concentrations of 12:2 FTOH, FTACs, perfluoroalkane sulfonamides (FASAs), and FASEs were considerably lower, with a mean of 2 ng/(sample·d) of the compounds' average concentrations. Estimated air concentrations for 8:2 FTOH and 10:2 FTOH were between 5.1 and 91.3 μg/m³ and 1.2 and 18.2 μg/m³, respectively (Table C-6). Previously reported air concentrations derived from passive sampling typically ranged from a few pg/m³ to several ng/m³ for both outdoor and residential indoor air.[185,210,219-223] Elevated indoor air concentrations were detected in stores selling furniture and outdoor equipment at up to 458 ng/m³ with 8:2 FTOH as the main compound.[185,224] However, those concentrations were still 2 orders of magnitude lower than the concentrations observed in our study.

Ionic PFASs. The ionic PFAS concentrations in air are shown in Table C-9. Fifteen compounds were detected with ΣPFASs concentrations ranging from 4.1 ng/(sample·d) (outdoors) to 80.6 ng/(sample·d) (drying in W1). In general, the concentrations were 2 orders of magnitude lower than those of neutral PFASs, reflecting not only the lower vapor pressure of PFCAs compared with that of neutral PFASs, but also the lower amount of PFCAs in fluorinated polymers. PFCAs were found in FTP dispersions as non-intended impurities with concentrations that were, likewise, 2 orders of magnitude lower than that of FTOHs.[188] Interestingly, the PFCA/FTOH ratios in our air samples were identical with those in a commercial DuPont FTP dispersion, i.e. 0.03:0.01:0.01:0.02 (PFHxA/6:2 FTOH:PFOA/8:2 FTOH:PFDA/10:2 FTOH:PFDoDA/12:2 FTOH).[188] The PUF disks were dominated by PFOA with a mean proportion of 53%, followed by PFHxA and PFDA with contributions of 20% and 11%, respectively. Interestingly, PFHxA had a higher contribution than its precursor compound 6:2 FTOH, whereas PFDA had a smaller contribution than 10:2 FTOH. These surprising findings may be explained by the decrease of the vapor pressure with increasing chain-length, influencing primarily the gas-particle partitioning of the PFCAs. PFHxA had, in accordance with its precursor compound 6:2 FTOH, the highest concentration (36.1 ng/(sample·d)) and the highest proportion (45%) at the drying process in W1. Although the air sample at the drying process in W1 had the highest ∑PFASs concentration, several compounds, such as PFDA, had higher concentrations next to the scouring process, assuming that the scouring is, likewise, a source of PFAS emissions by the use of PFAS-based surfactants.

Data for ionic PFASs in the gas phase are limited, because these compounds preferably attach to particles. However, PFOA concentrations ranging from not detected (n.d.) to 540 pg/(sample·d) were reported in European air.[208] Elevated concentrations were observed close to an ethylene tetrafluoroethylene manufacturing site (8.7 ng/(sample·d)) and close to a construction site of a new office block (27 ng/(sample·d)). Those concentrations were somewhat higher than ours observed outdoors (average of 1.7 ng/(sample·d)). Shoeib et al. reported mean concentrations of approximately 300 pg/m³ and 6 pg/m³ in indoor and outdoor air, respectively.[219] Mean air concentrations in this study were approximately 30 times (9610 pg/m³ indoors) and 175 times (1050 pg/m³ outdoors) higher.

5.3.4 PFASs in Airborne Particles

Neutral PFASs. As neutral PFASs have high vapor pressures and low log K_{OA} values, they occur mainly in the gas phase. Typically, less than 10% of FTOHs and FTACs are associated with particles. However, the gas-particle partitioning may vary significantly depending on the sampling site as well as the loading of total suspended particulate matter and ambient temperature.[225-229] The particle-phase percentages of FASAs and FASEs are typically higher, ranging from about 10 to 40% because of higher log K_{OA} values.[225,226,230]
Neutral PFAS concentrations in airborne particles are shown in Table C-10. Twelve compounds were detected with ΣPFASs concentrations ranging from 33800 ng/g (coating) to 1110000 ng/g (office). Samples were dominated by 10:2 FTOH, with a mean proportion of 56 ± 8%, followed by 8:2 FTOH with 32 ± 5%. In contrast to commercial FTP dispersions,[29,188] the concentrations of 10:2 FTOH exceeded that of 8:2 FTOH, reflecting possibly a stronger sorption potential to airborne particles due to a longer chain length. FTOHs accounted for approximately 96% of the total neutral PFASs, whereas FTACs accounted only for 2%. The percentages of 8:2 FTAC ranged from 3% to 37% in commercial FTP dispersions and were somewhat higher than in our airborne particle samples. The concentrations of 8:2 FTAC were predominantly higher than that of 6:2 FTAC, which is in accordance with the findings of FTOHs and with the composition of commercial FTP dispersions.[29,188] EtFOSE had, in general, concentrations ranging from <MDL to 41.0 ng/g, except at the coating treatment with a mean concentration of 219 ± 69 ng/g. It was assumed that this compound was used as a raw material or additive for coating agents rather than for DWR agents.

Ionic PFASs. Under environmentally relevant conditions, >99.99% of PFCA molecules will occur as anions.[231] The vapor pressure of the anionic form of PFOA is assumed as negligible.[21] The lower the vapor pressure of a compound, the higher the tendency to adsorb to surfaces and particles.[232] Assuming that the vapor pressure is negligible for all anionic conjugate bases of PFCAs and considering that the vapor pressure decreases with increasing chain-length, PFCAs should be found attached to particles rather than in the gas phase.[21,36,233] PFCAs might be released as impurities from textile finishes that are based on fluorinated polymers both associated with particles or unassociated followed by a rapid adsorption to particles.[234] Additionally, PFCAs may be formed during the degradation of FTOHs,[40,235] which can easily volatize because of their high vapor pressure from fluorinated polymer-based textile finishes. This hypothesis is supported by the semiquantitative findings for the FTUCAs, which are formed as intermediates during the transformation.

Ionic PFAS concentrations in airborne particles are shown in Table C-11. Fifteen compounds were detected with ΣPFASs concentrations ranging from 4730 ng/g (coating) to 224000 ng/g (office). The average concentrations of ionic PFASs totaled approximately 14% of those for neutral PFASs, reflecting the lower amount of PFCAs in fluorotelomer-based polymers compared with that of FTOHs.[188] Samples were dominated by PFOA and PFDA that, on average, accounted for 71% of the total ionic PFASs. These results were consistent with those of neutral PFASs, where the corresponding precursor substances 8:2 FTOH and 10:2 FTOH also dominated the distribution pattern. Interestingly, PFOA and PFDA had moderate relationships with their corresponding precursor substances ($r_{SP} = 0.40$), but statistically significant relationships with 12:2 FTOH ($r_{SP} > 0.62$) (Table C-12). A comparable observation was made for 8:2 FTOH and PFOA in indoor air, indicating a restriction on the mechanism of precursor transformation in the presence of NO_x.[40,219,235] PFHxA showed a statistically significant relationship with 6:2 FTOH ($r = 0.59$), whereas PFDoDA had a weak correlation with 12:2 FTOH ($r_{SP} = 0.25$).

5.3.5 PFASs in Settled Dust

Settled dust is a heterogeneous material containing varying percentages of inorganic and organic material and particle sizes ranging from a few µm to several mm. The presence of organic pollutants in settled dust strongly depends on the composition of the dust samples, leading to a reduced comparability among samples.[232] Additionally, the comparability among studies may be reduced when a sieving process is conducted. In contrast to the ΣPFASs concentrations in airborne particles, the ΣPFASs concentrations in settled dust were up to 2 orders of magnitude lower and in a comparable range across the samples (Table C-11). Sixteen compounds were detected with ΣPFASs concentrations ranging from 1390 ng/g (coating) to 6580 ng/g (workshop 1). Average concentrations that were up to 3 orders of magnitude higher than in our study, between approximately 49700 and 1170000 ng/g, were reported in dust from manufacturing plants producing fluorochemicals.[33,236,237] Mean concentrations of approximately 600 ng/g and 230 ng/g were found in house dust from Canada and Norway, respectively.[219,238] In offices, mean concentrations of 294 ng/g and 1540 ng/g were observed, which were 10 and 2 times lower, respectively, than our result (2950 ng/g).[239,240]

The main compound was PFOA with a mean contribution of 28% to ∑PFASs concentrations, followed by PFDA and PFNA with mean contributions of 18% and 12%, respectively. In general, the distribution pattern for settled dust varied more than that for airborne particles with average percent compositions of up to 7% for carboxylic acids with more than 11 carbon atoms. Besides, these compounds were the only ones that showed similar concentration levels in settled dust compared to those in airborne particles. In the literature, distribution patterns vary greatly among sampling sites and environments. For example, the distribution pattern in a Chinese fluoropolymer manufacturing plant was characterized mainly by PFOS, PFOA, and PFHxS, whereas PFHxA, PFNA, and PFDoDA were prevalent in home dust from Norway.[33]

Within the same workshop, the ΣPFASs concentrations differed by a factor of approximately 2 (workshop 1) and 3 (coating), indicating that there were different exposure times of the dust to the PFASs or different distances to the primary pollution source. Comparing the samples from the same workshop in more detail, it was seen that the short-chain PFCAs (PFBA, PFPeA, and PFHxA) showed higher concentrations in the samples where the long-chain PFCAs had lower concentrations. Statistical regressions showed that there were strong relationships among the short-chain PFCAs ($r > 0.51$) and even statistically significant correlations between PFBA and PFPeA ($r = 0.92$) and between PFHxA and PFHpA ($r = 0.85$) (Table C-13). Between the short-chain and long-chain PFCAs, there was generally a weaker (positive and negative) or no relationship ($0.40 > r > -0.36$). Exceptions were PFHpA and PFOA, which showed a statistically significant correlation with each other ($r = 0.90$) and moderate or strong relationships with both short and long-chain PFCAs. Similarly to the short-chain PFCAs, there are moderate or strong relationships among the long-chain PFCAs ($0.44 < r < 0.99$) with several statistically significant correlations. The results indicated that the uneven distribution and the age of the dust notably influenced the presence of PFASs in the dust. It might be that the dust samples within the same workshop were of different ages and, consequently, reflected a different exposure to PFASs. The results might indicate that various chemical formulations were used over time.

5.3.6 PFAS Emissions along the Textile Manufacturing Chain

Figure 5-3 shows the distribution of PFASs in air, airborne particles, and settled dust along the textile manufacturing chain.

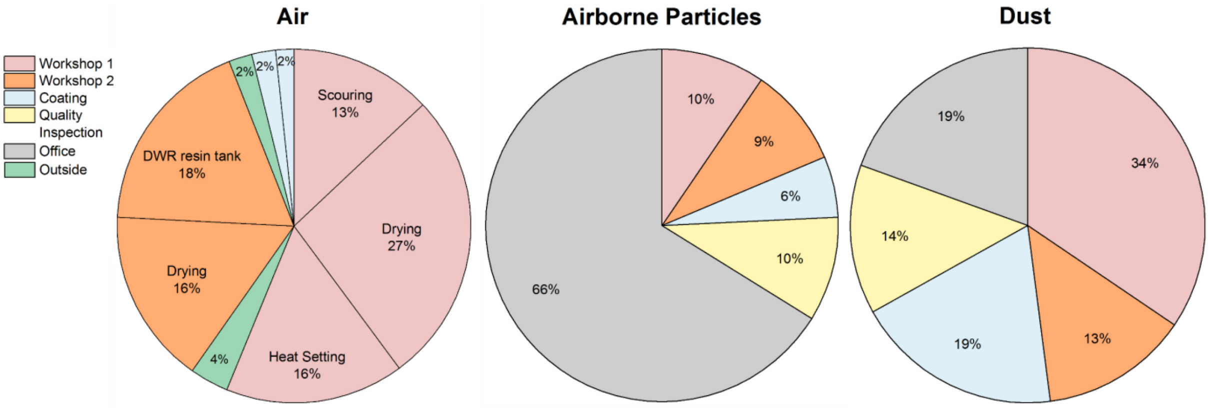

Figure 5-3. Distribution of PFASs in air, airborne particles, and settled dust along the textile manufacturing chain.

PFAS concentrations in air/airborne particles were similar in workshop 1 and workshop 2, contributing approximately 19%/10% and 17%/9%, respectively, which reflected the identical manufacturing processes of the textiles in both workshops. Interestingly, the scouring and heat setting contributed 13% and 16% to air pollution, respectively. PFAS concentrations may have resulted from the DWR treatment, which takes place in the same workshop, as observed in printing workshops for the detection of nonmethane hydrocarbons.[241] However, differences in the distribution of PFASs in air and airborne particle samples indicated that PFASs may be involved in manufacturing steps apart from the DWR treatment. For example, elevated concentrations were detected for 6:2 FTAC and 6:2 FTOH on GFFs that were deposited close to the drying process compared with the samples next to the scouring process and vice versa for 10:2 FTOH.

Because PFAS concentrations in airborne particles and dust observed in the coating workshop were comparable with those from the other workshops, similar air concentrations, or even lower than those observed outdoors, were unexpected. The low concentrations may be explained by higher humidity in the workshop caused by greater steam exhaustion, leading to a lesser extraction efficiency of the sampling medium. However, PFASs were detected in high concentrations in the coating workshop, although they were not used intentionally as coating ingredients. Additionally, the distribution pattern of PFASs in the airborne particles revealed that the coating treatment may be, likewise, a source of PFAS emissions. Thus, elevated amounts of primarily MeFBSA and EtFOSE were found in airborne particles during the coating treatment, whereas FTOHs and FTACs had lower concentrations, concluding that different fluorine-based auxiliary components or different amounts of these were used for the individual manufacturing steps. This hypothesis is supported by statistical regressions showing generally positive relationships among FTOHs and FTACs of up to $r_{SP} = 0.81$, whereas FTOHs/FTACs and MeFBSA/EtFOSE were mostly negatively correlated (Table C-12).

In the dust, 34% of total concentration was found in workshop 1, attributable to one sample showing a concentration of approximately twice that of the other samples. The other sampling locations contributed similarly to the total concentration. PFAS concentrations in airborne particles were highest in the office, which is located within workshop 2, and contributed 66% to the total concentration. Mainly responsible for the elevated concentrations were 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, MeFBSA, MeFOSA, PFOA, and PFDA, which all showed concentrations an order of magnitude higher in the office than in the other workshops. Contrarily, 6:2 FTAC had notably lower concentrations in the office than in workshop 1. However, there may be several reasons for the high concentrations in the office: (i) PFASs got to the office and adsorbed to particles because of a lower room temperature and lower humidity. (ii) PFASs got to the office, were trapped, and accumulated inside because only one door was regularly open, causing a lesser air exchange and a lesser air circulation. (iii) A smaller particle-size. It may be that coarse particles are found in the workshops because of abrasion from the production machines, whereas finer particles predominate in an office environment leading to a higher amount of particle-bound PFASs due to a higher particle surface area. (iv) The office provides entrance to a laboratory for quality tests, where the final product is tested on, among others, color fastness and elasticity. Therefore, the textile is prepared and cut in the office, possibly resulting in fine textile fibers depositing onto the GFFs. Overall, elevated amounts of particle-bound PFASs in the office are of concern, especially if fine particles are predominant because of their potential to reach the alveoli after inhalation.

Limited data are available about the emission of PFASs during their industrial use. Until now, peer-reviewed studies focused mainly on the emission of PFASs from fluorochemical or fluoropolymer manufacturing facilities.[33,236,237,242-244] Concentrations of ionic PFASs in settled dust and effluent water from the fluorochemical or fluoropolymer industry were typically up to 3 orders of magnitude higher than those from the textile manufacturing plant of this study. However, PFASs were detected along the textile manufacturing chain, involving high emissions into the atmosphere and into effluent water. Long-chain 8:2 FTOH, 10:2 FTOH, PFOA, and PFDA were the compounds emitted most from the manufacturing plant, although the plant workers stated to use "C_6" chemistry instead of "C_8" chemistry. Reasons may be the widespread use of PFASs as surfactants in scouring, dyeing, or coating agents as well as the detection of C_8 compounds as relics of the past.

5.3.7 Workers' Exposure to PFASs

Principally, diet is the dominant exposure pathway of PFASs for humans.[245] However, inhalation of air (gas and particle phase) and ingestion of dust become notably important when humans are exposed to PFASs during work. Several studies confirm that PFAS concentrations in human serum are significantly higher when workers were occupationally exposed.[33,245,246] However, those studies mainly focused on workers from fluorochemical or fluoropolymer manufacturing plants. To the best of our knowledge, there is no study focusing on the exposure to PFASs during the manufacturing of textiles. We therefore used PFAS concentrations in air, airborne particles, and dust to estimate the workers' exposure in the textile manufacturing plant. To consider the uncertainty of several input parameters, two exposure scenarios were assumed: a mean- and a high-intake scenario based on medium and 95th percentile concentrations, respectively. A detailed description of the calculations and the input parameters are given in the SI.

Figure 5-4 and Table C-15 show the workplace exposure for various scenarios and pathways.

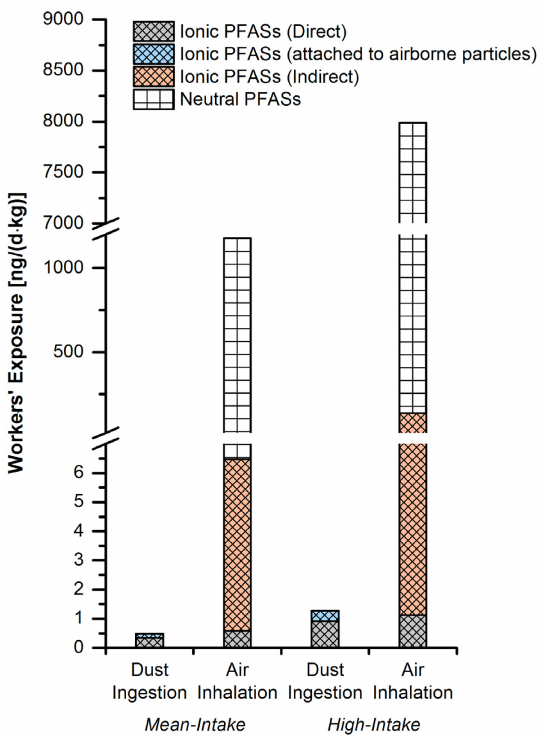

Figure 5-4. Exposure to neutral (direct) and ionic (direct and indirect through biotransformation of 8:2 and 10:2 FTOH) PFASs [ng/(d·kg)] for workers in a textile manufacturing plant based on median (mean-intake scenario) and 95th percentile (high-intake scenario) air and dust concentrations. The quantity of ionic PFASs (indirect) was subtracted from the quantity of neutral PFASs for the exposure scenarios via air inhalation.

Principally, direct exposure via inhalation was 3 orders of magnitude higher to neutral PFASs (1180–7990 ng/(d·kg), ranges represent estimates from the mean- and the high-intake scenario) than to ionic PFASs (0.6–1.1 ng/(d·kg)), reflecting the higher amount of neutral PFASs in the gas phase than that of ionic PFASs. Exposure to FTOHs was up to 5 orders of magnitude higher than the background exposure of the general western population (0.04–0.1 ng/(d·kg).[247] Schlummer et al. estimated the exposure to 8:2 FTOH at indoor sites dealing with materials containing fluorine treated surfaces. The estimates ranged from 3.4 to 23.4 ng/(d·kg), which is lower by 2 orders of magnitude than the intake of 8:2 FTOH in the textile manufacturing plant (933–6520 ng/(d·kg)).[224]

According to Vestergren et al., indirect exposure to PFOA rather results from the migration of FTOHs from packaging material into food than from the inhalation of FTOHs. Contribution of FTOHs to total PFCA exposure via inhalation was estimated between 0.3 and 11%, with clothing impregnation sprays and carpet care solutions being responsible for higher exposures if used indoors.[248,249] In this study, indirect exposure to ionic PFASs via biotransformation of FTOHs after respiration of the gaseous phase was estimated to be up to 2 orders of magnitude higher than direct exposure ranging from 5.9 to 136 ng/(d·kg). Indirect exposure accounted for 91–99% of the total ionic PFASs exposure via inhalation.

Exposure to ionic PFASs through dust ingestion was similar compared to direct exposure to ionic PFASs via air inhalation with 0.5–1.3 ng/(d·kg) and 0.6–1.1 ng/(d·kg), respectively. Fromme et al. assessed the background exposure for the general population in western countries based on PFAS findings from various studies.[247] Dust and air contributed a minor part to the overall exposure between 0.57 and 8.15% and 0.08 and 0.10%, respectively. The intake of PFOA via dust ranged from 0.02 to 1.0 ng/(d·kg), which is comparable, especially for the median-intake scenario, to the estimates for PFOA in this study (0.1–0.2 ng/(d·kg)). The intake of ionic PFASs via house dust in Catalonia, Spain, was estimated to be lower ranging from 0.05 and 0.3 ng/(d·kg).[250] Fu et al. calculated a daily intake of ionic PFASs via dust of 1680 ng/(d·kg) and 1.0 ng/(d·kg) for workers of a fluorochemical plant and ordinary residents, respectively.[33] The exposure of those workers was 3 orders of magnitude higher than of workers from the textile manufacturing plant.

Acknowledgements

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6 Conclusions

The studies presented in this thesis have shown that there are significant differences in the concentrations and substance patterns of PFASs in environmental samples from Germany and China, partly due to outsourcing a large part of the fluoropolymer industry to China in response to actual and pending regulations in Europe and North America. The overall conclusion of this thesis is as follows:

Activities to restrain and recycle per- and polyfluoroalkyl substances within manufacturing sites are yet to be effective, resulting in site-specific emissions of both legacy PFASs and fluorinated alternatives. While long-chain legacy PFASs are the main compounds observed in environmental samples from China, the fluorinated alternatives, especially HFPO-DA, are widespread in river basins and the coastal environment of Germany and the Netherlands. The exposure of the environment to fluorinated alternatives demonstrates the necessity to evaluate these compounds regarding their PBT/vPvB properties and their potential for long-range transport. Despite comprehensive efforts to reduce the direct emissions of the long-chain legacy compound PFOA in Europe, it is still emitted via diffuse sources and is, thus, widely dispersed in surface waters, suggesting that there is further need to continue the phase-out of PFOA in consumer products.

The results show that increasingly stringent regulations and the awareness of environmental concerns about long-chain legacy PFASs have reduced direct emissions in Germany and the Netherlands. It can be concluded that regulatory activities generally have a rapid effect on the decrease in direct emissions of targeted chemicals. Nevertheless, long-chain legacy PFASs are still observed in river basins in Germany and the Netherlands, as well as the coastal environment of the North Sea and the Baltic Sea, indicating that (i) their historically popular application in consumer products continues to act as an emission source and (ii) owing to their persistence, environmental exposure to PFASs, if any, will level-off rather than disappear. It can be expected that diffuse sources of long-chain legacy PFASs will become more important in the future because they exist as long as, for example, consumer products containing fluoroacrylate polymers are circulating in the environment. Thus, it is essential that a proper “end-of-life” treatment of PFASs-containing products and wastes is ensured to prevent PFASs from ending up in the environment.

Furthermore, the results demonstrate that regulatory activities in a few countries can be considered as a drop in the ocean, only resulting in “exporting” the problem rather than solving the problem. A large part of the fluoropolymer and textile industry has been outsourced to countries with fewer regulations, with the result that the Chinese samples studied show (i) a significantly different substance pattern dominated by the long-chain compound PFOA (or its precursor compound 8:2 FTOH) and (ii) PFAS concentrations that are several orders of magnitude higher than those in Germany. Investigations giving unique data on the emission of PFASs in a textile manufacturing plant in China reveal high emissions of long-chain legacy PFASs into the atmosphere and into effluent water, despite previous efforts to substitute the “long-chain chemistry" at the textile manufacturing site. Furthermore, the exposure of the textile workers to PFASs was estimated to be 4 orders of magnitude higher than the background exposure of the western population.[247] However, high emissions of especially PFOA and 8:2 FTOH in China also influence the environmental and human exposure in other regions, due to their potential for long-range transport in the environment. PFASs are known to be mobile substances that can be transported via the atmosphere and the oceans to regions that are devoid of industrial sources. In addition, a large portion of fluoropolymer and textile products produced in China is exported to western countries, including companies that joined the voluntary USEPA agreement on the phase-out of PFOA.[104] It seems that the global demand for fluoropolymers is currently very strong and possibly not compatible with the ambitious aims of a PFOA phase-out. Moreover, if the international market demands a steady supply of fluoropolymers, companies that are not participating in the voluntary PFOA phase-out or are not subject to national or international regulations may increase their production of PFOA to meet global demands. A ban on the import and sale of consumer products in Europe and North America may effectively reduce the use and, thus, the emissions of PFOA. In addition, people's awareness of the environmentally concerning properties of PFASs needs to be increased and consumers should be pointed towards more sustainable products.

The results of this thesis exemplarily reveal that banning one chemical leads to other chemicals with not-so-well-known environmental and toxicological properties popping up in the environment. The USEPA agreement on the voluntary phase-out of PFOA obliged the fluoropolymer manufacturers to develop their own PFOA alternative compounds. So far, the chemical structures of four fluorinated alternatives substituting PFOA have been identified.[12] The presented results provide first data on the widespread occurrence of the PFOA alternative compound HFPO-DA in surface waters. Furthermore, the alternative compound DONA was observed in the River Rhine, although it was probably not produced or directly applied there. As HFPO-DA and DONA are environmentally persistent and chemically stable,[11,114,128] their occurrence in the aquatic environment is of concern. The physicochemical properties of HFPO-DA and DONA, such as high water solubility and low pK_a, were estimated to be similar to that of their predecessor substance PFOA, indicating the same high mobility in water and the same ability to be transported from the river/estuary systems and coastal regions to remote areas via ocean currents.[128] The findings of HFPO-DA in water samples from the Norwegian Sea support this hypothesis. Additionally, a similar accumulation behavior and mode of toxic action as of PFOA is suggested for both alternative compounds.[11,99,115,251] In conclusion, fluorinated alternatives do not appear to be suitable replacement compounds for PFOA. In 2017, the Umweltbundesamt (UBA) will evaluate the ammonium salt of DONA, i.e. ADONA, as well as the ammonium salt of HFPO-DA, i.e. GenX, under the substance evaluation process of the REACH regulation because of their suspected PBT/vPvB properties, wide dispersive use, and exposure of the environment.[173] The results from this thesis may help to clarify whether there is wide dispersive use and an exposure of the environment regarding these compounds. The substance evaluation process of REACH is a long-term procedure, emphasizing the need to extend the burden of proof responsibilities of the manufacturers of fluorinated alternatives. So far, it is often the case that publicly funded research attempts to assess hazards and risks of newly identified substitutes. Instead, manufacturers should generate the information for a comprehensive hazard and risk assessment, and make this publicly available before alternative compounds are introduced in the market.

7 Materials and Methods

This chapter gives a summary of all experimental parameters. Parts of this chapter may be repetitive with the sections *Materials and Methods* and *Supplement* of the publications given in the Chapters 4.2, 5.2, A.1, and C.2.

7.1 Chemicals

Table 7-1. Solvents and laboratory chemicals used, including safety data information according to the *Globally Harmonized System of Classification and Labelling of Chemicals* (GHS).

Solvent/Chemical	Producer	Acronym	Formula	CAS-No.	Amount	Pictograms	H and P statements
Acetone Picograde®	LGC Standards	-	C_3H_6O	67-64-1	4 L	 Danger	H225 P210 H319 P241 H336 P303+P361+P353 P305+P351+P338 P405 P501
Acetone Distilled before usage	Sinopharm Chemical Reagent	-	C_3H_6O	67-64-1	0.5 L	 Danger	H225 P210 H319 P241 H336 P303+P361+P353 P305+P351+P338 P405 P501
Acetonitrile Chemsolute® für LC-MS	Th. Geyer	ACN	C_2H_3N	75-05-8	2.5 L	 Danger	H225 P210 H302+H312+H332 H319 P280 P305+P351+P338

Solvent/Chemical	Producer	Acronym	Formula	CAS-No.	Amount	Pictograms	H and P statements
Methanol LiChrosolv®	Merck	MeOH	CH_4O	67-56-1	2.5 L	 Danger	H225 P210 P308+P311 H301 P260 P320 H311 P270 P403+P233 H330 P271 P403+P235 H370 P301+P310 P405 P304+P340 P501
Methanol Picograde®	LGC Standards	MeOH	CH_4O	67-56-1	2.5 L	 Danger	H225 P210 P308+P311 H301 P260 P320 H311 P270 P403+P233 H330 P271 P403+P235 H370 P301+P310 P405 P304+P340 P501
Methanol Distilled before usage	Kermel	MeOH	CH_4O	67-56-1	0.5 L	 Danger	H225 P210 P308+P311 H301 P260 P320 H311 P270 P403+P233 H330 P271 P403+P235 H370 P301+P310 P405 P304+P340 P501
1-Methylpiperidine	Alfa Aesar	1-MP	$C_6H_{13}N$	626-67-5	100 g	 Danger	H225 P210 H331 P280 H302 P305+P351+P338 H314 P309 H318 P310
Millipore water supplied by Milli-Q Integral 5	Merck Millipore	H_2O	H_2O	7732-18-5	-	-	-
Purified water supplied by Pall Cascada LS system	Pall Corporation	H_2O	H_2O	7732-18-5	-	-	-
Ammonia solution 25% Suprapur®	Merck	NH_4OH	H_5NO	1336-21-6	0.25 L	 Danger	H209 P273 H314 P280 H335 P301+P330+P331 H400 P305+P351+P338 P308+P310

Solvent/Chemical	Producer	Acronym	Formula	CAS-No.	Amount	Pictograms	H and P statements
Ammonium acetate LC-MS ultra	Sigma-Aldrich	NH_4Ac	$C_2H_7NO_2$	631-61-8	25 g	-	-
Nitrogen liquid, for LC-MS/MS	Air Liquide	N	N	7727-37-9	1.8 m^3	 Warning	H281 P282 P336+P315 P403
Methane for GC-MS	Air Liquide	CH_4	CH_4	74-82-8	50 L, 200 bar	  Danger	H280 P210 H220 P377 P381 P403
Helium for GC-MS	Linde	Helium	He	7440-59-7	50 L, 300 bar	 Warning	H280 P410 P403

Table 7-2. Chemical mixtures used, including safety data information according to the *Globally Harmonized System of Classification and Labelling of Chemicals* (GHS).

Chemical Mixture	Producer	Substance	Acronym	Formula	CAS-No.	Amount	Pictograms	H and P statements
PFC-MXA in MeOH	Wellington Laboratories	Perfluorobutanoic acid	PFBA	$C_4HF_7O_2$	375-22-4	2 µg/mL	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
		Perfluoropentanoic acid	PFPeA	$C_5HF_9O_2$	2706-90-3	2 µg/mL		
		Perfluorohexanoic acid	PFHxA	$C_6HF_{11}O_2$	307-24-4	2 µg/mL		
		Perfluoroheptanoic acid	PFHpA	$C_7HF_{13}O_2$	375-85-9	2 µg/mL		
		Perfluorooctanoic acid	PFOA	$C_8HF_{15}O_2$	335-67-1	2 µg/mL		
		Perfluorononanoic acid	PFNA	$C_9HF_{17}O_2$	375-95-1	2 µg/mL		
		Perfluorodecanoic acid	PFDA	$C_{10}HF_{19}O_2$	335-76-2	2 µg/mL		
		Perfluoroundecanoic acid	PFUnDA	$C_{11}HF_{21}O_2$	2058-94-8	2 µg/mL		
		Perfluorododecanoic acid	PFDoDA	$C_{12}HF_{23}O_2$	307-55-1	2 µg/mL		
		Perfluorotridecanoic acid	PFTrDA	$C_{13}HF_{25}O_2$	72629-94-8	2 µg/mL		
		Perfluorotetradecanoic acid	PFTeDA	$C_{14}HF_{27}O_2$	376-06-7	2 µg/mL		
PFS-MXA in MeOH	Wellington Laboratories	Potassium perfluorobutane sulfonate	PFBS	$C_4HF_9O_3S\cdot K$	29420-49-3	2 µg/mL±5%	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
		Sodium perfluorohexane sulfonate	PFHxS	$C_6HF_{13}O_3S\cdot Na$	82382-12-5	2 µg/mL±5%		

Chemical Mixture	Producer	Substance	Acronym	Formula	CAS-No.	Amount	Pictograms	H and P statements
		Sodium perfluoroheptane sulfonate	PFHpS	$C_7HF_{15}O_3S{\cdot}Na$	21934-50-9	2 µg/mL±5%		
		Sodium perfluorooctane sulfonate	PFOS	$C_8HF_{17}O_3S{\cdot}Na$	4021-47-0	2 µg/mL±5%		
		Sodium perfluorodecane sulfonate	PFDS	$C_{10}HF_{21}O_3S{\cdot}Na$	2806-15-7	2 µg/mL±5%		
MPFAC-MXA in MeOH	Wellington Laboratories	Perfluoro-[1,2,3,4-$^{13}C_4$]butanoic acid	[$^{13}C_4$]-PFBA	$^{13}C_4HF_7O_2$	N.A.	2 µg/mL	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
		Perfluoro-[1,2-$^{13}C_2$]hexanoic acid	[$^{13}C_2$]-PFHxA	$^{13}C_2{}^{12}C_4HF_{11}O_2$	N.A.	2 µg/mL		
		Perfluoro-[1,2,3,4-$^{13}C_4$]octanoic acid	[$^{13}C_4$]-PFOA	$^{13}C_4{}^{12}C_4HF_{15}O_2$	N.A.	2 µg/mL		
		Perfluoro-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	[$^{13}C_5$]-PFNA	$^{13}C_5{}^{12}C_4HF_{17}O_2$	N.A.	2 µg/mL		
		Perfluoro-[1,2-$^{13}C_2$]decanoic acid	[$^{13}C_2$]-PFDA	$^{13}C_2{}^{12}C_8HF_{19}O_2$	N.A.	2 µg/mL		
		Perfluoro-[1,2-$^{13}C_2$]undecanoic acid	[$^{13}C_2$]-PFUnDA	$^{13}C_2{}^{12}C_9HF_{21}O_2$	N.A.	2 µg/mL		
		Perfluoro-[1,2-$^{13}C_2$]dodecanoic acid	[$^{13}C_2$]-PFDoDA	$^{13}C_2{}^{12}C_{10}HF_{23}O_2$	N.A.	2 µg/mL		
		Sodium perfluorohexane[$^{18}O_2$]sulfonate	[$^{18}O_2$]-PFHxS	$C_6HF_{13}S^{18}O_2{}^{16}O$	N.A.	2 µg/mL		
		Sodium perfluoro-[1,2,3,4-$^{13}C_4$]octane sulfonate	[$^{13}C_4$]-PFOS	$^{13}C_4{}^{12}C_4HF_{17}SO_3$	N.A.	2 µg/mL		

N.A. not available

Table 7-3. Pure chemicals used, including safety data information according to the *Globally Harmonized System of Classification and Labelling of Chemicals* (GHS).

Pure Chemical	Producer	Acronym	Formula	CAS-No.	Amount	Pictograms	H and P statements
2-(Perfluorohexyl)ethyl acrylate	Sigma Aldrich	6:2 FTAC	$C_{11}H_7F_{13}O_2$	17527-29-6	5 g	⚠ Warning	H315 P261 H319 P305, P351, P338 H335
2-(Perfluorooctyl)ethyl acrylate	Fluorochem	8:2 FTAC	$C_{13}H_7F_{17}O_2$	27905-45-9	1 g	-	-

Pure Chemical	Producer	Acronym	Formula	CAS-No.	Amount	Pictograms	H and P statements
1H,1H,2H,2H-Perfluoro-1-octanol	Lancaster Synthesis	6:2 FTOH	$C_8H_5F_{13}O$	647-42-7	5 g	 Warning	H315 P261 H319 P305, P351, P338 H335 P302+P352 P321 P405
1H,1H,2H,2H-Perfluoro-1-decanol	Lancaster Synthesis	8:2 FTOH	$C_{10}H_5F_{17}O$	678-39-7	1 g	-	-
1H,1H-Perfluoro-1-decanol	Sigma Aldrich	9:1 FTOH	$C_{10}H_3F_{19}O$	307-37-9	5 g	-	-
1H,1H,2H,2H-Perfluoro-1-dodecanol	Lancaster Synthesis	10:2 FTOH	$C_{12}H_5F_{21}O$	865-86-1	5 g	-	-
1H,1H,2H,2H-Perfluoro-1-tetradecanol	Fluorochem	12:2 FTOH	$C_{14}H_5F_{25}O$	39239-77-5	1 g	-	-
2H-Perfluoro-2-octenoic acid	Wellington Laboratories	6:2 FTUCA	$C_8H_2F_{12}O_2$	70887-88-6	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
2H-Perfluoro-2-decenoic acid	Wellington Laboratories	8:2 FTUCA	$C_{10}H_2F_{16}O_2$	70887-84-2	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
2H-Perfluoro-2-dodecenoic acid	Wellington Laboratories	10:2 FTUCA	$C_{12}H_2F_{20}O_2$	70887-94-4	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3,-heptafluoropropoxy)-propanoic acid	Wellington Laboratories	HFPO-DA	$C_6HF_{11}O_3$	13252-13-6	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Potassium 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxypropoxy) propionate	Dyneon	(K)DONA	$C_7H_2F_{12}O_4{\cdot}K$	1087271-46-2	N.A.	 Danger	H314 P260 P310 H290 P280 P305+P351+P338 P303+P361+P353
Sodium 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxypropoxy) propionate	Wellington Laboratories	(Na)DONA	$C_7H_2F_{12}O_4{\cdot}Na$	958445-44-8	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
N-Methylperfluorobutanesulfonamide	3M	MeFBSA	$C_5H_4F_9NO_2S$	68298-12-4	1 g	N.A.	N.A.

Pure Chemical	Producer	Acronym	Formula	CAS-No.	Amount	Pictograms	H and P statements
N-Methylperfluorooctanesulfonamide	3M	MeFOSA	$C_9H_4F_{17}NO_2S$	31506-32-8	20 g	 Warning	H302+H312+H332 P260 H315 P280 H319 P312 H335
N-Ethylperfluorooctanesulfonamide	ABCR	EtFOSA	$C_{10}H_6F_{17}NO_2S$	4151-50-2	1 g	 Warning	H302+H312 P261 H315 P280 H319 P312 H335 H411
N-Methylperfluorobutanesulfonamidoethanol	3M	MeFBSE	$C_7H_8F_9NO_3S$	34454-97-2	1 g	N.A.	N.A.
N-Methylperfluorooctanesulfonamidoethanol	3M	MeFOSE	$C_{11}H_8F_{17}NO_3S$	24448-09-7	20 g	 Warning	H302+H312+H332 P271 H315 P260 H319 P280 H335
N-Ethylperfluorooctanesulfonamidoethanol	3M	EtFOSE	$C_{12}H_{10}F_{17}NOS$	1691-99-2	20 g	 Warning	H315 P271 H319 P261 H335 P280
1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluoro-1-octanesulfonamide	Wellington Laboratories	FOSA	$C_7H_2F_{15}NO_2S$	754-91-6	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Perfluorobutanoic acid	Wellington Laboratories	PFBA	$C_4HF_7O_2$	375-22-4	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Perfluoropentanoic acid	Wellington Laboratories	PFPeA	$C_5HF_9O_2$	2706-90-3	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Perfluorohexanoic acid	Wellington Laboratories	PFHxA	$C_6HF_{11}O_2$	307-24-4	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Perfluoroheptanoic acid	Wellington Laboratories	PFHpA	$C_7HF_{13}O_2$	375-85-9	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Perfluoroheptanoic acid	Lancaster	PFHpA	$C_7HF_{13}O_2$	375-85-9	5 g	 Danger	H302 P280 H314 P305, P351, P338 P310

Pure Chemical	**Producer**	**Acronym**	**Formula**	**CAS-No.**	**Amount**	**Pictograms**	**H and P statements**	
Perfluorooctanoic acid	Wellington Laboratories	PFOA	$C_8HF_{15}O_2$	335-67-1	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*	
Perfluorooctanoic acid	Lancaster	PFOA	$C_8HF_{15}O_2$	335-67-1	5 g	 Danger	H302, H332 H318 H351 H360D H362 H372	P201 P260 P263 P280 P305, P351, P338, P310 P308, P313
Sodium 1H,1H,2H,2H-perfluorooctane sulfonate	Wellington Laboratories	6:2 FTS	$C_8H_5O_3F_{13}S$	27619-97-2	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*	
Sodium 1H,1H,2H,2H-perfluorooctylphosphate	Wellington Laboratories	6:2PAP	$C_8H_4F_{13}O_4PNa_2$	57678-01-0	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*	
Sodium 1H,1H,2H,2H-perfluorodecylphosphate	Wellington Laboratories	8:2PAP	$C_{10}H_4F_{17}O_4PNa_2$	57678-03-2	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*	
Sodium bis(1H,1H,2H,2H-perfluorooctyl)phosphate	Wellington Laboratories	6:2diPAP	$C_{16}H_8F_{26}O_4PNa$	57677-95-9	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*	
Sodium bis(1H,1H,2H,2H-perfluorodecyl)phosphate	Wellington Laboratories	8:2diPAP	$C_{20}H_8F_{34}O_4PNa$	678-41-1	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*	
Sodium 1H,1H,2H,2H-perfluorooctyl-1H,1H,2H,2H-perfluorodecylphosphate	Wellington Laboratories	6:2/8:2diPAP	$C_{18}H_8F_{30}O_4PNA$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*	
Mono[2-(perfluorodecyl)ethyl] phosphate	Chiron	10:2PAP	$C_{12}H_6F_{21}O_4P$	57678-05-4	50 µg	-	-	
Bis[2-(perfluorodecyl)ethyl] Phosphate	Chiron	10:2diPAP	$C_{24}H_9F_{42}O_4P$	1895-26-7	50 µg	-	-	
Tris[2-(perfluorohexyl)ethyl] phosphate	Chiron	6:2triPAP	$C_{24}H_{12}F_{39}O_4P$	165325-62-2	50 µg	-	-	
Sodium 2-N-ethylperfluorooctane-1-sulfonamidoethylphosphate	Wellington Laboratories	SAmPAP	$C_{12}H_9F_{17}NO_6PSNa_2$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*	
Sodium bis-[2-N-ethylperfluorooctane-1-sulfonamido)ethyl] phosphate	Wellington Laboratories	diSAmPAP	$C_{24}H_{18}F_{34}N_2O_8PS_2Na$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*	

Pure Chemical	**Producer**	**Acronym**	**Formula**	**CAS-No.**	**Amount**	**Pictograms**	**H and P statements**
Sodium bis(perfluorohexyl) phosphinate	Wellington Laboratories	6:6 PFPi	$C_{12}F_{26}O_2PNa$	1411714-08-3	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Sodium perfluorohexylperfluorooctyl phosphinate	Wellington Laboratories	6:8 PFPi	$C_{14}F_{30}O_2PNa$	1411714-10-7	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Sodium bis(perfluorooctyl) phosphinate	Wellington Laboratories	8:8 PFPi	$C_{16}F_{34}O_2PNa$	1411714-12-9	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Perfluorohexylphosphonic acid	Wellington Laboratories	PFHxPA	$C_6H_2F_{13}PO_3$	40143-76-8	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Perfluorooctylphosphonic acid	Wellington Laboratories	PFOPA	$C_8H_2F_{17}PO_3$	40143-78-0	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Perfluorodecylphosphonic acid	Wellington Laboratories	PFDPA	$C_{10}H_2F_{21}PO_3$	52299-26-0	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3,-heptafluoropropoxy)-$^{13}C_3$-propanoic acid	Wellington Laboratories	[$^{13}C_3$]-HFPO-DA	$^{13}C_3{}^{12}C_3HF_{11}O_3$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Perfluoro-n-(1,2-$^{13}C_2$)-octanoic acid	Wellington Laboratories	[$^{13}C_2$]-PFOA	$^{13}C_2{}^{12}C_6HF_{15}O_2$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Perfluoro-n[1,2,3,4,5,6,7,8-$^{13}C_8$]octanoic acid	Wellington Laboratories	[$^{13}C_8$]-PFOA	$^{13}C_8HF_{15}O_2$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
2-Perfluorohexyl-[1,1-$^2H_2$]-[1,2-$^{13}C_2$]-ethanol	Wellington Laboratories	[$^2H_2$,$^{13}C_2$]-6:2 FTOH	$^{13}C_2C_6{}^2H_2H_3F_{13}O$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
2-Perfluorooctyl-[1,1-$^2H_2$]-[1,2-$^{13}C_2$]-ethanol	Wellington Laboratories	[$^2H_2$,$^{13}C_2$]-8:2 FTOH	$^{13}C_2C_8{}^2H_2H_3F_{17}O$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
2-Perfluorodecyl-[1,1-$^2H_2$]-[1,2-$^{13}C_2$]-ethanol	Wellington Laboratories	[$^2H_2$,$^{13}C_2$]-10:2 FTOH	$^{13}C_2C_{10}{}^2H_2H_3F_{21}O$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
N-methyl-d3-perfluorooctanesulfonamide	Wellington Laboratories	d3-MeFOSA	$C_9D_3HF_{17}NO_2S$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
N-ethyl-d5-perfluorooctanesulfonamide	Wellington Laboratories	d5-EtFOSA	$C_{10}D_5HF_{17}NO_2S$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
2-(N-methyl-d3-perfluoro-1-octane-sulfonamido)-ethan-d4-ol	Wellington Laboratories	d7-MeFOSE	$C_{11}D_7HF_{17}NO_3S$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
2-(N-ethyl-d5-perfluoro-1-octane-sulfonamido)-ethan-	Wellington Laboratories	d9-EtFOSE	$C_{12}D_9HF_{17}NOS$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*

Pure Chemical	Producer	Acronym	Formula	CAS-No.	Amount	Pictograms	H and P statements
d4-ol							
2H-Perfluoro-[1,2-$^{13}C_2$]-2-octenoic acid	Wellington Laboratories	[$^{13}C_2$]-6:2 FTUCA	$^{13}C_2{}^{12}C_6H_2F_{12}O_2$	N.A.	50±2.5 µg/mL in Isopropanol	🔥 ❗ Danger	H225 P210 P312 P403+P233 H319 P271 P337+P313 P501 H336 P261 P403+P235 P280 P405 P370+P378 P305+P351+P338
2H-Perfluoro-[1,2-$^{13}C_2$]-2-decenoic acid	Wellington Laboratories	[$^{13}C_2$]-8:2 FTUCA	$^{13}C_2{}^{12}C_8H_2F_{16}O_2$	N.A.	50±2.5 µg/mL in Isopropanol	🔥 ❗ Danger	H225 P210 P312 P403+P233 H319 P271 P337+P313 P501 H336 P261 P403+P235 P280 P405 P370+P378 P305+P351+P338
2H-Perfluoro-[1,2-$^{13}C_2$]-2-dodecenoic acid	Wellington Laboratories	[$^{13}C_2$]-10:2 FTUCA	$^{13}C_2{}^{12}C_{10}H_2F_{20}O_2$	N.A.	50±2.5 µg/mL in Isopropanol	🔥 ❗ Danger	H225 P210 P312 P403+P233 H319 P271 P337+P313 P501 H336 P261 P403+P235 P280 P405 P370+P378 P305+P351+P338
Sodium 1H,1H,2H,2H-[1,2-$^{13}C_2$]perfluorooctylphosphate	Wellington Laboratories	[$^{13}C_2$]-6:2PAP	$^{13}C_2{}^{12}C_6H_4F_{13}O_4PNa_2$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Sodium 1H,1H,2H,2H-[1,2-$^{13}C_2$]perfluorodecyl phosphate	Wellington Laboratories	[$^{13}C_2$]-8:2PAP	$^{13}C_2{}^{12}C_8H_4F_{17}O_4PNa_2$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Sodium bis(1H,1H,2H,2H-[1,2$^{13}C_2$]perfluorooctyl) phosphate	Wellington Laboratories	[$^{13}C_4$]-6:2diPAP	$^{13}C_4{}^{12}C_{12}H_8F_{26}O_4PNa$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
Sodium bis(1H,1H,2H,2H-[1,2-$^{13}C_2$]perfluorodecyl) phosphate	Wellington Laboratories	[$^{13}C_4$]-8:2diPAP	$^{13}C_4{}^{12}C_{16}H_8F_{34}O_4PNa$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*
10:2 Fluorotelomer alcohol disubstituted phosphate surfactant-d4	Chiron	d4-10:2diPAP	$C_{24}D_4H_5F_{42}O_4P$	N.A.	50 µg	-	-
6-Chloroperfluorohexyl phosphonic acid	Wellington Laboratories	Cl-PFHxPA	$C_6H_2ClF_{12}PO_3$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*

Pure Chemical	Producer	Acronym	Formula	CAS-No.	Amount	Pictograms	H and P statements
8-Chloroperfluorooctyl phosphonic acid	Wellington Laboratories	Cl-PFOPA	$C_8H_2ClF_{16}PO_3$	N.A.	50±2.5 µg/mL in MeOH	See Table 7-1 for *Methanol*	See Table 7-1 for *Methanol*

N.A. not available

7.2 Instrumental Analyses

Table 7-4. Substance-specific mass-spectrometric parameters (API 3000) and retention times R_t [min]. Parameters marked with grey were adapted from Ahrens et al.[123]

Acronym	MRM transitions [m/z]	R_t [min]	DP	FP	CE	CXP	Acronym	MRM transitions [m/z]	DP	FP	CE	CXP
PFBA	213>169	5.1	-4	-80	-14	-3	$[^{13}C_4]$-PFBA	217>172	-3	-50	-14	-11
PFPeA	263>219	9.5	-3	-50	-14	-5						
PFHxA	313>269	10.6	-3	-50	-14	-7	$[^{13}C_2]$-PFHxA	315>270	-6	-50	-14	-7
PFHpA	363>319	11.5	-6	-50	-14	-9	$[^{13}C_4]$-PFOA	417>372	-11	-50	-14	-11
PFOA	413>369	12.5	-20	-60	-14	-11	$[^{13}C_2]$-PFOA	415>370	-8	-75	-15	-10
	413>219		-10	-75	-25	-5	$[^{13}C_8]$-PFOA	421>376	-10	-75	-15	-10
PFNA	463>419	13.7	-11	-50	-14	-13	$[^{13}C_5]$-PFNA	468>423	-16	-50	-14	-13
PFDA	513>469	15.2	-10	-50	-16	-15	$[^{13}C_2]$-PFDA	515>470	-10	-60	-16	-15
PFUnDA	563>519	17.1	-11	-60	-16	-15	$[^{13}C_2]$-PFUnDA	565>520	-16	-50	-18	-21
PFDoDA	613>569	19.3	-16	-50	-18	-19	$[^{13}C_2]$-PFDoDA	615>570	-11	-70	-18	-17
PFTrDA	663>619	21.8	-21	-60	-16	-21						
PFTeDA	713>669	24.3	-10	-90	-18	-17						
PFBS	299>99	9.8	-9	-150	-41	-4						
	299>80		-26	-100	-68	-5						
PFHxS	399>99	11.5	-26	-90	-62	-5	$[^{18}O_2]$-PFHxS	403>84	-6	-150	-62	-5
	399>80		-26	-90	-72	-5						
PFHpS	449>99	12.5	-21	-110	-74	-15						
PFOS	499>99	13.7	-36	-100	-68	-5	$[^{13}C_4]$-PFOS	503>80	-6	-200	-64	-13
	499>80		-36	-100	-82	-5						
PFDS	599>80	16.9	-26	-120	-94	-5						
HFPO-DA	329>285	10.9	-10	-50	-10	-7	$[^{13}C_3]$-HFPO-DA	332>287	-3	-50	-10	-7
	329>169		-25	-50	-20	-10						
6:2 FTUCA	357>293	11.8	-35	-150	-20	-5	$[^{13}C_2]$-6:2 FTUCA	359>294	-1	-60	-18	-7
	357>243		-40	-225	-50	-15						
8:2 FTUCA	457>393	14.2	-40	-200	-20	-10	$[^{13}C_2]$-8:2 FTUCA	459>394	-6	-60	-16	-13
	457>243		-40	-175	-40	-15						
10:2 FTUCA	557>493	18.0	-36	-50	-22	-15	$[^{13}C_2]$-10:2 FTUCA	559>494	-21	-50	-22	-1
4:2 FTS	327>307	10.5	-45	-200	-30	-20						
	327>287		-55	-225	-35	-5						
6:2 FTS	427>407	13.2	-50	-200	-35	-10						
	427>387		-45	-200	-40	-10						
8:2 FTS	527>507	15.2	-40	-200	-40	-15						
FOSA	498>78	17.9	-2	-140	-56	-3	$[^{13}C_8]$-FOSA	506>78	-15	-200	-54	-2
6:2PAP	443>97	13.1	-55	-175	-30	-5	$[^{13}C_2]$-6:2PAP	445>97	-55	-200	-30	-15
8:2PAP	543>97	14.7	-55	-175	-40	-5	$[^{13}C_2]$-8:2PAP	545>97	-55	-200	-35	-5
6:2diPAP	789>443	18.0	-55	-175	-30	-15	$[^{13}C_4]$-6:2diPAP	793>445	-55	-200	-30	-15
	789>97		-30	-175	-60	-5						
8:2diPAP	989>543	19.6	-55	-300	-35	-15	$[^{13}C_4]$-8:2diPAP	993>545	-50	-250	-35	-15
	989>97		-60	-250	-60	-5						
6:2/8:2 diPAP	889>443	18.9	-55	-200	-35	-15						
10:2PAP	643>97	15.8	-55	-175	-60	-5						
10:2diPAP	1189>643	20.8	-50	-250	-40	-45	d4-10:2diPAP	1193>645	-55	-250	-40	-20

Acronym	MRM transitions [m/z]	R_t [min]	DP	FP	CE	CXP	Acronym	MRM transitions [m/z]	DP	FP	CE	CXP
	1189>97		-50	-250	-60	-5						
6:2triPAP	789>443	22.8	-45	-200	-35	-25						
diSAmPAP	1203>650	20.2	-60	-200	-60	-15						
	1203>526		-60	-200	-60	-15						
6:6 PFPi	701>401	17.3	-40	-200	-60	-10						
	701>63		-60	-250	-60	-10						
6:8 PFPi	801>501	18.2	-55	-200	-60	-15						
	801>401		-45	-225	-60	-25						
8:8 PFPi	901>501	18.9	-55	-200	-60	-15						
	901>63		-55	-250	-60	-10						
PFHxPA	399>79	10.6	-40	-200	-55	-5	Cl-PFHxPA	415>79	-40	-200	-55	-5
PFOPA	499>130	15.5	-55	-200	-60	-10	Cl-PFOPA	515>79	-55	-175	-60	-10
	499>80		-55	-200	-60	-5						
PFDPA	599>79	14.6	-45	-200	-60	-5						

DP	declustering potential [V]
FP	focusing potential [V]
CE	collision energy [V]
CXP	collision cell exit potential [V]

Table 7-5. Substance-specific mass-spectrometric parameters (API 4000).

Acronym	**MRM transitions [m/z]**	**DP**	**FP**	**CE**	**CXP**	**Acronym**	**MRM transitions [m/z]**	**DP**	**FP**	**CE**	**CXP**
PFBA	213>169	-30	-5	-13	-9	$[^{13}C_4]$-PFBA	217>172	-20	-4	-13	-9
PFPeA	263>219	-26	-4	-12	-13						
PFHxA	313>269	-28	-6	-13	-16	$[^{13}C_2]$-PFHxA	315>270	-23	-4	-12	-16
PFHpA	363>319	-29	-4	-14	-19	$[^{13}C_4]$-PFOA	417>372	-32	-4	-13	-8
PFOA	413>369	-29	-6	-15	-8	$[^{13}C_2]$-PFOA	415>370	-29	-6	-15	-8
	413>219	-30	-3	-25	-11	$[^{13}C_8]$-PFOA	421>376	-30	-6	-14	-8
PFNA	463>419	-34	-7	-15	-9	$[^{13}C_5]$-PFNA	468>423	-30	-7	-14	-10
PFDA	513>469	-35	-7	-15	-11	$[^{13}C_2]$-PFDA	515>470	-39	-6	-16	-10
PFUnDA	563>519	-36	-5	-17	-13	$[^{13}C_2]$-PFUnDA	565>520	-33	-6	-16	-13
PFDoDA	613>569	-38	-9	-17	-15	$[^{13}C_2]$-PFDoDA	615>570	-40	-9	-17	-15
PFTrDA	663>619	-39	-8	-18	-14						
PFTeDA	713>669	-36	-9	-22	-15						
PFBS	299>99	-66	-12	-42	-16						
	299>80	-68	-12	-60	-2						
PFHxS	399>99	-90	-15	-50	-15	$[^{18}O_2]$-PFHxS	403>84	-82	-13	-55	-4
	399>80	-89	-14	-66	-2						
PFHpS	449>99	-58	-14	-61	-16						
PFOS	499>99	-73	-15	-74	-17	$[^{13}C_4]$-PFOS	503>80	-80	-15	-60	-4
	499>80	-91	-12	-65	-2						
PFDS	599>99	-11	-14	-60	-3						
	599>80	-10	-13	-64	-2						
HFPO-DA	329>285	-15	-4	-7	-18	$[^{13}C_3]$-HFPO-DA	332>287	-23	-3	-7	-14
	329>169	-22	-2	-18	-8						
DONA	377>285	-33	-6	-20	-22						
	377>85	-33	-4	-50	-14						

DP	declustering potential [V]
FP	focusing potential [V]
CE	collision energy [V]
CXP	collision cell exit potential [V]

Table 7-6. Target ions [m/z] and retention times R_t [min] in GC-MS analysis adapted from Dreyer et al. and Xie et al.[202,203]

Acronym	**Target ions [m/z]**	**R_t [min]**	**Acronym**	**Target ions [m/z]**
6:2 FTOH	365/327	14.7	$[^2H_2,^{13}C_2]$-6:2 FTOH	369/331
8:2 FTOH	465/427	16.0	$[^2H_2,^{13}C_2]$-8:2 FTOH	469/431
10:2 FTOH	565/527	17.3	$[^2H_2,^{13}C_2]$-10:2 FTOH	569/531
12:2 FTOH	665/627	18.5		
9:1 FTOH	501/481	16.7		
6:2 FTAC	419/447	13.4		
8:2 FTAC	519/547	15.1		
MeFBSA	314/315	23.0		
MeFOSA	514/515	23.3	d3-MeFOSA	517
EtFOSA	528/529	22.5	d5-EtFOSA	533
MeFBSE	340/358	24.8		
MeFOSE	540/558	24.9	d7-MeFOSE	547/565
EtFOSE	554/572	25.0	d9-EtFOSE	563/581

Table 7-7. Details of HPLC-MS/MS method (API 3000). Parameters marked with grey were adapted from Ahrens et al.[123]

	Analysis of *PFCAs, PFSAs, FTUCAs, HFPO-DA, FTSs, FOSA*	Analysis of *PAPs, PFPIAs, PFPAs*
Mass spectrometer	Applied Biosystems/MDS Sciex API 3000	
Ion source	TurboIonSpray	
Mode	Dynamic multiple reaction monitoring (DMRM)	
Source temperature	300°C	300°C
TurboIonSpray voltage	-3700 V	-3700 V
Entrance potential	-10 V	-10 V
Collision gas flow	4 L/min	4 L/min
Curtain gas flow	8 L/min	8 L/min
Nebulizer gas flow	14 L/min	8 L/min
TurboIonSpray gas	8 L/min	8 L/min
Vacuum	$3.8 \cdot 10^{-5}$ Torr	$3.8 \cdot 10^{-5}$ Torr
DF	-150 V	-150 V
CEM	-2700 V	-2700 V
HPLC system	Agilent HP 1100	
Column	Phenomenex Synergi 4 µm Fusion-RP-C$_{18}$ (150x2 mm)	
Security guard	Phenomenex SecurityGuard cartridge for Fusion-RP HPLC columns (4x2 mm)	
Injection	10 µL; Rinsing twice with MeOH prior injection	
Flow rate	0.200 mL/min	0.200 mL/min
Column temperature	30°C	
Gradient profile	Time A B	Time A B
	10 min 70% 30%	10 min 80% 20%
	0 min 70% 30%	0 min 80% 20%
	3 min 30% 70%	1 min 80% 20%
	29 min 10% 90%	9 min 25% 75%
	31 min 0% 100%	12 min 15% 85%
	41 min 0% 100%	17 min 0% 100%
		26 min 0% 100%
Mobile phase	A Water (10 mmol NH_4Ac)	A Water (5 mmol NH_4Ac, 5 mmol 1-MP)
	B MeOH (10 mmol NH_4Ac)	B MeOH (5 mmol NH_4Ac, 5 mmol 1-MP)
Filtration	Whatman® Puradisc™ 25 PP Disposable Filter Device; 0.2 µm Polypropylen Filter	

Table 7-8. Details of MS/MS method (API 4000).

	Analysis of *PFCAs, PFSAs, HFPO-DA, DONA*
Mass spectrometer	Applied Biosystems/MDS Sciex API 4000
Ion source	TurboIonSpray
Mode	Dynamic multiple reaction monitoring (DMRM)
Source temperature	400°C
TurboIonSpray voltage	-4500 V
Entrance potential	-10 V
Collision gas flow	6 L/min
Curtain gas flow	10 L/min
Nebulizer gas	50 psig
Heater gas	50 psig

Interface Heater	On
Vacuum	$2.2 \cdot 10^{-5}$ Torr
DF	-200 V
CEM	-2800 V

Table 7-9. Details of GC-MS method, adapted from Dreyer et al.[202]

Mass spectrometer	Agilent 5975 MSD
Ion source	Positive chemical ionization (PCI)
Mode	Selected ion monitoring (SIM)
Ion source temperature	300°C
Quadrupole temperature	150°C
Transfer line temperature	250°C
Reactant gas	Methane
GC system	Agilent 6890
Injection	2 µL; Pulsed splitless mode (40 psi) Initial inlet temperature: 60°C, hold for 0.1 min Heating rate: 400°C/min Final inlet temperature: 270°C, hold for 20 min
Oven temperature program	Initial 50°C for 2 min 3°C/min to 70°C 10°C/min to 130°C 20°C/min to 220°C 120°C/min to 275°C, hold for 5 min 10°C/min to 270°C, hold for 10 min
Run time	35 min
Column flow	1.5 mL/min
Carrier gas	Helium
Capillary column	Supelcowax10 (60 m x 0.25 mm I.D.; 0.25 µm film thickness)

7.3 Extraction of Environmental Samples

The Figures 7-1 to 7-4 give an overview of the sample preparations of all environmental media tested.

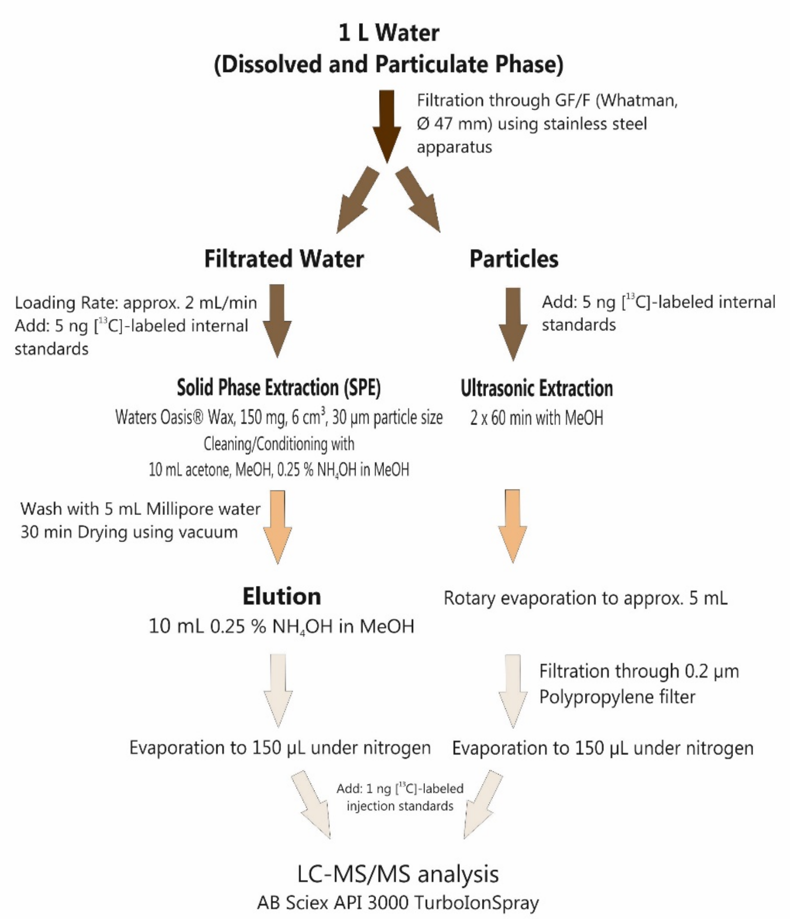

Figure 7-1. Sample extraction of water samples (dissolved and particulate phase). The extraction procedure of the dissolved phase was modified based on the method described by Ahrens et al.[123] The extraction procedure for the particulate phase was adapted from Ahrens et al.[123]

The recovery rates of the mass-labeled internal standards for the dissolved phase ranged from 48.9 ± 19.6% ([$^{13}C_4$]-PFOA) to 97.9 ± 69.8 ([$^{13}C_5$]-PFNA) and are listed in detail in Table D-1. The MDLs ranged from 0.001 ng/L (PFOS) to 2.08 ng/L (PFHpA) and are listed in detail in Table A-4. The MQLs ranged from 0.003 ng/L (PFOS) to 5.55 ng/L (PFHpA) and are listed in detail in Table A-4. The recovery rates of the mass-labeled internal standards for the particulate phase ranged from 51.2 ± 18.5% ([$^{13}C_4$]-PFOA) to 79.4 ± 35.8% ([$^{13}C_2$]-6:2 FTUCA) and are listed in detail in Table D-2. The MDLs ranged from 0.02 ng/L (PFTrDA) to 0.55 ng/L (PFHpA) and are listed in detail in Table A-4. The MQLs ranged from 0.06 ng/L (PFTrDA) to 1.64 ng/L (PFHpA) and are listed in detail in Table A-4.

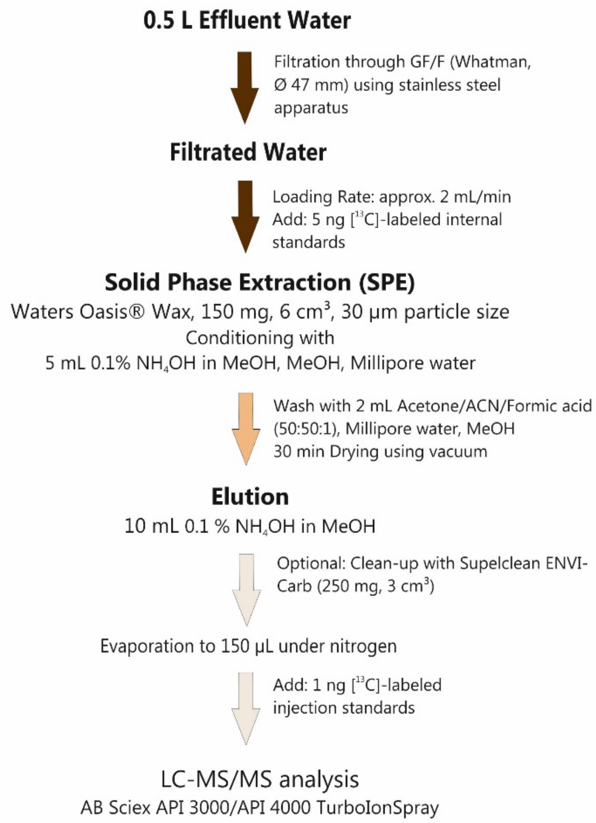

Figure 7-2. Sample extraction of effluent water from ChemPark Leverkusen according to DIN 38407-42.[148]

The recovery rates of the mass-labeled internal standards ranged from 43.0 ± 8.7% ([$^{13}C_2$]-PFDoDA) to 132.5 ± 32.5% ([$^{13}C_4$]-PFBA) and are listed in detail in Table D-3. The MDLs ranged from 0.00001 ng/L (DONA) to 0.30 ng/L (PFBA) and are listed in detail in Table B-5. The MQLs ranged from 0.00003 ng/L (DONA) to 1.01 ng/L (PFBA) and are listed in detail in Table B-5.

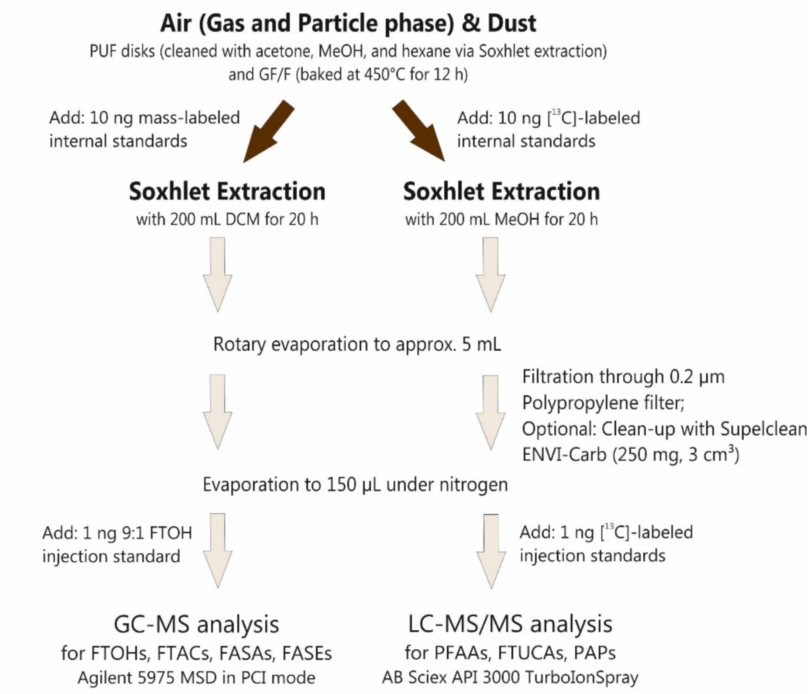

Figure 7-3. Sample extraction of air (gas and particle phase) and dust via Soxhlet extraction.

The recovery rates of the mass-labeled internal standards for the Soxhlet extraction ranged from 5.8 ± 8.4% ($[^{13}\text{C}_2]$-10:2 FTUCA) to 195.3 ± 60.1% (d9-EtFOSE) and are listed in detail in Table D-4 and Table D-5. The MDLs ranged from 0.002 ng/(sample·d) (PFHpA) to 16.8 ng/(sample·d) (6:2 FTOH) or 0.62 ng/g (PFTeDA) to 493 ng/g (8:2 FTOH) and are listed in detail in Table C-5. The MQLs ranged from 0.002 ng/(sample·d) (PFHpA) to 24.1 ng/(sample·d) (6:2 FTOH) or 2.07 ng/g (PFTeDA) to 708 ng/g (8:2 FTOH) and are listed in detail in Table C-5.

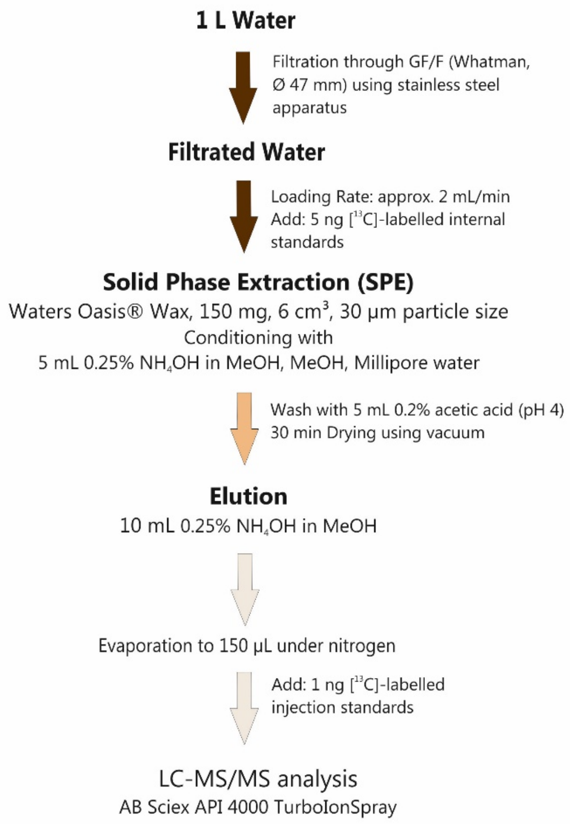

Figure 7-4. Sample extraction of water samples (Rhine 15-09 and Baltic Sea SB1-SB16).

The recovery rates of the mass-labeled internal standards ranged from 44.2 ± 10.6% ([$^{13}C_3$]-HFPO-DA) to 175.0 ± 34% ([$^{13}C_4$]-PFBA) and are listed in detail in Table D-3. The MDLs ranged from 0.000003 ng/L (PFUnDA) to 1.26 ng/L (PFPeA) and are listed in detail in Table B-7. The MQLs ranged from 0.00001 ng/L (PFUnDA) to 3.73 ng/L (PFPeA) and are listed in detail in Table B-7.

7.4 Calculations

Concentrations of analytes in the sample vials c_A [pg/µL] were calculated as follows:

$$c_A\ [\mathrm{pg/\mu L}] = \left(\frac{\mathrm{Area}_A}{\mathrm{Area}_{IS} \cdot b} - n \right) \cdot c_{IS} \tag{1}$$

with	Area_A	Peak area of the analyte in the sample
	Area_{IS}	Peak area of the [^{13}C]- labeled internal standard in the sample
	b	Slope of the calibration line
	n	Y-Intercept
	c_{IS}	Concentration of [^{13}C]-labeled internal standard in the sample vial

c_A was further used to calculate concentrations based on the amount of the environmental medium tested:

$$c_A = \frac{c_A[\mathrm{pg/\mu L}] \cdot 200\,\mathrm{\mu L}}{1000 \cdot m} \tag{2}$$

with	c_A [pg/µL]	Concentration of the analyte in the sample vial (derived from equation 1)
	200 µL	Amount of solution in the vial
	1000	Conversion factor from pg to ng
	m	Amount of sample (e.g. 1 L, 1 g)

The analytical standards of PFBS, PFHxS, PFOS, and DONA existed as salts. Thus, c_A needs to be multiplied with a conversion factor to calculate the amount of the free acid:

$$c_A\,[\mathrm{PFBS, PFHxS, PFOS, DONA}] = c_A \cdot x \tag{3}$$

with	x	Conversion factor from the salt to the free acid
		PFBS: x = 0.89 (potassium salt)
		PFHxS: x = 0.95 (sodium salt)
		PFOS: x = 0.96 (sodium salt)
		DONA: x = 0.95 (sodium salt)

For calculating the concentration of DONA, equation (2) was modified as follows:

$$c_A\,[\mathrm{pg/L}] = \frac{c_A[\mathrm{pg/\mu L}] \cdot 160\,\mathrm{\mu L} \cdot 10 \cdot 2 \cdot 0.91}{1\mathrm{L}} \tag{4}$$

with	c_A [pg/µL]	Concentration of the analyte in the sample vial (derived from equation 1)
	160 µL	Amount of solution in the vial
	10	Dilution factor
	2	Dilution factor
	0.91	Conversion from KDONA (potassium salt) to DONA
	1 L	Amount of water sample

Recoveries of [^{13}C]-labeled internal standards were calculated as follows:

$$\text{Recovery rate}\,[\%] = \frac{\mathrm{Area}_{\text{IS in sample}}}{\mathrm{Area}_{\text{InjS in sample}}} \cdot \frac{\mathrm{Area}_{\text{InjS in cal}}}{\mathrm{Area}_{\text{IS in cal}}} \cdot 100 \tag{5}$$

with	$\mathrm{Area}_{\text{IS in sample}}$	Peak area of the [^{13}C]-labeled internal standard in the sample
	$\mathrm{Area}_{\text{InjS in sample}}$	Peak area of the [^{13}C]-labeled injection standard in the sample
	$\mathrm{Area}_{\text{InjS in cal}}$	Peak area of the [^{13}C]-labeled injection standard in calibration point
	$\mathrm{Area}_{\text{IS in cal}}$	Peak area of the [^{13}C]-labeled internal standard in calibration point

Method detection limits (MDLs) and method quantification limits (MQLs) were calculated via two different approaches. For analytes that were detected in method blanks the MDLs and MQLs were calculated as follows:

$$\mathrm{MDL} = \frac{s_{\mathrm{Blank}} \cdot T_{98\%} \cdot 200\,\mu\mathrm{L}}{m \cdot 1000} \tag{6}$$

with s_{Blank} Standard deviation of procedural method blanks [pg/µL]

$T_{98\%}$ Student's t variable at 98% confidence (depending on the numbers of procedural method blanks)[124]

200 µL Amount of solution in the vial

m Amount of sample (e.g. 1 L, 1 g)

$$\mathrm{MQL} = \frac{s_{\mathrm{Blank}} \cdot 10 \cdot 200\,\mu\mathrm{L}}{m \cdot 1000} \tag{7}$$

For analytes that were not detected in method blanks the MDLs and MQLs were calculated as follows:

$$\mathrm{MDL} = \frac{3}{S/N_A} \cdot c_A \tag{8}$$

with S/N_A Signal to noise ratio of the analyte at its lowest concentration

c_A Lowest calculated concentration of the analyte (e.g. 1 ng/L, 1 ng/g)

$$\mathrm{MQL} = \frac{10}{S/N_A} \cdot c_A \tag{9}$$

The instrumental precision s_{rel} [%] was calculated as follows:

$$s_{\mathrm{rel}} = \frac{s}{\bar{x}} \cdot 100\% \tag{10}$$

with s Standard deviation of the peak areas (*N*=10)

$\bar{x}$ Mean of the peak areas (*N*=10)

A Supplement of Paper 1

A.1 Materials and Methods

Table A-1. Sampling stations and analytical parameters. No analytical parameters could have been determined for the 08/13 Rhine sampling campaign because of broken measurement devices. Thus, the outside temperature is given and the pH-value has been determined by pH 0-14 indicator strips by Merck.

No.	River | Name	Lon °E	Lat °N	Date | Time	T [°C]	pH	Sal [psu]	Turbidity [NTU]	Discharge Q [m^3/s]
R1	Lower Rhine | Leverkusen-Stammheim	6.97972	50.98606	19.08.2013 | 18:00	22.60	-	-	-	Cologne: 1270
R2	Lower Rhine | Leverkusen-Wiesdorf	6.97035	51.02987	19.08.2013 | 18:37	22.60	6-6.5	-	-	Cologne: 1270
R3	Lower Rhine | Monheim-Baumberg	6.87858	51.11587	19.08.2013 | 19:45	22.60	6.5-7	-	-	-
R4	Lower Rhine | Düsseldorf-Zentrum; Neuss	6.73327	51.20503	19.08.2013 | 20:30	22.60	6.5-7	-	-	1320
R5	Lower Rhine | Düsseldorf-Kaiserswerth	6.73158	51.3002	20.08.2013 | 11:23	22.60	6	-	-	1330
R6	Lower Rhine | Duisburg-Rheinhausen; L237 Moerser Straße	6.73978	51.41643	20.08.2013 | 12:15	22.60	6	-	-	1340
R7	Lower Rhine | Rheinberg-Orsoyerberg; Walsum	6.70595	51.52392	20.08.2013 | 12:58	22.60	6	-	-	-
R8	Lower Rhine | Wesel; Weseler Str.	6.60657	51.64683	20.08.2013 | 13:45	22.60	6-6.5	-	-	1350
R9	Lower Rhine | Rees	6.39022	51.75737	20.08.2013 | 14:26	22.60	7	-	-	1370
R10	Lower Rhine | Emmerich am Rhein; Emmericher Str.	6.23397	51.8305	20.08.2013 | 15:08	22.60	6-6.5	-	-	1370
R11	Lower Rhine | RWS; Lobith	6.1148	51.84985	20.08.2013 | 16:17	22.60	6.5-7	-	-	-
R12	Lower Rhine | Tolkamer	6.09807	51.85113	20.08.2013 | 16:35	22.60	6.5-7	-	-	-
R13	Lower Rhine | Arnhem	5.91165	51.97548	20.08.2013 | 17:38	22.60	6-6.5	-	-	-
R14	Waal | Ewijk	5.73737	51.88712	20.08.2013 | 18:16	22.60	7	-	-	-
R15	Waal | Tiel	5.44235	51.88533	20.08.2013 | 19:00	22.60	6	-	-	-
R16	Waal | Gorinchem	4.92855	51.83752	20.08.2013 | 19:35	22.60	6	-	-	-
R17	Oude Maas | Zwijndrecht	4.58027	51.80925	21.08.2013 | 10:44	22.60	7	-	-	-
R18	Hollands Diep | Willemstad	4.44343	51.696	21.08.2013 | 11:30	22.60	6.5-7	-	-	-
R19	New Waterway | Rozenburg	4.2433	51.91205	21.08.2013 | 12:22	22.60	7	-	-	-
R20	Ijssel | Kampen	5.92293	52.55487	21.08.2013 | 14:34	22.60	7	-	-	-
R21	Lower Ems | Leer; Emsstraße	7.42707	53.21597	22.08.2013 | 10:33	22.60	7	-	-	-

No.	River | Name	Lon °E	Lat °N	Date | Time	T [°C]	pH	Sal [psu]	Turbidity [NTU]	Discharge Q [m^3/s]
R22	Lower Ems | Gandersum	7.30592	53.32225	22.08.2013 | 11:32	22.60	6.5-7	-	-	-
R23	Lower Ems | Wybelsum	7.04187	53.33768	22.08.2013 | 12:27	22.60	-	-	-	-
E1	Upper Elbe | Dresden	13.74855	51.05416	02.09.2014 | 09:45	17.00	7.70	0.1	-	182
E2	Upper Elbe | Gohlis	13.64338	51.09621	02.09.2014 | 10:30	17.00	7.83	0.1	-	-
E3	Upper Elbe | Meißen	13.47801	51.16151	02.09.2014 | 11:17	17.10	7.90	0.1	-	-
E4	Middle Elbe | Boritz	13.40312	51.27085	02.09.2014 | 12:15	17.20	7.83	0.1	-	-
E5	Middle Elbe | Strehla	13.23556	51.35392	02.09.2014 | 12:55	17.40	8.10	0.1	-	Riesa: 152
E6	Middle Elbe | Torgau	13.01072	51.55757	02.09.2014 | 13:40	17.60	7.90	0.1	-	167
E7	Middle Elbe | Wittenberg	12.61178	51.86307	02.09.2014 | 15:50	18.80	8.10	0.2	-	175
E8	Middle Elbe | Barby	11.88835	51.97365	02.09.2014 | 18:25	18.80	7.95	1.5	-	287
E9	Middle Elbe | Sabke	11.67877	52.06767	02.09.2014 | 19:10	19.20	7.98	0.9	-	-
E10	Middle Elbe | Magdeburg	11.64887	52.13325	03.09.2014 | 10:00	17.80	7.94	0.9	-	287
E11	Middle Elbe | Derben	11.99558	52.43569	03.09.2014 | 11:10	18.90	8.02	0.6	-	Tangermünde: 283
E12	Middle Elbe | Sandau	12.03442	52.78592	03.09.2014 | 12:15	19.30	8.08	0.6	-	-
E13	Middle Elbe | Wittenberge	11.75917	52.98555	03.09.2014 | 13:20	20.20	8.11	0.5	-	-
E14	Middle Elbe | Schnackenburg	11.57216	53.04002	03.09.2014 | 13:55	19.90	8.23	0.5	-	-
E15	Middle Elbe | Dömitz	11.23641	53.14200	03.09.2014 | 14:50	20.00	8.33	0.5	-	Neu Darchau: 310
E16	Middle Elbe | Lauenburg	10.54306	53.37081	03.09.2014 | 17:45	19.90	8.75	0.6	-	-
E17	Middle Elbe | Grünhof	10.42344	53.40238	03.09.2014 | 18:20	20.40	8.87	0.6	-	-
E18	Lower Elbe | Oortkaten	10.09867	53.44151	09.09.2014 | 17:45	19.30	8.55	0.6	-	-
E19	Lower Elbe | Teufelsbrück	9.86320	53.54643	09.09.2014 | 16:40	19.20	8.05	0.6	-	-
E20	Lower Elbe | Wedel	9.70223	53.56797	09.09.2014 | 15:55	19.00	7.87	0.6	-	-
E21	Lower Elbe | Glückstadt	9.40948	53.78527	09.09.2014 | 13:40	19.00	8.10	0.9	-	-
E22	Lower Elbe | Brunsbüttel	9.09275	53.88750	09.09.2014 | 12:50	19.20	8.00	5.5	-	-
T1	Elbe estuary | Hamburg-Altona	9.9	53.54	24.03.2014 | 09:50	9.30	8.15	0.50	-	-
T2	Elbe estuary | Hamburg-Wedel	9.73	53.56	24.03.2014 | 10:30	9.17	7.82	0.56	-	-
T3	Elbe estuary | Lühesand	9.596888	53.600134	24.03.2014 | 11:02	8.85	7.81	0.60	35.71	-
T4	Elbe estuary | Pagensand	9.515887	53.66643	24.03.2014 | 11:34	8.77	7.86	0.64	37.84	-
T5	Elbe estuary | Glückstadt	9.426741	53.743679	24.03.2014 | 12:08	8.83	7.94	0.69	49.94	-

No.	River | Name	Lon °E	Lat °N	Date | Time	T [°C]	pH	Sal [psu]	Turbidity [NTU]	Discharge Q [m^3/s]
T6	Elbe estuary | Hollerwettern	9.365664	53.824502	24.03.2014 | 12:39	8.78	8.00	0.78	79.7	-
T7	Elbe estuary | Bütteler Hafen	9.260376	53.875967	24.03.2014 | 13:06	9.47	8.03	0.91	62.4	-
T8	Elbe estuary | Oste	8.968207	53.853102	24.03.2014 | 14:12	9.35	8.01	5.64	25.09	-
T9	Elbe estuary | Altenbruch	8.746437	53.862149	24.03.2014 | 15:19	8.43	8.05	15.84	8.37	-
T10	North Sea	8.509682	53.967967	25.03.2014 | 09:28	8.19	8.08	24.49	11.23	-
T11	North Sea	8.229092	53.983802	25.03.2014 | 10:26	8.82	8.09	30.61	9.17	-
T12	North Sea	7.952654	53.913998	25.03.2014 | 11:42	8.42	8.14	31.79	0.38	-
T13	North Sea	7.721291	53.857914	25.03.2014 | 12:42	9.31	8.11	31.08	2.77	-
T14	North Sea	7.490376	53.812302	25.03.2014 | 13:46	8.68	8.17	30.73	1.05	-
T15	North Sea	7.222304	53.749713	25.03.2014 | 15:01	8.96	8.18	30.15	6.95	-
T16	Lower Weser	8.5	53.39	27.03.2014 | 13:58	15.09	7.92	0.30	2.25	-
T17	Lower Weser	8.49	53.43	27.03.2014 | 14:14	13.79	7.81	0.80	35.71	-
T18	Lower Weser	8.49	53.47	27.03.2014 | 14:32	12.56	7.91	8.00	37.84	-
T19	Lower Weser	8.56	53.52	27.03.2014 | 14:56	11.38	7.81	7.95	49.94	-
S1	North Sea	8.294882	53.988391	04.08.2014 | 08:59	22.06	8.08	30.94	1.88	-
S2	North Sea	7.942224	53.909798	04.08.2014 | 10:28	20.21	8.17	32.96	-0.23	-
S3	North Sea	7.568550	53.816282	04.08.2014 | 12:07	21.55	8.07	32.65	0.18	-
S4	North Sea	7.225363	53.761533	04.08.2014 | 13:41	22.05	8.05	32.44	0.28	-
S11	North Sea	6.609757	53.688390	05.08.2014 | 08:35	22.00	8.01	31.47	3.45	-
S10	North Sea	6.684822	53.550203	05.08.2014 | 10:27	23.17	7.95	28.87	3.39	-
S9	Ems estuary	6.935445	53.410942	05.08.2014 | 11:41	24.82	7.86	22.51	8.00	-
S8	Ems estuary	7.021001	53.320232	06.08.2014 | 06:38	22.79	7.83	22.05	3.91	-
S7	Ems estuary	7.267713	53.322298	06.08.2014 | 08:19	22.98	7.55	9.54	30.47	-
S6	Ems estuary	7.372894	53.296584	06.08.2014 | 09:47	22.92	7.50	2.16	68.30	-
S5	Ems estuary	7.395839	53.263753	06.08.2014 | 11:35	23.20	7.36	0.37	46.08	-
S12	North Sea	6.590649	53.574989	07.08.2014 | 09:18	22.17	8.09	31.05	2.45	-
S13	North Sea	6.151409	53.546140	07.08.2014 | 11:05	21.58	8.13	32.58	-0.12	-
S14	North Sea	6.180173	53.420386	07.08.2014 | 13:02	22.33	8.16	32.43	4.39	-
S15	North Sea	5.801440	53.519967	08.08.2014 | 08:50	21.88	8.13	33.34	-0.21	-

No.	River | Name	Lon °E	Lat °N	Date | Time	T [°C]	pH	Sal [psu]	Turbidity [NTU]	Discharge Q [m^3/s]
S16	North Sea	5.578649	53.509771	08.08.2014 | 09:47	21.95	8.14	33.29	0.29	-
S17	North Sea	5.366887	53.475065	08.08.2014 | 10:54	21.33	8.13	33.22	-0.25	-
S18	North Sea	5.185081	53.441334	08.08.2014 | 11:38	20.89	8.14	33.15	-0.37	-
X1	Xiaoqing River	117.085	36.726	19.04.2014 | 15:40	18.20	7.44	0.62	-	-
X2	Xiaoqing River	117.093	36.733	19.04.2014 | 16:40	18.80	7.45	0.79	-	-
X3	Xiaoqing River	117.230	36.823	19.04.2014	18.70	7.50	0.69	-	-
X4	Xiaoqing River	117.360	36.909	19.04.2014 | 18:30	18.10	7.54	0.69	-	-
X5	Xiaoqing River	117.494	37.026	20.04.2014	17.60	7.78	0.87	-	-
X6	Xiaoqing River	117.695	37.069	20.04.2014	19.30	7.70	0.78	-	-
X7	Xiaoqing River	117.892	37.066	20.04.2014	20.90	7.76	1.01	-	-
X8	Xiaoqing River	117.917	37.071	20.04.2014	19.80	7.56	1.59	-	-
X9	Xiaoqing River	118.040	36.973	21.04.2014	19.80	7.58	3.94	-	-
X10	Xiaoqing River	118.038	37.007	21.04.2014	22.30	7.47	3.61	-	-
X11	Xiaoqing River	118.167	37.117	21.04.2014	23.70	7.68	1.66	-	-
X12	Xiaoqing River	118.376	37.143	22.04.2014	21.00	7.66	1.68	-	-
X13	Xiaoqing River	118.565	37.187	22.04.2014	20.70	7.86	1.62	-	-
X14	Xiaoqing River	118.547	37.154	22.04.2014	21.10	8.66	2.67	-	-
X15	Xiaoqing River	118.719	37.250	22.04.2014	22.80	8.18	2.44	-	-
X16	Xiaoqing River	118.832	37.274	22.04.2014	22.90	7.58	3.16	-	-
X17	Xiaoqing River	118.868	37.268	23.04.2014	20.40	7.49	9.22	-	-
X18	Xiaoqing River	118.892	37.279	23.04.2014	18.50	7.67	5.47	-	-
X19	Laizhou Bay	119.056	37.296	23.04.2014	19.20	7.50	24.95	-	-
X20	Laizhou Bay	119.107	37.304	23.04.2014	18.10	7.86	26.87	-	-
X21	Laizhou Bay	119.181	37.320	23.04.2014	17.20	7.97	27.20	-	-
X22	Laizhou Bay	119.265	37.344	23.04.2014	16.10	7.98	27.69	-	-
X23	Laizhou Bay	119.213	37.432	23.04.2014	15.70	8.06	27.74	-	-
X24	Laizhou Bay	119.161	37.392	23.04.2014	16.10	8.02	26.36	-	-
X25	Laizhou Bay	119.109	37.349	23.04.2014	16.50	7.93	27.16	-	-
X26	Laizhou Bay	119.047	37.316	23.04.2014	16.80	7.73	26.60	-	-

No.	River | Name	Lon °E	Lat °N	Date | Time	T [°C]	pH	Sal [psu]	Turbidity [NTU]	Discharge Q [m^3/s]
X27	Laizhou Bay	119.025	37.295	23.04.2014	18.60	7.58	20.71	-	-
X28	Xiaoqing River	118.983	37.277	23.04.2014	20.40	7.55	12.68	-	-
X29	Xiaoqing River	118.934	37.276	23.04.2014	19.30	7.61	10.23	-	-

Chemicals

All native and mass-labeled reference standards were purchased from Wellington Laboratories (Guelph, Canada). Additionally 5 g of PFOA and PFHpA were purchased from Lancaster Synthesis (UK), respectively.

Table A-2. Chemicals.

Acronym	Chemical name	Formula	CAS-No.	Amount	MRM transitions	Internal Standard
PFBA	Perfluoro-n-butanoic acid	$C_4HF_7O_2$	375-22-4	2 µg/mL (PFC-MXA); 50±2.5 µg/mL	212.9>168.7	[$^{13}C_4$]-PFBA
PFPeA	Perfluoro-n-pentanoic acid	$C_5HF_9O_2$	2706-90-3	2 µg/mL (PFC-MXA); 50±2.5 µg/mL	262.8>218.9	[$^{13}C_2$]-PFHxA
PFHxA	Perfluoro-n-hexanoic acid	$C_6HF_{11}O_2$	307-24-4	2 µg/mL (PFC-MXA); 50±2.5 µg/mL	312.9>268.8	[$^{13}C_2$]-PFHxA
PFHpA	Perfluoro-n-heptanoic acid	$C_7HF_{13}O_2$	375-85-9	2 µg/mL (PFC-MXA); 50±2.5 µg/mL; 5 g	363>318.8	[$^{13}C_4$]-PFOA
PFOA	Perfluoro-n-octanoic acid	$C_8HF_{15}O_2$	335-67-1	2 µg/mL (PFC-MXA); 50±2.5 µg/mL; 5 g	413>369>219>169	[$^{13}C_4$]-PFOA
PFNA	Perfluoro-n-nonanoic acid	$C_9HF_{17}O_2$	375-95-1	2 µg/mL (PFC-MXA)	462.9>418.9	[$^{13}C_5$]-PFNA
PFDA	Perfluoro-n-decanoic acid	$C_{10}HF_{19}O_2$	335-76-2	2 µg/mL (PFC-MXA)	512.9>469	[$^{13}C_2$]-PFDA
PFUnDA	Perfluoro-n-undecanoic acid	$C_{11}HF_{21}O_2$	2058-94-8	2 µg/mL (PFC-MXA)	562.8>519	[$^{13}C_2$]-PFUnDA
PFDoDA	Perfluoro-n-dodecanoic acid	$C_{12}HF_{23}O_2$	307-55-1	2 µg/mL (PFC-MXA)	613>568.9	[$^{13}C_2$]-PFDoDA
PFTrDA	Perfluoro-n-tridecanoic acid	$C_{13}HF_{25}O_2$	72629-94-8	2 µg/mL (PFC-MXA)	663.1>618.9	[$^{13}C_2$]-PFDoDA
PFTeDA	Perfluoro-n-tetradecanoic acid	$C_{14}HF_{27}O_2$	376-06-7	2 µg/mL (PFC-MXA)	713>669	[$^{13}C_2$]-PFDoDA
PFBS	Perfluorobutane sulfonate	$C_4F_9O_3S$	375-73-5	2 µg/mL±5% (PFS-MXA)	298.9>99>79.8	[$^{18}O_2$]-PFHxS

Acronym	Chemical name	Formula	CAS-No.	Amount	MRM transitions	Internal Standard
PFHxS	Perfluorohexane sulfonate	$C_6HF_{13}SO_3$	355-46-4	2 µg/mL±5% (PFS-MXA)	398.9>98.8>79.8	[$^{18}O_2$]-PFHxS
PFHpS	Perfluoroheptane sulfonate	$C_7HF_{15}O_3S$	375-92-8	2 µg/mL±5% (PFS-MXA)	449>79.3	[$^{13}C_4$]-PFOS
PFOS	Perfluorooctane sulfonate	$C_8HF_{17}SO_3$	1763-23-1	2 µg/mL±5% (PFS-MXA)	499>98.8>79.6	[$^{13}C_4$]-PFOS
PFDS	Perfluorodecane sulfonate	$C_{10}HF_{21}O_3S$	335-77-3	2 µg/mL±5% (PFS-MXA)	598.9>79.5	[$^{18}O_2$]-PFHxS
HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3,-heptafluoropropoxy)-propanoic acid	$C_6HF_{11}O_3$	13252-13-6	50±2.5 µg/mL	329>285>168.9	[$^{13}C_3$]-HFPO-DA [$^{13}C_2$]-PFHxA
6:2 FTS	Sodium 1H,1H,2H,2H-perfluorooctane sulfonate	$C_8H_5O_3F_{13}S$	27619-97-2	50±2.5 µg/mL	427>407	[$^{18}O_2$]-PFHxS
FOSA	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluoro-1-octanesulfonamide	$C_7H_2F_{15}NO_2S$	754-91-6	50±2.5 µg/mL	498>77.8	[$^{13}C_4$]-PFOS
[$^{13}C_3$]-HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3,-heptafluoropropoxy)-$^{13}C_3$-propanoic acid	$^{13}C_3{}^{12}C_3HF_{11}O_3$	N.A.	50±2.5 µg/mL	332>287	-
[$^{13}C_4$]-PFBA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	$^{13}C_4HF_7O_2$	N.A.	2 µg/mL (MPFAC-MXA)	216.8>171.8	-
[$^{13}C_2$]-PFOA	Perfluoro-n-(1,2-13C2)-octanoic acid	$^{13}C_2{}^{12}C_6HF_{15}O_2$	N.A.	50±2.5 µg/mL	415>369.9	-
[$^{13}C_4$]-PFOA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	$^{13}C_4{}^{12}C_4HF_{15}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	417>371.8	-
[$^{13}C_8$]-PFOA	Perfluoro-n[1,2,3,4,5,6,7,8-$^{13}C_{8]}$octanoic acid	$^{13}C_8HF_{15}O_2$	N.A.	50±2.5 µg/mL	421>375.9	-
[$^{13}C_2$]-PFHxA	Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	$^{13}C_2{}^{12}C_4HF_{11}\ O_2$	N.A.	2 µg/mL (MPFAC-MXA)	314.9>269.9	-
[$^{13}C_5$]-PFNA	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	$^{13}C_5{}^{12}C_4HF_{17}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	467.9>423	-
[$^{13}C_2$]-PFDA	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	$^{13}C_2{}^{12}C_8HF_{19}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	514.9>469.8	-
[$^{13}C_2$]-PFUnDA	Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	$^{13}C_2{}^{12}C_9HF_{21}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	565>519.8	-
[$^{13}C_2$]-PFDoDA	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	$^{13}C_2{}^{12}C_{10}HF_{23}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	614.9>569.9	-
[$^{18}O_2$]-PFHxS	Perfluoro-1-hexane[$^{18}O_2$]sulfonate	$C_6HF_{13}S^{18}O_2{}^{16}O$	N.A.	2 µg/mL (MPFAC-MXA)	403>83.9	-
[$^{13}C_4$]-PFOS	Perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	$^{13}C_4{}^{12}C_4HF_{17}SO_3$	N.A.	2 µg/mL (MPFAC-MXA)	503>79.5	-

Quality Assurance and Quality Control

Table A-3. Recoveries of the mass-labeled internal standards spiked into the environmental samples.

Internal standard	**Mean ± SD [%]**
[$^{18}O_2$]-PFHxS	57.7 ± 23.6
[$^{13}C_4$]-PFOS	68.7 ± 43.2
[$^{13}C_4$]-PFBA	65.9 ± 40.2
[$^{13}C_2$]-PFHxA	55.5 ± 22.6
[$^{13}C_4$]-PFOA	48.9 ± 19.6
[$^{13}C_5$]-PFNA	97.9 ± 69.8
[$^{13}C_2$]-PFDA	73.2 ± 52.5
[$^{13}C_2$]-PFUnDA	85.1 ± 67.5
[$^{13}C_2$]-PFDoDA	90.7 ± 82.6
[$^{13}C_3$]-HFPO-DA	49.8 ± 8.4

Table A-4. PFASs, that have been detected in this study, and their Limit of Detections (LOD), Limit of Quantifications (LOQ), Method Detection Limits (MDL) and Method Quantification Limits (MQL) referred to the specific sampling campaigns. For analytes present in the method blanks (blue), the MDL and the MQL were calculated with the blank standard deviations multiplied by 3.747 or 2.821 (variable from Student's t table at 98% confidence, depending on the numbers of procedural blank samples) and 10, respectively. For analytes absent in the method blanks (green), the sample with the lowest concentration was chosen to extrapolate from the calculated S/N at this concentration to a S/N at 3 and 10, respectively.

			Rhine 08/13		**Elbe 09/14**		**LP 03/14**		**XQ River 04/14**		**LP 08/14**	
Analyte	**LOD [pg]**	**LOQ [pg]**	**MDL [ng/L]**	**MQL [ng/L]**	**MDL [ng/L]**	**MQL [ng/L]**	**MDL [ng/L]**	**MQL [ng/L]**	**MDL [ng/L]**	**MQL [ng/L]**	**MDL [ng/L]**	**MQL [ng/L]**
HFPO-DA	0.4	1.2	0.14	0.47	n.d.	n.d.	0.13	0.42	0.31	1.02	0.13	0.44
PFBS	0.2	0.5	0.09	0.29	0.16	0.53	0.04	0.13	n.d.	n.d.	0.05	0.17
PFHxS	0.1	0.4	0.08	0.27	0.03	0.08	0.03	0.10	n.d.	n.d.	0.06	0.20
PFOS	0.1	0.3	0.001	0.003	0.01	0.05	0.40	1.07	0.98	2.61	0.10	0.35
PFBA	0.7	2.2	0.03	0.09	0.03	0.09	0.37	0.99	1.29	3.45	0.01	0.05
PFPeA	0.7	2.4	0.20	0.66	0.10	0.33	0.25	0.66	1.90	5.06	0.20	0.66
PFHxA	0.3	1.0	0.09	0.31	0.09	0.29	0.09	0.25	0.23	0.60	0.07	0.25
PFHpA	0.3	0.9	0.23	0.81	0.22	0.81	0.63	1.68	2.08	5.55	0.22	0.81
PFOA	0.5	1.7	0.30	1.07	0.56	1.98	0.40	1.07	1.30	3.48	0.01	0.02
PFNA	0.3	0.9	0.01	0.05	0.04	0.13	0.01	0.05	0.07	0.24	0.02	0.06
PFDA	0.2	0.5	0.003	0.01	0.54	2.05	0.002	0.01	0.51	1.36	0.09	0.32
PFUnDA	0.4	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.06	0.03	0.09
PFDoDA	0.1	0.4	0.002	0.006	n.d.	n.d.	n.d.	n.d.	0.02	0.05	n.d.	n.d.
6:2 FTS	0.1	0.3	0.01	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOSA	0.04	0.1	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. not detected

A.2 Results and Discussion

Table A-5. PFASs concentrations [ng/L] of all sampling sites. Substances which showed no peak are reported as not detected (n.d.). Substances which showed peaks, but the values were calculated with <0, are reported as <0. Values less than a blank-defined MDL are reported as <MDL. Values in brackets are below the MQL.

No.	HFPO-DA	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	6:2 FTS	FOSA	ΣPFASs
R1	n.d.	1.75	1.87	3.08	2.52	4.32	2.52	1.70	5.08	0.37	0.27	n.d.	n.d.	n.d.	0.08	23.56
R2	107.6	10.96	1.69	1.84	1.32	4.70	2.22	1.91	6.56	0.34	0.11	n.d.	n.d.	0.29	0.05	139.58
R3	n.d.	25.00	1.75	2.48	2.44	4.42	2.68	2.50	4.92	0.47	0.22	n.d.	n.d.	0.19	0.08	47.15
R4	n.d.	25.40	2.12	1.89	1.80	4.66	3.12	2.38	4.44	0.40	0.22	n.d.	n.d.	0.47	0.08	46.98
R5	n.d.	18.26	2.04	2.42	1.72	4.20	2.74	2.04	4.64	0.44	0.21	n.d.	n.d.	0.55	0.09	39.36
R6	n.d.	17.00	1.74	1.23	2.38	4.94	2.66	2.32	4.54	0.40	0.18	n.d.	n.d.	0.30	0.07	37.76
R7	n.d.	18.78	1.64	2.32	2.56	5.48	2.76	2.36	4.38	0.37	0.16	n.d.	n.d.	n.d.	0.06	40.87
R8	n.d.	23.20	2.38	1.96	2.72	6.18	3.60	2.82	6.40	0.42	0.22	n.d.	n.d.	n.d.	0.09	49.98
R9	n.d.	26.60	2.12	n.d.	1.67	6.74	3.82	2.20	5.90	0.41	0.36	n.d.	0.02	n.d.	0.06	49.90
R10	n.d.	32.60	2.20	3.36	2.46	5.98	3.62	3.10	6.48	0.50	0.22	n.d.	n.d.	n.d.	0.09	60.61
R11	n.d.	31.00	4.44	1.05	3.32	7.52	4.84	2.26	8.88	0.76	0.38	n.d.	n.d.	n.d.	0.08	64.54
R12	0.75	18.84	2.26	3.12	2.70	5.00	3.16	2.76	6.44	0.46	0.20	n.d.	n.d.	n.d.	0.09	45.79
R13	n.d.	22.60	2.40	1.92	1.91	6.22	3.14	2.16	6.32	0.49	0.23	n.d.	n.d.	n.d.	0.07	47.46
R14	n.d.	29.00	2.12	0.15	2.02	4.32	3.22	1.55	5.38	0.44	0.24	n.d.	n.d.	n.d.	0.06	48.50
R15	n.d.	50.00	2.24	1.32	2.78	5.58	2.82	2.88	5.94	0.40	0.24	n.d.	n.d.	n.d.	0.06	74.26
R16	n.d.	10.90	1.70	n.d.	3.24	5.02	3.82	2.04	7.98	0.68	0.28	n.d.	n.d.	n.d.	0.04	35.71
R17	n.d.	30.00	1.91	2.70	1.55	5.64	3.12	2.32	5.62	0.41	0.22	n.d.	n.d.	0.29	0.06	53.84
R18	n.d.	18.08	2.16	2.06	1.95	5.92	3.48	3.68	7.38	0.55	0.25	n.d.	n.d.	n.d.	0.07	45.58
R19	91.40	14.16	2.40	1.71	2.12	4.90	3.28	2.62	7.50	0.61	0.29	n.d.	n.d.	n.d.	0.10	131.09
R20	n.d.	13.36	2.06	n.d.	1.31	4.60	3.18	2.58	5.68	0.48	0.20	n.d.	n.d.	n.d.	0.07	33.53
R21	n.d.	4.90	2.68	n.d.	2.45	13.33	6.80	2.98	8.53	0.45	0.16	n.d.	n.d.	n.d.	n.d.	42.26
R22	n.d.	3.32	1.75	n.d.	0.53	10.06	3.90	2.34	5.48	0.09	0.02	n.d.	n.d.	n.d.	n.d.	27.49
R23	1.80	2.12	1.04	n.d.	0.27	5.06	2.62	2.02	4.64	0.21	0.04	n.d.	n.d.	n.d.	n.d.	19.83
E1	n.d.	1.38	0.87	6.30	0.52	0.54	2.58	<0	(1.75)	0.60	<MDL	0.03	0.03	2.86	<0	17.46

No.	HFPO-DA	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	6:2 FTS	FOSA	ΣPFASs
E2	n.d.	0.96	0.79	<0	0.67	1.08	2.86	<0	(1.46)	0.65	(0.96)	0.24	0.17	2.36	0.04	12.23
E3	n.d.	2.62	0.73	<0	1.39	1.39	2.80	<0	(1.61)	0.80	(1.17)	0.58	0.58	2.86	0.09	16.63
E4	n.d.	2.18	1.01	<0	1.23	0.61	2.34	<0	(1.68)	0.57	(1.17)	0.30	0.30	1.98	<0	13.38
E5	n.d.	1.92	0.91	1.67	1.01	0.83	2.78	<0	(1.79)	1.03	(1.92)	1.91	1.40	2.38	0.33	19.87
E6	n.d.	2.46	0.94	13.14	0.77	2.16	2.94	<0	2.02	0.93	2.80	1.00	0.73	1.78	0.19	31.87
E7	n.d.	2.48	0.65	<0	1.13	2.04	3.24	<0	(1.87)	0.78	(1.71)	0.54	0.43	1.56	0.09	16.52
E8	n.d.	3.42	0.59	<0	1.90	4.06	4.30	2.10	3.18	0.97	3.34	0.73	0.23	1.34	0.09	26.26
E9	n.d.	3.00	0.75	<0	1.01	2.22	3.74	(0.58)	3.20	0.91	(1.92)	0.25	0.09	1.10	0.09	18.87
E10	n.d.	2.60	0.68	<0	1.75	2.60	4.08	(0.39)	2.52	0.69	(2.00)	0.23	n.d.	1.22	n.d.	18.75
E11	n.d.	3.42	1.44	<0	1.13	2.86	4.08	(0.65)	3.12	1.08	2.18	0.14	0.03	0.40	0.07	20.60
E12	n.d.	3.48	1.21	<0	2.34	2.94	4.14	(0.62)	3.02	1.31	(1.47)	0.15	n.d.	n.d.	0.07	20.75
E13	n.d.	3.12	0.69	<0	1.68	3.58	3.84	1.14	2.26	0.60	(0.95)	n.d.	n.d.	n.d.	<0	17.85
E14	n.d.	2.98	0.85	<0	2.26	4.58	4.06	1.57	2.88	0.65	(1.27)	0.19	n.d.	0.20	n.d.	21.50
E15	n.d.	1.03	0.35	<0	<0	0.66	1.88	<0	(1.03)	0.35	(0.43)	0.06	<0	n.d.	n.d.	5.80
E16	n.d.	3.20	0.74	<0	0.11	3.52	3.56	(0.34)	2.12	0.56	(0.64)	n.d.	n.d.	n.d.	n.d.	14.78
E17	n.d.	3.24	0.67	<0	<0	3.50	3.44	0.87	2.34	0.83	(0.71)	0.12	0.10	n.d.	n.d.	15.82
E18	n.d.	3.68	0.96	9.60	1.89	5.18	3.98	2.22	2.74	0.87	(1.10)	0.14	n.d.	n.d.	0.07	32.43
E19	n.d.	3.10	1.22	4.04	1.87	4.44	4.04	1.15	3.12	1.23	2.16	0.37	n.d.	n.d.	0.11	26.83
E20	n.d.	3.56	1.62	3.34	1.31	5.28	5.08	1.34	2.94	0.72	(1.36)	0.17	n.d.	n.d.	0.03	26.75
E21	n.d.	4.55	1.73	9.75	1.93	6.55	5.48	1.46	4.48	1.14	(1.20)	n.d.	n.d.	0.49	0.06	38.80
E22	n.d.	4.16	1.64	6.00	1.61	6.00	4.12	2.16	3.24	0.99	(1.77)	n.d.	n.d.	n.d.	n.d.	31.68
T1	n.d.	1.39	0.66	2.06	1.53	1.06	2.71	<MDL	2.09	0.23	0.09	n.d.	n.d.	n.d.	n.d.	11.81
T2	n.d.	1.38	0.68	3.29	2.22	1.10	2.25	<MDL	2.12	0.28	<0	n.d.	n.d.	n.d.	n.d.	13.32
T3	n.d.	1.43	0.63	2.39	1.63	0.72	3.10	<MDL	2.01	0.20	<0	n.d.	n.d.	n.d.	n.d.	12.11
T4	n.d.	1.41	0.66	2.12	1.59	1.56	3.21	(1.25)	2.31	0.43	0.02	n.d.	n.d.	n.d.	n.d.	14.55
T5	n.d.	1.49	0.84	2.23	1.67	1.12	2.81	(1.22)	2.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	13.41
T6	n.d.	1.66	0.45	2.27	1.67	1.68	3.07	(1.30)	1.92	0.25	0.03	n.d.	n.d.	n.d.	n.d.	14.32
T7	n.d.	1.39	0.67	2.21	1.65	1.71	3.14	<MDL	1.97	0.23	0.02	n.d.	n.d.	n.d.	n.d.	12.98
T8	0.61	1.47	0.59	(0.87)	(0.34)	1.15	2.29	(0.19)	2.43	0.23	n.d.	n.d.	n.d.	n.d.	n.d.	10.17

No.	HFPO-DA	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	6:2 FTS	FOSA	ΣPFASs
T9	1.46	1.14	0.46	2.02	1.49	1.01	1.66	(0.70)	6.37	0.15	<0	n.d.	n.d.	n.d.	n.d.	16.45
T10	2.18	0.99	0.38	1.52	0.99	(0.44)	0.96	(1.00)	(1.04)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.49
T11	2.82	1.18	0.23	1.13	(0.60)	(0.61)	0.58	(0.75)	(0.44)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.35
T12	2.10	0.92	0.14	<MDL	(0.91)	0.74	0.54	(1.59)	(0.62)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.56
T13	2.66	1.13	0.23	1.10	(0.57)	(0.58)	0.52	(1.02)	(0.46)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.26
T14	2.78	0.84	0.27	(0.89)	(0.36)	(0.26)	0.64	(1.03)	1.36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.43
T15	3.70	1.18	0.26	1.14	(0.61)	(0.41)	0.58	<MDL	(0.59)	0.11	<0	n.d.	n.d.	n.d.	n.d.	8.47
T16	n.d.	1.29	0.78	1.42	(0.89)	1.30	4.57	(0.87)	2.73	0.14	<0	n.d.	n.d.	n.d.	n.d.	13.97
T17	n.d.	1.67	0.81	2.32	1.79	1.58	4.37	(1.29)	2.57	0.18	<0	n.d.	n.d.	n.d.	n.d.	16.58
T18	n.d.	2.02	1.23	1.57	1.04	1.34	4.99	(1.21)	4.17	0.24	0.02	n.d.	n.d.	n.d.	n.d.	17.83
T19	n.d.	1.52	0.73	1.59	1.06	1.23	3.35	(1.00)	1.67	0.09	<0	n.d.	n.d.	n.d.	n.d.	12.24
S1	1.47	1.04	n.d.	<0	<0	<0	0.94	0.87	4.08	0.27	(0.29)	n.d.	n.d.	n.d.	n.d.	8.96
S2	1.27	0.70	0.22	<0	<0	<0	0.34	<MDL	2.02	0.17	(0.17)	n.d.	n.d.	n.d.	n.d.	4.90
S3	1.51	0.90	0.31	<0	<0	<0	0.48	(0.35)	2.76	0.18	(0.21)	n.d.	n.d.	n.d.	n.d.	6.69
S4	1.60	0.73	0.40	<0	<0	<0	0.64	(0.40)	2.96	0.22	(0.18)	n.d.	n.d.	n.d.	n.d.	7.13
S5	n.d.	3.38	1.54	0.59	4.56	4.71	1.00	5.91	13.17	1.75	1.31	0.31	n.d.	n.d.	n.d.	42.63
S6	n.d.	3.03	1.88	0.88	3.55	4.38	5.01	7.33	13.21	2.58	2.42	0.39	n.d.	n.d.	n.d.	44.66
S7	0.62	3.30	1.66	<0	0.67	3.98	4.52	6.74	10.70	1.29	0.82	n.d.	n.d.	n.d.	n.d.	34.29
S8	1.25	1.56	0.99	<0	<0	2.06	2.16	5.38	6.62	0.62	(0.32)	n.d.	n.d.	n.d.	n.d.	20.96
S9	1.32	2.44	0.87	<0	<0	1.67	2.74	9.68	11.04	1.80	0.65	n.d.	n.d.	n.d.	n.d.	32.21
S10	1.60	1.12	0.52	<0	<0	<0	1.33	(0.81)	5.56	0.28	(0.21)	n.d.	n.d.	n.d.	n.d.	11.44
S11	1.73	0.90	n.d.	<0	0.26	<0	0.95	<MDL	1.79	0.19	n.d.	n.d.	n.d.	n.d.	n.d.	5.82
S12	1.62	0.96	n.d.	<0	1.63	<0	0.80	6.19	4.99	0.67	n.d.	n.d.	n.d.	n.d.	n.d.	16.86
S13	1.30	1.71	n.d.	<0	<0	<0	0.32	10.51	7.37	0.99	n.d.	n.d.	n.d.	n.d.	n.d.	22.20
S14	1.59	1.22	n.d.	<0	0.08	<0	0.86	5.30	6.30	0.42	n.d.	n.d.	n.d.	n.d.	n.d.	15.76
S15	1.81	0.86	n.d.	<0	1.75	<0	0.47	1.50	3.06	0.22	(0.21)	n.d.	n.d.	n.d.	n.d.	9.88
S16	1.88	0.93	0.23	<0	0.67	<0	0.55	<MDL	2.46	0.15	(0.18)	n.d.	n.d.	n.d.	n.d.	7.03
S17	2.04	0.79	0.30	<0	1.06	<0	0.54	<MDL	2.08	0.14	(0.22)	n.d.	n.d.	n.d.	n.d.	7.17
S18	2.02	1.05	n.d.	<0	<0	<0	0.49	(0.31)	2.50	0.14	<0	n.d.	n.d.	n.d.	n.d.	6.51

No.	HFPO-DA	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	6:2 FTS	FOSA	ΣPFASs
X1	n.d.	n.d.	n.d.	3.65	8.25	0.31	5.31	3.98	86.69	0.90	<MDL	<MDL	n.d.	n.d.	n.d.	109.1
X2	n.d.	n.d.	n.d.	<MDL	5.95	0.43	3.06	2.91	40.07	0.56	<MDL	<MDL	n.d.	n.d.	n.d.	52.97
X3	n.d.	n.d.	n.d.	3.05	7.15	0.45	3.15	4.09	38.07	0.79	<MDL	<MDL	n.d.	n.d.	n.d.	56.75
X4	n.d.	n.d.	n.d.	2.87	7.40	1.80	4.28	5.69	72.82	0.74	<MDL	<MDL	n.d.	n.d.	n.d.	95.60
X5	n.d.	n.d.	n.d.	2.74	8.20	1.16	3.83	4.09	43.57	0.99	(0.63)	0.11	<0	n.d.	n.d.	65.32
X6	n.d.	n.d.	n.d.	1.74	37.00	5.47	6.93	8.94	372.3	1.29	<MDL	<MDL	<0	n.d.	n.d.	433.7
X7	n.d.	n.d.	n.d.	(1.31)	13.70	4.52	6.58	9.44	181.3	3.16	(0.90)	0.08	n.d.	n.d.	n.d.	221.0
X8	3.30	n.d.	n.d.	(2.07)	29.65	8.02	18.38	21.09	4005	2.60	(0.74)	0.11	<0	n.d.	n.d.	4090
X9	5.55	n.d.	n.d.	n.d.	30.45	11.12	22.88	25.74	9950	1.97	<MDL	(0.06)	n.d.	n.d.	n.d.	10048
X10	2722	n.d.	n.d.	4.01	5963*	13903*	25243*	53209*	723713*	93.50	11.53	1.07	<0	n.d.	n.d.	824862
X11	2125	n.d.	n.d.	<MDL	1615	2075	4115	7550	115000*	8.90	1.43	0.22	n.d.	n.d.	n.d.	132491
X12	3825	n.d.	n.d.	(2.01)	1305	3835	6500	9800	152500*	14.70	1.88	0.24	<0	n.d.	n.d.	177784
X13	212.5	n.d.	n.d.	(2.13)	1115	1345	2990	4045	65500*	7.05	(1.20)	0.19	<0	n.d.	n.d.	75218
X14	142.5	n.d.	n.d.	<MDL	1595	1495	3215	4560	67500*	5.85	(0.70)	<MDL	n.d.	n.d.	n.d.	78514
X15	103.5	n.d.	n.d.	(1.36)	1230	1120	2675	3560	76500*	6.85	(1.09)	0.12	<0	n.d.	n.d.	85198
X16	143.0	n.d.	n.d.	(1.29)	1060	1160	3060	4775	79500*	7.90	(1.24)	0.12	n.d.	n.d.	n.d.	89709
X17	102.0	n.d.	n.d.	(1.82)	1225	1695	3495	4835	82000*	6.00	(0.98)	0.10	n.d.	n.d.	n.d.	93361
X18	103.0	n.d.	n.d.	(1.47)	845.0	1825	4150	6250	69500*	6.90	(0.97)	<MDL	n.d.	n.d.	n.d.	82682
X29	95.50	n.d.	n.d.	(1.87)	975.0	2105	4055	5300	80000*	7.00	(1.10)	<MDL	n.d.	n.d.	n.d.	92540
X28	105.0	n.d.	n.d.	<MDL	1264	1841	3614	5422	63329*	6.05	(1.05)	0.09	n.d.	n.d.	n.d.	75581
X27	55.00	n.d.	n.d.	<MDL	199.6	1105	2125	2730	52500*	3.48	<MDL	<MDL	n.d.	n.d.	n.d.	58718
X19	34.15	n.d.	n.d.	2.98	134.6	178.6	361.7	264.0	17084	2.19	<MDL	<MDL	n.d.	n.d.	n.d.	18062
X26	18.75	n.d.	n.d.	<MDL	49.60	84.07	155.7	153.0	15100	1.53	<MDL	<MDL	n.d.	n.d.	n.d.	15563
X20	8.70	n.d.	n.d.	n.d.	36.50	50.57	84.23	82.04	12100	1.09	<MDL	<MDL	n.d.	n.d.	n.d.	12363
X25	7.50	n.d.	n.d.	n.d.	16.05	27.57	47.48	46.29	4380	0.65	<MDL	<MDL	n.d.	n.d.	n.d.	4526
X21	6.65	n.d.	n.d.	4.47	10.85	27.27	46.08	35.19	4067	1.00	<MDL	<MDL	n.d.	n.d.	n.d.	4199
X24	6.00	n.d.	n.d.	4.97	9.95	17.37	27.53	28.99	3252	1.18	<MDL	0.26	(0.05)	n.d.	n.d.	3348
X22	10.60	n.d.	n.d.	(1.79)	21.75	66.07	88.23	91.54	1074	0.77	<MDL	<MDL	n.d.	n.d.	n.d.	1355
X23	6.05	n.d.	n.d.	(1.80)	8.25	16.17	25.53	16.19	1050	0.59	<MDL	<MDL	n.d.	n.d.	n.d.	1125

*These values have to be considered as semiquantitative because they are outside the calibration range

Table A-6. Frequency of detection at >MDL [%] and statistics of the individual PFASs [ng/L] in the different sampling areas. Values <MQL were used unaltered to calculate arithmetic means. Nondetects and values <MDL were considered as zero to calculate arithmetic means.

	Rhine 08/13					**Elbe 09/14**					**LP 03/14**					**XQ Riv 04/14**					**LP 08/14**				
Substance	***n [%] >* MDL**	**Max**	**Min**	**Mean**	**Median**	***n [%] >* MDL**	**Max**	**Min**	**Mean**	**Median**	***n [%] >* MDL**	**Max**	**Min**	**Mean**	**Median**	***n [%] >***	**Max**	**Min**	**Mean**	**Median**	***n [%] >* MDL**	**Max**	**Min**	**Mean**	**Median**
HFPO-DA	17	107.6	0.0	8.8	0.0	0	-	-	-	-	42	3.7	0.0	1.0	0.0	76	3825	0.0	339.3	10.6	89	2.0	0.0	1.4	1.5
PFBS	100	50.0	1.8	19.5	18.8	100	4.6	1.0	2.8	3.1	100	2.0	0.8	1.3	1.4	0	-	-	-	-	100	3.4	0.7	1.5	1.0
PFHxS	100	4.4	1.0	2.1	2.1	100	1.7	0.4	1.0	0.9	100	1.2	0.1	0.6	0.6	0	-	-	-	-	61	1.9	0.0	0.5	0.3
PFOS	74	3.4	0.0	1.5	1.8	36	13.1	0.0	2.4	0.0	95	3.3	0.0	1.7	1.6	69	5.0	0.0	1.7	1.8	11	0.9	0.0	0.1	0.0
PFBA	100	3.3	0.3	2.1	2.1	91	2.3	0.0	1.3	1.3	100	2.2	0.3	1.2	1.1	100	5962	6.0	649.2	37.0	50	4.6	0.0	0.8	0.0
PFPeA	100	13.3	4.2	5.9	5.1	100	6.6	0.5	3.0	2.9	100	1.7	0.3	1.0	1.1	100	13902	0.3	1173	66.1	28	4.7	0.0	0.9	0.0
PFHxA	100	6.8	2.2	3.4	3.2	100	5.5	1.9	3.6	3.8	100	5.0	0.5	2.4	2.7	100	25243	3.1	2281	88.2	100	5.4	0.3	1.6	0.8
PFHpA	100	3.7	1.6	2.4	2.3	68	2.2	0.0	0.8	0.6	74	1.6	0.0	0.8	1.0	100	53209	2.9	3891	91.5	78	10.5	0.0	3.4	1.2
PFOA	100	8.9	4.4	6.1	5.9	100	4.5	1.0	2.5	2.4	100	6.4	0.4	2.0	2.0	100	723713	38.1	58636	12100	100	13.2	1.8	5.7	4.5
PFNA	100	0.8	0.1	0.4	0.4	100	1.3	0.3	0.8	0.8	68	0.4	0.0	0.1	0.1	100	93.5	0.6	6.8	2.2	100	2.6	0.1	0.7	0.3
PFDA	100	0.4	0.0	0.2	0.2	95	3.3	0.0	1.5	1.3	26	0.1	0.0	0.0	0.0	48	11.5	0.0	0.9	0.0	72	2.4	0.0	0.4	0.2
PFUnDA	0	-	-	-	-	91	1.9	0.0	0.3	0.2	0	-	-	-	-	45	1.1	0.0	0.1	0.0	11	0.4	0.0	0.0	0.0
PFDoDA	4	0.0	0.0	0.0	0.0	50	1.4	0.0	0.2	0.0	0	-	-	-	-	3	0.1	0.0	0.0	0.0	0	-	-	-	-
6:2 FTS	26	0.6	0.0	0.1	0.0	59	2.9	0.0	0.9	0.4	0	-	-	-	-	0	-	-	-	-	0	-	-	-	-
FOSA	87	0.1	0.0	0.1	0.1	64	0.3	0.0	0.1	0.0	0	-	-	-	-	0	-	-	-	-	0	-	-	-	-
∑PFASs	-	139.6	19.8	52.4	47.0	-	38.8	5.8	21.2	19.4	-	17.8	7.6	12.2	12.2	-	824862	53.0	66978	12363	-	44.7	4.9	16.9	10.7

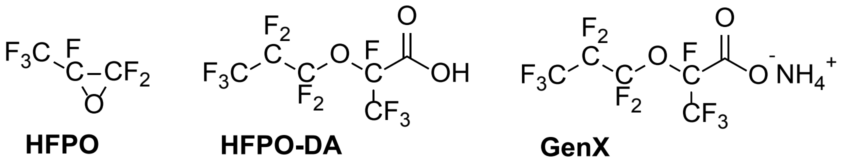

Figure A-1. Structure of the monomer HFPO. the dimer acid HFPO-DA and its ammonium salt GenX.

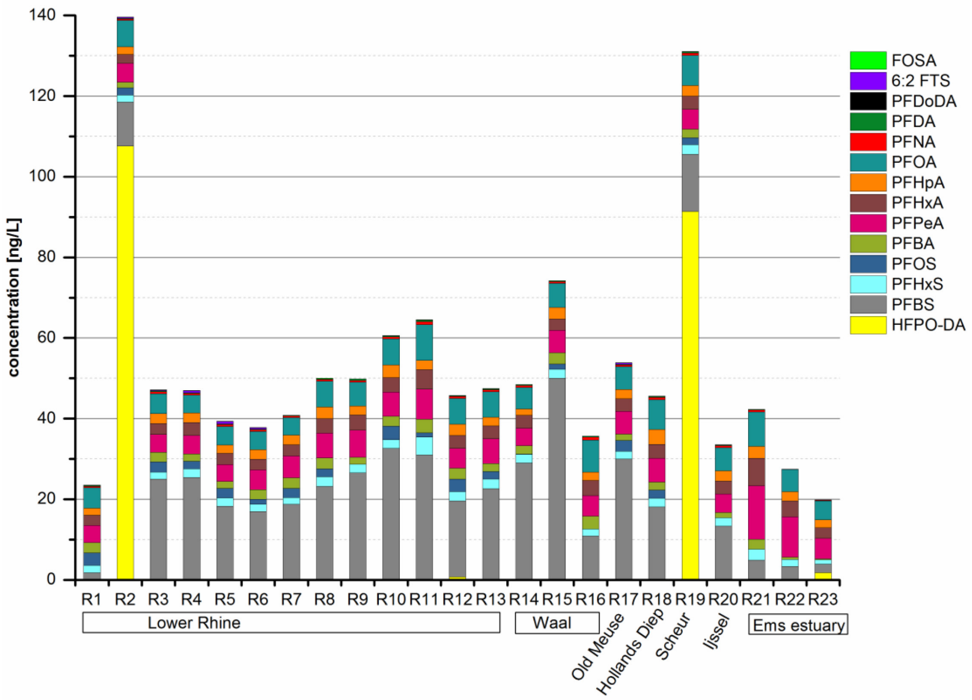

Figure A-2. PFASs concentrations [ng/L] in surface water along the Lower Rhine and its branch streams including the Ems estuary in August 2013.

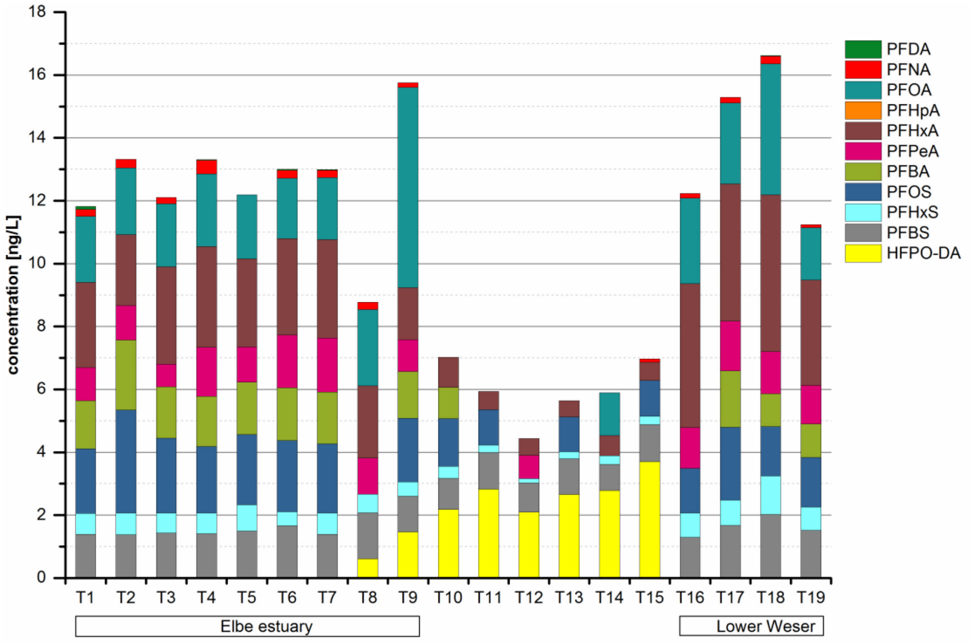

Figure A-3. PFASs concentrations [ng/L] in surface water along the coastline of Germany including the estuaries of Elbe and Weser (March 2014).

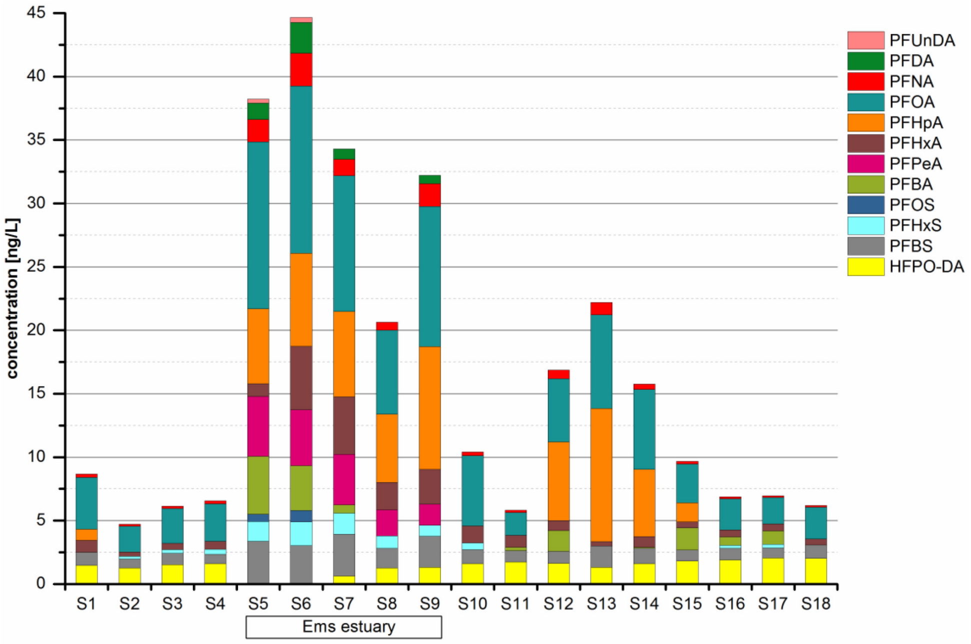

Figure A-4. PFASs concentrations [ng/L] in surface water along the coastline of the Netherlands and Germany including the estuary of Ems (August 2014).

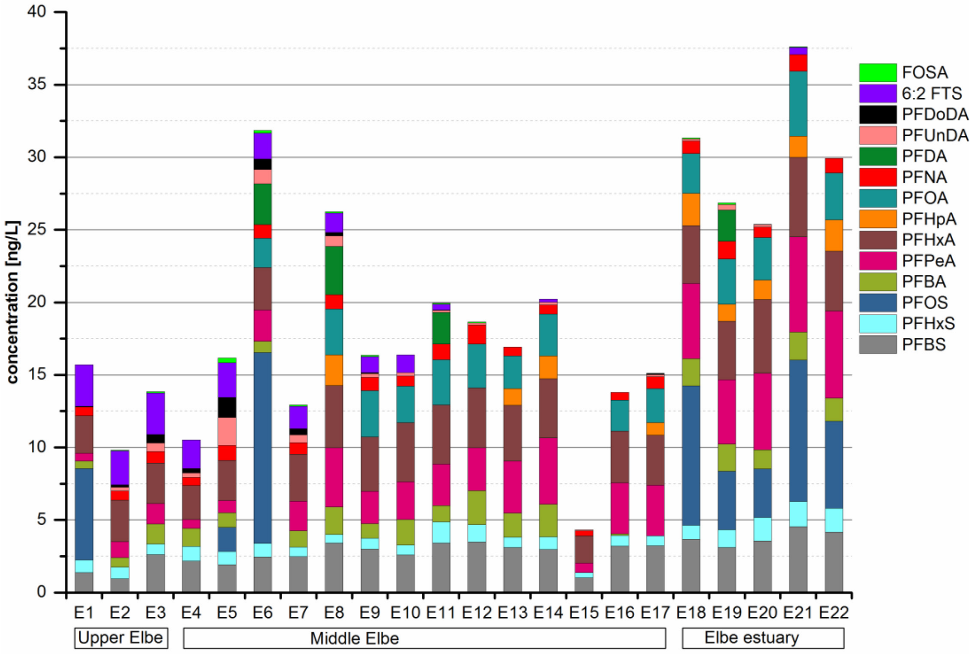

Figure A-5. PFASs concentrations [ng/L] along the River Elbe (September 2014).

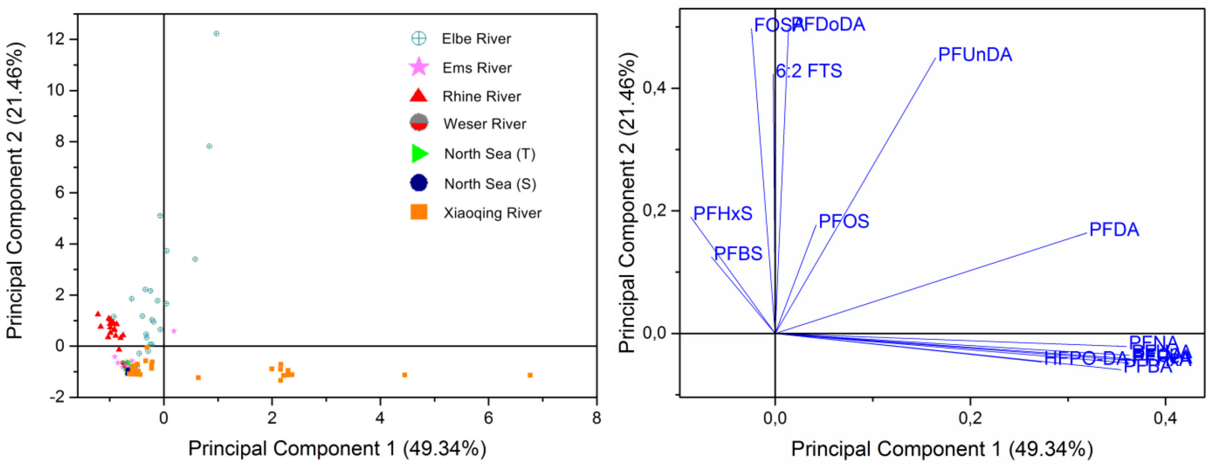

Figure A-6. Score plot and loading plot for Principal Components 1 and 2. The orange sampling points on the negative side of PC1 already belong to the area of Laizhou Bay. All orange sampling points on the positive side of PC1 belong to the Xiaoqing River behind the point source.

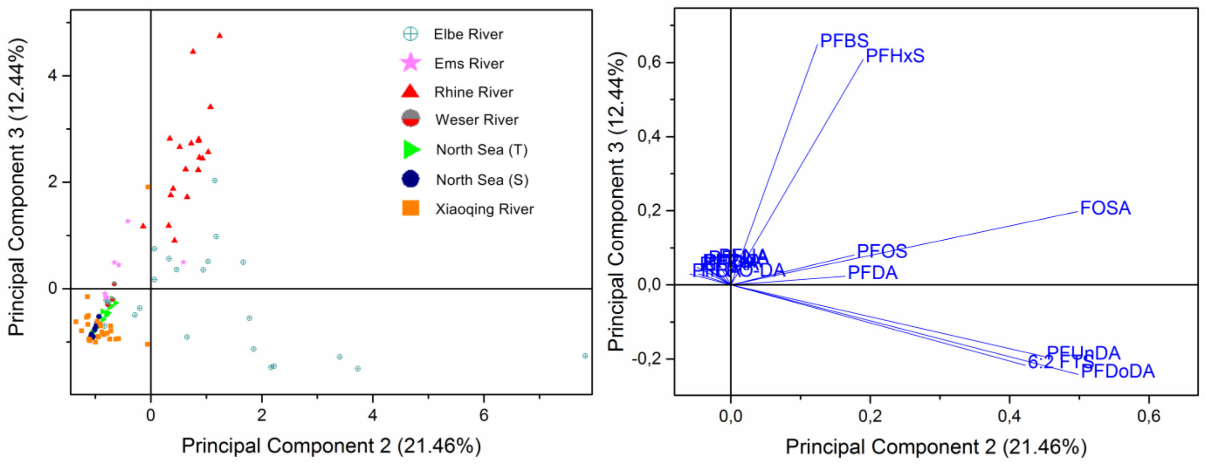

Figure A-7. Score plot and loading plot for Principal Components 2 and 3.

B Supplement of Add-on Studies

B.1 Study on the Long-Range Transport of the Fluorinated Alternative Substance HFPO-DA

Table B-1. Detailed information on sampling locations from cruise PS85-2 (ARK-XXVIII/2) with the *R/V* Polarstern.

No.	Lon °E	Lat °N	Date | Time	T [°C]	pH	Sal [psu]
PS1	3.730	59.382	08.06.2014 | 8:14	14.6	7.63	29.48
PS2	3.167	61.240	08.06.2014 | 19:30	14.0	7.60	32.50
PS3	2.198	63.560	09.06.2014 | 9:06	11.9	7.66	33.92
PS4	0.338	67.000	10.06.2014 | 8:45	8.7	7.65	35.13
PS5	0.945	68.437	10.06.2014 | 17:07	8.7	7.65	35.14

Table B-2. PFASs that were detected in this study and their method detection limits (MDLs) and method quantification limits (MQLs). For analytes present in the method blanks (blue), the MDLs and MQLs were calculated according to equations (6) and (7). For analytes absent in the method blanks (green), the MDLs and MQLs were calculated according to equations (8) and (9).

Analyte	PS-85 ARK-XXVIII/2	
	MDL [pg/L]	MQL [pg/L]
HFPO-DA	23	76
PFBS	22	75
PFHxS	5	15
PFOS	132	440
PFBA	38	127
PFPeA	324	1079
PFHxA	4	14
PFHpA	242	806
PFOA	134	447

B.2 Study on the Fluorinated Alternative Substance DONA

Table B-3. Concentration [pg/L] of DONA in 20 selected samples from the Rivers Rhine, Waal, and Xiaoqing; the Rhine-Meuse delta; and the German Bight.

No.	Sampling Location	DONA [pg/L]
R1	Lower Rhine | Leverkusen-Stammheim	n.d.
R2	Lower Rhine | Leverkusen-Wiesdorf	n.d.
R3	Lower Rhine | Monheim-Baumberg	79
R12	Lower Rhine | Tolkamer	n.d.
R15	Waal | Tiel	347
R17	Oude Maas | Zwijndrecht	n.d.
R18	Hollands Diep | Willemstad	n.d.
R19	New Waterway | Rozenburg	n.d.
T7	Elbe estuary | Bütteler Hafen	n.d.
T11	North Sea	n.d.
T12	North Sea	n.d.
T13	North Sea	n.d.
T14	North Sea	n.d.
S6	Ems estuary	n.d.
S8	Ems estuary	n.d.
S13	North Sea	n.d.
S18	North Sea	n.d.
X7	Xiaoqing River	n.d.
X9	Xiaoqing River	n.d.
X13	Xiaoqing River	n.d.

n.d. not detected

B.3 Study on Effluent Water from a Chemical Park Situated Along the Rhine River

Table B-4. Detailed information on sampling locations in effluent water of the ChemPark in Leverkusen and in the Lower Rhine (R/15-09).

No.	Name	Lon °E	Lat °N	Date | Time	T [°C]	pH	Sal [psu]
Y2	WWTP ChemPark	6.97328	51.02690	30.09.2015	N.A.	7.70	N.A.
X	WWTP ChemPark	6.97406	51.01429	30.09.2015	N.A.	8.27	N.A.
Bürrig	WWTP ChemPark	6.94294	51.04345	30.09.2015	N.A.	7.82	N.A.
R1/15-09	Lower Rhine | Bonn	7.12941	50.71926	30.09.2015 | 09:20	14.8	8.20	0.2
R2/15-09	Lower Rhine | Köln	7.01525	50.86269	30.09.2015 | 10:25	15.3	8.33	0.2
R3/15-09	Lower Rhine | Leverkusen-Stammheim	6.98648	50.98395	30.09.2015 | 11:35	16.0	8.24	0.2
R3-A/15-	Lower Rhine | Leverkusen-Stammheim	6.98648	50.98395	29.09.2015 | 16:35	17.8	8.29	0.2
R4/15-09	Lower Rhine | Leverkusen-Wiesdorf	6.97015	51.02985	30.09.2015 | 12:20	17.2	7.99	0.2
R4-A/15-	Lower Rhine | Leverkusen-Wiesdorf	6.97015	51.02985	29.09.2015 | 16:05	18.6	8.05	0.2
R5/15-09	Wupper | Bürrig	6.97728	51.05780	30.09.2015 | 12:50	14.2	8.15	0.1
R6/15-09	Lower Rhine | Hitdorf	6.91837	51.05648	30.09.2015 | 15:55	17.8	8.25	0.2
R6-A/15-	Lower Rhine | Hitdorf	6.91837	51.05648	29.09.2015 | 15:20	18.2	8.26	0.2
R7/15-09	Lower Rhine | Monheim-Baumberg	6.87856	51.11591	01.10.2015 | 08:05	14.4	8.16	0.2
R8/15-09	Lower Rhine | Düsseldorf-Zentrum; Neuss	6.73338	51.20507	01.10.2015 | 09:05	15.0	8.19	0.2
R9/15-09	Lower Rhine | Düsseldorf-Kaiserswerth	6.72963	51.29756	01.10.2015 | 10:15	15.1	8.22	0.2
R10/15-09	Lower Rhine | Duisburg-Rheinhausen	6.73310	51.41761	01.10.2015 | 11:10	16.0	8.17	0.2
R11/15-09	Lower Rhine | Rheinberg-Walsum	6.70003	51.52572	01.10.2015 | 11:55	16.3	8.22	0.2
R12/15-09	Lower Rhine | Xanten	6.48127	51.66483	01.10.2015 | 12:50	16.9	8.16	0.3
R13/15-09	Lower Rhine | Rees	6.39024	51.75729	01.10.2015 | 14:25	17.2	8.29	0.3
R14/15-09	Lower Rhine | Emmerich	6.23402	51.83054	01.10.2015 | 15:15	17.2	8.15	0.3
R15/15-09	Lower Rhine | Tolkamer	6.09832	51.85120	01.10.2015 | 15:45	17.3	8.16	0.3

WWTP	wastewater treatment plant
N.A.	not analyzed

Table B-5. Method detection limits (MDLs) and method quantification limits (MQLs) for compounds analyzed in the effluent samples from the ChemPark Leverkusen. The sample with the lowest concentration was chosen to extrapolate from the calculated S/N at this concentration to a S/N at 3 and 10, respectively. HFPO-DA and DONA were analyzed using the API 4000 (AB Sciex), whereas the legacy PFASs were analyzed via the API 3000 (AB Sciex).

Analyte	MDL [ng/L]	MQL [ng/L]
HFPO-DA	0.002	0.005
DONA	0.00001	0.00003
PFBS	0.07	0.23
PFHxS	0.03	0.11
PFOS	0.07	0.24
PFBA	0.30	1.01
PFPeA	0.30	0.99
PFHxA	0.19	0.63
PFHpA	0.17	0.57
PFOA	0.03	0.10
PFNA	0.07	0.23
PFDA	0.003	0.01

B.4 Study on PFASs along the German coast of the Baltic Sea

Table B-6. Detailed information on sampling locations in the Baltic Sea and the River Schlei (SB15).

No.	Name	Lon °E	Lat °N	Date | Time	T [°C]	pH	Sal [psu]
SB1	Binz	13.61794	54.40355	15.03.2016 | 11:00	4.7	8.69	8.0
SB2	Stralsund	13.09527	54.31843	15.03.2016 | 09:45	4.3	8.48	7.6
SB3	Prerow	12.57057	54.45522	15.03.2016 | 12:15	6.7	8.10	9.2
SB4	Wustrow	12.38314	54.35272	15.03.2016 | 13:30	7.1	8.23	10.1
SB5	Warnemünde	12.09059	54.18055	15.03.2016 | 14:50	6.1	8.21	10.2
SB6	Kühlungsborn	11.76279	54.15592	15.03.2016 | 16:30	5.9	8.33	9.4
SB7	Hohen Wieschendorf	11.34778	53.94818	15.03.2016 | 18:00	6.2	8.45	13.0
SB8	Timmendorfer Strand	10.78360	54.00137	16.03.2016 | 09:05	4.7	8.49	11.5
SB9	Grömitz	10.96468	54.14124	16.03.2016 | 10:00	5.1	8.29	10.8
SB10	Großenbrode	11.09159	54.35593	16.03.2016 | 11:30	5.9	8.29	9.0
SB11	Hohwacht	10.66704	54.32498	16.03.2016 | 12:10	6.3	8.33	14.7
SB12	Schönberg	10.41542	54.41575	16.03.2016 | 12:55	6.4	8.28	18.3
SB13	Strande	10.17164	54.42723	16.03.2016 | 14:00	8.1	8.28	18.2
SB14	Eckernförde	9.84339	54.46199	16.03.2016 | 15:10	8.8	8.16	16.1
SB15	Kappeln	9.93451	54.65958	16.03.2016 | 15:55	7.0	8.52	10.2
SB16	Langballigholz	9.65426	54.82290	16.03.2016 | 16:40	6.2	8.34	13.9

Table B-7. Method detection limits (MDLs) and method quantification limits (MQLs) for compounds analyzed in the Baltic Sea. For analytes present in the method blanks (blue), the MDLs and the MQLs were calculated with the blank standard deviations multiplied by 3.365 (variable from Student's t table at 98% confidence, numbers of procedural blank samples = 6) and 10, respectively. For analytes absent in the method blanks (green), the sample with the lowest concentration was chosen to extrapolate from the calculated S/N at this concentration to a S/N at 3 and 10, respectively.

Analyte	MDL [ng/L]	MQL [ng/L]
HFPO-DA	0.012	0.041
DONA	0.00001	0.00003
PFBS	0.041	0.136
PFHxS	0.012	0.037
PFOS	0.00004	0.0002
PFBA	*	*
PFPeA	1.256	3.732
PFHxA	0.017	0.051
PFHpA	0.025	0.082
PFOA	0.033	0.097
PFNA	0.003	0.010
PFDA	0.008	0.023
PFUnDA	0.000003	0.00001
PFDoDA	0.00004	0.0001

* Not calculated because of poor chromatographic separation

C Supplement of Paper 2

C.1 Introduction

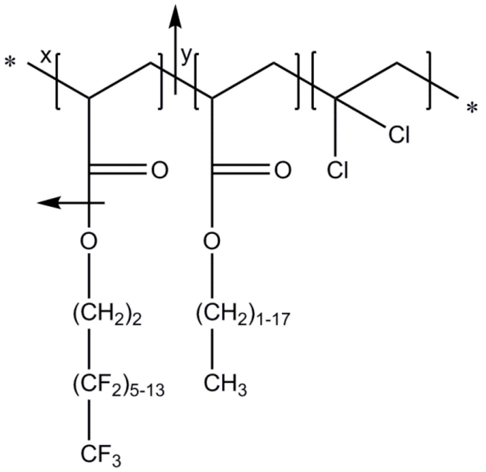

Figure C-1. Simplified structure of a fluoroacrylate polymer product, including potential polymer degradation sites (tagged with an arrow), adapted from Russell et al.[29]

C.2 Materials and Methods

Table C-1. Particle associated fraction [%] and amount of suspended particulate matter (SPM) [mg] in effluent water and Yangtze River surface water.

Sample Name	m_{SPM} [mg]	Particle associated fraction [%]
EW1	25.8	5.4
EW2	26.3	4.8
EW3	26.1	5.8
Y1	64.2	11.5
Y2	68.9	12.3
Y3	61.6	13.1

Table C-2. Particle deposition fluxes *F* in mg/(m^2·d).

Sample Name	Manufacturing Step	*F* [mg/(m^2·d)]
GFF 75	Workshop 1 (A)	35
GFF 77	Workshop 1 (A)	31
GFF 71	Workshop 1 (B)	41
GFF 72	Workshop 1 (B)	42
GFF 81	Workshop 2	25
GFF 85	Workshop 2	29
GFF 76	Office (Workshop 2)	12
GFF 80	Office (Workshop 2)	12
GFF 73	Coating (C)	21
GFF 79	Coating (C)	21
GFF 70	Coating (D)	47

Sample Name	**Manufacturing Step**	***F*** **[mg/(m²·d)]**
GFF 74	Quality Inspection	29
GFF 78	Quality Inspection	27

Chemicals

The following solvents and reagents were used: Acetone and dichloromethane (Picograde®) were purchased from LGC Standards (Wesel, Germany). Methanol (LiChroSolv®) and ammonia solution 25% (Suprapur®) were purchased from Merck (Darmstadt, Germany). Ammonium acetate (LC-MS ultra) was purchased from Sigma Aldrich (Steinheim, Germany). Millipore water was supplied by a Milli-Q Integral 5 (Darmstadt, Germany). In China, purified water was supplied by a Pall Cascada LS system. Methanol and hexane were purchased from Kermel (Tianjin, China), whereas acetone was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). These solvents were distilled before usage.

Table C-3. Chemicals.

Acronym	**Chemical name**	**Formula**	**CAS-No.**	**Amount**	**Quantifier Ions (Qualifier Ions) [m/z]**	**Internal Standard**	**Supplier**
6:2 FTOH	2-(Perfluorohexyl)ethanol	$C_8H_5F_{13}O$	647-42-7	Solid	365 (327)	$[^{2}H_{2},{}^{13}C_{2}]$-8:2 FTOH	Lancaster Synthesis
8:2 FTOH	2-(Perfluorooctyl)ethanol	$C_{10}H_5F_{17}O$	678-39-7	Solid	465 (427)	$[^{2}H_{2},{}^{13}C_{2}]$-8:2 FTOH	Lancaster Synthesis
10:2 FTOH	2-(Perfluorodecyl)ethanol	$C_{12}H_5F_{21}O$	865-86-1	Solid	565 (527)	$[^{2}H_{2},{}^{13}C_{2}]$-10:2 FTOH	Lancaster Synthesis
12:2 FTOH	2-(Perfluorododecyl)ethanol	$C_{14}H_5F_{25}O$	39239-77-5	Solid	665 (627)	$[^{2}H_{2},{}^{13}C_{2}]$-8:2 FTOH	Fluorochem
6:2 FTAC	2-(Perfluorohexyl)ethyl acrylate	$C_{11}H_7F_{13}O_2$	17527-29-6	Solid	419 (447)	$[^{2}H_{2},{}^{13}C_{2}]$-8:2 FTOH	Sigma Aldrich
8:2 FTAC	2-(Perfluorooctyl)ethyl acrylate	$C_{13}H_7F_{17}O_2$	27905-45-9	Solid	519 (547)	$[^{2}H_{2},{}^{13}C_{2}]$-8:2 FTOH	Fluorochem
MeFBSA	N-Methylperfluorobutanesulfonamide	$C_5H_4F_9NO_2S$	68298-12-4	Solid	314 (315)	d5-EtFOSA	3M
MeFOSA	N-Methylperfluorooctanesulfonamide	$C_9H_4F_{17}NO_2S$	31506-32-8	Solid	514 (515)	d3-MeFOSA	3M
EtFOSA	N-Ethylperfluorooctanesulfonamide	$C_{10}H_6F_{17}NO_2S$	4151-50-2	Solid	528 (529)	d5-EtFOSA	ABCR
MeFBSE	N-Methylperfluorobutanesulfonamidoethanol	$C_7H_8F_9NO_3S$	34454-97-2	Solid	340 (358)	d9-EtFOSE	3M
MeFOSE	N-Methylperfluorooctanesulfonamidoethanol	$C_{11}H_8F_{17}NO_3S$	24448-09-7	Solid	540 (558)	d7-MeFOSE	3M
EtFOSE	N-Ethylperfluorooctanesulfonamidoethanol	$C_{12}H_{10}F_{17}NOS$	1691-99-2	Solid	554	d9-EtFOSE	3M

Acronym	Chemical name	Formula	CAS-No.	Amount	Quantifier Ions (Qualifier Ions) [m/z]	Internal Standard	Supplier
					(572)		
PFBA	Perfluorobutanoic acid	$C_4HF_7O_2$	375-22-4	2 µg/mL (PFC-MXA)	212.9 (168.7)	[$^{13}C_4$]-PFBA	Wellington Laboratories
PFPeA	Perfluoropentanoic acid	$C_5HF_9O_2$	2706-90-3	2 µg/mL (PFC-MXA)	262.8 (218.9)	[$^{13}C_2$]-PFHxA	Wellington Laboratories
PFHxA	Perfluorohexanoic acid	$C_6HF_{11}O_2$	307-24-4	2 µg/mL (PFC-MXA)	312.9 (268.8)	[$^{13}C_2$]-PFHxA	Wellington Laboratories
PFHpA	Perfluoroheptanoic acid	$C_7HF_{13}O_2$	375-85-9	2 µg/mL (PFC-MXA)	363 (318.8)	[$^{13}C_4$]-PFOA	Wellington Laboratories
PFOA	Perfluorooctanoic acid	$C_8HF_{15}O_2$	335-67-1	2 µg/mL (PFC-MXA)	413 (369, 219, 169)	[$^{13}C_4$]-PFOA	Wellington Laboratories
PFNA	Perfluorononanoic acid	$C_9HF_{17}O_2$	375-95-1	2 µg/mL (PFC-MXA)	462.9 (418.9)	[$^{13}C_5$]-PFNA	Wellington Laboratories
PFDA	Perfluorodecanoic acid	$C_{10}HF_{19}O_2$	335-76-2	2 µg/mL (PFC-MXA)	512.9 (469)	[$^{13}C_2$]-PFDA	Wellington Laboratories
PFUnDA	Perfluoroundecanoic acid	$C_{11}HF_{21}O_2$	2058-94-8	2 µg/mL (PFC-MXA)	562.8 (519)	[$^{13}C_2$]-PFUnDA	Wellington Laboratories
PFDoDA	Perfluorododecanoic acid	$C_{12}HF_{23}O_2$	307-55-1	2 µg/mL (PFC-MXA)	613 (568.9)	[$^{13}C_2$]-PFDoDA	Wellington Laboratories
PFTrDA	Perfluorotridecanoic acid	$C_{13}HF_{25}O_2$	72629-94-8	2 µg/mL (PFC-MXA)	663.1 (618.9)	[$^{13}C_2$]-PFDoDA	Wellington Laboratories
PFTeDA	Perfluorotetradecanoic acid	$C_{14}HF_{27}O_2$	376-06-7	2 µg/mL (PFC-MXA)	713 (669)	[$^{13}C_2$]-PFDoDA	Wellington Laboratories
PFBS	Perfluorobutane sulfonate	$C_4F_9O_3SNa$	375-73-5	2 µg/mL±5% (PFS-MXA)	298.9 (99, 79.8)	[$^{18}O_2$]-PFHxS	Wellington Laboratories
PFHxS	Perfluorohexane sulfonate	$C_6F_{13}SO_3Na$	355-46-4	2 µg/mL±5% (PFS-MXA)	398.9 (98.8, 79.8)	[$^{18}O_2$]-PFHxS	Wellington Laboratories
PFHpS	Perfluoroheptane sulfonate	$C_7F_{15}SO_3Na$	375-92-8	2 µg/mL±5% (PFS-MXA)	449 (99)	[$^{13}C_4$]-PFOS	Wellington Laboratories
PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_3Na$	1763-23-1	2 µg/mL±5% (PFS-MXA)	499 (98.8, 79.6)	[$^{13}C_4$]-PFOS	Wellington Laboratories
PFDS	Perfluorodecane sulfonate	$C_{10}F_{21}SO_3Na$	335-77-3	2 µg/mL±5% (PFS-MXA)	599 (99)	[$^{13}C_4$]-PFOS	Wellington Laboratories
6:2 FTUCA	2H-Perfluoro-2-octenoic acid	$C_8H_2F_{12}O_2$	70887-88-6	50±2.5 µg/mL	356.9	[$^{13}C_2$]-6:2	Wellington

Acronym	Chemical name	Formula	CAS-No.	Amount	Quantifier Ions (Qualifier Ions) [m/z]	Internal Standard	Supplier
					(293)	FTUCA	Laboratories
8:2 FTUCA	2H-Perfluoro-2-decenoic acid	$C_{10}H_2F_{16}O_2$	70887-84-2	50±2.5 µg/mL	456.8 (392.8)	[$^{13}C_2$]-8:2 FTUCA*	Wellington Laboratories
10:2 FTUCA	2H-Perfluoro-2-dodecenoic acid	$C_{12}H_2F_{20}O_2$	70887-94-4	50±2.5 µg/mL	556.9 (493.1)	[$^{13}C_2$]-10:2 FTUCA*	Wellington Laboratories
HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3,-heptafluoropropoxy)-propanoic acid	$C_6HF_{11}O_3$	13252-13-6	50±2.5 µg/mL	329 (285, 168.9)	[$^{13}C_3$]-HFPO-DA	Wellington Laboratories
[$^2H_2$,$^{13}C_2$]-6:2 FTOH	2-Perfluorohexyl-[1,1-$^2H_2$]-[1,2-$^{13}C_2$]-ethanol	$^{13}C_2C_6{}^2H_2H_3F_{13}O$	N.A.	50±2.5 µg/mL	369.1 (331)	-	Wellington Laboratories
[$^2H_2$,$^{13}C_2$]-8:2 FTOH	2-Perfluorooctyl-[1,1-$^2H_2$]-[1,2-$^{13}C_2$]-ethanol	$^{13}C_2C_8{}^2H_2H_3F_{17}O$	N.A.	50±2.5 µg/mL	469 (431)	-	Wellington Laboratories
[$^2H_2$,$^{13}C_2$]-10:2 FTOH	2-Perfluorodecyl-[1,1-$^2H_2$]-[1,2-$^{13}C_2$]-ethanol	$^{13}C_2C_{10}{}^2H_2H_3F_{21}O$	N.A.	50±2.5 µg/mL	569 (531)	-	Wellington Laboratories
d3-MeFOSA	N-methyl-d3-perfluorooctanesulfonamide	$C_9D_3HF_{17}NO_2S$	N.A.	50±2.5 µg/mL	517	-	Wellington Laboratories
d5-EtFOSA	N-ethyl-d5-perfluorooctanesulfonamide	$C_{10}D_5HF_{17}NO_2S$	N.A.	50±2.5 µg/mL	533.1	-	Wellington Laboratories
d7-MeFOSE	2-(N-methyl-d3-perfluoro-1-octane-sulfonamido)-ethan-d4-ol	$C_{11}D_7HF_{17}NO_3S$	N.A.	50±2.5 µg/mL	547.1 (565.1)	-	Wellington Laboratories
d9-EtFOSE	2-(N-ethyl-d5-perfluoro-1-octane-sulfonamido)-ethan-d4-ol	$C_{12}D_9HF_{17}NOS$	N.A.	50±2.5 µg/mL	563.1 (581.1)	-	Wellington Laboratories
[$^{13}C_4$]-PFBA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	$^{13}C_4HF_7O_2$	N.A.	2 µg/mL (MPFAC-MXA)	216.8 (171.8)	-	Wellington Laboratories
[$^{13}C_2$]-PFOA	Perfluoro-n-(1,2-$^{13}C_2$)-octanoic acid	$^{13}C_2{}^{12}C_6HF_{15}O_2$	N.A.	50±2.5 µg/mL	415 (369.9)	-	Wellington Laboratories
[$^{13}C_4$]-PFOA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	$^{13}C_4{}^{12}C_4HF_{15}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	417 (371.8)	-	Wellington Laboratories
[$^{13}C_8$]-PFOA	Perfluoro-n[1,2,3,4,5,6,7,8-$^{13}C_8$]octanoic acid	$^{13}C_8HF_{15}O_2$	N.A.	50±2.5 µg/mL	421 (375.9)	-	Wellington Laboratories
[$^{13}C_2$]-PFHxA	Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	$^{13}C_2{}^{12}C_4HF_{11}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	314.9 (269.9)	-	Wellington Laboratories
[$^{13}C_5$]-PFNA	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	$^{13}C_5{}^{12}C_4HF_{17}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	467.9 (423)	-	Wellington Laboratories

Acronym	Chemical name	Formula	CAS-No.	Amount	Quantifier Ions (Qualifier Ions) [m/z]	Internal Standard	Supplier
[$^{13}C_2$]-PFDA	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	$^{13}C_2{}^{12}C_8HF_{19}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	514.9 (469.8)	-	Wellington Laboratories
[$^{13}C_2$]-PFUnDA	Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	$^{13}C_2{}^{12}C_9HF_{21}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	565 (519.8)	-	Wellington Laboratories
[$^{13}C_2$]-PFDoDA	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	$^{13}C_2{}^{12}C_{10}HF_{23}O_2$	N.A.	2 µg/mL (MPFAC-MXA)	614.9 (569.9)	-	Wellington Laboratories
[$^{18}O_2$]-PFHxS	Perfluoro-1-hexane[$^{18}O_2$]sulfonate	$C_6HF_{13}S^{18}O_2{}^{16}O$	N.A.	2 µg/mL (MPFAC-MXA)	403 (83.9)	-	Wellington Laboratories
[$^{13}C_4$]-PFOS	Perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	$^{13}C_4{}^{12}C_4HF_{17}SO_3$	N.A.	2 µg/mL (MPFAC-MXA)	503 (79.5)	-	Wellington Laboratories
[$^{13}C_2$]-6:2 FTUCA	2H-Perfluoro-[1,2-$^{13}C_2$]-2-octenoic acid	$^{13}C_2{}^{12}C_6H_2F_{12}O_2$	N.A.	50±2.5 µg/mL	259.9 (294)	-	Wellington Laboratories
[$^{13}C_2$]-8:2 FTUCA	2H-Perfluoro-[1,2-$^{13}C_2$]-2-decenoic acid	$^{13}C_2{}^{12}C_8H_2F_{16}O_2$	N.A.	50±2.5 µg/mL	458.9 (394.2)	-	Wellington Laboratories
[$^{13}C_2$]-10:2 FTUCA	2H-Perfluoro-[1,2-$^{13}C_2$]-2-dodecenoic acid	$^{13}C_2{}^{12}C_{10}H_2F_{20}O_2$	N.A.	50±2.5 µg/mL	559 (494)	-	Wellington Laboratories
[$^{13}C_3$]-HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3,-heptafluoropropoxy)-[$^{13}C_3$]-propanoic acid	$^{13}C_3{}^{12}C_3HF_{11}O_3$	N.A.	50±2.5 µg/mL	332 (287)	-	Wellington Laboratories

* For the extraction of the dissolved and particulate phase of the water samples, [$^{13}C_2$]-8:2 and [$^{13}C_2$]-10:2 FTUCA were not available. For these samples, [$^{13}C_2$]-6:2 FTUCA was used to correct 6:2 FTUCA, 8:2 FTUCA, and 10:2 FTUCA.

Quality Assurance and Quality Control

Table C-4. Recoveries of the mass-labeled internal standards spiked into the environmental samples. Recoveries were determined by comparing the MS response of the internal standard (e.g. $[^{13}C_2]$-PFHxA) to the MS response of the injection standard ($[^{13}C_2]$-PFOA):
Area ($[^{13}C_2]$-PFHxA sample)/Area ($[^{13}C_2]$-PFOA sample)=Area ($[^{13}C_2]$-PFHxA cal)/Area ($[^{13}C_2]$-PFOA cal). Calibration solutions were non-matrix standard solutions in methanol. With this approach, we assume that the sample matrix in the ion source interferes with the internal standards and the injection standard in the same way. However, sample matrix will influence $[^{13}C_2]$-PFOA in a different way than e.g. $[^{13}C_2]$-PFHxA, resulting perhaps in an apparent lower or higher recovery rate.

Internal standard	Dissolved Phase Water Mean ± SD [%]	Particulate Phase Water Mean ± SD [%]	Air Mean ± SD [%]	Dust/Airbone Particles Mean ± SD [%]	Native standard	Extraction efficiency (using DCM[202,203] or MeOH$^{\mu}$) Mean ± SD [%]
$[^{2}H_2,^{13}C_2]$-8:2 FTOH	N.A.	N.A.	106.6 ± 70.9	56.8 ± 19.5	6:2 FTOH	See [202,203]
$[^{2}H_2,^{13}C_2]$-10:2 FTOH	N.A.	N.A.	143.0 ± 75.9	89.9 ± 33.7	8:2 FTOH	See [202,203]
d3-MeFOSA	N.A.	N.A.	66.1 ± 34.4	58.6 ± 45.7	10:2 FTOH	See [202,203]
d5-EtFOSA	N.A.	N.A.	90.0 ± 29.1	108.9 ± 32.3	12:2 FTOH	See [202,203]
d7-MeFOSE	N.A.	N.A.	160.7 ± 51.3	174.4 ± 48.0	6:2 FTAC	See [202,203]
d9-EtFOSE	N.A.	N.A.	172.0 ± 60.1	195.3 ± 60.1	8:2 FTAC	See [202,203]
$[^{18}O_2]$-PFHxS	59.5 ± 29.9	56.9 ± 19.0	65.1 ± 27.3	70.7 ± 18.9	MeFSA	See [202,203]
$[^{13}C_4]$-PFOS	69.2 ± 36.0	61.0 ± 20.0	35.3 ± 9.9	55.0 ± 19.1	MeFOSA	See [202,203]
$[^{13}C_4]$-PFBA	79.4 ± 40.6	62.7 ± 27.9	109.9 ± 50.2	83.7 ± 55.6	EtFOSA	See [202,203]
$[^{13}C_2]$-PFHxA	40.0 ± 19.2	65.3 ± 29.3	41.0 ± 19.6	59.4 ± 16.0	MeFBSE	See [202,203]
$[^{13}C_4]$-PFOA	33.2 ± 15.3	51.2 ± 18.5	43.8 ± 8.6	62.1 ± 15.9	MeFOSE	See [202,203]
$[^{13}C_5]$-PFNA	68.7 ± 37.3	67.8 ± 25.3	35.0 ± 8.5	54.5 ± 17.0	EtFOSE	See [202,203]
$[^{13}C_2]$-PFDA	71.6 ± 35.9	64.7 ± 21.6	19.8 ± 4.4	38.4 ± 13.9	PFBS	78.1 ± 10.1$^{\mu}$
$[^{13}C_2]$-PFUnDA	79.3 ± 42.7	68.5 ± 22.6	22.6 ± 5.6	45.1 ± 17.4	PFHxS	67.1 ± 7.5$^{\mu}$
$[^{13}C_2]$-PFDoDA	78.1 ± 40.7	63.4 ± 21.2	21.8 ± 6.7	45.5 ± 19.4	PFHpS	71.3 ± 6.0$^{\mu}$
$[^{13}C_2]$-6:2 FTUCA	35.3 ± 12.6	79.4 ± 35.8	12.7 ± 8.2	6.3 ± 8.7	PFOS	41.2 ± 3.4$^{\mu}$
$[^{13}C_2]$-8:2 FTUCA	-*	-*	23.7 ± 11.0	7.9 ± 12.2	PFDS	70.5 ± 10.0$^{\mu}$
$[^{13}C_2]$-10:2 FTUCA	-*	-*	11.5 ± 5.2	5.8 ± 8.4	PFBA	92.1 ± 14.6$^{\mu}$
					PFPeA	61.1 ± 7.9$^{\mu}$
					PFHxA	85.8 ± 10.3$^{\mu}$
					PFHpA	66.1 ± 6.6$^{\mu}$
					PFOA	72.5 ± 5.9$^{\mu}$
					PFNA	82.6 ± 7.4$^{\mu}$
					PFDA	73.4 ± 7.5$^{\mu}$
					PFUnDA	75.0 ± 10.5$^{\mu}$

PFDoDA	71.0 ± 18.2 $^{\mu}$
HFPO-DA	42.9 ± 4.5 $^{\mu}$
6:2 FTUCA	10.0 ± 5.3 $^{\mu}$
8:2 FTUCA	10.1 ± 5.6 $^{\mu}$
10:2 FTUCA	11.2 ± 7.1 $^{\mu}$

N.A. not analyzed

* For the extraction of the dissolved and particulate phase of the water samples, [$^{13}C_2$]-8:2 and [$^{13}C_2$]-10:2 FTUCA were not available. For these samples, [$^{13}C_2$]-6:2 FTUCA was used to correct 6:2 FTUCA, 8:2 FTUCA, and 10:2 FTUCA

$^{\mu}$Determined via matrix-spiked experiments

Table C-5. PFASs, that have been detected in this study, and their Method Detection Limits (MDL) and Method Quantification Limits (MQL) referred to the sample types. For analytes present in the method blanks (blue), the MDL and the MQL were calculated with the blank standard deviations multiplied by Student's t-value (at 98% confidence, depending on the numbers of procedural blank samples) and 10, respectively. Number of blank samples: 5 (water - dissolved phase); 6 (water – particulate phase); 3 (air); 6 (dust and airborne particles, ionic PFASs); 3 (airborne particles, neutral PFASs). For analytes absent in the method blanks (green), the sample with the lowest concentration was chosen to extrapolate from the calculated S/N at this concentration to a S/N at 3 and 10, respectively. For the MDL and MQL of PFASs in airborne particles and settled dust, the average mass of particles was used as the reference value.

	Dissolved phase		**Particulate Phase**		**Air**		**Dust and Airborne Particles**	
Analyte	**MDL [ng/L]**	**MQL [ng/L]**	**MDL [ng/L]**	**MQL [ng/L]**	**MDL [ng/(sample·d)]**	**MQL [ng/(sample·d)]**	**MDL [ng/g]**	**MQL [ng/g]**
6:2 FTOH	N.A.	N.A.	N.A.	N.A.	16.8	24.1	88.6	127
8:2 FTOH	N.A.	N.A.	N.A.	N.A.	1.03	1.48	493	708
10:2 FTOH	N.A.	N.A.	N.A.	N.A.	1.76	2.53	216	311
12:2 FTOH	N.A.	N.A.	N.A.	N.A.	0.14	0.19	63.2	90.7
6:2 FTAC	N.A.	N.A.	N.A.	N.A.	0.14	0.19	34.1	48.9
8:2 FTAC	N.A.	N.A.	N.A.	N.A.	0.23	0.33	37.2	53.5
MeFBSA	N.A.	N.A.	N.A.	N.A.	0.02	0.02	10.4	14.9
MeFOSA	N.A.	N.A.	N.A.	N.A.	0.02	0.03	11.7	16.8
EtFOSA	N.A.	N.A.	N.A.	N.A.	0.004	0.01	7.5	10.7
MeFBSE	N.A.	N.A.	N.A.	N.A.	0.007	0.01	15.4	22.1
MeFOSE	N.A.	N.A.	N.A.	N.A.	0.02	0.03	7.7	11.1
EtFOSE	N.A.	N.A.	N.A.	N.A.	0.009	0.01	7.7	11.1
PFBS	1.22	4.07	0.10	0.32*	N.A.	N.A.	N.A.	N.A.
PFHxS	0.14	0.45	0.10	0.32*	N.A.	N.A.	N.A.	N.A.
PFOS	0.96	2.55	0.10	0.32*	0.07	0.10	5.33	15.8
PFBA	0.44	1.16	0.10	0.32*	0.004	0.01	35.9	107

PFPeA	0.80	2.14	0.11	0.34	0.08	0.12	19.5	57.8
PFHxA	0.04	0.10	0.04	0.12	0.03	0.04	4.82	14.3
PFHpA	0.70	1.87	0.55	1.64	0.002	0.002	22.9	68.1
PFOA	0.31	0.82	0.22	0.65	0.02	0.03	7.30	21.7
PFNA	0.03	0.12	0.05	0.18	0.01	0.02	4.36	14.5
PFDA	0.02	0.06	0.17	0.49	0.03	0.04	4.79	14.2
PFUnDA	0.01	0.02	0.13	0.40	0.002	0.01	1.48	4.41
PFDoDA	0.02	0.05	0.07	0.20	0.01	0.03	0.85	2.83
PFTrDA	0.10	0.32*	0.02	0.06	0.001	0.004	0.68	2.26
PFTeDA	0.10	0.32*	0.02	0.06	0.004	0.01	0.62	2.07
6:2 FTUCA	0.35	1.18	0.06	0.20	0.09	0.30	4.09	13.6
8:2 FTUCA	4.37	14.6	0.27	0.91	0.03	0.11	1.72	5.74
10:2 FTUCA	0.10	0.32*	0.10	0.32*	0.04	0.15	14.3	47.8

N.A. not analyzed

*MQL = lowest calibration point (1000 ng/L) / enrichment factor (3125)

×estimated via matrix recovery experiments

C.3 Results and Discussion

Table C-6. Estimated air concentrations [µg/m^3]. Air concentrations of 8:2 FTOH and 10:2 FTOH [µg/m^3] were calculated as follows: $c_{Air} = \frac{c_{PUF}}{K_{PUF-A}}$ using PUF-air partition coefficients K_{PUF-A} of 1570[207] and 4484[207], respectively, and a Volume of the PUF disk V_{PUF} of 0.000207816 m^3.[207] Air concentrations of ionic PFASs [pg/m^3] were calculated as follows: $c_{Air} = \frac{M_{PUF}}{\Delta t \cdot R}$ using a sampling time Δt of 17 d and a sampling rate R of 4 m^3/d.[200,209-211]

Sample Name	Manufacturing Step	8:2 FTOH [µg/m^3]	10:2 FTOH [µg/m^3]	PFOS [pg/m^3]	PFBA [pg/m^3]	PFPeA [pg/m^3]	PFHxA [pg/m^3]	PFHpA [pg/m^3]	PFOA [pg/m^3]	PFNA [pg/m^3]	PFDA [pg/m^3]	PFUnDA [pg/m^3]	PFDoDA [pg/m^3]	PFTrDA [pg/m^3]	PFTeDA [pg/m^3]
PAS 1	Workshop 1: Scouring	31.8	8.3	<MDL	339	571	2133	587	6512	369	1607	131	36	5	15
PAS 2	Workshop 1: Drying	87.7	11.7	4	226	901	9018	434	8482	221	784	54	26	n.d.	12
PAS 3	Workshop 1: Heat Setting	91.3	9.5	3	241	213	2845	163	5188	156	523	61	21	n.d.	8
PAS 4	Outdoors	23.0	2.7	<MDL	173	117	169	50	405	44	99	24	7	n.d.	n.d.
PAS 5	Outdoors	9.7	2.6	<MDL	206	63	81	35	444	49	114	27	n.d	n.d.	n.d.
PAS 6	Workshop 2: Drying	55.4	18.2	<MDL	137	154	1274	264	6129	372	2025	91	16	n.d.	n.d.
PAS 7	Workshop 2: DWR resin tank	63.1	14.2	<MDL	129	200	3577	228	6100	320	1237	66	17	n.d.	n.d.
PAS 8	Workshop 2A: Coating	7.0	1.2	<MDL	35	<MDL	209	18	1255	29	141	5	10	n.d.	n.d.
PAS 9	Workshop 2A: Coating	5.1	1.6	<MDL	94	<MDL	121	41	785	53	207	14	n.d	n.d.	n.d.

Table C-7. Ionic PFAS concentrations [ng/L] in fresh water, effluent water from the textile factory's in-house wastewater treatment plant, and in the Yangtze River. Substances that showed no peak are reported as not detected (n.d.). Values in brackets are below the MQL.

Sample Name	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	6:2 FTUCA	8:2 FTUCA	10:2 FTUCA	ΣPFASs
FW1	15.5	2.59	(0.96)	11.9	(2.15)	1.77	(1.15)	14.0	0.32	0.10	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	50.5
FW2	11.8	2.14	<MDL	11.0	(1.25)	1.74	(1.03)	14.8	0.33	0.10	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	44.2
EW1	n.d.	n.d.	1.72	69.4	842.2	392.2	1666.9	1972.3	261.7	723.9	44.6	0.71	n.d.	n.d.	53.8	628.0	41.60	6698.9
EW2	n.d.	n.d.	0.45	67.2	866.2	412.2	1790.9	2076.3	279.7	911.9	47.0	0.65	n.d.	n.d.	58.2	742.0	52.0	7304.6
EW3	n.d.	n.d.	1.58	66.6	642.2	304.2	1458.9	1788.3	255.7	751.9	40.6	0.74	n.d.	n.d.	49.2	658.0	44.0	6061.8
Y1	4.51	1.18	n.d.	8.84	<MDL	8.44	17.3	56.7	2.72	3.06	2.70	0.16	n.d.	n.d.	n.d.	n.d.	n.d.	105.6
Y2	5.33	1.47	n.d.	8.08	(1.38)	6.36	16.8	60.7	2.96	3.82	3.20	0.20	n.d.	n.d.	n.d.	n.d.	n.d.	110.3
Y3	3.22	0.84	n.d.	7.60	<MDL	6.24	16.6	47.9	2.56	3.22	2.68	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	91.0
EW1, SPM	n.d.	n.d.	n.d.	n.d.	10.1	8.96	22.2	69.4	15.7	144.3	18.0	0.93	1.86	0.36	6.46	41.5	40.0	379.8
EW2, SPM	n.d.	n.d.	n.d.	n.d.	9.22	9.05	20.8	70.1	15.7	145.1	18.4	1.03	1.96	0.35	5.61	37.6	38.1	373.1
EW3, SPM	n.d.	n.d.	n.d.	n.d.	10.7	9.4	23.6	80.8	18.2	153.0	17.6	1.00	1.87	0.32	5.92	48.4	37.0	407.9
Y1, SPM	n.d.	n.d.	n.d.	n.d.	0.56	0.18	1.54	2.80	0.60	1.63	3.28	1.01	1.43	0.56	n.d.		n.d.	13.7
Y2, SPM	n.d.	n.d.	n.d.	n.d.	0.63	0.19	2.19	2.74	0.62	1.86	3.68	1.14	1.64	0.82	n.d.	n.d.	n.d.	15.5
Y3, SPM	n.d.	n.d.	n.d.	n.d.	0.61	0.16	2.30	2.83	0.49	1.35	2.90	0.96	1.52	0.67	n.d.	n.d.	n.d.	13.8

FW: Fresh/tap water

EW: Effluent water, concentrations calculated in fresh water were subtracted from concentrations in effluent water

Y: Yangtze River

SPM: Suspended Particulate Matter

Table C-8. Neutral PFAS concentrations [ng/(sample·day)] in air. Values less than a blank-defined MDL are reported as <MDL. Values in brackets are below the MQL.

Sample Name	Manufacturing Step	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTAC	8:2 FTAC	MeFBSA	MeFOSA	EtFOSA	MeFBSE	MeFOSE	EtFOSE	ΣPFASs (neutral)
PAS 1	Workshop 1: Scouring	<MDL	610.5	457.6	3.79	1.86	5.88	1.70	0.21	<MDL	0.03	0.03	<MDL	1081.6
PAS 2	Workshop 1: Drying	897.6	1683.5	641.1	2.94	16.9	9.08	4.02	1.96	<MDL	0.08	<MDL	<MDL	3257.1
PAS 3	Workshop 1: Heat Setting	235.2	1753.0	519.3	0.77	4.13	2.74	1.53	0.33	<MDL	0.02	<MDL	0.02	2517.0
PAS 4	Outdoors	132.8	441.9	149.5	1.33	0.64	0.47	0.36	0.06	(0.004)	0.01	<MDL	<MDL	727.1
PAS 5	Outdoors	38.6	185.7	143.2	0.90	0.65	0.85	0.43	0.09	<MDL	<MDL	<MDL	<MDL	370.5
PAS 6	Workshop 2: Drying	122.8	1063.1	996.8	5.50	8.30	37.1	5.19	1.77	<MDL	0.03	0.04	<MDL	2240.7
PAS 7	Workshop 2: DWR resin tank	525.7	1211.1	776.1	2.91	6.82	15.3	4.73	1.67	<MDL	0.02	0.06	(0.009)	2544.5
PAS 8	Workshop 3: Coating	<MDL	134.9	64.6	1.47	2.02	1.14	0.08	0.06	0.01	0.02	<MDL	0.06	244.7
PAS 9	Workshop 3: Coating	<MDL	97.0	87.9	0.79	0.70	1.14	0.17	0.04	<MDL	0.01	<MDL	0.01	187.8

Table C-9. Ionic PFAS concentrations [ng/(sample·day)] in air. Values less than a blank-defined MDL are reported as <MDL. Substances that showed no peak are reported as not detected (n.d.).

Sample Name	Manufacturing Step	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	6:2 FTUCA*	8:2 FTUCA*	10:2 FTUCA*	ΣPFASs (ionic)
PAS 1	Workshop 1: Scouring	<MDL	1.36	2.29	8.53	2.35	26.0	1.48	6.43	0.52	0.14	0.02	0.06	6.09	13.8	16.6	49.2
PAS 2	Workshop 1: Drying	0.01	0.90	3.60	36.1	1.74	33.9	0.88	3.14	0.22	0.10	n.d.	0.05	17.2	18.4	14.4	80.6
PAS 3	Workshop 1: Heat Setting	0.01	0.96	0.85	11.4	0.65	20.8	0.63	2.09	0.24	0.08	n.d.	0.03	8.00	16.9	11.2	37.7
PAS 4	Outdoors	<MDL	0.69	0.47	0.68	0.20	1.62	0.18	0.40	0.10	0.03	n.d.	n.d.	4.12	2.29	2.45	4.36
PAS 5	Outdoors	<MDL	0.82	0.25	0.32	0.14	1.78	0.19	0.46	0.11	n.d.	n.d.	n.d.	0.83	1.07	1.75	4.08
PAS 6	Workshop 2: Drying	<MDL	0.55	0.61	5.10	1.06	24.5	1.49	8.10	0.36	0.06	n.d.	n.d.	2.89	6.61	24.4	41.8
PAS 7	Workshop 2: DWR resin tank	<MDL	0.52	0.80	14.3	0.91	24.4	1.28	4.95	0.27	0.07	n.d.	n.d.	4.38	7.55	23.6	47.5
PAS 8	Workshop 3: Coating	<MDL	0.14	<MDL	0.84	0.07	5.02	0.11	0.57	0.02	0.04	n.d.	n.d.	0.87	1.48	1.70	6.81

Sample Name	Manufacturing Step	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	6:2 FTUCA*	8:2 FTUCA*	10:2 FTUCA*	ΣPFASs (ionic)
PAS 9	Workshop 3: Coating	<MDL	0.37	<MDL	0.48	0.16	3.14	0.21	0.83	0.06	n.d.	n.d.	n.d.	0.63	1.40	2.68	5.26

*The results for the Fluorotelomer unsaturated carboxylic acids 6:2 FTUCA, 8:2 FTUCA, and 10:2 FTUCA have to be considered as semiquantitative because the ^{13}C-labeled internal standards showed poor recoveries with a mean of 8.3% ± 9.0%, 12.9% ± 13.9%, and 7.6% ± 8.0%, respectively. The results are not used for the calculation of ΣPFASs.

Table C-10. Neutral PFAS concentrations [ng/g] in airborne particles (GFF). Values less than a blank-defined MDL are reported as <MDL. Values in brackets are below the MQL.

Sample Name	Manufacturing Step	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTAC	8:2 FTAC	MeFBSA	MeFOSA	EtFOSA	MeFBSE	MeFOSE	EtFOSE	ΣPFASs (neutral)
GFF 75	Workshop 1 (A)	11064.3	54642.8	96436.8	2582.6	726.3	1523.0	464.4	267.9	15.4	52.0	48.3	14.0	167837.8
GFF 77	Workshop 1 (A)	11831.1	59147.5	128612.9	3957.1	794.6	1999.6	691.9	423.7	14.3	71.3	58.3	(10.2)	207612.7
GFF 71	Workshop 1 (B)	19260.7	45958.1	66957.4	4870.9	4610.2	4466.8	198.5	388.9	<MDL	59.7	92.6	41.0	146904.6
GFF 72	Workshop 1 (B)	22483.8	85377.2	74221.1	2164.8	1951.6	1785.7	364.9	489.3	<MDL	74.1	48.4	27.7	188988.7
GFF 81	Workshop 2	5669.5	51663.4	109339.1	5712.4	1258.5	4327.3	217.5	1046.6	33.9	60.0	30.4	<MDL	179358.5
GFF 85	Workshop 2	6495.4	55679.5	98553.4	4975.0	1157.1	4142.0	234.6	912.8	16.8	60.4	38.3	12.9	172278.2
GFF 76	Office (Workshop 2)	11902.9	299560.0	751797.2	24263.6	683.1	4909.0	6317.3	7125.2	86.2	57.0	29.6	21.6	1106752.8
GFF 80	Office (Workshop 2)	17024.7	324318.8	686698.2	28333.1	757.5	4585.2	6488.7	10053.7	<MDL	468.4	52.4	35.3	1078815.9
GFF 73	Coating (C)	4281.5	31503.9	60938.3	4303.6	215.9	1415.0	1657.3	630.9	<MDL	69.3	17.9	210.2	105243.8
GFF 79	Coating (C)	3708.2	33935.1	58752.0	4926.6	214.6	1555.1	1770.4	790.0	<MDL	50.0	(10.5)	155.9	105868.4
GFF 70	Coating (D)	1693.0	9290.0	16556.2	866.7	161.2	1102.6	741.5	2680.3	<MDL	22.3	402.3	292.3	33808.4
GFF 74	Quality Inspection	9524.4	63124.6	93437.0	5241.9	859.6	3389.0	321.5	666.5	51.1	(21.2)	14.5	19.9	176671.2
GFF 78	Quality Inspection	10760.9	79450.8	123257.9	3856.5	502.0	1464.6	1360.7	2290.7	<MDL	22.6	12.9	20.1	222999.6

Table C-11. Ionic PFAS concentrations [ng/g] in airborne particles (GFF) and settled dust (S). Substances which showed no peak are reported as not detected (n.d.). Values in brackets are below the MQL.

Sample Name	Manufacturing Step	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	6:2 FTUCA*	8:2 FTUCA*	10:2 FTUCA*	ΣPFASs (ionic)
GFF 75	Workshop 1 (A)	104.1	3308.8	3227.8	3247.9	2887.6	10127.5	1647.5	6477.0	451.5	495.0	84.4	314.9	1350.5	5861.4	2348.5	32374
GFF 77	Workshop 1 (A)	106.8	1195.5	1238.1	1216.1	858.6	4948.3	679.3	2991.9	153.7	215.9	24.5	100.6	n.d.	n.d.	n.d.	13729
S6	Workshop 1 (A)	(10.6)	230.8	301.2	268.5	258.0	1111.7	384.1	497.8	189.4	246.0	58.0	293.3	n.d.	n.d.	n.d.	3849.4
GFF 71	Workshop 1 (B)	(15.0)	1553.5	1184.0	1869.9	1632.5	6445.4	1117.1	3931.2	334.4	401.3	53.5	215.7	963.2	n.d.	n.d.	18754
GFF 72	Workshop 1 (B)	70.8	1933.4	1902.0	3036.1	2081.9	9067.9	1566.1	5205.1	551.9	538.7	103.7	369.1	904.4	3956.8	1373.2	26427
S7	Workshop 1 (B)	(8.5)	143.2	243.5	196.9	369.0	1901.3	658.1	1057.6	461.3	726.8	163.8	645.3	n.d.	n.d.	n.d.	6575.4
GFF 81	Workshop 2	28.4	877.5	951.9	1266.0	1222.1	10218.3	1166.4	5477.0	261.3	225.6	17.3	113.3	n.d.	n.d.	n.d.	21825
GFF 85	Workshop 2	n.d.	845.6	984.8	1069.9	726.1	9598.0	1149.6	4925.5	256.7	229.0	18.9	165.4	1366.3	6878.7	5512.4	19970
S1	Workshop 2	(6.5)	(96.8)	169.9	78.7	(63.6)	587.3	219.8	407.3	106.4	118.4	27.1	153.5	21.9	133.6	123.1	2035.2
GFF 76	Office (Workshop 2)	391.4	2342.8	1535.1	4315.1	3478.1	155486.4	1488.4	53667.9	204.6	679.1	49.8	197.7	712.8	3186.0	1232.6	223836
GFF 80	Office (Workshop 2)	252.2	575.8	567.9	2452.7	1350.3	100714.6	783.6	27981.7	96.2	385.9	n.d.	81.6	n.d.	n.d.	n.d.	135243
S2	Office (Workshop 2)	n.d.	189.9	381.4	69.5	<MDL	683.0	173.1	669.0	143.7	299.7	54.3	282.1	n.d.	n.d.	75.5	2945.7
GFF 73	Coating (C)	202.0	2148.9	1198.8	1378.1	808.7	12829.0	788.1	9771.1	192.0	266.2	20.2	96.0	401.3	2741.7	854.3	29699
GFF 79	Coating (C)	54.0	1024.9	567.7	755.2	501.6	7660.7	431.4	4824.3	89.4	237.7	22.5	130.2	n.d.	n.d.	n.d.	16300
S4	Coating (C)	38.5	(42.9)	(51.5)	28.9	(34.1)	767.3	1011.1	831.3	674.0	353.7	137.0	358.5	n.d.	152.2	198.5	4329.0
GFF 70	Coating (D)	26.4	594.8	280.5	363.4	157.4	1644.8	238.5	1285.4	61.1	44.0	6.0	25.8	n.d.	n.d.	n.d.	4728
S3	Coating (D)	(6.6)	(69.9)	70.3	62.7	90.8	515.3	186.7	231.5	82.0	38.2	11.4	25.7	n.d.	n.d.	n.d.	1391.0
GFF 74	Quality Inspection	72.8	1924.5	914.1	1409.2	721.4	10917.2	702.0	9354.3	163.9	277.5	28.8	133.3	455.6	2365.1	838.6	26619
GFF 78	Quality Inspection	75.0	697.0	344.8	700.1	237.3	6272.2	322.4	4022.5	91.7	143.5	9.5	69.5	n.d.	n.d.	n.d.	12986
S5	Quality Inspection	n.d.	(104.8)	160.3	113.9	159.5	646.1	225.8	381.7	114.8	79.0	13.6	61.2	n.d.	n.d.	n.d.	2060.6

*The results for the Fluorotelomer unsaturated carboxylic acids 6:2 FTUCA, 8:2 FTUCA, and 10:2 FTUCA have to be considered as semiquantitative because the ^{13}C-labeled internal standards showed poor recoveries with means of 6.3 ± 8.7%, 7.9 ± 12.2%, and 5.8 ± 8.4%, respectively. The results are not used for the calculation of ΣPFASs.

Table C-12. Pearson correlations r and Spearman correlations r_{SP} (marked with *) among PFASs in airborne particles.

	PFOS	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA***	**PFNA**	**PFDA***	**PFUnDA**	**PFDoDA**	**PFTrDA**	**PFTeDA**	**6:2 FTOH**	**8:2 FTOH***	**10:2 FTOH***	**12:2 FTOH***	**6:2 FTAC**	**8:2 FTAC**	**MeFBSA**	**MeFOSA**	**EtFOSA**	**MeFBSE***	**MeFOSE***	**EtFOSE***
PFOS	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFBA	0.29	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFPeA	0.14	**0.88**	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFHxA	**0.66**	**0.68**	**0.69**	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFHpA	0.56	**0.73**	**0.77**	**0.97**	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFOA*	**0.61**	0.36	0.31	**0.66**	0.50	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFNA	0.29	**0.68**	**0.83**	**0.82**	**0.87**	0.53	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFDA*	**0.69**	0.41	0.34	**0.70**	0.51	**0.98**	0.53	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFUnDA	-0.14	**0.62**	**0.81**	**0.56**	**0.62**	0.29	**0.86**	0.28	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFDoDA	**0.59**	**0.68**	**0.67**	**0.97**	**0.94**	**0.61**	**0.83**	**0.64**	**0.61**	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFTrDA	0.12	**0.72**	**0.82**	**0.78**	**0.76**	0.29	**0.80**	0.35	**0.91**	**0.81**	1	-	-	-	-	-	-	-	-	-	-	-	-	-
PFTeDA	0.01	**0.69**	**0.82**	**0.69**	**0.72**	0.22	**0.85**	0.23	**0.94**	**0.76**	**0.97**	1	-	-	-	-	-	-	-	-	-	-	-	-
6:2 FTOH	0.12	0.22	0.35	**0.59**	0.50	0.16	0.50	0.20	**0.57**	**0.64**	**0.77**	0.61	1	-	-	-	-	-	-	-	-	-	-	-
8:2 FTOH*	0.57	0.01	0.23	0.51	0.43	0.40	0.27	0.46	0.15	0.43	0.41	0.20	**0.71**	1	-	-	-	-	-	-	-	-	-	-
10:2 FTOH*	**0.67**	-0.06	0.23	0.35	0.42	0.39	0.25	0.40	0.09	0.15	0.07	-0.01	0.49	**0.79**	1	-	-	-	-	-	-	-	-	-
12:2 FTOH*	0.34	-0.12	-0.10	0.29	0.23	**0.71**	0.15	**0.62**	-0.02	0.25	-0.01	0.01	0.09	0.38	0.52	1	-	-	-	-	-	-	-	-
6:2 FTAC	-0.31	0.07	0.16	0.18	0.24	0.08	0.38	0.02	0.51	0.30	0.41	0.44	**0.64**	0.31	0.23	0.21	1	-	-	-	-	-	-	-
8:2 FTAC	0.40	-0.11	-0.08	0.37	0.37	0.51	0.38	0.41	0.03	0.40	0.01	0.04	0.30	0.55	**0.62**	**0.81**	0.44	1	-	-	-	-	-	-
MeFBSA	**0.88**	-0.04	-0.14	0.52	0.39	0.27	0.05	0.35	-0.34	0.46	0.00	-0.17	0.18	0.25	0.21	0.15	-0.26	0.42	1	-	-	-	-	-
MeFOSA	**0.73**	-0.23	-0.25	0.40	0.27	0.27	-0.03	0.25	-0.38	0.31	-0.10	-0.26	0.20	0.30	0.35	0.46	-0.21	0.48	**0.94**	1	-	-	-	-
EtFOSA	0.77	0.23	-0.21	0.61	0.51	**0.94**	0.18	**0.83**	-0.37	0.66	0.06	-0.04	0.27	0.49	0.09	0.89	-0.34	0.67	**0.84**	**0.88**	1	-	-	-
MeFBSE*	0.35	-0.01	0.45	0.35	0.49	0.25	0.40	0.23	0.37	0.26	0.30	0.13	0.49	0.32	0.34	0.18	0.42	0.35	0.07	-0.09	-0.25	1	-	-
MeFOSE*	-0.23	-0.18	0.18	0.12	0.27	-0.35	0.09	-0.38	0.18	0.01	0.18	0.03	0.36	-0.08	-0.04	-0.30	0.31	0.12	-0.26	-0.15	-0.43	0.36	1	-
EtFOSE*	-0.35	-0.18	-0.41	-0.20	-0.25	-0.04	-0.30	-0.03	-0.34	-0.04	-0.21	-0.33	-0.27	-0.45	**-0.66**	-0.13	-0.48	-0.33	0.36	0.26	**0.90**	-0.08	0.09	1

Values in **bold**: statistically significant with $p < 0.05$

Table C-13. Pearson correlations r among PFASs in settled dust.

	PFOS	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFTrDA**	**PFTeDA**
PFOS	1	-	-	-	-	-	-	-	-	-	-	-
PFBA	-0.46	1	-	-	-	-	-	-	-	-	-	-
PFPeA	-0.51	**0.92**	1	-	-	-	-	-	-	-	-	-
PFHxA	-0.44	0.75	0.51	1	-	-	-	-	-	-	-	-
PFHpA	-0.42	0.73	0.80	**0.85**	1	-	-	-	-	-	-	-
PFOA	-0.14	0.37	0.33	0.67	**0.90**	1	-	-	-	-	-	-
PFNA	0.87	-0.33	-0.36	-0.04	0.03	0.44	1	-	-	-	-	-
PFDA	0.42	0.11	0.24	0.17	0.50	**0.77**	0.73	1	-	-	-	-
PFUnDA	0.83	-0.31	-0.29	-0.08	0.06	0.47	**0.99**	**0.80**	1	-	-	-
PFDoDA	0.17	0.23	0.31	0.36	0.69	**0.90**	0.61	**0.96**	0.68	1	-	-
PFTrDA	0.52	-0.02	0.03	0.18	0.43	**0.77**	**0.86**	**0.96**	**0.90**	**0.93**	1	-
PFTeDA	0.21	0.28	0.34	0.40	0.66	**0.89**	0.65	**0.96**	0.70	**0.99**	**0.93**	1

Values in **bold**: statistically significant with $p < 0.05$

Table C-14. Pearson correlations *r* and Spearman correlations r_{SP} (marked with *) among PFASs in air.

	PFOS*	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA*	PFTeDA	6:2 FTUCA	8:2 FTUCA	10:2 FTUCA	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTAC	8:2 FTAC	MeFBSA	MeFOSA	EtFOSA*	MeFBSE	MeFOSE	EtFOSE
PFOS*	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFBA	0.52	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFPeA	0.62	0.65	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFHxA	0.62	0.35	0.88	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFHpA	0.31	**0.72**	**0.85**	0.62	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFOA	0.41	0.48	**0.79**	**0.81**	**0.85**	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFNA	0.10	0.44	0.50	0.41	**0.82**	**0.84**	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFDA	0.10	0.33	0.38	0.27	**0.73**	**0.76**	**0.98**	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFUnDA	0.10	**0.71**	0.54	0.31	**0.88**	**0.76**	**0.92**	**0.88**	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFDoDA	0.52	**0.67**	**0.78**	0.61	**0.92**	**0.85**	**0.75**	0.65	**0.83**	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFTrDA*	-0.19	0.55	0.41	0.14	0.55	0.41	0.41	0.41	0.55	0.55	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PFTeDA	0.61	**0.81**	**0.87**	0.64	**0.85**	**0.68**	0.45	0.33	0.63	0.85	0.65	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6:2 FTUCA	**0.72**	0.51	**0.91**	**0.95**	0.63	**0.75**	0.33	0.19	0.32	0.65	0.27	**0.75**	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8:2 FTUCA	**0.72**	**0.68**	**0.82**	**0.81**	**0.76**	**0.86**	0.55	0.42	0.62	0.84	0.27	**0.86**	**0.87**	1	-	-	-	-	-	-	-	-	-	-	-	-	-
10:2 FTUCA	0.10	0.26	0.42	0.47	**0.67**	**0.85**	**0.96**	**0.93**	**0.79**	0.64	0.27	0.28	0.34	0.53	1	-	-	-	-	-	-	-	-	-	-	-	-
6:2 FTOH	0.63	0.15	**0.71**	**0.94**	0.40	0.67	0.30	0.16	0.12	0.39	-0.42	0.36	**0.84**	0.62	0.44	1	-	-	-	-	-	-	-	-	-	-	-
8:2 FTOH	**0.72**	0.38	0.60	**0.78**	0.49	**0.82**	0.53	0.42	0.45	0.61	0.00	0.48	**0.78**	**0.86**	0.65	**0.75**	1	-	-	-	-	-	-	-	-	-	-
10:2 FTOH	0.31	0.23	0.42	0.52	0.58	**0.84**	**0.88**	**0.86**	**0.70**	0.56	0.00	0.23	0.42	0.56	**0.96**	0.51	**0.75**	1	-	-	-	-	-	-	-	-	-
12:2 FTOH	-0.21	0.20	0.40	0.29	**0.68**	**0.69**	**0.88**	**0.94**	**0.75**	0.56	0.41	0.25	0.21	0.30	**0.84**	0.20	0.32	**0.81**	1	-	-	-	-	-	-	-	-
6:2 FTAC	0.52	0.12	**0.74**	**0.91**	0.52	**0.80**	0.47	0.41	0.27	0.47	-0.14	0.40	**0.82**	0.65	0.58	**0.89**	**0.75**	0.68	0.50	1	-	-	-	-	-	-	-
8:2 FTAC	0.21	-0.08	0.10	0.17	0.33	0.54	**0.74**	**0.84**	0.52	0.24	0.14	-0.11	0.05	0.14	**0.81**	0.19	0.38	0.87	**0.88**	0.48	1	-	-	-	-	-	-
MeFBSA	0.21	0.10	0.45	0.60	0.55	**0.82**	**0.82**	**0.80**	0.58	0.48	0.14	0.16	0.44	0.47	**0.93**	0.63	**0.69**	0.96	**0.80**	**0.77**	**0.85**	1	-	-	-	-	-
MeFOSA	0.52	0.00	0.52	**0.72**	0.47	**0.78**	**0.67**	0.64	0.39	0.39	0.00	0.15	0.55	0.46	**0.80**	**0.78**	**0.69**	0.87	**0.69**	**0.89**	**0.76**	**0.96**	1	-	-	-	-
EtFOSA*	-0.22	-0.58	-0.50	-0.25	-0.58	-0.25	-0.58	-0.41	-0.58	-0.25	-0.14	-0.28	-0.25	-0.25	-0.58	-0.42	-0.41	-0.58	-0.08	-0.08	-0.33	-0.58	-0.41	1	-	-	-
MeFBSE	0.42	0.27	**0.89**	**0.91**	**0.68**	**0.79**	0.43	0.36	0.33	0.64	0.35	0.66	**0.89**	**0.73**	0.44	**0.79**	0.64	0.50	0.46	**0.91**	0.28	0.57	**0.69**	-0.09	1	-	-
MeFOSE	-0.37	0.04	0.06	0.09	0.42	0.51	**0.82**	**0.80**	0.64	0.39	0.33	-0.05	-0.09	0.10	**0.85**	0.15	0.25	0.72	**0.71**	0.19	**0.69**	**0.74**	0.57	-0.28	0.03	1	-
EtFOSE	0.14	-0.61	-0.39	-0.24	-0.42	-0.29	-0.43	-0.37	-0.47	-0.15	-0.28	-0.26	-0.29	-0.23	-0.39	-0.26	-0.23	-0.40	-0.34	-0.22	-0.29	-0.40	-0.34	0.68	-0.15	-0.33	1

Values in **bold**: statistically significant with $p < 0.05$

Workers Exposure to PFASs

Dust ingestion is an important route of exposure, especially for children due to their intense hand-to-mouth contact. For adults, the ingestion of dust is a minor source of exposure compared with the inhalation of air. However, adults may also ingest dust particles that adhere to their hands during work. Thus, dust ingestion can become a significant exposure pathway in a high-exposure scenario.[249,252] The workplace exposure to PFASs via the ingestion of dust E_{Dust} (ng/(d·kg)) was estimated using[253]

$$E_{\mathrm{Dust}} = \frac{C_{\mathrm{Dust}} \cdot Q_{\mathrm{Dust}} \cdot f_{\mathrm{time\_in}}}{m_{\mathrm{bw}}} \cdot F_{\mathrm{uptake}} \tag{11}$$

where C_{dust} is the sum of ionic PFAS concentrations in settled dust or airborne particles (ng/g). Only large particles (>4 µm) were included, supposing that they are not able to reach the alveoli. Instead, they can be deposited onto the mucosa after inhalation and transported into the intestine.[254] According to Barton et al., 5.6% of PFOA was distributed in the larger particle-size fraction close to a fluoropolymer manufacturing site.[234] Because PFCAs seem to distribute similarly among the fractions,[255] we multiplied PFCA concentrations in airborne particles by a factor of 0.056. Q_{Dust} is the dust ingestion rate (g/d). Studies estimating adult dust ingestions are limited and various rates are given depending on the scenarios. For instance, the U.S. Environmental Protection Agency (U.S. EPA) recommends a dust ingestion rate of 0.03 g/d, whereas the Dutch National Institute for Public Health and the Environment (RIVM) assumes 0.05 g/d.[256,257] Authors of peer-reviewed literature estimated E_{Dust} using, for example, 0.004 g/d or 0.02 g/d for mean-intake scenarios and 0.055 g/d or 0.05 g/d for high-intake scenarios.[219,240] We included dust ingestion rates of 0.03 g/d and 0.05 g/d for the mean- and the high-intake scenario, respectively. f_{time_in} is the fraction of time spent at the workplace and was set to 0.280 (unitless), reflecting a mean 49-hour workweek and 2 weeks of vacation per year. Blue-collar workers and quality assurance inspectors normally work 12 hours per day, including lunch and dinner breaks totaling 1.5 hours per day, and 4 days in a row followed by 2 days off. m_{bw} is the body weight assuming an average Asian body weight of 57.7 kg.[258] F_{Uptake} is the absorption fraction of a compound (unitless). On the basis of rodent studies and the evidence of extensive enterohepatic circulation, high absorption has been generally assumed using uptake fractions varying from 0.66 to 1.[219,240,252,254,259,260] Uptake fractions were set to 0.8 and 0.91 for the mean- and the high-intake scenario, respectively.

The workplace exposure to PFASs through inhalation E_{Air} (ng/(d·kg)) was estimated using

$$E_{\mathrm{Air}} = \frac{C_{\mathrm{Air}} \cdot V_{\mathrm{Air}} \cdot f_{\mathrm{time\_in}}}{m_{\mathrm{bw}}} \cdot F_{\mathrm{uptake}} \tag{12}$$

where C_{Air} is the ΣPFASs concentration in air [ng/m^3]. Airborne particle concentrations are not included in the calculation leading to an underestimation of the inhalation exposure, because the fine particle fraction (<4 µm) is respirable and will be transmitted into the blood.[261] V_{Air} is the inhalation rate [m^3/d]. The U.S. EPA recommends inhalation rates (long-term exposure for the Age-Group 21–51) of 15.9 and 21.3 for a mean- and a high-intake scenario, respectively.[256] V_{Air} is strongly activity-dependent and the workers exposure might be underestimated when inhalation rates increase during physical work as observed for ski wax technicians.[262] The absorption fraction F_{uptake} of neutral PFASs was set to 0.38 and 1 for the mean- and high-intake scenario, respectively.[219,250,263] For consistency, 0.8 and 0.91 were used for ionic PFASs according to dust ingestion. Because of a lack of inhalation studies, estimates for F_{uptake} differ greatly among peer-reviewed literature, suggesting values ranging from 0.38 to 1 and 0.5 to 1 for neutral and ionic PFASs, respectively.[219,248,250,260,264] Himmelstein et al. observed a rapid clearance and metabolization of 8:2 FTOH to PFCAs in rats.[265] To assess the indirect exposure to PFCAs through biotransformation of 8:2 and 10:2 FTOH, E_{Air} was multiplied by biotransformation factors (0.005 and 0.017 for the mean- and the high-intake scenario, respectively).[248,249]

Table C-15. Estimation of workers exposure to ionic and neutral PFASs via dust ingestion and air inhalation [ng/d/kg].

	Dust Ingestion [ng/d/kg]				**Air Inhalation [ng/d/kg]**					
	Mean-intake		High-intake		Mean-intake			High-intake		
	Ionic	Ionic (airborne particles)	Ionic	Ionic (airborne particles)	Ionic	Ionic (Biotrans-formation of FTOHs)	Neutral	Ionic	Ionic (Biotrans-formation of FTOHs)	Neutral
5th percentile	0.16	0.03	0.31	0.06	0.06	0.98	195	0.10	11.7	688
Median	0.34	0.14	0.65	0.27	0.58	5.89	1177	0.89	70.6	4151
95th percentile	0.48	0.19	0.90	0.37	0.73	11.33	2265	1.12	136	7986

Dust ingestion rates Q_{Dust} of 0.03 g/d[256] and 0.05 g/d[257] were assumed in the mean-intake and in the high-intake scenario, respectively.

Absorption fractions F_{uptake} of 0.8[219,249,254] and 0.91[249,254,260] for ionic PFASs were assumed in the mean-intake and in the high-intake scenario, respectively.

Absorption fractions F_{uptake} of 0.38 and 1 for neutral PFASs were assumed in the mean-intake and in the high-intake scenario, respectively.[219,250,263]

Inhalation rates V_{Air} of 15.9 m^3/d and 21.3 m^3/d were assumed in the mean-intake and in the high-intake scenario, respectively.[256]

Biotransformation factors of 0.005 and 0.017 were assumed in the mean-intake and in the high-intake scenario, respectively.[248,249]

f_{time_in} = 0.280

m_{bw} = 57.7 kg[258]

D Appendix of Materials and Methods

D.1 Recoveries

The Table D-1 to Table D-5 list the recovery rates of the internal standards for all samples extracted. Calculations were done according to equation 3.

Table D-1. Recovery rates [%] of [^{13}C]-labeled, deuterated, and chlorinated internal standards for water samples of paper 1.

Sample	[^{18}O$_2$]-PFHxS	[^{13}C$_4$]-PFOS	[^{13}C$_4$]-PFBA	[^{13}C$_2$]-PFHxA	[^{13}C$_4$]-PFOA	[^{13}C$_5$]-PFNA	[^{13}C$_2$]-PFDA	[^{13}C$_2$]-PFUnDA	[^{13}C$_2$]-PFDoDA	[^{13}C$_3$]-HFPO-DA	[^{13}C$_2$]-6:2PAP	[^{13}C$_2$]-8:2PAP	[^{13}C$_4$]-6:2diPAP	[^{13}C$_4$]-8:2diPAP	d4-10:2diPAP	Cl-PFHxPA	Cl-PFOPA
R1	69.9	96.5	44.2	49.3	54.7	84.3	111.4	126.7	147.8	38.0	N.A.	N.A.	135.8	82.7	96.9	N.A.	N.A.
R2	64.9	111.7	82.9	49.2	57.9	88.4	109.4	112.6	131.6	36.2	N.A.	N.A.	90.5	59.7	70.3	N.A.	N.A.
R3	111.8	145.2	59.8	72.0	72.1	128.5	168.4	196.6	234.1	57.7	N.A.	N.A.	178.3	123.4	173.6	N.A.	N.A.
R4	85.8	140.2	62.4	68.4	74.7	121.6	160.3	191.1	225.6	58.8	N.A.	N.A.	169.9	116.8	168.8	N.A.	N.A.
R5	86.9	129.0	52.5	66.8	68.1	114.5	138.8	170.7	200.5	49.6	N.A.	N.A.	136.5	97.5	155.9	N.A.	N.A.
R6	105.4	155.5	56.4	72.8	77.5	125.1	154.3	180.6	220.3	57.4	N.A.	N.A.	149.4	102.7	150.8	N.A.	N.A.
R7	61.8	106.3	45.6	58.9	62.6	96.3	114.2	132.5	151.0	49.8	N.A.	N.A.	98.3	75.8	116.3	N.A.	N.A.
R8	78.9	131.7	49.1	67.1	67.4	114.8	131.9	162.4	188.4	55.5	N.A.	N.A.	134.4	101.5	163.6	N.A.	N.A.
R9	67.8	118.0	52.3	65.3	69.0	107.2	120.7	145.2	171.0	62.4	N.A.	N.A.	127.2	82.3	128.3	N.A.	N.A.
R10	70.6	112.4	49.7	62.7	65.2	105.4	117.9	151.7	173.9	54.6	N.A.	N.A.	110.7	83.2	150.0	N.A.	N.A.
R11	58.9	94.5	44.4	51.4	56.2	81.8	89.6	116.9	133.0	43.1	N.A.	N.A.	96.2	54.6	51.1	N.A.	N.A.
R12	56.3	87.1	45.5	54.3	56.3	87.3	97.4	115.6	133.9	49.1	N.A.	N.A.	81.2	56.3	93.2	N.A.	N.A.
R13	56.3	100.7	44.6	49.7	54.1	80.1	91.4	113.0	132.5	49.0	N.A.	N.A.	90.7	63.0	109.1	N.A.	N.A.
R14	52.9	82.9	39.0	47.6	56.2	79.5	86.2	125.5	147.1	41.6	N.A.	N.A.	112.1	56.3	97.2	N.A.	N.A.
R15	65.4	115.1	51.7	61.3	58.1	92.7	99.5	123.1	140.6	57.1	N.A.	N.A.	75.5	52.9	99.5	N.A.	N.A.
R16	77.7	114.7	44.1	59.8	73.6	97.9	113.3	148.4	184.5	56.7	N.A.	N.A.	123.9	80.9	143.4	N.A.	N.A.
R17	75.9	110.4	56.3	67.5	72.6	107.4	116.3	152.2	186.1	61.0	N.A.	N.A.	121.7	78.5	162.3	N.A.	N.A.
R18	54.9	90.0	45.7	52.4	49.5	74.3	83.7	113.3	131.2	39.6	N.A.	N.A.	93.9	65.3	134.4	N.A.	N.A.
R19	56.7	102.8	41.9	56.4	61.6	86.6	92.7	122.4	152.2	44.9	N.A.	N.A.	95.4	62.0	131.8	N.A.	N.A.
R20	64.5	93.1	50.8	55.8	57.8	91.0	95.0	120.7	146.4	53.7	N.A.	N.A.	94.0	65.2	129.4	N.A.	N.A.
R21	75.4	111.0	36.3	52.8	62.2	109.7	112.9	146.8	180.7	50.5	N.A.	N.A.	114.7	102.6	162.5	N.A.	N.A.
R22	42.1	66.1	33.3	34.1	35.8	64.5	62.0	74.1	86.0	31.7	N.A.	N.A.	41.2	31.2	68.0	N.A.	N.A.
R23	58.4	84.8	53.7	48.4	53.4	83.0	84.0	105.4	129.4	46.6	N.A.	N.A.	76.0	46.1	90.4	N.A.	N.A.

Sample	$[^{18}O_2]$-PFHxS	$[^{13}C_4]$-PFOS	$[^{13}C_4]$-PFBA	$[^{13}C_2]$-PFHxA	$[^{13}C_4]$-PFOA	$[^{13}C_5]$-PFNA	$[^{13}C_2]$-PFDA	$[^{13}C_2]$-PFUnDA	$[^{13}C_2]$-PFDoDA	$[^{13}C_3]$-HFPO-DA	$[^{13}C_2]$-6:2PAP	$[^{13}C_2]$-8:2PAP	$[^{13}C_4]$-6:2diPAP	$[^{13}C_4]$-8:2diPAP	d4-10:2diPAP	Cl-PFHxPA	Cl-PFOPA
E1	55.8	62.9	61.7	39.9	56.7	61.1	50.4	33.5	22.9	N.A.$^{\#}$	N.A.	N.A.	86.5	57.7	92.5	N.A.	N.A.
E2	45.7	35.6	58.9	38.7	48.3	52.6	25.9	16.1	10.0	N.A.$^{\#}$	N.A.	N.A.	40.4	21.6	52.2	N.A.	N.A.
E3	#	#	#	#	#	#	#	#	#	N.A.$^{\#}$	N.A.	N.A.	#	#	#	N.A.	N.A.
E4	#	#	#	#	#	#	#	#	#	N.A.$^{\#}$	N.A.	N.A.	#	#	#	N.A.	N.A.
E5	#	#	#	#	#	#	#	#	#	N.A.$^{\#}$	N.A.	N.A.	#	#	#	N.A.	N.A.
E6	36.6	33.4	27.0	28.1	35.8	44.0	25.0	16.7	8.8	N.A.$^{\#}$	N.A.	N.A.	32.9	15.6	49.4	N.A.	N.A.
E7	49.4	28.7	42.9	33.2	45.0	42.4	17.3	11.2	7.7	N.A.$^{\#}$	N.A.	N.A.	29.2	18.6	n.d.	N.A.	N.A.
E8	35.6	16.0	39.3	28.2	33.4	30.0	12.1	8.9	7.3	N.A.$^{\#}$	N.A.	N.A.	18.5	13.0	42.1	N.A.	N.A.
E9	45.8	22.7	52.7	38.6	42.4	37.0	14.7	12.3	9.9	N.A.$^{\#}$	N.A.	N.A.	15.4	13.1	31.1	N.A.	N.A.
E10	52.0	26.1	45.2	41.0	48.6	48.2	15.8	9.8	7.5	N.A.$^{\#}$	N.A.	N.A.	33.5	23.3	82.3	N.A.	N.A.
E11	34.2	20.4	42.0	28.7	35.6	29.0	12.4	9.6	7.2	N.A.$^{\#}$	N.A.	N.A.	25.0	18.4	52.5	N.A.	N.A.
E12	34.0	19.9	27.1	29.0	35.9	30.5	13.2	8.7	7.2	N.A.$^{\#}$	N.A.	N.A.	16.1	10.4	40.6	N.A.	N.A.
E13	47.2	38.6	42.1	39.8	54.9	56.9	23.1	13.3	10.2	N.A.$^{\#}$	N.A.	N.A.	20.7	14.5	69.4	N.A.	N.A.
E14	33.7	20.5	28.8	26.3	31.4	31.7	11.0	7.1	5.8	N.A.$^{\#}$	N.A.	N.A.	13.4	8.7	35.2	N.A.	N.A.
E15	111.1	42.9	108.6	79.2	85.9	72.2	26.1	18.8	15.4	N.A.$^{\#}$	N.A.	N.A.	29.9	18.7	76.8	N.A.	N.A.
E16	37.1	18.0	37.8	27.3	37.2	31.5	12.1	8.0	5.9	N.A.$^{\#}$	N.A.	N.A.	20.6	15.6	65.4	N.A.	N.A.
E17	46.0	23.0	28.4	33.1	42.8	39.3	14.4	10.3	8.2	N.A.$^{\#}$	N.A.	N.A.	24.9	15.9	55.3	N.A.	N.A.
E18	23.3	16.4	28.1	18.5	24.3	21.8	10.5	9.9	8.7	N.A.$^{\#}$	N.A.	N.A.	14.2	11.0	33.0	N.A.	N.A.
E19	37.7	15.0	41.2	29.1	32.9	27.2	10.0	8.6	6.0	N.A.$^{\#}$	N.A.	N.A.	26.5	12.2	57.3	N.A.	N.A.
E20	37.1	21.3	60.3	24.8	34.9	33.4	13.8	9.5	7.2	N.A.$^{\#}$	N.A.	N.A.	26.2	17.5	69.0	N.A.	N.A.
E21	27.4	12.7	38.9	22.0	24.5	24.7	10.3	6.8	5.2	N.A.$^{\#}$	N.A.	N.A.	19.6	11.6	41.9	N.A.	N.A.
E22	36.7	13.0	66.7	27.0	30.9	19.7	5.4	4.8	3.8	N.A.$^{\#}$	N.A.	N.A.	8.7	5.8	30.7	N.A.	N.A.
T1	88.5	77.3	120.8	68.9	70.6	114.2	198.8	147.3	75.0	N.A.$^{\#}$	N.A.	N.A.	94.3	14.9	5.0	N.A.	N.A.
T2	89.0	77.7	97.5	68.2	73.4	89.5	173.6	125.9	77.2	N.A.$^{\#}$	N.A.	N.A.	104.3	17.2	1.5	N.A.	N.A.
T3	79.3	76.3	95.2	70.1	67.0	110.2	152.6	110.1	46.6	N.A.$^{\#}$	N.A.	N.A.	n.d.	n.d.	n.d.	N.A.	N.A.
T4	48.5	40.0	50.0	39.7	39.2	66.2	86.7	52.5	25.4	N.A.$^{\#}$	N.A.	N.A.	n.d.	n.d.	n.d.	N.A.	N.A.
T5	66.5	36.8	78.8	63.2	50.4	63.3	22.5	n.d.	n.d.	N.A.$^{\#}$	N.A.	N.A.	n.d.	n.d.	n.d.	N.A.	N.A.
T6	64.6	65.7	86.7	62.6	59.6	106.9	89.6	29.9	1.4	N.A.$^{\#}$	N.A.	N.A.	n.d.	n.d.	n.d.	N.A.	N.A.
T7	54.2	74.0	77.3	64.7	62.8	128.2	148.3	131.2	82.0	N.A.$^{\#}$	N.A.	N.A.	20.9	n.d.	n.d.	N.A.	N.A.
T8	93.2	26.1	385.5	100.2	70.7	33.6	6.2	n.d.	n.d.	N.A.$^{\#}$	N.A.	N.A.	n.d.	n.d.	n.d.	N.A.	N.A.
T9	36.3	35.7	80.1	36.0	38.1	52.3	81.4	68.3	48.4	N.A.$^{\#}$	N.A.	N.A.	62.2	19.8	2.6	N.A.	N.A.
T10	29.6	30.1	25.2	29.9	23.1	51.5	59.6	50.0	36.6	N.A.$^{\#}$	N.A.	N.A.	37.3	24.8	5.7	N.A.	N.A.
T11	63.8	59.1	96.3	71.0	55.9	83.2	77.8	35.8	13.9	N.A.$^{\#}$	N.A.	N.A.	n.d.	n.d.	2.5	N.A.	N.A.
T12	65.8	59.3	97.1	66.3	51.0	82.6	73.9	34.8	14.4	N.A.$^{\#}$	N.A.	N.A.	2.0	n.d.	n.d.	N.A.	N.A.

Sample	**$[^{18}O_2]$-PFHxS**	**$[^{13}C_4]$-PFOS**	**$[^{13}C_4]$-PFBA**	**$[^{13}C_2]$-PFHxA**	**$[^{13}C_4]$-PFOA**	**$[^{13}C_5]$-PFNA**	**$[^{13}C_2]$-PFDA**	**$[^{13}C_2]$-PFUnDA**	**$[^{13}C_2]$-PFDoDA**	**$[^{13}C_3]$-HFPO-DA**	**$[^{13}C_2]$-6:2PAP**	**$[^{13}C_2]$-8:2PAP**	**$[^{13}C_4]$-6:2diPAP**	**$[^{13}C_4]$-8:2diPAP**	**d4-10:2diPAP**	**Cl-PFHxPA**	**Cl-PFOPA**
T13	73.7	73.6	113.2	75.7	62.9	106.4	117.8	68.5	28.8	N.A.$^{\#}$	N.A.	N.A.	6.7	7.6	2.0	N.A.	N.A.
T14	63.0	70.2	46.3	61.0	55.8	96.0	109.8	89.4	71.0	N.A.$^{\#}$	N.A.	N.A.	69.9	46.3	20.5	N.A.	N.A.
T15	64.5	63.5	68.9	58.8	58.2	88.3	134.7	98.3	70.1	N.A.$^{\#}$	N.A.	N.A.	95.1	47.7	10.4	N.A.	N.A.
T16	51.0	53.9	88.8	51.1	52.2	101.4	141.2	123.9	80.3	N.A.$^{\#}$	N.A.	N.A.	69.3	24.7	8.0	N.A.	N.A.
T17	45.2	60.9	79.5	59.9	61.9	113.5	139.6	129.8	86.7	N.A.$^{\#}$	N.A.	N.A.	96.9	80.6	32.4	N.A.	N.A.
T18	47.3	77.5	36.7	66.4	68.8	145.7	156.7	159.6	116.2	N.A.$^{\#}$	N.A.	N.A.	168.7	129.9	103.2	N.A.	N.A.
T19	54.0	73.6	44.5	70.8	69.0	160.4	156.0	155.1	113.7	N.A.$^{\#}$	N.A.	N.A.	125.4	104.1	61.3	N.A.	N.A.
S1	33.2	17.3	32.4	41.2	15.3	44.9	15.7	12.5	9.4	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S2	40.7	36.3	70.5	42.0	17.3	50.6	18.2	13.5	10.1	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S3	30.0	29.8	50.7	35.8	14.9	42.2	16.8	9.6	6.7	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S4	28.2	25.0	48.1	42.2	15.1	45.2	20.2	14.6	10.8	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S5	50.6	22.7	57.3	44.4	22.1	100.6	47.8	33.7	28.0	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S6	42.2	31.0	58.6	44.5	19.0	56.6	17.0	19.7	17.3	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S7	54.0	43.1	81.1	54.3	23.5	85.8	23.0	15.1	10.5	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S8	43.4	16.5	177.9	39.7	17.2	53.6	17.2	11.0	9.0	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S9	33.9	19.2	38.6	37.1	10.3	21.9	5.9	5.7	5.5	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S10	37.1	29.6	28.5	35.8	15.7	56.8	22.1	19.3	13.8	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S11	33.8	34.6	33.1	32.7	27.2	29.1	15.7	12.3	9.9	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S12	38.5	62.0	69.7	42.5	13.6	20.1	5.0	4.6	4.4	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S13	17.0	2.2	80.5	36.1	6.1	9.9	3.8	3.9	4.0	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S14	38.4	4.4	28.0	47.3	13.3	25.0	10.1	10.5	10.0	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S15	42.7	12.6	73.5	42.1	16.8	57.8	21.5	18.1	14.7	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S16	43.2	28.5	32.8	48.6	19.6	51.9	24.2	19.1	16.1	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S17	52.4	38.7	44.7	53.7	28.5	65.1	24.7	16.9	12.5	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
S18	32.2	25.1	24.7	35.4	16.3	49.7	17.2	13.6	10.1	N.A.$^{\#}$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
X1	45.5	71.9	43.8	51.3	54.7	89.1	55.4	80.9	87.6	N.A.$^{\#}$	36.6	75.2	113.6	135.5	100.7	100.8	113.0
X2	41.7	67.1	36.7	44.3	58.8	102.6	56.9	97.0	110.9	N.A.$^{\#}$	42.6	72.6	160.5	143.3	113.2	103.1	130.6
X3	30.8	49.7	33.5	38.5	47.8	89.1	42.3	60.6	84.0	N.A.$^{\#}$	31.0	50.7	105.4	95.4	79.3	103.2	123.8
X4	33.3	55.7	33.8	41.0	50.4	87.4	44.0	62.9	84.5	N.A.$^{\#}$	35.8	62.1	130.3	104.6	78.7	111.5	134.2
X5	37.8	49.2	30.5	37.2	53.3	89.6	38.9	66.2	79.1	N.A.$^{\#}$	32.5	36.9	149.5	96.7	103.0	116.0	81.4
X6	47.8	73.2	104.3	59.7	56.1	129.0	56.8	96.7	106.5	N.A.$^{\#}$	52.3	96.3	229.5	137.9	119.9	120.3	161.0
X7	58.0	85.5	58.5	68.3	63.9	145.0	66.6	105.0	118.9	N.A.$^{\#}$	72.0	161.4	115.7	122.4	81.3	115.6	181.4
X8	38.6	57.8	37.6	43.7	50.1	96.8	45.7	80.1	90.2	N.A.$^{\#}$	42.6	66.7	126.8	88.3	41.5	128.4	138.2
X9	61.7	76.1	64.9	65.4	57.0	165.5	73.8	139.9	145.3	N.A.$^{\#}$	45.6	72.3	177.7	144.0	122.2	142.5	126.3
X10	29.6	38.8	52.7	59.8	25.2	86.9	41.7	78.6	106.7	N.A.$^{\#}$	319.6	212.9	551.2	418.7	367.7	437.7	698.6

Sample	**$[^{18}O_2]$-PFHxS**	**$[^{13}C_4]$-PFOS**	**$[^{13}C_4]$-PFBA**	**$[^{13}C_2]$-PFHxA**	**$[^{13}C_4]$-PFOA**	**$[^{13}C_5]$-PFNA**	**$[^{13}C_2]$-PFDA**	**$[^{13}C_2]$-PFUnDA**	**$[^{13}C_2]$-PFDoDA**	**$[^{13}C_3]$-HFPO-DA**	**$[^{13}C_2]$-6:2PAP**	**$[^{13}C_2]$-8:2PAP**	**$[^{13}C_4]$-6:2diPAP**	**$[^{13}C_4]$-8:2diPAP**	**d4-10:2diPAP**	**Cl-PFHxPA**	**Cl-PFOPA**
X11	84.0	139.0	90.2	94.6	55.9	242.6	107.1	183.7	223.3	N.A.$^{\#}$	84.7	107.8	205.6	184.6	160.3	248.9	192.8
X12	105.5	142.8	159.8	113.3	77.3	317.7	147.0	243.2	302.1	N.A.$^{\#}$	124.2	119.7	313.3	238.7	198.5	487.3	289.5
X13	127.5	168.9	198.6	119.4	84.3	333.4	151.8	240.9	299.0	N.A.$^{\#}$	127.4	155.4	321.7	183.1	82.1	443.5	276.7
X14	82.8	149.8	154.9	102.9	71.6	288.0	132.3	203.7	247.0	N.A.$^{\#}$	100.0	102.1	229.5	106.8	46.5	313.1	161.3
X15	110.0	150.2	232.1	121.0	84.7	309.9	142.3	233.6	296.4	N.A.$^{\#}$	91.1	81.5	228.9	134.7	22.6	257.1	169.9
X16	94.2	132.4	131.8	91.9	66.1	261.7	127.7	203.6	248.0	N.A.$^{\#}$	74.9	72.0	151.8	149.1	101.6	170.9	114.0
X17	95.3	137.7	156.7	102.2	68.3	278.9	128.6	196.6	241.5	N.A.$^{\#}$	79.8	93.2	179.6	152.1	146.7	172.9	133.3
X18	90.9	105.9	145.4	91.4	62.2	247.8	111.0	173.1	221.6	N.A.$^{\#}$	62.1	54.6	175.8	116.5	41.7	6.6	107.3
X19	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.$^{\#}$	26.5	33.6	102.1	84.0	72.1	27.3	61.3
X20	63.4	79.9	76.8	64.1	51.1	129.3	56.5	94.0	104.1	N.A.$^{\#}$	24.0	37.6	91.7	118.9	78.1	65.6	70.8
X21	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.$^{\#}$	28.1	38.1	88.1	98.6	56.1	17.8	57.1
X22	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.*	N.A.$^{\#}$	29.7	38.5	77.6	59.7	23.0	5.1	65.3
X23	36.7	43.8	44.7	39.9	40.9	80.7	34.8	55.2	63.0	N.A.$^{\#}$	19.2	30.1	46.3	58.9	33.1	9.5	49.2
X24	26.9	146.5	29.1	27.7	27.5	59.0	28.2	46.0	52.0	N.A.$^{\#}$	19.8	34.9	99.8	135.5	58.8	90.9	59.7
X25	54.1	79.4	69.8	61.4	50.3	120.6	59.0	92.3	106.6	N.A.$^{\#}$	14.6	25.7	49.2	55.0	35.5	7.8	48.1
X26	66.8	79.8	72.2	67.7	51.4	156.1	70.9	113.4	125.2	N.A.$^{\#}$	21.4	28.6	84.9	98.6	62.7	2.8	52.3
X27	102.5	132.7	121.9	94.4	68.3	219.0	104.7	151.5	182.5	N.A.$^{\#}$	59.0	61.7	132.4	115.5	114.0	4.9	104.8
X28	94.9	162.2	108.7	100.8	62.2	258.5	130.9	216.7	228.7	N.A.$^{\#}$	55.1	46.4	86.8	84.9	39.5	7.1	94.3
X29	106.8	146.5	187.2	117.9	68.2	268.0	129.5	179.7	226.8	N.A.$^{\#}$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

N.A.$^{\#}$	Internal standards were not available at that time
N.A.	Substances were not analyzed
N.A.*	Recovery rates cannot be calculated because different amounts of $[^{13}C]$-labeled internal standards were given to the samples compared with the calibration solutions
#	Injection standard was not available
n.d.	not detected

Table D-2. Recovery rates [%] of $[^{13}C]$-labeled internal standards for water samples of paper 2.

Sample	**$[^{18}O_2]$-PFHxS**	**$[^{13}C_4]$-PFOS**	**$[^{13}C_4]$-PFBA**	**$[^{13}C_2]$-PFHxA**	**$[^{13}C_4]$-PFOA**	**$[^{13}C_5]$-PFNA**	**$[^{13}C_2]$-PFDA**	**$[^{13}C_2]$-PFUnDA**	**$[^{13}C_2]$-PFDoDA**	**$[^{13}C_3]$-HFPO-DA**	**$[^{13}C_2]$-6:2 FTUCA**
FW1	38.6	45.4	66.4	23.7	29.1	49.5	72.0	63.0	64.3	N.A.$^{\#}$	75.1
FW2	85.3	107.2	82.3	33.2	45.1	76.3	116.1	117.4	110.5	N.A.$^{\#}$	101.5
EW1	38.9	76.6	69.2	23.0	34.6	59.1	69.3	100.1	88.8	N.A.$^{\#}$	29.5
EW2	67.4	112.3	93.7	32.2	29.6	86.0	87.3	142.6	131.2	N.A.$^{\#}$	41.2
EW3	100.8	189.8	169.3	70.6	46.9	150.4	195.1	255.0	221.4	N.A.$^{\#}$	75.2
Y1	52.0	55.2	150.9	51.0	21.5	111.2	58.3	66.7	74.6	N.A.$^{\#}$	63.2

Sample	$[^{18}O_2]$-PFHxS	$[^{13}C_4]$-PFOS	$[^{13}C_4]$-PFBA	$[^{13}C_2]$-PFHxA	$[^{13}C_4]$-PFOA	$[^{13}C_5]$-PFNA	$[^{13}C_2]$-PFDA	$[^{13}C_2]$-PFUnDA	$[^{13}C_2]$-PFDoDA	$[^{13}C_3]$-HFPO-DA	$[^{13}C_2]$-6:2 FTUCA
Y2	37.0	38.7	73.6	45.2	20.1	95.8	48.4	55.1	59.9	N.A.[#]	53.6
Y3	32.4	34.5	75.2	30.3	11.4	68.8	24.5	23.9	19.4	N.A.[#]	28.1
EW1-A_SPM	54.7	72.5	96.1	84.3	65.3	95.9	73.3	79.5	77.9	N.A.[#]	107.0
EW1-B_SPM	47.9	60.5	78.2	86.9	57.6	81.6	64.4	73.4	66.3	N.A.[#]	99.8
EW1-C_SPM	33.1	32.5	23.4	19.2	18.1	24.9	33.3	30.8	29.8	N.A.[#]	22.4
EW1-D_SPM	97.3	100.6	64.2	56.5	51.3	80.7	108.1	97.1	96.2	N.A.[#]	64.8
EW2-A_SPM	39.9	54.1	67.2	73.9	50.8	71.3	54.0	63.5	58.0	N.A.[#]	84.8
EW2-B_SPM	62.4	84.3	120.9	123.5	75.1	117.0	89.8	108.7	99.3	N.A.[#]	127.5
EW2-C_SPM	105.9	101.4	66.6	66.9	61.3	88.6	115.6	108.3	105.2	N.A.[#]	77.1
EW2-D_SPM	58.9	61.8	36.5	33.8	33.6	49.8	66.4	63.5	60.4	N.A.[#]	42.3
EW3-A_SPM	52.0	72.8	103.4	102.3	56.7	90.0	66.7	84.8	72.7	N.A.[#]	109.1
EW3-B_SPM	49.9	62.7	106.0	102.3	57.7	87.7	67.5	84.6	72.0	N.A.[#]	105.6
EW3-C_SPM	58.9	56.9	44.2	35.1	33.6	52.2	64.5	62.3	63.4	N.A.[#]	40.1
EW3-D_SPM	19.5	17.3	11.8	11.1	10.4	16.2	19.9	19.4	19.0	N.A.[#]	13.1
Y1-A_SPM	57.5	59.2	55.9	73.7	67.7	69.2	61.3	66.2	60.6	N.A.[#]	105.3
Y1-B_SPM	66.4	58.3	60.9	55.0	46.0	57.4	68.7	66.5	63.3	N.A.[#]	53.5
Y2-A_SPM	54.0	56.4	58.6	75.6	65.7	74.7	60.5	67.3	59.6	N.A.[#]	98.2
Y2-B_SPM	54.9	47.8	39.7	41.4	36.7	43.0	56.7	52.4	50.8	N.A.[#]	44.3
Y3-A_SPM	63.8	67.3	73.2	87.9	70.5	85.2	69.9	78.2	68.7	N.A.[#]	120.1
Y3-B_SPM	33.9	30.5	25.6	24.9	22.3	26.5	35.2	33.0	30.9	N.A.[#]	28.4

Table D-3. Recovery rates [%] of [^{13}C]-labeled and deuterated internal standards for water samples of add-on studies.

Sample	$[^{18}O_2]$-PFHxS	$[^{13}C_4]$-PFOS	$[^{13}C_4]$-PFBA	$[^{13}C_2]$-PFHxA	$[^{13}C_4]$-PFOA	$[^{13}C_5]$-PFNA	$[^{13}C_2]$-PFDA	$[^{13}C_2]$-PFUnDA	$[^{13}C_2]$-PFDoDA	$[^{13}C_3]$-HFPO-DA	$[^{13}C_4]$-6:2diPAP	$[^{13}C_4]$-8:2diPAP	d4-10:2diPAP
PS1	98.4	125.6	233.1	77.3	90.0	104.4	114.0	110.8	113.8	94.2	72.6	76.1	100.2
PS2	52.4	62.4	128.1	48.5	54.1	61.3	63.7	65.5	66.3	50.0	54.1	54.5	86.8
PS3	79.6	95.1	183.5	70.8	84.3	85.3	89.5	93.8	94.4	86.8	65.2	64.3	107.3
PS4	66.8	90.7	176.6	69.6	61.9	72.9	75.6	81.5	86.6	70.1	52.6	52.1	71.9
PS5	63.2	83.7	157.4	61.0	67.1	75.6	75.5	75.8	80.7	68.5	72.1	72.0	108.0
Currenta Y2-A2	53.3	50.8	120.1	51.1	57.1	48.9	44.0	45.2	41.4	53.9	N.A.	N.A.	N.A.
Currenta Y2-B2	47.8	49.6	106.8	45.6	49.9	46.6	40.9	39.7	35.0	45.7	N.A.	N.A.	N.A.
Currenta X-A2	50.6	44.2	136.9	50.4	65.6	52.4	47.6	41.8	38.9	50.2	N.A.	N.A.	N.A.
Currenta X-B2	62.0	51.8	184.3	55.1	66.7	57.6	53.1	45.9	41.9	63.8	N.A.	N.A.	N.A.
Currenta Bürrig A2	53.5	50.4	95.1	34.8	45.9	41.5	45.0	47.0	40.9	n.d.*	N.A.	N.A.	N.A.

Sample	**$[^{18}O_2]$-PFHxS**	**$[^{13}C_4]$-PFOS**	**$[^{13}C_4]$-PFBA**	**$[^{13}C_2]$-PFHxA**	**$[^{13}C_4]$-PFOA**	**$[^{13}C_5]$-PFNA**	**$[^{13}C_2]$-PFDA**	**$[^{13}C_2]$-PFUnDA**	**$[^{13}C_2]$-PFDoDA**	**$[^{13}C_3]$-HFPO-DA**	**$[^{13}C_4]$-6:2diPAP**	**$[^{13}C_4]$-8:2diPAP**	**d4-10:2diPAP**
Currenta Bürrig B2	85.4	73.2	151.8	29.2	57.9	51.9	69.0	64.7	60.1	n.d.*	N.A.	N.A.	N.A.
R1/15-09	71.1	50.9	168.9	65.2	54.2	58.5	60.5	47.5	50.1	61.4	N.A.	N.A.	N.A.
R2/15-09	85.4	68.8	206.7	77.2	66.4	75.2	72.4	53.4	59.8	58.2	N.A.	N.A.	N.A.
R3/15-09	111.4	65.1	225.6	77.2	66.8	70.3	70.2	58.5	57.4	65.6	N.A.	N.A.	N.A.
R3-A/15-09	68.4	45.3	197.9	63.7	51.1	64.9	59.6	45.9	44.4	47.9	N.A.	N.A.	N.A.
R4/15-09	60.6	41.7	167.8	53.7	48.3	52.1	49.5	37.9	37.4	34.9	N.A.	N.A.	N.A.
R4-A/15-09	66.0	49.8	176.6	59.6	43.9	57.3	50.4	35.7	37.2	33.3	N.A.	N.A.	N.A.
R5/15-09	62.4	29.9	199.0	56.7	43.8	56.2	47.8	32.0	32.6	36.6	N.A.	N.A.	N.A.
R6/15-09	54.9	51.1	201.9	63.8	46.9	64.6	56.4	40.2	38.8	45.8	N.A.	N.A.	N.A.
R6-A/15-09	47.3	21.6	122.5	38.6	36.5	34.2	40.1	23.2	22.2	37.2	N.A.	N.A.	N.A.
R7/15-09	46.6	39.0	153.1	45.9	38.2	38.1	39.7	25.9	24.8	27.4	N.A.	N.A.	N.A.
R8/15-09	36.5	48.0	176.1	53.0	37.6	42.0	43.3	29.9	26.1	36.5	N.A.	N.A.	N.A.
R9/15-09	55.0	43.4	168.9	54.9	41.3	44.5	45.5	23.7	26.1	25.0	N.A.	N.A.	N.A.
R10/15-09	46.2	31.7	237.9	50.3	39.7	47.6	47.1	29.1	27.7	27.7	N.A.	N.A.	N.A.
R11/15-09	35.5	30.6	166.9	49.6	41.6	51.3	40.2	26.7	23.7	26.9	N.A.	N.A.	N.A.
R12/15-09	41.3	42.0	185.4	47.2	38.8	54.6	44.5	29.8	23.1	25.3	N.A.	N.A.	N.A.
R13/15-09	85.6	65.1	104.8	52.1	47.5	57.5	55.0	49.7	52.9	40.3	N.A.	N.A.	N.A.
R14/15-09	78.8	56.7	150.4	62.3	51.5	55.0	52.9	50.0	46.6	55.1	N.A.	N.A.	N.A.
R15/15-09	79.6	52.3	139.8	61.4	49.1	54.1	48.6	43.4	41.5	48.1	N.A.	N.A.	N.A.
SB1	49.3	58.6	n.d.#	30.1	56.3	63.2	76.9	73.8	64.4	39.0	N.A.	N.A.	N.A.
SB2	61.0	76.6	n.d.#	35.4	66.1	80.2	100.2	105.0	93.1	44.0	N.A.	N.A.	N.A.
SB3	64.1	74.8	n.d.#	41.0	73.3	81.9	109.0	99.8	91.9	49.4	N.A.	N.A.	N.A.
SB4	64.4	78.4	n.d.#	39.1	69.4	82.6	101.7	100.1	87.9	51.3	N.A.	N.A.	N.A.
SB5	53.9	62.8	n.d.#	33.4	60.8	69.0	82.5	86.0	77.5	45.6	N.A.	N.A.	N.A.
SB6	66.0	71.1	n.d.#	37.7	68.9	77.3	99.4	94.3	86.7	50.2	N.A.	N.A.	N.A.
SB7	64.9	73.9	n.d.#	34.0	63.6	74.5	98.0	90.8	86.7	47.0	N.A.	N.A.	N.A.
SB8A	73.7	86.9	n.d.#	41.7	74.4	86.1	106.8	101.5	97.9	60.8	N.A.	N.A.	N.A.
SB8B	65.3	74.6	n.d.#	37.5	64.8	77.7	91.2	86.5	83.7	54.9	N.A.	N.A.	N.A.
SB8C	59.0	72.1	n.d.#	35.0	60.0	69.6	89.1	83.3	78.4	39.5	N.A.	N.A.	N.A.
SB9	66.2	71.3	n.d.#	34.7	64.3	74.9	97.5	90.6	84.8	42.9	N.A.	N.A.	N.A.
SB10	55.6	64.1	n.d.#	31.6	58.6	66.3	91.6	88.3	80.3	43.0	N.A.	N.A.	N.A.
SB11	49.7	55.7	n.d.#	33.0	56.2	61.5	79.2	68.1	63.5	40.0	N.A.	N.A.	N.A.
SB12	64.7	74.1	n.d.#	41.1	68.4	77.3	98.1	91.1	83.5	50.3	N.A.	N.A.	N.A.
SB13	54.8	61.3	n.d.#	36.3	60.1	65.4	92.2	83.6	75.2	47.2	N.A.	N.A.	N.A.
SB14	54.6	57.2	n.d.#	35.8	58.4	63.9	80.5	72.9	65.2	50.4	N.A.	N.A.	N.A.

Sample	$[^{18}O_2]$-PFHxS	$[^{13}C_4]$-PFOS	$[^{13}C_4]$-PFBA	$[^{13}C_2]$-PFHxA	$[^{13}C_4]$-PFOA	$[^{13}C_5]$-PFNA	$[^{13}C_2]$-PFDA	$[^{13}C_2]$-PFUnDA	$[^{13}C_2]$-PFDoDA	$[^{13}C_3]$-HFPO-DA	$[^{13}C_4]$-6:2diPAP	$[^{13}C_4]$-8:2diPAP	d4-10:2diPAP
SB15	57.7	72.1	n.d.#	34.7	65.2	77.5	105.0	95.7	86.1	44.2	N.A.	N.A.	N.A.
SB16	65.2	73.2	n.d.#	37.2	68.2	79.6	101.8	87.1	78.9	57.1	N.A.	N.A.	N.A.

N.A. not analyzed

n.d.* Substance was not detected because its concentration was too low after diluting the sample 1:5

n.d.# Recovery rate could not be determined because of poor chromatographic performance

Table D-4. Recovery rates [%] of $[^{13}C]$-labeled internal standards for ionic analytes extracted via Soxhlet and analyzed via LC-MS/MS.

Sample	$[^{18}O_2]$-PFHxS	$[^{13}C_4]$-PFOS	$[^{13}C_4]$-PFBA	$[^{13}C_2]$-PFHxA	$[^{13}C_4]$-PFOA	$[^{13}C_5]$-PFNA	$[^{13}C_2]$-PFDA	$[^{13}C_2]$-PFUnDA	$[^{13}C_2]$-PFDoDA	$[^{13}C_3]$-HFPO-DA	$[^{13}C_2]$-6:2 FTUCA	$[^{13}C_2]$-8:2 FTUCA	$[^{13}C_2]$-10:2 FTUCA
PAS 1	111.4	50.6	217.6	92.5	59.6	47.4	26.1	22.3	20.7	57.3	30.3	40.0	21.0
PAS 2	89.9	29.7	129.4	45.8	51.4	35.6	20.5	20.2	17.1	59.1	23.3	28.6	17.5
PAS 3	41.3	25.2	54.2	26.8	32.8	21.5	14.4	11.6	10.3	24.6	7.4	13.2	8.4
PAS 4	82.8	40.4	81.0	41.8	47.0	33.2	15.5	18.8	17.2	30.8	11.0	24.0	10.9
PAS 5	97.3	51.5	54.0	26.9	32.5	22.2	17.4	17.5	18.3	13.1	6.4	16.4	10.5
PAS 6	58.4	23.1	105.2	47.5	44.8	31.6	17.8	25.0	25.4	39.8	15.5	37.6	13.8
PAS 7	74.4	46.3	187.0	56.1	48.8	38.8	18.6	25.1	25.2	63.8	19.1	33.4	14.4
PAS 8	73.3	35.6	114.9	44.3	42.5	39.1	22.1	23.2	21.4	29.0	10.8	24.2	12.4
PAS 9	53.2	29.5	74.3	31.8	33.5	29.9	14.4	21.0	16.5	26.4	8.6	24.7	8.9
GFF 70	107.2	78.6	67.7	75.7	87.6	69.6	55.0	71.3	79.3	49.3	0.2	0.1	0.0
GFF 71	81.2	67.3	108.4	65.1	62.3	57.6	49.1	57.8	61.6	40.3	0.5	0.4	0.0
GFF 72	45.9	37.6	46.0	37.7	40.5	37.3	26.6	30.2	30.0	58.0	22.4	23.3	24.6
GFF 73	52.7	39.2	60.9	42.2	50.4	42.2	28.8	36.6	36.3	59.7	12.9	14.1	11.4
GFF 74	31.4	24.7	24.4	25.5	31.1	23.8	17.5	21.7	19.8	39.0	4.0	3.6	3.3
GFF 75	36.8	26.0	33.0	31.9	34.4	27.4	19.2	23.1	24.0	40.6	9.2	8.9	9.7
GFF 76	48.7	33.8	41.9	40.9	37.2	37.7	26.4	34.3	31.8	50.9	4.0	4.1	3.4
GFF 77	47.9	31.5	48.3	37.9	43.1	32.4	22.2	27.0	28.1	16.7	0.0	0.0	0.0
GFF 78	64.5	41.7	51.5	55.1	62.7	54.2	33.8	39.1	41.2	25.6	0.3	0.4	0.0
GFF 79	65.3	52.5	50.5	53.9	61.6	48.9	33.0	40.3	39.9	27.8	0.0	0.0	0.0
GFF 80	83.6	55.2	58.8	60.9	56.5	52.5	36.7	44.9	46.0	26.8	0.0	0.0	0.0
GFF 81	55.1	43.5	63.4	40.5	48.0	44.4	28.2	30.9	32.0	24.9	0.1	0.0	0.0
GFF 85	70.2	42.4	68.6	57.5	70.2	43.4	23.8	23.4	26.6	50.3	8.9	13.8	6.4
S1	101.0	58.3	261.7	81.1	59.4	56.2	42.0	52.8	36.7	31.5	31.3	43.6	27.5
S2	75.1	77.5	240.8	65.1	59.7	77.6	37.0	45.8	37.1	15.7	20.2	36.4	20.4
S3	85.5	49.9	80.9	70.6	71.1	49.4	35.9	37.7	42.3	37.4	0.0	0.0	0.0

S4	70.5	54.6	125.6	83.5	70.1	54.4	42.7	44.6	42.1	43.0	21.0	26.9	16.3
S5	85.1	58.1	107.6	68.3	71.6	53.9	28.3	31.6	32.0	44.5	0.9	0.1	0.0
S6	82.3	47.3	102.0	64.2	69.8	47.5	31.5	35.5	34.7	38.0	0.4	0.0	0.0
S7	70.5	43.8	120.4	68.9	59.9	49.6	32.8	29.5	26.7	26.9	1.1	0.0	0.0

Table D-5. Recovery rates [%] of $[^{13}C]$-labeled and deuterated internal standards for neutral analytes extracted via Soxhlet and analyzed via GC-MS.

Sample	**$[^2H_2.^{13}C_2]$-8:2 FTOH**	**$[^2H_2.^{13}C_2]$-10:2 FTOH**	**d3-MeFOSA**	**d5-EtFOSA**	**d7-MeFOSE**	**d9-EtFOSE**
PAS 1	105.7	171.3	65.4	84.9	185.6	221.6
PAS 2	222.9	178.5	40.3	79.7	176.8	160.0
PAS 3	202.1	127.6	24.8	62.6	151.1	141.4
PAS 4	69.4	91.5	66.1	81.7	168.2	157.4
PAS 5	68.6	110.9	74.1	93.1	204.1	182.4
PAS 6	137.9	282.1	48.7	114.3	147.3	261.9
PAS 7	216.9	283.6	36.0	102.0	190.9	232.3
PAS 8	31.2	44.7	32.1	35.5	61.0	63.3
PAS 9	74.7	122.1	101.5	115.0	211.8	211.7
GFF 70	63.0	105.7	26.7	125.3	200.1	218.0
GFF 71	18.5	33.6	48.7	66.0	122.6	131.1
GFF 72	60.2	81.1	38.7	88.2	145.2	149.2
GFF 73	69.8	108.9	29.6	112.6	178.0	176.7
GFF 74	12.9	22.9	32.0	47.7	131.0	156.1
GFF 75	58.7	91.7	47.4	105.7	188.0	241.3
GFF 76	39.8	69.3	16.9	63.2	124.0	138.1
GFF 77	55.5	82.4	42.7	96.8	163.7	234.4
GFF 78	40.6	86.5	25.0	93.6	192.5	185.7
GFF 79	61.7	105.6	23.8	107.8	167.4	207.6
GFF 80	82.9	169.3	29.3	145.2	317.8	280.9
GFF 81	63.2	94.7	67.3	113.7	212.9	334.2
GFF 85	69.8	115.0	73.3	123.0	204.7	248.1

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Eidesstattliche Versicherung

Hiermit versichere ich an Eides statt, die vorliegende Dissertation selbst verfasst und keine anderen als die angegebenen Hilfsmittel benutzt zu haben. Ich versichere, dass diese Dissertation nicht in einem früheren Promotionsverfahren eingereicht wurde.

Hamburg, den 9. Januar 2017