Environmental Mobility of Short Chain Perfluoroalkyl Carboxylic Acids
–
Partition Behaviour and Resulting Environmental Concern

Der Fakultät Nachhaltigkeit der Leuphana Universität Lüneburg
zur Erlangung des Grades Doktorin der Naturwissenschaften
- Dr. rer. nat. -

vorgelegte kumulative Dissertation von

Lena Vierke

geboren am 13.12.1985 in OIdenburg (Oldb.)

Eingereicht am:	25.04.2014
Gutachter und Vorsitzender:	Prof. Dr. Klaus Kümmerer
	Institut für Nachhaltige Chemie und Umweltchemie
	Leuphana Universität Lüneburg
Betreuer und Gutachter:	Prof. Dr. Ralf Ebinghaus
	Institut für Küstenforschung
	Helmholtz-Zentrum Geesthacht
Gutachter:	PD Dr. Martin Scheringer
	Institut für Chemie- und Bioingenieurwissenschaften
	Eidgenössische Technische Hochschulte (ETH) Zürich
Tag der Disputation:	02.10.2014

Summary

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been widely used since 1950 in various consumer products as well as in industrial applications owing to their unique properties, e.g. being hydrophobic and lipophobic at the same time. Nowadays, some of these persistent and man-made PFASs can ubiquitously be found in humans, wildlife and various environmental media. One prominent representative of concern, belonging to the subgroup of perfluorocarboxylates (PFCs) and their conjugate acids (PFCAs), is perfluorooctanoat (PFO) and its conjugate acid (PFOA). Because of its adverse effects on human health and its persistency in the environment industry has started to replace PFO(A) and related long chain chemicals (with seven and more fully fluorinated carbon atoms) with so-called short chain PFASs (less than seven fully fluorinated carbon atoms), including precursors of PFC(A)s. Also these short chain PFC(A)s are persistent and can already be found in humans, ground- and drinking water and in remote regions. However, knowledge gaps exist in understanding the partitioning and the resulting mobility of short chain PFC(A)s in the environment. This is due to the fact that partitioning data of PFC(A)s from standardised experiments can easily be biased by various artefacts, e.g. self-aggregation of the molecules.

Therefore, the objectives of this thesis are (i) to quantify the partitioning of PFC(A)s into mobile environmental media, (ii) to show how results from non-standard tests can be used to assess substance properties of concern and (iii) to conclude on whether the environmental exposure to short chain PFC(A)s is of concern from a regulatory point of view.

In the first part of this thesis, the environmental mobility of short chain C_{4-7}-PFC(A)s was investigated by quantifying their partitioning under non-standardised semi-environmental conditions into mobile environmental media, focusing on water and air, and comparing it to long chain PFC(A)s. Results are:

- Partitioning between water and particles in the aeration tank, primary and secondary clarifier of a wastewater treatment plant (WWTP) showed no distinct differences for short chain PFC(A)s compared to their long chain homologues (Paper 1). In a water-saturated sandy sediment column short chain PFC(A)s were not retarded, whereas long chain homologues were retarded by sorption to the sediment (Paper 2).
- Atmospheric particle-gas partitioning showed a lower fraction sorbed to particles for short chain PFC(A)s compared to long chain ones in samples from a WWTP (Paper 3).
- Air-water concentration ratios based on samples from the tanks of a WWTP were found to be higher for short chain PFC(A)s compared to long chain PFC(A)s (Paper 1). Additionally, in a newly developed experimental set-up the water to air transfer was used to derive that the pK_a of C_{4-11}-PFCAs must be <1.6 instead of up to 3.8 as reported in the literature (Paper 4).

Overall, in the investigated systems short chain PFC(A)s showed a higher mobility due to a more pronounced partitioning into mobile environmental media compared to long chain PFC(A)s.

In the second part of the thesis it was shown how PFO(A) - owing to its persistent, bioaccumulative and toxic (PBT-)properties – was in the context of this thesis successfully assessed as a substance of very high concern according to the criteria of the European REACH Regulation (EC No 1907/2006) by using data from non-standard tests (Paper 5).

In conclusion, based on the knowledge of the high environmental mobility of short chain PFC(A)s and taking into account the argumentation of the PBT-concern of PFO(A), environmental exposure to short chain PFC(A)s is of concern and existing knowledge is already sufficient to initiate measures to prevent emissions of short chain PFC(A)s and their precursors into the environment.

Research papers included in this cumulative Ph.D. thesis

The following research papers are part of this cumulative dissertation and can be found in Appendix A.

Paper 1 air-water and particle-water partitioning WWTP

***In situ* air-water and particle-water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant**

by Lena Vierke, Lutz Ahrens, Mahiba Shoeib, Wolf-Ulrich Palm, Eva M. Webster, David A. Ellis, Ralf Ebinghaus and Tom Harner

published in Chemosphere 2013, 92: 941–948.

Additional material

Response to comment on "*In situ* air-water and particle-water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant"

by Lena Vierke, Lutz Ahrens, Mahiba Shoeib, Wolf-Ulrich Palm, Eva M. Webster, David A. Ellis, Ralf Ebinghaus and Tom Harner

published in Chemosphere 2013, 93: 2207.

Paper 2 sediment-water partitioning enclosure

Transport of perfluoroalkyl acids in a water-saturated sediment column investigated under near-natural conditions

by Lena Vierke, Axel Möller and Sondra Klitzke

published in Environmental Pollution 2014, 186: 7–13.

Paper 3 particle-gas partitioning WWTP

Air concentrations and particle-gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant

by Lena Vierke, Lutz Ahrens, Mahiba Shoeib, Eric J. Reiner, Rui Guo, Wolf-Ulrich Palm, Ralf Ebinghaus and Tom Harner

published in Environmental Chemistry 2011, 8: 363–371.

Paper 4 pK_a via water-to-air transport

Estimation of the acid dissociation constant of perfluoroalkyl carboxylic acids through an experimental investigation of their water-to-air transport

by Lena Vierke, Urs Berger and Ian T. Cousins

published in Environmental Science and Technology 2013, 47: 11032–11039.

Paper 5 PFOA concerns and regulatory developments

Perfluorooctanoic acid (PFOA) - main concerns and regulatory developments in Europe from an environmental point of view

by Lena Vierke, Claudia Staude, Annegret Biegel-Engler, Wiebke Drost and Christoph Schulte

published in Environmental Science Europe 2012, 24: 16–27.

Acknowledgement

Dessau, Lüneburg, Geesthacht, Berlin, Hannover, Toronto, Stockholm - Perfluoroalkyl carboxylic acids around the world, but I found more: Great and helpful people, inspiring working atmospheres, pleasant journeys and activities!

There are numerous people who supported me and my work outstandingly in the last years – my gratitude cannot be adequately expressed in this acknowledgement. But my sincere thanks are given to…

- … Ralf Ebinghaus for the supervision of my thesis and the support of my work on all levels.
- … Klaus Kümmerer for the support of my thesis from the university side and helpful discussions.
- … Martin Scheringer for reviewing my thesis and final corrections.
- … Annegret Biegel-Engler, Adolf Eisenträger, Christoph Schulte, Klaus Günter Steinhäuser, Claudia Staude and all colleagues from the German Federal Environment Agency (UBA) for the possibility to work on the topic of per- and polyfluoroalkyl substances, for the institutional framework, the freedom, flexibility and support in all steps of my thesis and work beside the thesis. I am grateful for the opportunity to work as PhD student at UBA and to experience and combine research and regulation.
- … Wolf-Ulrich Palm for promoting my way in environmental chemistry research from my first seminar at university on with his enthusiasm and his patience and for inspiring discussions.
- … Lutz Ahrens for his advice and support in every step of my thesis.
- … Mahiba Shoeib, Tom Harner and all colleagues and friends from Toronto and other parts of Canada for their support especially in the beginning of my thesis.
- … Michael McLachlan, Ian Cousins and Urs Berger and all colleagues and friends from Stockholm for the great collaboration.
- … Sondra Klitzke, Ingrid Chorus, Hartmut Bartel, Dieter Litz and other colleagues from UBA in Marienfelde for their support and the possibility to combine knowledge and facilities available at UBA.
- … Axel Möller, Renate Sturm, Jürgen Gandraß, Zhiyong Xie and all colleagues and friends from Helmholtz-Zentrum Geesthacht for their support and for making me part of their group even if I wasn´t there very often.
- … Mieke, Gerlinde, Annika, Jenni, Tobi & Tanja, Lars & Mareike, Christian, Moritz, Lea, Til, Karen & Jürgen, Kai & Gundula, Dirk, Jenni & Sören, Kirsten, Frauke and Claudia, and all the others from and around Großenkneten, Lüneburg, Dessau and Hannover for being friends.
- … my parents Heike & Uwe, my sister Svenja, my brother Markus, my grandmother Marianne and the rest of my family as well as Manus family for being the best family I could think of.
- … Manu for simply everything! Especially, your love, confidence and support, independent of the spatial distance between us. I am looking forward to our future!

Table of content

Abbreviations

APFO	ammonium perfluorooctanoate
C_4-PFC(A)	perfluorobutanoate and its conjugate acid
C_5-PFC(A)	perfluoropentanoate and its conjugate acid
C_6-PFC(A)	perfluorohexanoate and its conjugate acid
C_7-PFC(A)	perfluoroheptanoate and its conjugate acid
C_8-PFC(A)	perfluorooctanoate and its conjugate acid
$c_{air,\ gas}$	concentrations in the gas phase
$c_{particle}$	concentrations in the particle phase
$c_{water,\ dissolved}$	concentrations in the dissolved phase
FTOHs	fluorotelomer alcohols
GC-MS	gas chromatography mass spectrometry
HPLC-MS/MS	high pressure liquid chromatography mass spectrometry
K_{AW}	air-water partition coefficient
K_d	solid-water partition coefficient
long chain PFC(A)s	perfluoroalkyl carboxylates and their conjugate acids with seven and more fully fluorinated C-atoms, which is eight and more C-atoms in total, ≥C_8-PFCAs
n_e	effective porosity
PBT	persistent, bioaccumulative and toxic
PFASs	perfluoroalkyl and polyfluoroalkyl substances
PFB(A)	perfluorobutanoate and its conjugate acid
PFC(A)s	perfluoroalkyl carboxylates and their conjugate acids
PFHp(A)	perfluoroheptanoate and its conjugate acid
PFHx(A)	perfluorohexanoate and its conjugate acid
PFN(A)	perfluorononanoate and its conjugate acid
PFO(A)	perfluorooctanoate and its conjugate acid
PFOS	perfluorooctane sulfate
PFP(A)	perfluoropentanoate and its conjugate acid
PFSAs	perfluoroalkyl sulfonates
pK_a	acid dissociation constant
POP	persistent organic pollutant
Q_{AW}	air-water concentration ratio
QSAR	quantitative structure-activity relationship
R	retardation factor
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals, EC regulation No 1907/2006
short chain PFC(A)s	perfluoroalkyl carboxylates and their conjugate acids with three to six fully fluorinated C-atoms, which is four to seven C-atoms in total, C_{4-7}-PFCAs
SIMULAF	facility for the simulation of riverbank and slow sand filtration
UPLC-MS/MS	ultra performance liquid chromatography tandem mass spectrometry
vPvB	very persistent and very bioaccumulative
WWTP	wastewater treatment plant
ρ_B	sediment density

1 Motivation – Background and aim of the thesis

1.1 Perfluoroalkyl and polyfluoroalkyl substances (PFASs)

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) (Buck et al. 2011) have been used in different industrial as well as consumer applications since 1950 (OECD 2013; Prevedouros et al. 2006). The group of PFASs comprises more than 800 substances(OECD 2007). At the beginning of the 21st century, research started to focus on environmental aspects of these substances. Concerns raised when some PFASs were ubiquitously found in the environment and in humans (Giesy and Kannan 2001; Hansen et al. 2001). PFASs can be detected in almost all environmental media, even in remote regions, whereby natural sources are unknown. For example, findings are reported for rivers (McLachlan et al. 2007), tap water from Europe (Llorca et al. 2012; Skutlarek et al. 2006) and Australia (Thompson et al. 2011), remote surface waters such as the Greenland Sea or the Atlantic Ocean (Zhao et al. 2012), the global atmosphere (Dreyer et al. 2009) and polar bear liver (Martin et al. 2004). In addition, PFASs are also present in human blood of the general population (Yeung et al. 2013; Hölzer et al. 2008).

Due to their hydrophobic and lipophobic properties, PFASs are used in different consumer products to make them water-, grease- and stain-repellent (Kissa 2001; OECD 2013). Examples are papers and textiles, such as carpets and outdoor clothing (Herzke et al. 2012; Wang et al. 2013). Furthermore, certain PFASs are used in fire fighting foams or in industrial processes, such as chrome plating or as processing aid in the production of fluorpolymers (Prevedouros et al. 2006; Wang et al. 2013). PFASs are released into the environment from industrial sites, where they are produced or used (Prevedouros et al. 2006). In addition, PFASs-containing products are sources of PFASs-emissions into the environment during their whole life cycle, i.e. during their production, use (e.g. laundering of textiles) and disposal (Wang et al. 2013; Prevedouros et al. 2006).

The most known and best investigated long chain PFASs are perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFO, and its conjugate acid, PFOA). PFOS has been included as a persistent organic pollutant (POP) into the international Stockholm Convention and therefore the parties of this convention restricted the production and use of PFOS (United Nations 2009). PFO(A) and its ammonium salt both are listed as substances of very high concern according to the European REACH Regulation (Registration, Evaluation, Authorization and Restriction of Chemicals, EC No 1907/2006) due to their persistent, bioaccumulative and toxic (PBT-)properties as well as due to their toxicity for reproduction (European Chemicals Agency 2013a, b). PFOS has eight and PFO(A) has seven fully fluorinated C-atoms and both are part of the so called long-chain homologues (minimum of seven fully fluorinated C-atoms) within the PFASs-group. PFOS belongs to the subgroup of perfluoroalkyl sulfonates (PFSAs) whereas PFO(A) belongs to the subgroup of perfluoroalkyl carboxylic acids (PFCAs, and their conjugate bases, PFCs, see Figure 1).

Furthermore, substances which can degrade under environmental conditions to PFC(A)s and PFSAs, the so called precursors, belong to the group of PFASs (Buck et al. 2011). Known precursors for PFC(A)s are for example fluorotelomer alcohols (FTOHs). FTOHs are also globally distributed in the environment, as for example shown by findings in the atmosphere over the Atlantic Ocean and the Antarctic (Dreyer et al. 2009).

When humans and the environment are exposed to POP- and PBT-substances like PFOS and PFO(A) long-term effects are not predictable and therefore exposure of humans and the

environment to such substances needs to be minimized. Based on structural similarities and environmental findings it is expected that other PFSAs and PFC(A)s are also persistent. In addition, long chain homologues are known to be highly bioaccumulative. Hence, C_{11-14}-PFCAs have been identified as substances of very high concern under REACH due to their very persistent and very bioaccumulative (vPvB) properties (European Chemicals Agency 2012a – d).

1.2 Shift to short chain PFASs

Due to the restriction of PFOS-uses and the knowledge of the critical properties of long chain ≥C_8-PFC(A)s, use patterns of PFASs in their various applications are nowadays shifting to short chain PFASs at least in the US and Europe (Ritter 2010; Herzke et al. 2012). Short chain PFC(A)s are defined as PFC(A)s with less than seven fully fluorinated C-atoms (C_{4-7}-PFC(A)s). Eight of the main PFASs producers have agreed with the Environmental Protection Agency of the United States to eliminate long chain PFC(A)s, such as PFO(A), its precursors and even longer chain homologue substances from products and emissions until 2015 (Environmental Protection Agency United States 2013). Besides these producers, also downstream users are planning to phase-out certain PFASs, as for example announced by brands of the apparel and footwear industry (Zero Discharge of Hazardous Chemicals Programme 2013). Due to the special properties of PFASs, short chain PFASs are used as alternatives for the long chain PFASs in many applications (Wang et al. 2013; Rotander et al. 2012; Ritter 2010). Some of these alternatives are precursors of PFC(A)s, like 6:2 FTOH and 4:2 FTOH. Under environmental conditions these precursors may then degrade to the respective short chain PFC(A)s (Buck et al. 2011), e.g. perfluorohexanoate and its acid (PFHx(A), C_6-PFC(A)) or perfluorobutanoate and its acid (PFB(A), C_4-PFC(A)) (see Figure 1).

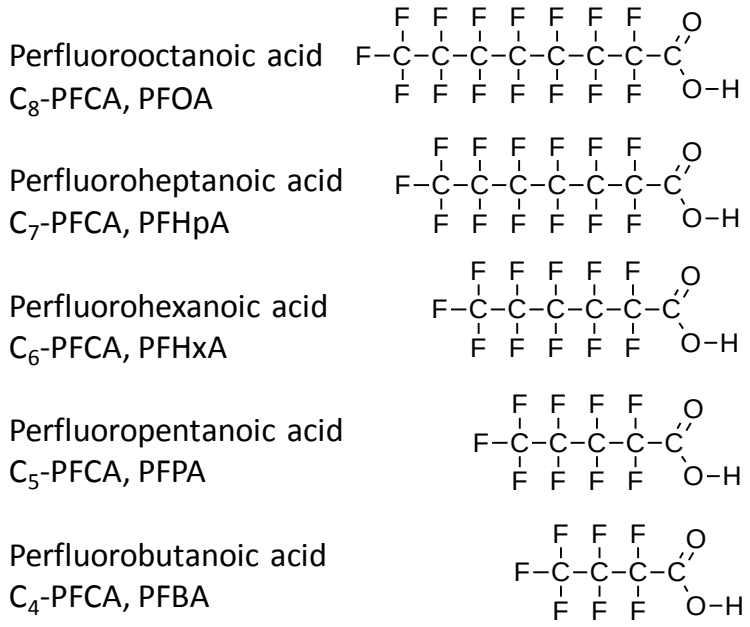


Figure 1: Chemical structures of C_8-PFCA (representative of long chain PFCAs) and short chain (<C_8-PFCAs) perfluoroalkyl carboxylic acids (PFCAs).

The shift from long chain PFASs to short chain homologues is backed by data on e.g. hepatotoxicity or reproductive toxicity of short chain PFC(A)s, which indicate that short chain PFC(A)s are not as toxic as their long chain homologues (Agency for Toxic Substances and Disease Registry

2009; Das et al. 2008; Borg et al. 2013). Furthermore, PFHx(A) has a greater elimination rate in rats and in humans compared to PFO(A) (Russell et al. 2013; Chang et al. 2008), which might indicate a lesser bioaccumulation potential for short chain PFC(A)s compared to long chain PFC(A)s. PFC(A)s generally do not enrich in lipids but strongly bind to proteins (Bischel et al. 2011), which triggers the need to take results from non-standard bioaccumulation test into account instead of e.g. bioconcentration studies in fish. Besides PFO(A) and other long chain PFC(A)s also short chain PFC(A)s have already been found in humans (see Table 1). In the blood of occupationally exposed humans all homologues of short chain PFC(A)s were present (Nilsson et al. 2010). Additionally, in the blood and breast milk of the general population short chain PFC(A)s were already detected (Yeung et al. 2013; Kubwabo et al. 2013). Furthermore, short chain PFC(A)s have been found in groundwater samples (Gellrich et al. 2012; Gellrich et al. 2013) and in snow and surface water samples from remote regions (Benskin et al. 2012; Kirchgeorg et al. 2013) (see Table 1). Overall, these findings are of concern, because short chain PFC(A)s or their precursors must have been released into the environment and are obviously able to reach humans and different environmental media. Under environmental conditions short chain PFC(A)s are persistent, as confirmed by structural similarities to long chain PFC(A)s and estimated atmospheric half-lives of over 130 days for PFBA and Perfluoropentanoic acid (PFPA). The half-life estimation is based on measurements of the reaction with OH radicals (at 700 Torr of air at 296 K) (Hurley et al. 2004).

Table 1: Examples of findings of PFB(A), PFP(A), PFHx(A), PFHp(A) and PFO(A) in humans and the environment.

	PFB(A)	PFP(A)	PFHx(A)	PFHp(A)	PFO(A)	Reference
Human blood general population	-	-	<0.01 – 0.1 ng mL^{-1} in less than 10% of all samples	0.02 – 2.2 ng mL^{-1} in all samples	0.1 – 39 ng mL^{-1} in all samples	(Yeung et al. 2013)
Human blood occupationally exposed ski waxers	<0.6 – 1.1 ng mL^{-1}	<0.6 – 0.1 ng mL^{-1}	<0.07 – 12 ng mL^{-1}	<0.4 – 20 ng mL^{-1}	4.8 – 470 ng mL^{-1}	(Nilsson et al. 2010)
Groundwater	3 ng L^{-1} median in 17% of the samples	8 ng L^{-1} median in 9% of the samples	4 ng L^{-1} median in 14% of the samples	2 ng L^{-1} median in 10% of the samples	3 ng L^{-1} median in 27% of the samples	(Gellrich et al. 2012)
Tap water	2 ng L^{-1} median in 19% of the samples	2 ng L^{-1} median in 19% of the samples	2 ng L^{-1} median in 23% of the samples	1.5 ng L^{-1} median in 12% of the samples	2.6 ng L^{-1} median in 19% of the samples	(Gellrich et al. 2013)
Arctic surface water	-	-	2.9 – 65 pg L^{-1}	11 – 84 pg L^{-1}	6.5 – 54 pg L^{-1}	(Benskin et al. 2012)
Alpine snow	0.3 – 1.8 ng L^{-1}	n.d. – 0.4 ng L^{-1}	0.06 – 0.34 ng L^{-1}	0.04 – 0.22 ng L^{-1}	0.2 – 0.6 ng L^{-1}	(Kirchgeorg et al. 2013)

1.3 Research needs

Short chain PFC(A)s seem to have a lesser potential for bioaccumulation (Russell et al. 2013; Chang et al. 2008) and for some endpoints a lesser acute toxicity (Agency for Toxic Substances and Disease Registry 2009; Das et al. 2008; Borg et al. 2013) compared to long chain PFC(A)s. But findings of short chain PFC(A)s in human bodies and the environment including remote regions (see Table 1) raise questions on the mobility and distribution of these substances in the environment. It can be assumed that the properties and behaviour of short chain PFC(A)s in the environment can be derived from those of long chain PFC(A)s due to the structural similarities of these homologues. Nevertheless, such a read-across is challenged by two facts: (i) Also for long chain PFC(A)s the mobility in the environment is not yet fully understood. (ii) There are indications that the environmental behaviour, e.g. partitioning to solids, does not solely correlate with the chain length of PFC(A)s (Li et al. 2011). Therefore, the mobility of short chain PFC(A)s is in the focus of this thesis.

In general, the environmental mobility of a substance is determined by its occurrence in mobile environmental media like water and air. Data to quantify, to understand and to predict this mobility of short chain PFC(A)s are so far missing. Investigations of short and long chain PFC(A)s in the atmosphere are rare and only very few data are available on their occurrence in the gas phase (Kim and Kannan 2007; Weinberg et al. 2011; Ahrens et al. 2011a; Ahrens et al. 2011b). The gas-particle partitioning had not been investigated so far. In the aqueous environment PFC(A)s are present in equilibrium between their acids and conjugate bases, whereby the contribution of each species remains unclear because of high uncertainties in the experimentally determined pK_a values of PFCAs (Goss and Arp 2009; Burns et al. 2009). This is of relevance when acids and conjugate bases of PFC(A)s have different properties, for example a higher vapour pressure of neutral acids compared to their ionic bases (Barton et al. 2007). Furthermore, sorption to soil and sediment has been investigated for long chain PFC(A)s with environmental samples (Ahrens et al. 2010; Kwadijk et al. 2010) or in laboratory studies (Enevoldsen and Juhler 2010) but only to a limited extent for short chain PFC(A)s. There are indications that partitioning does not solely correlate with the chain length of PFC(A)s (Li et al. 2011). Therefore, investigations under conditions relevant to assess the concern of mobility are needed, e.g. related to drinking water.

1.4 Objectives of the thesis

Given the evidence from monitoring data that demonstrate the presence of short chain PFC(A)s in different environmental media and in humans and the substantial uncertainties about the PBT-properties of short chain PFC(A)s, this thesis has the following objectives:

i) To investigate the environmental mobility of short chain PFC(A)s by quantifying their a) solid-water partitioning (Paper 1 air-water and particle-water partitioning WWTP Appendix A1, Paper 2 sediment-water partitioning enclosure Appendix A2), b) particle-gas partitioning (Paper 3 particle-gas partitioning WWTP Appendix A3) and c) air-water partitioning (Paper 1 air-water and particle-water partitioning WWTP Appendix A1, Paper 4 pK_a via water-to-air transport Appendix A4; see chapter 2).

ii) To show in analogy to the PFOA-case that and how results from non-standard tests can be used in a weight of evidence approach to identify substances of very high concern under REACH (Paper 5 PFOA concerns and regulatory developments Appendix A5; see chapter 3).

iii) To come to a conclusion whether the environmental exposure to short chain PFC(A)s is of concern from a regulatory point of view (see chapter 4).

1.5 Approach and methods

The first part of the thesis is focused on the partitioning of PFC(A)s into mobile environmental media (see chapter 1). In general, the partitioning behaviour of organic chemicals can be determined with different standardised laboratory experiments. However, due to the surface activity of PFC(A)s results from laboratory experiments can easily be biased by various artefacts, such as enrichment of these substances at interfaces (Psillakis et al. 2009; Higgins and Luthy 2006; Arp and Goss 2008) and aggregation events (Cheng et al. 2009; López-Fontán et al. 2005). Beside experiments, it is possible to calculate partition coefficients with established computational models, e.g. quantitative structure-activity relationship (QSAR)-models. However, the application of such calculations for PFC(A)s is limited because properties can only be estimated for the acids of PFC(A)s, e.g. with quantum chemistry-based models like COSMOtherm (Wang et al. 2011), and measured data for validating model results are missing (Arp et al. 2006; Rayne and Forest 2009).

Within this thesis different experiments were developed and conducted to quantify the partitioning of PFC(A)s into mobile environmental media. It is an outstanding feature of this thesis that these experiments were mainly conducted under semi-environmental conditions. Experiments under semi-environmental conditions were neither performed in a laboratory nor were samples taken directly from the environment. Experimental sites were:

i) a wastewater treatment plant (WWTP) (Paper 1 air-water and particle-water partitioning WWTP Appendix A1 and Paper 3 particle-gas partitioning WWTP Appendix A3) and
ii) an experimental facility for the simulation of riverbank and slow sand filtration (SIMULAF) (Paper 2 sediment-water partitioning enclosure Appendix A2).

The SIMULAF facility can in part be controlled under well defined conditions and is located outside under natural influences (Grützmacher et al. 2005). Compared to investigations in the environment the WWTP and the SIMULAF facility both have the advantage of applying higher but still environmentally relevant concentrations of PFASs. The semi-environmental test conditions help to minimize the influence of biases on test results as observed in laboratory studies, for example the enrichment of PFC(A)s at interfaces (Ju et al. 2008). A challenge of using these semi-environmental conditions is the question to which extent results are comparable and transferable to other settings. For example composition of particles within the WWTP (sludge) might differ from particles found in the environment. Therefore, the particles from the WWTP are described as bio-solids in the following.

Extraction and analysis of samples from the WWTP as well as the SIMULAF facility were performed with established methods (Ahrens et al. 2010; Vestergren et al. 2012; Ahrens et al. 2007). High-volume samplers and passive samplers were used for air sampling (Paper 1 air-water and particle-water partitioning WWTP Appendix A1 and Paper 3 particle-gas partitioning WWTP Appendix A3). Cartridges, for enrichment of the gaseous phase in high-volume air-sampling, were soxhlet extracted. Soxhlet extraction was also used for the extraction of sorbent impregnated polyurethane disks, which were used as passive air samplers. Filters from high-volume air samples were extracted with solvents in a sonication bath. Water samples from the WWTP were filtrated and filters were also

extracted with solvents in a sonication bath (Paper 1 air-water and particle-water partitioning WWTP Appendix A1). For water samples from the SIMULAF-facility (Paper 2 sediment-water partitioning enclosure Appendix A2) as well as from the WWTP solid-phase extraction was applied. For all extracts different concentration and clean-up steps, like nitrogen blow-down and sodium sulfate to remove moisture, were needed before instrumental analysis could be performed. Instrumental analysis was performed with high pressure liquid chromatography tandem mass spectrometry (HPLC-MS/MS) for PFC(A)s and PFSAs and gas chromatography mass spectrometry (GC-MS) for other PFASs. Details of sampling, sample preparation and instrumental analysis can be found in the respective papers (papers 1, 2, and 3). The used instrumental analytics do not allow to distinguish between acid and conjugate base of PFC(A)s. Due to an ionization step during analysis the sum of PFC(A) acids and their conjugated bases is quantified in each sample.

In addition to the tests under semi-environmental conditions, a laboratory experiment was designed to estimate the pK_a values of PFCAs (Paper 4 pK_a via water-to-air transport Appendix A4). Due to biases reported for former experimentally determined pK_a values, e.g. solvation in water-solvent systems or aggregation (Kutsuna et al. 2012), it was necessary to develop a new experimental set-up to avoid such artefacts. For example in a previous study using a classical titration set-up a pK_a of 3.8 was derived for PFOA (Burns et al. 2008), which was questioned by others (Goss and Arp 2009). Basically, the set-up developed and used in this thesis consisted of plastic vessels with pH adjusted water. Except of pH adjustment and solvent addition no sample preparation was needed and a ultra performance liquid chromatography system coupled to tandem mass spectrometer (UPLC-MS/MS) was used for instrumental analysis and quantification. Details can be found in paper 4.

The second part of the thesis is focusing on the regulatory perspective (see chapter 3). For the PBT-assessment of PFO(A) under REACH it was necessary to take results from non-standard tests into account, because bioaccumulation of PFO(A) is not covered by standard tests. Such a weight of evidence approach (European Chemicals Agency 2010) was applied under REACH for the first time to identify a substance of very high concern. The assessment of PFOA was done in connection with this thesis (Paper 5 PFOA concerns and regulatory developments Appendix A5).

Finally, to come to a conclusion whether the environmental exposure to short chain PFC(A)s is of concern from a regulatory point of view, results and knowledge from the first and second part of the thesis are combined in a tiered approach (see chapter 4). Firstly, the mobility of short chain PFC(A)s is compared to the mobility of their long chain homologues, which are known to be of concern (e.g. PFO(A) is a PBT-substance). Secondly, the argumentation behind the PBT-concern of PFO(A) is transferred to the findings on the mobility of short chain PFC(A)s.

2 Mobility of short chain PFC(A)s in the environment

2.1 Relevant physical-chemical processes for the mobility of substances

The mobility of a substance in the environment is governed by its occurrence in mobile environmental media, e.g. air and water, and the mobility of these media (Ballschmiter 1992). Diffusive and non-diffusive transport mechanisms are of relevance (Mackay 2001; Schwarzenbach et al. 2003). Non-diffusive transport takes place as advection, e.g. in water or air currents and in rain or snowfall. Diffusive transport is the dispersion of a substance between different environmental media, e.g. from soil or water to air and from water to sediment (Mackay 2001; Schwarzenbach et al. 2003). The chemicals' properties, like vapour pressure or solubility, as well as the characteristics of the environmental media, e.g. sediment properties, are decisive for the partitioning behaviour (Ballschmiter 1992). Ballschmiter (1992) defined five classes for transport processes of organic compounds in the environment:

1. in the technosphere
2. in the hydrosphere
3. in the atmosphere
4. in the lithosphere
5. in the biosphere.

This thesis focuses on the classes 2–4 stated above. Investigated processes are (i) solid-water, (ii) particle-gas and (iii) air-water partitioning as shown in Figure 2. The mobile media addressed with these processes are water and air.

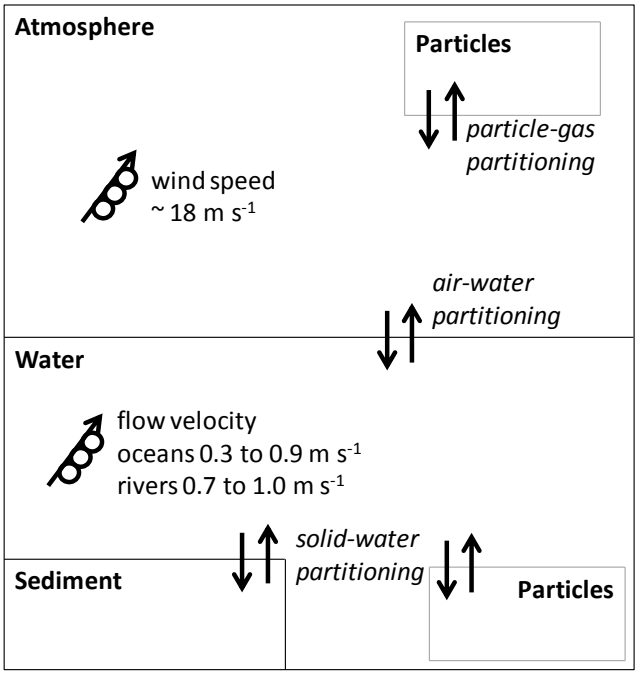


Figure 2: Distribution of substances (equilibrium arrows) to mobile environmental media (circled arrows) investigated within this thesis (based on Ballschmiter (1992) and multimedia models (Mackay 2001; Scheringer 2002)).

Transport in water is slower compared to transport in air. For example flow velocities of 0.7 m s^{-1} to 1.0 m s^{-1} were reported for large European rivers, 0.3 m s^{-1} to 0.9 m s^{-1} for ocean currents, whereby the wind speed 10 m above the ground can be 4 m s^{-1} and even higher in the upper regions of the atmosphere (on average 18 m s^{-1}) (Zarfl et al. 2011). Furthermore, air is capable of reaching all remote regions including alpine regions. A substance in air is thus considered to be more mobile compared to a substance in water. In both media adsorption of substances to particles lower the mobility of these substances (Ballschmiter 1992). In the atmosphere wet deposition takes place for gaseous substances (rain washout velocity 19.4 m h^{-1}, global average value used for multimedia models) and substances sorbed to particles ($9.7 * 10^{-5}$ m h^{-1}). Additionally, particle-associated substances undergo dry deposition (10.8 m h^{-1}) (Mackay and Paterson 1991; Scheringer 2002). An exception are very small particles in the so called "accumulation mode" (0.1 – 2.5 µm) which can be transported over long distances (Seinfeld, Pandis 1998) because dry deposition is negligible (Ballschmiter 1992). In this thesis, substances associated with particles are considered to be less mobile compared to their gaseous forms. For wet deposition the air-water partitioning is of relevance (Scheringer 2002).

The partitioning of substances between suspended particles and the dissolved phase in water bodies is one aspect of solid-water partitioning. These particles could be deposited (Ballschmiter 1992) and if deposition takes place substances sorbed to deposited particles have a lower mobility compared to substances in the dissolved phase. Furthermore, sorption to sediment in a water body, e.g. the riverbed, is another aspect of solid-water partitioning. Sorption to sediment in water bodies results in a lesser mobility compared to the dissolved phase. These processes are relevant for the long-range transport of substances in surface waters. Furthermore, solid-water partitioning is of relevance when water passes through soil or sediment in the subsurface environment. Also particles and therefore sorption of substances to these particles could lead to a transport of substances in the subsurface environment (McCarthy and Zachara 1989). Nevertheless, higher sorption to the immobile solid phase results in a lesser mobility. Subsurface solid-water partitioning is of relevance in different scenarios related to the production of drinking water. Examples are groundwater or riverbank filtrate, which are often used as a resource for drinking water and are fed by surface water after subsurface passage.

2.2 Solid-water partitioning

The partitioning of chemicals between water and solid materials can be quantified by the partition coefficient K_d (Schwarzenbach et al. 2003). In this thesis two approaches for determining this coefficient were applied. For a bulk water phase and suspended (bio-)particle K_d is the ratio of analyte concentrations in the particle phase ($c_{particle}$) and in the dissolved phase ($c_{water,\ dissolved}$) (see Equation 1). Under flow through conditions with a stationary sediment phase, characteristics of this stationary phase, such as porosity and density, are taken into account for calculating K_d (see Equation 2, n_e effective porosity, ρ_B sediment density, R retardation factor, for details see Paper 2 sediment-water partitioning enclosure Appendix A2). According to the concentration units used K_d can have different units or is dimensionless. All species of PFC(A)s, i.e. their acids and conjugate bases, were taken into account for calculating the solid-water partitioning.

Equation 1 $$K_{\mathrm{d}} = \frac{\mathrm{c}_{\mathrm{particles}}}{\mathrm{c}_{\mathrm{water,\ dissolved}}}$$

Equation 2 $$K_{\mathrm{d}} = \frac{n_{\mathrm{e}}}{\rho_{\mathrm{B}}} * (\mathrm{R} - 1)$$

The partitioning of PFC(A)s from an aqueous phase to solid materials, e.g. sediment, has mostly been investigated in laboratory batch experiments (Pan et al. 2009; Enevoldsen and Juhler 2010) or in field studies using environmental samples (Ahrens et al. 2010). Most of these studies focus on PFO(A) and PFOS, only very few data are available for short chain PFC(A)s (for details see supplementary information of paper 1 air-water and particle-water partitioning WWTP Appendix A1 or paper 2 sediment-water partitioning enclosure Appendix A2). Sorption of PFB(A) has not been quantified before and partition coefficients of PFC(A)s have not been determined from a column study before.

2.2.1 Paper 1 air-water and particle-water partitioning WWTP

Background

On a WWTP the partitioning between water and particles was investigated for PFOS and PFO(A) only (Yu et al. 2009). PFC(A)s are known to be present in WWTPs and hence WWTPs are a source for the introduction of PFC(A)s into the environment (Ahrens et al. 2009; Filipovic et al. 2013). Processes in the WWTP are of course artificial but for some aspects, i.e. when it comes to the partitioning of substances between different media, like bio-solids and water, they are comparable to processes in the environment or in the laboratory. This comparability was proven within this study by a comparison of solid-water partition coefficients derived in laboratory test systems under equilibrium conditions or from environmental samples and bio-solid-water partition coefficients from the WWTP, which showed good agreement.

Study design

In this study the partitioning of PFC(A)s between the bio-solid and the aqueous phase in three different tanks of a WWTP was investigated. Samples were collected from a primary clarifier, an aeration tank and a secondary clarifier and were divided by filtration into a particle (bio-solid) and a dissolved phase (particle retention 1.6 µm). Concentrations of PFC(A)s were determined separately in both phases.

Results and discussion

Partition coefficients (see Equation 1) for PFB(A) were 350 $cm^3\ g^{-1}$ at the primary clarifier and 370 $cm^3\ g^{-1}$ at the aeration tank. These were higher compared to PFHx(A) (34 $cm^3\ g^{-1}$ at the primary clarifier, 110 $cm^3\ g^{-1}$ at the aeration tank and 56 $cm^3\ g^{-1}$ at the secondary clarifier). For long chain PFC(A)s, e.g. PFO(A) and PFN(A), partition coefficients were similar compared to PFHx(A). Variations in partitioning of one analyte in different tanks can be explained by differences in processes in the tanks in combination with the sampling procedure. In the aeration tank particles were well mixed whereby in the secondary clarifier at least bigger particles are allowed to settle and were due to grab sampling not included in the samples taken. Results from the clarifiers were in agreement with results from studies conducted under equilibrium conditions, whereby mainly long chain PFC(A)s were investigated in these laboratory studies (Higgins and Luthy 2006). There was no clear trend

observable of partitioning and chain length for C_{4-9}-PFC(A)s in the tanks of the WWTP, which is in line with results from field studies (Li et al. 2011). This indicates that sorption is not mainly driven by hydrophobic interaction of solid material with the perfluorinated chain but by interactions with the carboxylic group, which is equal for all analytes. An increase inpartition coefficients with increasing chain length was reported in laboratory or field studies for >C_7-PFC(A)s only (Ahrens et al. 2010; Higgins and Luthy 2006).

2.2.2 Paper 2 sediment-water partitioning enclosure

Background

To investigate the transport of PFC(A)s within soil or sediment column studies have been used. All previous studies have been conducted under water-unsaturated conditions (Murakami et al. 2008; Murakami et al. 2009; Gellrich et al. 2012; Stahl et al. 2013). Removal of PFC(A)s from the water phase within these studies increased with increasing chain length and was found to be partly competitive (Gellrich et al. 2012). Furthermore, PFC(A)s have already been found in riverbank filtrate (Lange et al. 2007). Riverbank filtration is one possible step in the production of drinking water from surface water resources. The sediment of a riverbank filtration system is water-saturated and transport might differ from water-unsaturated conditions. In this study, the transport in a riverbank filtration scenario was simulated in a water-saturated sediment column (termed enclosure) within the SIMULAF facility. For the first time, sorption coefficients for PFC(A)s were derived from a column study.

Study design

A water-saturated sediment column (enclosure) was used to investigate the breakthrough of PFC(A)s and quantify the sediment-water partitioning under flow-through conditions. Transport of PFC(A)s in the enclosure was compared to a tracer (sodium chloride), which was known to have negligible interactions with the sediment ("conservative tracer") and therefore passes through the column with the same flow velocity as water. Water samples were collected from different depths of the column in certain time intervals and the concentrations of the tracer and analytes were compared.

Results and discussion

Compared to the tracer PFB(A) and PFHx(A) showed no retardation and a complete breakthrough whereby long chain PFC(A)s, here PFO(A) and PFN(A), were retarded by sorption to the sediment. Partition coefficients (see Equation 2) increased from PFB(A) (0.004 $cm^3\ g^{-1}$ in 40 cm and 0.37 $cm^3\ g^{-1}$ in 80 cm) to PFHx(A) (0.66 $cm^3\ g^{-1}$ in 40 cm and 2.9 $cm^3\ g^{-1}$ in 80 cm) and PFO(A) (6.5 $cm^3\ g^{-1}$ in 40 cm and 4.9 $cm^3\ g^{-1}$ in 80 cm). These results from a simulated riverbank filtration scenario showed that short chain PFC(A)s might not be eliminated by sorption to the sediment and therefore can reach raw water sources without retardation. The faster breakthrough of short chain PFC(A)s is in line with results from other column studies, conducted under water unsaturated conditions (Gellrich et al. 2012; Murakami et al. 2008; Murakami et al. 2009). These findings indicate an influence of the length of the perfluorinated chain on sorption (hydrophobic interaction) within the enclosure instead of a dominating influence of the carboxylic group, which is equal for all PFC(A)s.

2.2.3 Conclusion on solid-water partitioning

For samples from the WWTP the comparison of partitioning of long and short chain PFC(A)s exhibited no distinct differences. In the enclosure breakthrough of short chain PFC(A)s was more pronounced compared to their long chain homologues. In the tanks of the WWTP sorption of substances took place to particles distributed in a bulk water reservoir. In the water saturated sediment column sorption to the sediment took place under flow-through conditions to a stationary phase. In addition to these differences, the composition of the solid phase differed between the WWTP and the water-saturated sediment column, e.g. the organic carbon fraction of the solid phase was 0.07% for the water saturated sediment column and up to 19% in the primary clarifier of the WWTP. These two different scenarios resulted in clearly different partition coefficients for PFC(A)s and therefore demonstrated the complexity of sorption. Nevertheless, results from the enclosure experiment indicate a higher mobility of short chain PFC(A)s compared to long chain PFC(A)s.

2.3 Particle-gas partitioning

Particle-gas partitioning was quantified as the fraction of the total amount of analytes found in the atmosphere (gas and particle phase) bound to particles (in %).

2.3.1 Paper 3 particle-gas partitioning WWTP

Background

So far, PFC(A)s in the atmospheric gas phase have been reported in very few studies (Weinberg et al. 2011; Kim and Kannan 2007; Ahrens et al. 2011b). None of these studies investigated the particle-gas partitioning.

Atmospheric concentrations of PFC(A)s might be biased by sampling artefacts, i.e. when in high-volume sampling air is pumped through a filter to sample the particle phase followed by a cartridge to enrich gas phase compounds: Due to sorption of gaseous analytes on the filter gas phase concentrations might be underestimated and particle phase concentrations might be overestimated (Arp and Goss 2008). Conversely, the particle phase concentrations might be underestimated and the gas phase concentrations might be overestimated due to the breakthrough of small particles through the filter or blow-off of analytes from the filter and subsequent sampling in the gas phase sample media. The influence of PFC(A)s incorporated in atmospheric water droplets is unknown. Therefore, two different samplers were used for sampling on the WWTP in this study. A passive sampler, which was supposed to sample compounds from the gas phase only, and an active sampler used to sample the particle and gas phase separately. This thesis reports particle bound fractions of PFC(A)s in the atmosphere for the first time.

Study design

To determine the particle-gas partitioning atmospheric gas and particle phases were sampled with high volume samplers above the aeration tank and the secondary clarifier of a WWTP. The gas phase concentrations determined within these samples were compared to gas phase concentrations derived from samples of a passive sampler at the same sampling sites.

Results and discussion

The gas phase concentrations determined with the passive sampler and the high volume sampler differed by a mean factor of 1.5 only indicating a good comparability of the determined gas phase concentrations. Approximately 64% of PFB(A) and 78% of PFHx(A) were bound to particles in the

atmosphere, the remaining fraction was found in the gas phase. The percentage bound to particles increased for long chain PFC(A)s. For PFO(A) the fraction was about 86%. This indicates, based on particle-gas separation with the high volume sampler that short chain PFC(A)s are present in the gas phase to a larger extent compared to their long chain homologues, which might be caused by a higher vapour pressure and a lesser sorption affinity.

2.3.2 Conclusion on particle-gas partitioning

Up to now, no air sampling technique for PFC(A)s has been reported that is free of possible biases when it comes to the separation of gas and particle phase. Ahrens et al. (Ahrens et al. 2012) investigated the gas-particle partitioning of PFC(A)s by using a high volume sampler and a denuder. In the denuder the gas phase was sampled first followed by the particle phase and sorption of gaseous analytes to the filter was expected to be excluded. The fraction of PFC(A)s sorbed to particles was higher if derived from high volume samples (60 – 100% for $C_{8\text{-}12}$-PFC(A)s) compared to denuder samples (10 – 40% for $C_{8\text{-}12}$-PFC(A)s). $C_{4\text{-}7}$-PFCAs were not detected in the gas phase in that study. Overall fractions sorbed to particles were slightly increasing with increasing chain length for $C_{8\text{-}12}$-PFC(A)s in the study by Ahrens et al. (Ahrens et al. 2012). The higher particle associated fraction of PFC(A)s in the high volume sampler compared to the denuder might have been caused by gas phase PFCAs sorbed to the filter. Nevertheless, for the denuder it cannot be ruled out that small particles were sampled as part of the gas phase and therefore gas phase concentrations might have been overestimated (Ahrens et al. 2012).

Further research is needed to ensure an artefact free sampling for the determination of atmospheric gas and particle phase concentrations of PFC(A)s. Nevertheless, results derived from high volume samples within this study as well as denuder samples (Ahrens et al. 2012) showed for different locations in agreement that long chain PFC(A)s have higher particle bound fractions compared to their short chain homologues. Hence, short chain PFC(A)s with higher fractions in the gas phase are expected to have a higher mobility compared to their long chain homologues.

2.4 Air-water partitioning

Air-water partitioning is the ratio between concentrations of substances in the gas phase ($c_{air,\ gas}$) and the dissolved phase ($c_{water,\ dissolved}$) (see Equation 3). Again, depending on concentration units this coefficient can be expressed with different units or is dimensionless.

Equation 3 $$K_{\mathrm{AW}} = \frac{c_{\mathrm{air\ ,\ gas}}}{c_{\mathrm{water,\ \ dissolved}}}$$

Occurrence of PFC(A)s in the atmospheric gas phase is expected for the protonated species of PFCAs only (e.g. PFOA 2.2 Pa at 20 °C), because the ionic ones have a negligible vapour pressure (Barton et al. 2007). Therefore, air-water partitioning does not occur for ionic bases.

2.4.1 Paper 1 air-water and particle-water partitioning WWTP

Background

Air-water partition coefficients have so far been determined in two laboratory studies for PFOA only (Kutsuna and Hori 2008; Li et al. 2007). The laboratory determination of these coefficients is challenged by possible biases influencing the results, like sorption of PFC(A)s to surfaces (Li et al.

2007) or self-aggregation of PFC(A)s because of concentrations above the critical micelle concentration (López-Fontán et al. 2005). Furthermore, due to different sampling artefacts determination of PFCA gas phase concentrations is difficult (see chapter 2.3).

Study design

Based on gas phase and water phase concentrations from different tanks of the WWTP air-water concentration ratios were estimated. The concentration of the acid in the dissolved phase is needed to quantify this partitioning, because only the protonated species of PFCAs are expected to have a sufficiently high vapour pressure to undergo air-water partitioning (Barton et al. 2007). This concentration was calculated from the measured total concentration of all species in water samples using the pK_a of the acids and the pH of the aqueous solution in the tanks. The pK_a values of PFCAs is an intensively discussed topic in the literature, e.g. reported pK_as for PFOA ranged from -0.2 to 3.8 (Steinle-Darling and Reinhard 2008; Burns et al. 2008), whereby measured pK_as were with a few exceptions available for PFOA only (1.0 – 3.8) (Igarashi and Yotsuyanagi 1992; Burns et al. 2008) (for an overview of pK_as reported in the literature see supplementary information of Paper 1 air-water and particle-water partitioning WWTP Appendix A1).

Results and discussion

Highest uncertainties in air-water concentration ratios (Q_{AW}) resulted from the uncertainties in pK_a values of PFCAs. For PFBA Q_{AW} ranged from 8.1 (for maximum pK_a values reported in the literature of 0.7) to 34 (for minimum pK_a values reported in the literature of 0.08) and from 5.8 to 24 at the aeration tank and the secondary clarifier, respectively. For PFOA with reported pK_a values in the range of -3.8 to 0.2 Q_{AW} ranged from 4.6×10^{-3} to 46 at the aeration tank and 9.2×10^{-4} to 9.2 at the secondary clarifier. The lowest Q_{AW} for PFOA was in good agreement with K_{AW} derived from laboratory experiments (Kutsuna and Hori 2008; Li et al. 2007). Due to the uncertainties in pK_a values a comparison of short chain and long chain PFC(A)s was not possible. But elevated atmospheric gas phase concentrations of PFC(A)s above the tanks of a WWTP, as derived from high volume samples, indicate that a water to air transfer occurred.

2.4.2 Paper 4 air-water partitioning to estimate the pK_a

Background

For PFCAs the experimental determination of pK_a values is challenged by the enrichment of PFC(A)s at surfaces (Ju et al. 2008; Reth et al. 2011), their self-aggregation (López-Fontán et al. 2005) and the influence of solvents in the systems (López-Fontán et al. 2005; Kutsuna et al. 2012). pK_a values of PFCAs were almost exclusively reported for PFOA and they were in the range from -0.2 to 3.8 (Steinle-Darling and Reinhard 2008; Burns et al. 2008). For the presence of the acidic species under environmental relevant conditions this has a big influence: at pH 5 the fraction of the acid would be 6×10^{-4}% for a pK_a of -0.2 or 6% for a pK_a of 3.8. The influence of these uncertainties is for example reflected in the above reported air-water concentration ratios (see chapter 2.4.1). Therefore, an experimental set-up which aims to avoid these artefacts was developed within this thesis.

Study design

The air-water transport of PFCAs was investigated to estimate the pK_a values. For this purpose aqueous pH values below the pH values usually found in the environment were needed and the

experiment was conducted in a laboratory test system. In theory, the fraction of the acids of PFC(A)s in water depends on the pK_a of these acids and the pH of the water phase. Only the non-dissociated acids are able to partition from water to air. In the experiment the pK_a of the acid was estimated from the amount of acids found in the gas phase in dependence of the water pH. The laboratory test system was a polypropylene vessel, which was partly filled with water adjusted to a defined pH and spiked with PFC(A)s. The vessels walls above the water surface served as a passive sampler for gaseous PFC(A)s.

Results and discussion

Closed mass balances, increasing PFCA gas phase concentrations with decreasing pH values and results from a reference chemical (8:2 fluorotelomer unsaturated acid) proved the suitability of this new experimental set-up. The water to air transfer at different water pH values showed that the pK_a of $C_{4\text{-}11}$-PFCAs must be <1.6. The resolution of the data was not sufficient to draw a conclusion on a trend with chain length. Volatilization within this set-up was described with a simple model but this model could be applied for PFOA only, because only for PFOA an air-water partitioning coefficient is reported in the literature (Kutsuna and Hori 2008; Li et al. 2007). With the least-square method modelled data were fit to experimental results giving a pK_a of 0.5 for PFOA.

2.4.3 Conclusion on air-water partitioning

With pK_a values below 1.6 only less than 0.1% of PFC(A)s would be present as protonated acids under environmentally relevant aqueous pH conditions (i.e. 5 – 7). Furthermore, in the laboratory test system no transfer of PFCAs from water to the atmosphere has been observed at pH ≥3.6. Therefore, under environmental conditions water to air transfer of PFCAs itself seems not to be a very important process. Anyhow, air samples from the WWTP, which were supposed to sample the gas phase, indicate that the transfer from water to the atmosphere is of relevance. This could have been caused by biases in the sampling of PFCAs in the gas phase: PFC(A)s sorbed to small particles incl. water droplets could have passed the filter during high volume sampling and subsequently were collected as part of the gas phase (filters had >1.0 µm particle retention). With respect to a potential for long-range transport also small particles are of relevance, because they can be transported over long distances (Seinfeld and Pandis 1998). Furthermore, the ammonium salt of PFO(A) (APFO) has a vapour pressure of 0.008 Pa (at 20°C) (2.3 Pa at 20°C for PFOA) (Washburn et al. 2005) and can therefore be expected to be in the atmospheric gas phase. It is unclear whether PFC(A) salts could be responsible for findings of PFC(A)s in the gas phase.

Because of these possibilities it is more appropriate to calculate air-water concentration ratios for all species. Within that ratio, gas phase concentrations comprise PFC(A)s in their protonated form or as a salt in the gas phase and PFC(A)s bound to small particles. The concentrations in water cover dissolved PFC(A)s as well as PFC(A)s bound on small particles, which have passed the filter.

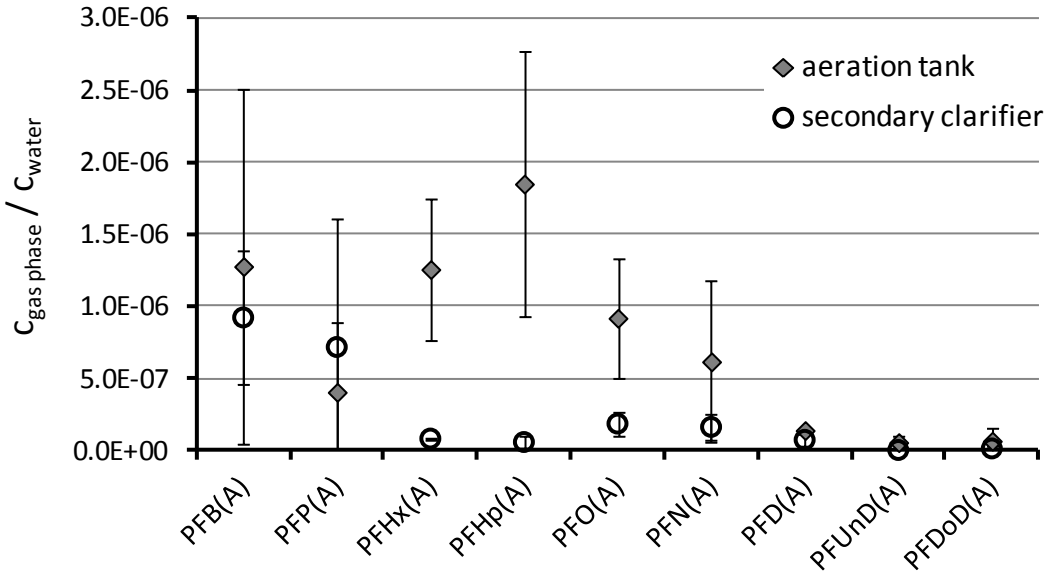


Figure 3: Concentration ratio of gas phase concentrations based on the gas phase sample media ($c_{gas\ phase}$) and water concentrations based on filtered water samples (c_{water}) of PFC(A)s derived from samples from an aeration tank and a secondary clarifier of a wastewater treatment plant (n = 3, respectively).

Air-water concentration ratios for all investigated species give indications that short chain PFC(A)s had higher ratios compared to their long chain homologues and were transferred into the atmosphere to a larger extent (see Figure 3). Transfer from water to the atmosphere was higher at the aeration tank compared to the clarifier, which can be explained by turbulent condition in the aeration tank due to aeration whereas there was a calm water surface at the clarifier. This air-water partitioning is not only relevant for water reservoirs and the air above, but also for rain washout of PFC(A)s from the atmosphere. Overall, due to higher fractions in the gas phase compared to the water phase short chain PFC(A)s are expected to be more mobile than their long chain homologues.

Furthermore, indication for a particle bound transfer of PFC(A)s from the water of the tanks of the WWTP to the atmosphere was given by higher atmospheric particle phase concentrations at the WWTP compared to other studies outside of WWTPs (see Paper 3 particle-gas partitioning WWTP Appendix A3). Aerosol mediated air-water transfer has already been investigated in other studies (Reth et al. 2011; McMurdo et al. 2008) and was not in the focus of this thesis.

3 Assessment of the PBT-properties of PFO(A)

3.1 PBT-assessment

Globally, several regulatory measures are in force to protect the environment from damages caused by the release of hazardous substances. A risk exists when humans or the environment are exposed to a substance with hazardous properties in concentrations leading to adverse effects. This risk can be quantified by a comparison of exposure and effect concentrations. For toxic substances, which are also persistent and enrich in biota (e.g. PBT-substances), such a quantification of the risk is not appropriate. These substances accumulate in the environment and their long-term adverse effects are not predictable. Moreover, they have the potential to contaminate remote regions (European Chemicals Agency 2007; European Chemicals Agency 2012e). Therefore, the European chemicals regulation REACH defines PBT- and very persistent and very bioaccumulative (vPvB-) substances as substances of very high concern, for which no safe environmental concentration can be derived and hence their release into the environment should be minimized. The assessment of such substances is solely based on their inherent hazard properties, such as PBT-properties, without taking the environmental exposure into consideration. Usually, results from laboratory test systems are compared to numerical criteria, defined in REACH Annex XIII. These are for example environmental half-lives to assess the persistency, bioaccumulation factors which describe the bioaccumulation potential and no-observed-effect concentrations for assessing the toxicity. For PBT- or vPvB-substances all three or two criteria have to be fulfilled, respectively.

3.2 Weight of evidence: Non-standard tests in the PBT-assessment

If information on a substance is not directly comparable with the numerical criteria of REACH Annex XIII, but indicates that the substance might be PBT this information can be used within a weight of evidence approach. Furthermore, the weight of evidence approach can be applied if the specific behaviour of a substance is not covered by the respective standard tests. For a weight of evidence approach it is important that all relevant information is taken into account and weighted based on their relevance (European Chemicals Agency 2010). Results from simulation tests or monitoring data can be used to assess the persistency. For the assessment of the bioaccumulation potential, for example data from human body fluids, information on the toxicokinetic behaviour of the substance, biomagnification factors or trophic magnification factors may be used. Results from long-term toxicity tests with fish, birds and invertebrates are applicable in the T-assessment. So far, such a weight of evidence approach was used only once under REACH: to identify PFO(A) as a PBT-substance in 2013. The assessment was done in connection with this thesis.

3.2.1 Paper 5 PFOA concerns and regulatory developments

Background

Since the early 21st century, environmental science has increasingly focused on PFO(A) and other PFASs among other compounds of interest. Several studies show the widespread contamination of the environment with PFO(A). Also in humans PFO(A) was found. Together with indications that PFO(A) might have toxic effects and that it might be able to accumulate in food chains first regulatory activities were initiated. One example is the identification of PFO(A) as a PBT-substance under REACH in 2013 (European Chemicals Agency 2013b). In this research paper it is shown how scientific

knowledge and findings were transferred into regulatory measures in a weight of evidence approach, e.g. the PBT-assessment. Furthermore, the regulatory strategy for PFO(A) is presented and further research needs are defined.

Study design

Information on the use of PFO(A), its sources, its occurrence and its fate in the environment were collected to investigate the need for regulatory measures and to develop a regulatory strategy. Within that strategy it is the first step to identify PFO(A) as a PBT-substance under REACH, although the numerical B-criterion is not fulfilled, followed by a restriction proposal. Furthermore, the paper includes an overview of the PBT-assessment, which was done in the context of this thesis.

Results and discussion

Numerous scientific findings show that human and environmental exposure to PFO(A) is of concern. PFO(A) is stable under environmentally relevant conditions, therefore no half-lives could be measured in laboratory test systems verifying the fulfilment of the P-criterion. With the classification (EC No 1272/2008) of PFO(A) as toxic for reproduction Cat. 1B and a specific target organ toxicity (STOT RE1) (European Commission (2013) the T-criterion is fulfilled. Bioconcentration factors for PFO(A) in fish are far below the threshold for bioaccumulative substances of 2000, meaning that PFO(A) is not bioaccumulative in fish. But gill-breathing organisms are not the most relevant endpoint to be considered for this substance. Because of the high water solubility of PFO(A) fish might have a different possibility of elimination compared to air breathing organisms. Biomagnification of PFO(A) in food webs, investigated in field studies, was shown by biomagnification factors and trophic magnification factors >1 in certain food chains. Furthermore, PFO(A) can be found in the blood of the general population and concentrations are increasing with age. Half-lives of PFO(A) in humans of around three years indicate a bioaccumulation potential of PFO(A). Taken all these information together in a weight of evidence approach it was concluded that PFO(A) is a bioaccumulative substance in line with REACH Annex XIII.

One aim of REACH is that exposure of humans and the environment to PBT-substances is minimized. An authorization for the use of such substances is one foreseen way to achieve this minimization. That means that industry needs an approval from the European Commission to use a substance. As there are indications that PFO(A) (or its precursors)-containing articles are imported into the EU and comprise a relevant source for PFO(A) (or its precursors) into the environment an authorization is not expected to efficiently minimize PFO(A) emissions, as imported articles are not covered by an authorization. Therefore, a restriction for PFO(A) including its precursors is needed.

3.2.2 Conclusion on weight of evidence

The conclusion from the research paper that PFO(A) is a PBT-substance was later unanimously supported by the member states of the European Union, leading to the identification of PFO(A) as a PBT-substance under REACH (European Chemicals Agency 2013a, b). The PFOA-case shows that it is possible to identify PBT-substances even if one numerical criterion is not fulfilled, in this case the BFC for the B-criterion. A weight of evidence approach delivered the possibility to take results from non-standard tests, for example results from field studies, into account. The PBT-assessment of PFO(A) as done in the context of this thesis is a precedent-setting within the chemicals regulation.

4 Overall evaluation of the results

4.1 Background – State of the art

It is nowadays known that - within the group of PFASs - long chain PFASs, which have been widely used since 1950, are of special concern. PFO(A) for example, the most investigated representative out of the subgroup of PFC(A)s, is of concern, because of its persistency, its bioaccumulation potential and its toxicity. Industry has started to replace these long chain PFASs with short chain ones, e.g. with short chain PFC(A)s or their precursors. But also these short chain PFC(A)s have already been found in humans and the environment. In remote regions concentrations of these short chain PFC(A)s are already similar to those of long chain ones. This indicates a high mobility of short chain PFC(A)s in the environment.

At the same time knowledge of the transport behaviour in the environment was poor:

i) No data were available on partitioning between the atmospheric gas and particle phase,
ii) uncertainties of the pK_a values of PFCAs lead to uncertainties regarding the role of the acids in the environment, for example in air-water partitioning and
iii) sorption to sediment has been investigated for short chain PFC(A)s to a limited extent only.

Therefore, it was one objective of this thesis to investigate the mobility of short chain PFC(A)s in the environment by quantifying their partitioning to mobile environmental media, e. g. air and water. Furthermore, the thesis addresses the question of whether the environmental exposition with short chain PFC(A)s is actually of concern from a regulatory point of view. Therefore, the argumentation behind the PBT-concern of PFO(A) was transferred to the findings on the mobility of short chain PFC(A)s.

4.2 Mobility in the environment – A comparison of short chain and long chain PFC(A)s

The mobility of PFC(A)s in the environment was determined with their partitioning to mobile environmental media. The partitioning of PFC(A)s was exemplary quantified with experiments under semi-environmental conditions on a WWTP (see chapters 2.2.1, 2.3.1 and 2.4.1) and on an experimental field site representing a riverbank filtration scenario (enclosure, see chapter 2.2.2). Furthermore, also a laboratory experiment was performed (see chapter 2.4.2). These experiments aimed at avoiding experimental artefacts that have been reported for other laboratory experiments. Compared to the environment higher PFC(A) concentrations were used in these settings. Results of these experiments are summarized in the following with a focus on the comparison of partitioning of short and long chain PFC(A)s.

a) Solid-water partitioning

Solid-water partitioning is of relevance for the mobility of PFC(A)s in (surface) water bodies and under flow-through conditions in soil or sediment, e.g. in drinking water production. Substances in the dissolved aqueous phase are more mobile compared to substances sorbed to solid phases. Within this thesis tanks of a WWTP represented bulk water with suspended particles (bio-solids). In these tanks particle-water partitioning of short chain PFC(A)s showed no distinct differences compared to their long chain homologues (see chapter 2.2.1 Paper 1 air-water and particle-water

partitioning WWTP). Under flow-through conditions in the water-saturated sediment column (enclosure) on an experimental field site, short chain PFC(A)s were not retarded whereas long chain PFC(A)s were retarded by sorption to the stationary sediment (see chapter 2.2.2 Paper 2 sediment-water partitioning enclosure). Thus, sorption processes did not eliminate short chain PFC(A)s from water in such a riverbank filtration scenario. From laboratory batch experiments or from field studies sometimes an increasing trend of sorption of $>C_7$-PFC(A)s with increasing chain length was observed (Ahrens et al. 2010; Higgins and Luthy 2006), while other results contradict this finding (Li et al. 2011). Results from column studies under water unsaturated conditions reported in the literature showed – in agreement to water saturated conditions in the enclosure within this thesis – a faster breakthrough of short chain compared to long chain PFC(A)s (Gellrich et al. 2012; Murakami et al. 2008; Murakami et al. 2009). Hence, under specific conditions, especially flow-through conditions, short chain PFC(A)s have a higher mobility compared to their long chain homologues.

b) Particle-gas partitioning

The occurrence in the atmosphere leads to a high mobility of substances, whereby substances in the gas phase are even more mobile compared to particle-bound substances. In the atmosphere above the tanks of a WWTP fractions of long-chain PFC(A)s sorbed to particles were higher compared to their short chain homologues (see chapter 2.3.1 Paper 3 particle-gas partitioning WWTP). No other particle-gas partition coefficients have so far been reported in the literature for short chain PFC(A)s, but an increasing sorption to particles with increasing chain length was also found for long chain PFC(A)s (Ahrens et al. 2012). Therefore, the mobility of short chain PFCAs in the atmosphere seems to be higher compared to long chain PFC(A)s.

c) Air-water partitioning

Air has a higher mobility in the environment than water. In the tanks of a WWTP short chain PFC(A)s were transferred from water to air to a larger extent compared to their long chain homologues (see chapter 2.4.1 Paper 3 air-water and particle-water partitioning WWTP). For PFC(A)s in the atmospheric gas phase, this trend in air-water partitioning might lead to a more pronounced rain washout of long chain PFC(A)s compared to short chain PFC(A)s. As the pK_a values of PFCAs were found to be below 1.6, only <0.1% of PFC(A)s are present as protonated acids in water under environmental conditions and the relevance of air-water transfer of PFCA acids is expected to be negligible (see chapter 2.4.2 Paper 4 pK_a via water-to-air transport). Air-water transfer could have been caused by PFC(A)salts and/or by PFC(A)s bound to small particles. These small particles can be transported over long-distances and therefore short chain PFC(A)s are more mobile compared to long chain PFC(A)s.

Overall, in the investigated systems short chain PFC(A)s have a higher mobility than their long chain homologues due to a more pronounced partitioning into mobile environmental media.

4.3 Regulatory implications – Comparing the mobility of short chain PFC(A)s with the PBT-concern of PFO(A)

PFO(A) and C_{11-14}-PFC(A)s were identified as PBT and vPvB-substances according to the criteria of REACH, and are therefore included in the list of substances of very high concern. A comprehensive PBT-assessment of short chain PFC(A)s is not yet available. Nevertheless, the weight of evidence

approach, which was successfully applied in the PBT-assessment of PFO(A) in connection with this thesis, showed that a substance might be considered as a PBT-substance under REACH even though the numerical criteria are not fulfilled (see chapter 3.2.1 Paper 5 PFOA concerns and regulatory developments). Furthermore, REACH foresees the possibility to identify a substance of very high concern if there is an equivalent level of concern, e.g. compared to PBT- or vPvB-substances. From the structural similarities of short and long chain PFC(A)s and from the results of a degradation study (Hurley et al. 2004), it can be assumed that short chain PFC(A)s are persistent. In addition, the results of this thesis show that short chain PFC(A)s are more mobile in the environment than long chain PFC(A)s. Reasons for the hypothesis that environmental exposure to short chain PFC(A)s is of concern from a regulatory point of view are given in the following.

a) The environmental mobility and persistency of short chain PFC(A)s trigger the same concerns as PBT-substances

PBT-/vPvB-substances are substances of very high concern under REACH because of the following reasons:

i) "Hazardous substances may accumulate in parts of the environment, including the marine environment and remote areas and the effects of such accumulation are unpredictable in the long-term and such accumulation would be difficult to reverse." (European Chemicals Agency 2007)
ii) "Remote areas should be protected from further contamination by hazardous substances resulting from human activity, and the intrinsic value of pristine environments should be protected." (European Chemicals Agency 2007)

The inherent properties of mobility and persistency lead to a long-term circulation and wide-range distribution of short chain PFC(A)s in the environment with unknown effects once these substances have been released into the environment. Furthermore, it will be impossible to remove these substances from the environment because of their low sorption potential. They will accumulate in the environment. A release of these substances into the environment is thus of concern for the same reasons as environmental exposure to PBT-substances.

b) Short chain PFC(A)s have a potential for long-range transport

The only aspect of mobility of a substance in the environment dealt within the REACH guidance is long-range transport: "This [a potential for long-range transport through the air, with accompanying evidence that wide distribution could occur], in addition to specific real or 'borderline' PBT/vPvB properties, can be considered as evidence giving rise to an equivalent level of concern and to consider the substance in question as a PBT or vPvB." (European Chemicals Agency 2012e). REACH does not define how the long range transport potential of a substance can be proven, whereas in the Stockholm Convention it is foreseen that monitoring data as well as environmental fate properties or model results can be used to prove the long-range transport potential of a substance (Secretariat of the Stockholm Convention 2009).

Models cannot be applied to short chain PFC(A)s because they are ionic under environmentally relevant conditions (Scheringer 2002). Alternatively, the conclusion that short chain PFC(A)s have the potential for long-range transport can be derived from monitoring data and from their partition

behaviour in the environment, as quantified within this thesis. Findings of short chain PFC(A)s in remote regions (Kirchgeorg et al. 2013; Benskin et al. 2012) show that these substances can be transported over long distances, whereby also uncharged and volatile precursors can be responsible for this transport. Furthermore, their partitioning to the aqueous dissolved phase and the atmospheric gas phase indicate a potential for long-range transport.

The definition of criteria for a long-range transport potential, as laid down in the Stockholm Convention, shows that long-range transport potential of substance is a globally accepted concern. The fact that short chain PFC(A)s have a potential for long-range transport is one important argument to show that environmental exposure to short chain PFC(A)s is of concern.

c) Short chain PFC(A)s have a potential for drinking water contamination

Results of the present thesis show that the environmental mobility of short chain PFC(A)s is characterized by a second aspect besides the potential for long range transport: Short chain PFC(A)s may contaminate surface and ground water as important sources for drinking water. The direct breakthrough through a sediment column under flow-through conditions, as shown in a riverbank filtration scenario indicates a high mobility of short chain PFC(A)s. This is proven by findings of short chain PFC(A)s in groundwater (Gellrich et al. 2012) and in drinking water (Gellrich et al. 2013). Furthermore, it was already shown that short chain PFC(A)s are not removed by treatment processes during drinking water production (Eschauzier et al. 2012). Therefore, the high mobility of short chain PFC(A)s could lead to a circulation of these substances in the water cycle including drinking water.

The potential for drinking water contamination is so far not included in the assessment of substances of very high concern under REACH. It is, however, of relevance because of human exposure due to consumption of drinking water. For short chain PFC(A)s it can be assumed that even if future emissions in the environment reach a steady-state on today's emissions, concentrations in the environment, including drinking water, will increase because of their environmental persistency. Already today, there are first findings of short chain PFC(A)s in human blood, not only of highly exposed populations (Nilsson et al. 2010) but also of the general population (Yeung et al. 2013). In the same way as environmental concentrations, these can be expected to increase in the future. In addition, contaminated drinking water would lead to an ongoing PFC(A) exposure of humans even if these substances do not bioaccumulate. Therefore, the potential of short chain PFC(A)s to contaminate drinking water is of great concern.

d) Current knowledge on behaviour of short chain PFC(A)s in the environment indicates that these are substances of very high concern

From the identification of PFO(A) as a substance of very high concern in line with REACH criteria, two things can be learned:

i) Standard tests do not cover the bioaccumulation properties of PFO(A). This might also be true for similar substances, which do not enrich in lipid tissues but enrich by binding to proteins.
ii) Data from human and biota monitoring were needed to prove the bioaccumulation potential of PFO(A) within a weight of evidence approach.

Both aspects required an exposure of humans and the environment to PFO(A) before its identification as a substance of very high concern was possible.

PFO(A) has been produced since 1947 (Prevedouros et al. 2006), whereby production of short chain PFC(A)s and their precursors increased presumably from 2000 on the earliest (Wang et al. 2013). PFO(A) is ubiquitously distributed in the environment, but also short chain PFC(A)s have already been found in humans and the environment (see Table 1 in chapter 1.2) despite their production in high volumes started approximately 50 years later. Results of the present thesis deliver the explanation for these findings: Short chain PFC(A)s are persistent substances with high mobility in the environment. It is very likely that if emissions of PFC(A)s into the environment will continue, concentrations will increase. The effects of this remain unknown. It can be expected that due to the increasing contamination of drinking water, exposure of humans will increase as well, leading to higher blood concentrations. Higher concentrations can also be expected in biota. To avoid this scenario emissions of short chain PFC(A)s into the environment need to be minimized immediately.

4.4 Future steps – For research and beyond

This thesis provides knowledge which adds further to the understanding of the fate of short chain PFC(A)s in the environment. Nevertheless, there are still open questions that should be addressed by future research. Furthermore, the thesis shows that exposure of the environment to short chain PFC(A)s is of concern and therefore delivers a starting point for measures by industry and regulatory authorities.

a) Research to understand the fate of PFC(A)s in the environment with special focus on the role of the acids, their occurrence in the atmosphere and their long range transport

Under environmental relevant aqueous conditions the role of the acid is expected to be negligible, given that the pK_a is <1.6 for $C_{4\text{-}11}$-PFCAs as derived from an experiment of this thesis. Nevertheless, there might be conditions, especially in humans and biota, where media with a low pH are available and species differentiation needs further exploration because of differences in their properties. Furthermore, findings of PFC(A)s in gas phase sample media within this thesis show the need for reliable sampling methods in order to identifying the species of PFC(A)s, their sources and their contribution to long-range transport. The pK_a values and partition coefficients derived within this thesis can be used to update model calculations on the fate of PFC(A)s in the environment. This could also be useful to investigate the relative relevance of their transport through air and water.

b) Research to identify sources of PFC(A)s and their precursors in the environment

There are indications that mostly precursors, like FTOHs, of short chain PFC(A)s are produced and used (Wang et al. 2013; OECD 2013). Knowledge about their sources and fate in the environment is needed to fully understand the fate of these compounds and their role in the occurrence of short chain PFC(A)s.

c) Measures to prevent future exposure of humans and the environment to short chain PFC(A)s

In line with the responsibilities under REACH and especially in line with the principles of a green chemistry (Anastas and Warner 2000), industry should develop and use alternatives for short chain PFC(A)s and their precursors which neither have properties of concern, nor degrade to substances with properties of concern. However, industry is currently producing and using short chain PFC(A)s

and their precursors, respectively. Therefore, a regulatory strategy should be developed to prevent human and environmental exposure. Such a regulatory strategy can take possibilities under REACH (restriction or authorization) but also other measures (e.g. emission limits for industrial plants or limits values for environmental media like drinking water) into account. Alternatively to the use of other substances it should be evaluated by industry as well as consumers for which uses and applications the properties provided by PFASs are unavoidably needed and whether these products are necessary at all.

d) Advancement of criteria for defining substances' properties of very high concern

From the PBT-assessment of PFOA it is obvious that the numerical PBT-criteria and the associated testing requirements are not sufficient to cover all potential substances of very high concern. The possibilities within a weight of evidence approach address this gap. At the same time the PFOA-case shows that for such a weight of evidence approach monitoring data are needed, which requires an exposure of humans and/or the environment before regulatory measures can be initiated. Therefore, new test or other methods needs to be developed to cover for example the bioaccumulation mechanism of PFASs. Before that a better understanding of this mechanism is needed.

Furthermore, the procedure applied in this thesis, to investigate the partitioning of persistent substances to mobile environmental media, should be considered as a possibility to define criteria for substances of very high concern with respect to their mobility. For example, criteria for the assessment of the partition behaviour should be developed. Such criteria would make the process of identifying substances of very high concern with respect to their environmental mobility transparent and reproducible. With respect to the mobility of substances, first attempts have already been made for raw water relevant substances (Skark et al. 2011) and substances with a potential for long-range transport (Zarfl et al. 2012).

4.5 Conclusion

The experimental results obtained within this thesis showed that short chain PFC(A)s are more mobile in the environment compared to their long chain homologues. This mobility in combination with the persistency of PFC(A)s is of concern from a regulatory point of view. Therefore, emissions of these substances into the environment need to be minimized.

5 References

Agency for Toxic Substances and Disease Registry (2009): Draft toxicological profile for perfluoroalkyls. Georgia. http://www.atsdr.cdc.gov/toxprofiles/tp200.pdf (05.11.2013).

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

Ahrens, L.; Felizeter, S.; Xie, Z.; Sturm, R.; Ebinghaus, R. (2009): Polyfluorinated compounds in wastewater treatment plant effluents and surface waters along the river Elbe, Germany. Mar. Pollut. Bull. 58: 1326–1333.

Ahrens, L.; Taniyasu, S.; Yeung, L. W.; Yamashita, N.; Lam, P. K.; Ebinghaus, R. (2010): Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 79: 266–272.

Ahrens, L.; Shoeib, M.; Harner, T.; Lane, D. A.; Guo, R.; Reiner, E. J. (2011a): Comparison of annular diffusion denuder and high volume air samplers for measuring per- and polyfluoroalkyl substances in the atmosphere. Anal. Chem. 83: 9622–9628.

Ahrens, L.; Shoeib, M.; Harner, T.; Lee, S. C.; Guo, R.; Reiner, E. (2011b): Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. Environ. Sci. Technol. 45: 8098–8105.

Ahrens, L.; Harner, T.; Shoeib, M.; Lane, D. A.; Murphy, J. G. (2012): Improved characterization of gas−particle partitioning for per- and polyfluoroalkyl substances in the atmosphere using annular diffusion denuder samplers. Environ. Sci. Technol. 46: 7199–7206.

Anastas, P. T.; Warner, J. C. (2000): Green chemistry. Theory and pratice. Oxford University Press: Oxford.

Arp, H. P. H.; Niederer, C.; Goss, K.-U. (2006): Predicting partitioning behavior of various highly fluorinated compounds. Environ. Sci. Technol. 40: 7298–7304.

Arp, H. P. H.; Goss, K.-U. (2008): Irreversible sorption of trace concentrations of perfluorocarboxylic acids to fiber filters used for air sampling. Atmos. Environ. 42: 6869–6872.

Ballschmiter, K. (1992): Transport and fate of organic compounds in the global environment. Angew. Chem. Int. Edit. 31: 487–664.

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

Benskin, J. P.; Muir, D. C. G.; Scott, B. F.; Spencer, C.; De Silva, A. O.; Kylin, H.; Martin, J. W.; Morris, A.; Lohmann, R.; Tomy, G.; Rosenberg, B.; Taniyasu, S.; Yamashita, N. (2012): Perfluoroalkyl acids in the Atlantic and Canadian Arctic Oceans. Environ. Sci. Technol. 46: 5815–5823.

Bischel, H. N.; MacManus-Spencer, L.; Zhang, C.; Luthy, R. G. (2011): Strong associations of short-chain perfluoroalkyl acids with serum albumin and investigation of binding mechanisms. Environ. Toxicol. Chem. 30: 2423–2430.

Borg, D.; Lund, B.-O.; Lindquist, N.-G.; Hakanssson, H. (2013): Cumulative health risk assessment of 17 perfluoroalkylated and polyfluoroalkylated substances (PFASs) in the Swedish population. Environ. Int. 59: 112–123.

Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; Voogt, P. de; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J. (2011): Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. Integr. Environ. Assess. Manage. 7: 513–541.

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

Burns, D. C.; Ellis, D. A.; Webster, E. M.; McMurdo, C. J. (2009): Response to comment on "Experimental pK_a determination for perfluorooctanoic acid (PFOA) and the potential impact of pK_a concentration dependence on laboratory-measured partitioning phenomena and environmental modeling". Environ. Sci. Technol. 43: 5152–5154.

Chang, S.-C.; Das, K. P.; Ehresman, D. J.; Ellefson, M. E.; Gorman, G. S.; Hart, J. A.; Noker, P. E.; Tan, Y.-M.; Lieder, P. H.; Lau, C.; Olsen, G. W.; Butenhoff, J. L. (2008): Comparative pharmacokinetics of perfluorobutyrate in rats, mice, monkeys, and humans and relevance to human exposure via drinking water. Toxicol. Sci. 104: 40–53.

Cheng, J.; Psillakis, E.; Hoffmann, M. R.; Colussi, A. J. (2009): Acid dissociation versus molecular association of perfluoroalkyl oxoacids: Environmental implications. J. Phys. Chem. A 113: 8152–8156.

Das, K. P.; Grey, B. E.; Zehr, R. D.; Wood, C. R.; Butenhoff, J. L.; Chang, S.-C.; Ehresman, D. J.; Tan, Y.-M.; Lau, C. (2008): Effects of perfluorobutyrate exposure during pregnancy in the mouse. Toxicol. Sci. 105: 173–181.

Dreyer, A.; Weinberg, I.; Temme, C.; Ebinghaus, R. (2009): Polyfluorinated compounds in the atmosphere of the Atlantic and Southern Ocean: Evidence for a global distribution. Environ. Sci. Technol. 43: 6507–6514.

Enevoldsen, R.; Juhler, R. K. (2010): Perfluorinated compounds (PFCs) in groundwater and aqueous soil extracts: using inline SPE-LC-MS/MS for screening and sorption characterisation of perfluorooctane sulphonate and related compounds. Anal. Bioanal. Chem. 398: 1161–1172.

Environmental Protection Agency United States (2013): 2010/2015 PFOA Stewardship Programm. http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html (10.01.2014).

Eschauzier, C.; Beerendonk, E.; Scholte-Veenendaal, P.; Voogt, P. de (2012): Impact of treatment processes on the removal of perfluoroalkyl acids from the drinking water production chain. Environ. Sci. Technol. 46: 1708–1715.

European Chemicals Agency (2007): Guidance for the preparation of an annex XV dossier on the identification of substances of very high concern. http://echa.europa.eu/documents/10162/13638/svhc_en.pdf (30.10.2013).

5 References

European Chemicals Agency (2010): Practical guide 2: How to report weight of evidence. http://echa.europa.eu/documents/10162/13655/pg_report_weight_of_evidence_en.pdf (22.11.2013).

European Chemicals Agency (2012a): Agreement of the member state committee on the identification of henicosafluoroundecanoic acid as a substance of very high concern. http://echa.europa.eu/documents/10162/a6b5d648-3b56-4bf2-a3ce-428205151e53 (10.01.2014).

European Chemicals Agency (2012b): Agreement of the member state committee on the identification of heptacosafluorotetradecanoic acid as a substance of very high concern. http://echa.europa.eu/documents/10162/53e64b10-3d33-4c52-91d2-2fac292ef3bd (10.01.2014).

European Chemicals Agency (2012c): Agreement of the member state committee on the identification of pentacosafluorotridecanoic acid as a substance of very high concern. http://echa.europa.eu/documents/10162/c4c5e92c-afb7-46b9-b4d3-f83d2812cb09 (10.01.2014).

European Chemicals Agency (2012d): Agreement of the member state committee on the identification of tricosafluorododecanoic acid as a substance of very high concern. http://echa.europa.eu/documents/10162/bbec40cc-c8f8-4924-bce3-7201f0650f46 (10.01.2014).

European Chemicals Agency (2012e): Guidance on information requirements and chemical safety assessment Chapter R.11: PBT Assessment. http://echa.europa.eu/documents/10162/13632/information_requirements_r11_en.pdf (30.10.2013).

European Chemicals Agency (2013a): Agreement of the member state committee on the identification of ammonium pentadecafluorooctanoate (APFO) as a substance of very high concern. http://echa.europa.eu/documents/10162/21f8c2f6-dbbd-48a4-a92e-b8f62f658341 (10.01.2014).

European Chemicals Agency (2013b): Agreement of the member state committee on the identification of pentadecafluorooctanoic acid (PFOA) as a substance of very high concern. http://echa.europa.eu/documents/10162/86f13df6-a078-475c-b0b2-2eb9536ebc5d (10.01.2014).

European Commission (2013): Commission Regulation (EU) No 944/2013 of 2 October 2013 amending, for the purposes of its adaptation to technical and scientific progress, Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures. Official Journal of the European Union L 261: 5–22.

Filipovic, M.; Berger, U.; McLachlan, M. S. (2013): Mass balance of perfluoroalkyl acids in the Baltic Sea. Environ. Sci. Technol. 47: 4088–4095.

Gellrich, V.; Stahl, T.; Knepper, T. P. (2012): Behavior of perfluorinated compounds in soils during leaching experiments. Chemosphere 87: 1052–1056.

Gellrich, V.; Brunn, H.; Stahl, T. (2013): Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in mineral water and tap water. J. Environ. Sci. Health, Part A 48: 129–135.

Giesy, J. P.; Kannan, K. (2001): Global distribution of perfluorooctance sulfonate in wildlife. Environ. Sci. Technol. 35: 1339–1342.

Goss, K.-U.; Arp, H. P. H. (2009): Comment on “Experimental pK_a determination for perfluorooctanoic acid (PFOA) and the potential impact of pK_a concentration dependence on laboratory-measured partitioning phenomena and environmental modeling”. Environ. Sci. Technol. 43: 5150–5151.

Grützmacher, G.; Wessel, G.; Chorus, I.; Bartel, H. (2005): Are there limits to cyanobacterial toxin (microcystin) elimination by sand passage. ISMAR.

Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Johnson, H. (2001): Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. Environ. Sci. Technol. 35: 766–770.

Herzke, D.; Olsson, E.; Posner, S. (2012): Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway - A pilot study. Chemosphere 88: 980–987.

Higgins, C. P.; Luthy, R. G. (2006): Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. 40: 7251–7256.

Hölzer, J.; Midasch, O.; Rauchfuss, K.; Kraft, M.; Reupert, R.; Angerer, J.; Kleeschulte, P.; Marschall, N.; Wilhelm, M. (2008): Biomonitoring of perfluorinated compounds in children and adults exposed to perfluorooctanoate-contaminated drinking water. Environ. Health Persp. 116: 651–657.

Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. (2004): Atmospheric chemistry of perfluorinated carboxylic acids: Reaction with OH radicals and atmospheric lifetimes. J. Phys. Chem. A 108: 615–620.

Igarashi, S.; Yotsuyanagi, T. (1992): Homogeneous liquid-liquid extraction by pH dependent phase separation with a fluorocarbon ionic surfactant and its application to the preconcentration of porphyrin compounds. Mikrochim. Acta 106: 37–44.

Ju, X.; Jin, Y.; Sasaki, K.; Saiti, M. (2008): Perfluorinated surfactants in surface, subsurface water and microlayer from Dalian coastal waters in China. Environ. Sci. Technol. 42: 3538–3542.

Kim, S. K.; Kannan, K. (2007): Perfluorinated acids in air, rain, snow, surface runoff, and lakes: Relative importance of pathways to contamination of urban lakes. Environ. Sci. Technol. 41: 8328–8334.

Kirchgeorg, T.; Dreyer, A.; Gabrieli, J.; Kehrwald, N.; Sigl, M.; Schwikowski, M.; Boutron, C.; Gambaro, A.; Barbante, C.; Ebinghaus, R. (2013): Temporal variations of perfluoroalkyl substances and polybrominated diphenyl ethers in alpine snow. Environ. Pollut. 178: 367–374.

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

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

Kutsuna, S.; Hori, H. (2008): Experimental determination of Henry's law constant of perfluorooctanoic acid (PFOA) at 298 K by means of an inert-gas stripping method with a helical plate. Atmos. Environ. 42: 8883–8892.

Kutsuna, S.; Hori, H.; Sonoda, T.; Iwakami, T.; Wakisaka, A. (2012): Preferential solvation of perfluorooctanoic acid (PFOA) by methanol in methanol-water mixtures: A potential

overestimation of the dissociation constant of PFOA using a Yasuda-Shedlovsky plot. Atmos. Environ. 49: 411–414.

Kwadijk, C. J. A. F.; Korytar, P.; Koelmans, A. A. (2010): Distribution of perfluorinated compounds in aquatic systems in The Netherlands. Environ. Sci. Technol. 44: 3746–3751.

Lange, F. T.; Wenz, M.; Schmidt, C. K.; Brauch, H. J. (2007): Occurrence of perfluoroalkyl sulfonates and carboxylates in German drinking water sources compared to other countries. Water Sci. Technol. 56: 151–158.

Li, H.; Ellis, D. A.; Mackay, D. (2007): Measurement of low air-water partition coefficients of organic acids by evaporation from a water surface. J. Chem. Eng. Data 52: 1580–1584.

Li, F.; Sun, H.; Hao, Z.; He, N.; Zhao, L.; Zhang, T.; Sun, T. (2011): Perfluorinated compounds in Haihe River and Dagu Drainage Canal in Tianjin, China. Chemosphere 84: 265–271.

Llorca, M.; Farré, M.; Picó, Y.; Müller, J.; Knepper, T. P.; Barceló, D. (2012): Analysis of perfluoroalkyl substances in waters from Germany and Spain. Sci. Total Environ. 431: 139–150.

López-Fontán, J. L.; Sarmiento, F.; Schulz, P. C. (2005): The aggregation of sodium perfluorooctanoate in water. Colloid Polym. Sci. 283: 862–871.

Mackay, D.; Paterson, S. (1991): Evaluation the multimedia fate of organic chemicals: A level III fugacity model. Environ. Sci. Technol. 25: 427–436.

Mackay, D. (2001): Multimedia environmental models. The fugacity approach. 2nd Ed. Lewis Publishers: Boca Raton.

Martin, J. W.; Smithwick, Marla, M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C. G.; Mabury, S. A. (2004): Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. Environ. Sci. Technol. 38: 373–380.

McCarthy, J. F.; Zachara, J. M. (1989): Subsurface transport of contaminants. Mobile colloids in the subsurface environment may alter the transport of contaminants. Environ. Sci. Technol. 23: 496–502.

McLachlan, M. S.; Holmström, K. E.; Reth, M.; Berger, U. (2007): Riverine discharge of perfluorinated carboxylates from the European continent. Environ. Sci. Technol. 41: 7260–7265.

McMurdo, C. J.; Ellis, D. A.; Webster, E.; Butler, J.; Christensen, R.; Reid, L. K. (2008): Aerosol enrichment of the surfactant PFO and mediation of the water-air transport of gaseous PFOA. Environ. Sci. Technol. 42: 3969–3974.

Murakami, M.; Nobuyuki, S.; Anegawa, A.; Nakada, N.; Harada, A.; Komatsu, T.; Takada, H.; Tanaka, H.; Ono, Y.; Furumai, H. (2008): Multiple evaluations of the removal of pollutants in road runoff by soil infiltration. Water Res. 42: 2745–2755.

Murakami, M.; Kuroda, K.; Sato, N.; Fukushi, T.; Takizawa, S.; Takada, H. (2009): Groundwater pollution by perfluorinated surfactants in Tokyo. Environ. Sci. Technol. 43: 3480–3486.

Nilsson, H.; Kärrman, A.; Westberg, H.; Rotander, A.; van Bavel, B.; Lindström, G. (2010): A time trend study of significantly elevated perfluorocarboxylate levels in humans after using fluorinated ski wax. Environ. Sci. Technol. 44: 2150–2155.

OECD (2007): Lists of PFOS, PFAS, PFOA, PFCA, related compounds and chemicals that may degrade to PFCA. http://search.oecd.org/officialdocuments/displaydocumentpdf/?doclanguage=en&cote=env/jm/mono%282006%2915 (10.01.2014).

OECD (2013): OECD/UNEP global PFC group, synthesis paper on per- and polyfluorinated chemicals (PFCs). www.oecd.org/env/ehs/risk-management/PFC_FINAL-Web.pdf (19.11.2013).

Pan, G.; Jia, C.; Zhao, D.; You, C.; Chen, H.; Jiang, G. (2009): Effect of cationic and anionic surfactants on the sorption and desorption of perfluorooctane sulfonate (PFOS) on natural sediments. Environ. Pollut. 157: 325–330.

Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. (2006): Sources, fate and transport of perfluorocarboxylates. Environ. Sci. Technol. 40: 32–44.

Psillakis, E.; Cheng, J.; Hoffmann, M. R.; Colussi, A. J. (2009): Enrichment factors of perfluoroalkyl oxoanions at the air/water interface. J. Phys. Chem. A 113: 8826–8829.

Rayne, S.; Forest, K. (2009): Perfluoroalkyl sulfonic and carboxylic acids: A critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. J. Environ. Sci. Health, Part A 44: 1145–1199.

Reth, M.; Berger, U.; Broman, D.; Cousins, I. T.; Nilsson, E. D.; McLachlan, M. S. (2011): Water-to-air transfer of perfluorinated carboxylates and sulfonates in a sea spray simulator. Environ. Chem. 8: 381–388.

Ritter, S. K. (2010): Fluorochemicals go short. Chem. Eng. News 88: 12–17.

Rotander, A.; Kärrman, A.; van Bavel, B.; Polder, A.; Rigét, F.; Audunsson, G. A.; Víkingsson, í.; Gabrielsen, G. W.; Bloch, D.; Dam, M. (2012): Increasing levels of long-chain perfluorocarboxylic acids (PFCAs) in Arctic and North Atlantic marine mammals, 1984 - 2009. Chemosphere 86: 278–285.

Russell, M. H.; Nilsson, H.; Buck, R. C. (2013): Elimination kinetics of perfluorohexanoic acid in humans and comparison with mouse, rat and monkey. Chemosphere 93: 2419–2425.

Scheringer, M. (2002): Persistence and spatial range of environmental chemicals. New ethical and scientific concepts for risk assessment. Wiley-VCH: Weinheim.

Schwarzenbach, R.; Gschwend, P. M.; Imboden, D. M. (2003): Environmental organic chemistry. Wiley-Interscience: Hoboken/New Jersey.

Secretariat of the Stockholm Convention (2009): Stockholm Convention on persistent organic pollutants (POPs) as amended in 2009. chm.pops.int/TheConvention/Overview/TextoftheConvention/tabid/2232/Default.aspx (11.11.2013).

Seinfeld, J. H.; Pandis, S. N. (1998): Atmospheric chemistry and physics. John Wiley & Sons, Inc: New York.

Skark, C.; Kuhlmann, B.; Zullei-Seibert, N. (2011): Verfeinerung und Validierung des Screenings nach Trinkwasserrelevanten Chemikalien im Geltungsbereich der REACH-Verordnung. www.reach-info.de/dokumente/Rohwasserrelevanz_2011_FKZ36001059_Langfassung.pdf (15.11.2013).

Skutlarek, D.; Exner, M.; Färber, H. (2006): Perfluorinated surfactants in surface and drinking waters. Environ. Sci. Pollut. Res. 13: 299–307.

5 References

Stahl, T.; Riebe, R. A.; Falk, S.; Failing, K.; Brunn, H. (2013): Long-term lysimeter experiment to investigate the leaching of perfluoroalkyl substances (PFASs) and the carry-over from soil to plants: Results of a pilot study. J. Agr. Food Chem. 61: 1784–1793.

Steinle-Darling, E.; Reinhard, M. (2008): Nanofiltration for trace organic contaminant removal: Structure, solution, and membrane fouling effects on the rejection of perfluorochemicals. Environ. Sci. Technol. 42: 5292–5297.

Thompson, J.; Eaglesham, G.; Mueller, J. (2011): Concentrations of PFOS, PFOA and other perfluorinated alkyl acids in Australian drinking water. Chemosphere 83: 1320–1325.

United Nations (2009): Stockholm Convention on Persistent Organic Pollutants. C.N. 524.2009.TREATIES-4. New York. http://chm.pops.int/Portals/0/download,aspx?d=UNEP-POPS-TREATY-NOTIF-CN703-2011.En.pdf (18.03.2014).

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

Wang, Z.; Macleod, M.; Cousins, I. T.; Scheringer, M.; Hungerbühler, K. (2011): Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs). Environ. Chem. 8: 389–398.

Wang, Z.; Cousins, I. T.; Scheringer, M.; Hungerbühler, K. (2013): Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. Environ. Int. 60: 242–248.

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

Weinberg, I.; Dreyer, A.; Ebinghaus, R. (2011): Waste water treatment plants as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air. Environ. Pollut. 159: 125–132.

Yeung, L. W.; Robinson, S. J.; Koschorreck, J.; Mabury, S. A. (2013): Part I. A temporal study of PFCAs and their precursors in human plasma from two German cities 1982−2009. Environ. Sci. Technol. 47: 3865–3874.

Yu, Q.; Zhang, R.; Deng, S.; Huang, J.; Yu, G. (2009): Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study. Water Res. 43: 1150–1158.

Zarfl, C.; Scheringer, M.; Matthies, M. (2011): Screening criteria for long-range transport potential of organic substances in water. Environ. Sci. Technol. 45: 10075–10081.

Zarfl, C.; Hotopp, I.; Kehrein, N.; Matthies, M. (2012): Identification of substances with potential for long-range transport as possible substances of very high concern. Environ. Sci. Pollut. Res. 19: 3152–3161.

Zero Discharge of Hazardous Chemicals Programme (2013): Joint roadmap version 2. www.roadmaptozero.com/joint-roadmap.php (19.11.2013).

Zhao, Z.; Xia, Z.; Möller, A.; Sturm, R.; Tang, J.; Zhang, G.; Ebinghaus, R. (2012): Distribution and long-range transport of polyfluoroalkyl substances in the Arctic, Atlantic Ocean and Antarctic coast. Environ. Pollut. 170: 71–77.

Appendix A - Papers included in this cumulative Ph.D. thesis

A1 Paper 1 air-water and particle-water partitioning WWTP

Chemosphere 92 (2013) 941–948

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

In situ air–water and particle–water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant

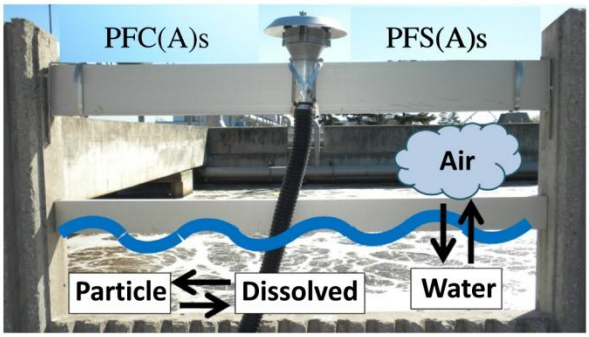
Lena Vierke [a,b,*], Lutz Ahrens [c,1], Mahiba Shoeib [c], Wolf-Ulrich Palm [b], Eva M. Webster [d], David A. Ellis [d], Ralf Ebinghaus [e], Tom Harner [c]

[a] Federal Environment Agency (UBA), Section Chemicals, Wörlitzer Platz 1, Dessau-Roßlau, Germany
[b] Leuphana University of Lüneburg, Institute of Sustainable and Environmental Chemistry, Scharnhorststr. 1, Lüneburg, Germany
[c] Environment Canada, Air Quality Processes Research Section, 4905 Dufferin Street, Toronto, ON, Canada
[d] Trent University, Centre for Environmental Modelling and Chemistry, 1600 West Bank Drive, Peterborough, ON, Canada
[e] Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, Max-Planck Str. 1, Geesthacht, Germany

HIGHLIGHTS

- PFCAs, PFSAs and HFOSA were measured in different phases at a WWTP.
- Particle-dissolved (R_d) and air–water (Q_{AW}) concentration ratios were determined.
- R_d values agreed well with equilibrium partition coefficients from the literature.
- Q_{AW} values derived for PFOA agreed well with K_{AW} values reported in the literature.
- Uncertainties in Q_{AW} values are attributed to the wide range of pK_a values reported.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 December 2012
Received in revised form 26 February 2013
Accepted 27 February 2013
Available online 2 April 2013

Keywords:
PFCA
PFSA
Henry's-law
K_{AW}
K_d
Fate

ABSTRACT

In situ measurements of air and water phases at a wastewater treatment plant (WWTP) were used to investigate the partitioning behavior of perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs) and perfluorooctyl sulfonamide (HFOSA) and their conjugate bases (PFC^-s, PFS^-s, and $FOSA^-$, respectively). Particle-dissolved (R_d) and air–water (Q_{AW}) concentration ratios were determined at different tanks of a WWTP. Sum of concentrations of $C_{4-12,14}$ PFC(A)s, $C_{4,6,8,10}$ PFS(A)s and (H)FOSA were as high as 50 pg m^{-3} (atmospheric gas phase), 2300 ng L^{-1} (aqueous dissolved phase) and 2500 ng L^{-1} (aqueous particle phase). Particle-dissolved concentration ratios of total species, log R_d, ranged from −2.9 to 1.3 for PFS(A)s, from −1.9 to 1.1 for PFC(A)s and was 0.71 for (H)FOSA. These field-based values agree well with equilibrium partitioning data reported in the literature, suggesting that any *in situ* generation from precursors, if they are present in this system, occurs at a slower rate than the rate of approach to equilibrium. Acid Q_{AW} were also estimated. Good agreement between the Q_{AW} and the air–water equilibrium partition coefficient for C_8PFCA suggests that the air above the WWTP tanks is at or near equilibrium with the water. Uncertainties in these Q_{AW} values are attributed mainly to variability in pK_a values reported in

* Corresponding author at: Federal Environment Agency (UBA), Section Chemicals, Wörlitzer Platz 1, Dessau-Roßlau, Germany. Tel.: +49 34021036620; fax: +49 34021046620.
E-mail addresses: Lena.Vierke@uba.de (L. Vierke), Lutz.Ahrens@slu.se (L. Ahrens), Mahiba.Shoeib@ec.gc.ca (M. Shoeib), Palm@uni.leuphana.de (W.-U. Palm), Ewebster@trentu.ca (E.M. Webster), Davidellis@trentu.ca (D.A. Ellis), Ralf.Ebinghaus@hzg.de (R. Ebinghaus), Tom.Harner@ec.gc.ca (T. Harner).
[1] Present address: Swedish University of Agricultural Sciences, Institutionen för vatten och miljö, Lennart Hjelms väg 9, Uppsala, Sweden.

0045-6535/$ - see front matter
http://dx.doi.org/10.1016/j.chemosphere.2013.02.067

the literature. The WWTP provides a unique environment for investigating environmental fate processes of the PFCAs and PFSAs under 'real' conditions in order to better understand and predict their fate in the environment.

1. Introduction

Perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs) and perfluorooctyl sulfonamide (HFOSA) and their conjugate bases (PFC^-s, PFS^-s, and $FOSA^-$, respectively) have been produced since 1950 (Prevedouros et al., 2006). Today, these anthropogenic compounds are ubiquitous in the environment and wastewater treatment plants (WWTPs) are known to be one source for per- and polyfluorinated compounds into the environment (Houde et al., 2006; Ahrens, 2011).

To better understand and to be able to model the fate of PFC(A)s, PFS(A)s and (H)FOSA, knowledge of their partitioning between different environmental phases (e.g. between water and particles or between air and water) is crucial. Several studies have investigated the particle-dissolved partitioning under controlled conditions (Ochoa-Herrera and Sierra-Alvarez, 2008; Pan et al., 2009; Enevoldsen and Juhler, 2010) as well as in the field (Ahrens et al., 2010; Kwadijk et al., 2010; Labadie and Chevreuile, 2011; Li et al., 2011); whereas limited data are available for air–water partitioning of these compounds (Li et al., 2007; Kutsuna and Hori, 2008). Absence of such data can be attributed to the challenges associated with the design of reliable laboratory experiments. For example the surface active behavior of $PFCs^-$ and $PFSs^-$ might bias the results (Li et al., 2007). The present study combines new waterside measurements at different tanks of a WWTP with previously reported air-side results (Vierke et al., 2011) to investigate the particle-dissolved partitioning behavior in water and air–water partitioning behavior of PFC(A)s, PFS(A)s and (H)FOSA.

The overall process of wastewater treatment is dynamic. Chemicals within the wastewater are partitioning between the freely dissolved phase and particles present in the wastewater. At the same time, chemicals present in the dissolved phase, surface water are subject to exchange with the overlying atmosphere. It is possible that sub-processes such as particle–water and air–water partitioning are able to approach equilibrium. This would require that the rate of approach to equilibrium is much faster than, for example, any rate of formation associated with precursor degradation.

The aim of the present study is to derive *in situ* particle-dissolved (R_d) and air–water (Q_{AW}) concentration ratios for PFC(A)s, PFS(A)s and (H)FOSA for a WWTP, while taking into account the ionizability of these compounds. The derived values are then compared to reported thermodynamic equilibrium partition coefficients. Uncertainties associated with both the *in situ* values and the reported values are discussed in light of improvements that can be made to future investigations. To our knowledge, this is the first field-based study investigating air–water partitioning of PFCAs, PFSAs and HFOSA.

2. Methods and materials

2.1. Terminology

In the aqueous environment, acids are in equilibrium with their conjugate bases. The acid–base equilibrium depends on the pH of the medium and the pK_a of the acids. As suggested in the literature (Buck et al., 2011) we refer to the PFCA acids by adding an "A" to the acronym (Table 1). This system was also applied to PFSAs (Table 1). To facilitate the readers' understanding of acronyms the conjugate bases are indicated with a minus symbol. It is in line with this definition to name the perfluoroctanesulfonic acid as PFOSA, which in other studies was used for the HFOSA. Here, HFOSA represents the acid and $FOSA^-$ represents the conjugate base. For both species parenthesis are used, i.e. PFS(A), PFC(A) and (H)FOSA.

2.2. Chemicals

The present study focuses on $C_{4-12,14}$ PFC(A)s (Perfluorobutanoate PFB^-, Perfluoropentanoate PFP^-, Perfluorohexanoate $PFHx^-$, Perfluorohepantoate $PFHp^-$, Perfluorooctanoate PFO^-, Perfluorononanoate PFN^-, Perfluorodecanoate PFD^-, Perfluoroundecanoate $PFUnD^-$, Perfluorododecanoate $PFDoD^-$, Perfuorotetradecanoate $PFTD^-$ and the respective acids), $C_{4,6,8,10}$ PFS(A)s (Perfluorobutane sulfonate $PFBS^-$, Perfluorohexane sulfonate $PFHxS^-$, Perfluorooctane sufonate $PFOS^-$, Perfluorodecanesulfonate $PFDS^-$ and the respective acids) and (H)FOSA. Detailed information on analytes, mass-labeled internal standards and other chemicals used are provided in Tables SM1 and SM2.

2.3. Sampling

Sampling was conducted on a WWTP in Ontario, Canada with all samples being collected between 15th and 28th of April 2010. Air and water sampling were carried out at an aeration tank and at a secondary clarifier. Water samples were also collected from a primary clarifier. Results for the gas-phase concentrations of PFCAs, PFSAs and HFOSA were previously reported (Vierke et al., 2011) and are summarized briefly below. In that study active and passive air sampling was performed. The comparison of the results obtained from active and passive air sampling was used to produce reliable results for PFCAs, PFSAs and HFOSA in the gas phase.

For air sampling, as part of the previously reported study (Vierke et al., 2011), one high volume air sampler was installed at each sampling site at the rail of the tanks (approximately 2 m above the water surface) and samples were collected once a week over 24 h, resulting in an average air volume of 140 m^3. The particulate phase was collected on glass fiber filters (GFFs) (Pall, Quebec, Canada, Type A/E Glass 102 mm diameter, baked at 250 °C before sampling) and the gas phase was collected on PUF/XAD/PUF cartridges (precleaned large PUF plug, Supelco, Oakville, ON, Canada, 7.6 cm length, 6 cm diameter, 15 g of XAD-2 (SupelcoTM-2), Supelco) (Vierke et al., 2011). At the end of the 24 h air sampling period, water samples were collected from the corresponding tanks (note: the water component of this study was not part of the previous publication). Approximately 1 L water was collected in a brown glass bottle. The bottles and a bucket, by which the water was carried, were rinsed several times with the corresponding water from the tank. Surface water temperatures were not measured as they were expected to be in a similar range as the air temperatures recorded above the tanks, given the time of the year. Average temperatures for each 24 h sampling period ranged from 7 to 12 °C.

2.4. Extraction and instrumental analysis

Extraction and instrumental analysis are described elsewhere (Ahrens et al., 2010; Vierke et al., 2011) and in Table SM 3 and in Chapter 2 in the SM.

Table 1
Acronyms for the acids and their conjugate bases of PFC(A)s, PFS(A)s and (H)FOSA.

Number of $(CF)_2$ groups	**PerFluoroSulfonic Acid** PFSA $CF_3(CF_2)_xSO_2OH$	⟺	**PerFluoroSulfonate** PFS^- $CF_3(CF_2)_xSO_2O^-$
$x = 3$	**PerFluoroButaneSulfonic Acid** PFBSA		**PerFluoroButaneSulfonate** $PFBS^-$
$x = 5$	**PerFluoroHexaneSulfonic Acid** PFHxSA		**PerFluoroHexaneSulfonate** $PFHxS^-$
$x = 7$	**PerFluoroOctaneSulfonic Acid** PFOSA		**PerFluoroOctaneSulfonate** $PFOS^-$
$x = 9$	**PerFluoroDecaneSulfonic Acid** PFDSA		**PerFluoroDecaneSulfonate** $PFDS^-$
	PerFluoroOctaneSulfonAmide HFOSA $CF_3(CF_2)_7SO_2NH_2$	⟺	PerFluoroOctaneSulfonAmide Anion $FOSA^-$ $CF_3(CF_2)_7SO_2NH^-$
	PerFluoroCarboxylic Acid PFCA $CF_3(CF_2)_xCOOH$	⟺	**PerFluoroCarboxylate** PFC^- $CF_3(CF_2)_xCOO^-$
$x = 2$	**PerFluoroButanoic Acid** PFBA		**PerFluoroButanoate** PFB^-
$x = 3$	**PerFluoroPentanoic Acid** PFPA		**PerFluoroPentanoate** PFP^-
$x = 4$	**PerFluoroHexanoic Acid** PFHxA		**PerFluoroHexanoate** $PFHx^-$
$x = 5$	**PerFluoroHeptanoic Acid** PFHpA		**PerFluoroHeptanoate** $PFHp^-$
$x = 6$	**PerFluoroOctanoic Acid** PFOA		**PerFluoroOctanoate** PFO^-
$x = 7$	**PerFluoroNonanoic Acid** PFNA		**PerFluoroNonanoate** PFN^-
$x = 8$	**PerFluoroDecanoic Acid** PFDA		**PerFluoroDecanoate** PFD^-
$x = 9$	**PerFluoroUnDecanoic Acid** PFUnDA		**PerFluoroUnDecanoate** $PFUnD^-$
$x = 10$	**PerFluoroDoDecanoic Acid** PFDoDA		**PerFluoroDoDecanoate** $PFDoD^-$
$x = 12$	**PerFluoroTetraDecanoic Acid** PFTDA		**PerFluoroTetraDecanoate** $PFTD^-$

2.5. Quantification and quality control

Quantification was performed based on response factors of the target compounds and their corresponding mass-labeled internal standards added prior to extraction. Recoveries were calculated from the mass-labeled internal standard and the injection standard added prior to analysis. An eight point calibration curve was used that ranged from 0.005 to 5.0 ng mL^{-1}.

Omnisol water was used as blank for the dissolved phase ($n = 3$) and tap water was used as blank for the particle phase ($n = 1$) in water samples.

Instrument detection limits (IDLs) were calculated by extrapolating instrument response to a concentration that would give a signal to noise ratio of three. For air samples IDLs were based on blank samples (see Vierke et al., 2011) and for water, tap water was used for determining IDLs. Sample concentrations below the concentrations of the blank or below the IDL were not considered in calculation of concentration ratios.

2.6. Calculation of the concentrations of PFCAs and PFSAs in water

The measured concentration in the dissolved phase is the sum of the concentration of all species, including the neutral acid (HA) and the anionic conjugate base (A^-). For the partitioning behavior of PFC(A)s and PFS(A)s in the environment it is important to distinguish between species as they behave differently (Webster et al., 2010). Using the general definition of the acid dissociation constant and the Henderson–Hasselbalch equation the concentrations of HA in the dissolved phase can be calculated as shown in Eq. (1).

$$c(\mathrm{HA}) = \frac{c_{\mathrm{dissolved}}(\mathrm{total})}{1 + 10^{\mathrm{pH} - \mathrm{p}K_a}} \quad (1)$$

$c_{\mathrm{dissolved}}(\mathrm{total})$ is the measured concentration of all species dissolved in the aqueous phase at the given pH.

The pH of the WWTP tanks was 7.5 (measured by the operator of the WWTP) and so accordingly the aqueous phase pH is 7.5. Different pK_a values for linear PFCAs and PFSAs are reported and discussed in the literature (Table 2 and Table SM4). To calculate concentrations of PFCAs and PFSAs in the dissolved phase, minimum and maximum pK_a values reported in the literature were used (Table 2).

2.7. Calculation of particle-dissolved partitioning in water

It is recognized that in the case of ionizing organic acids, several species have the potential to partition to organic matter (Jafvert et al., 1990). R_d was calculated for each analyte including all species (Eq. (2)). The particle-dissolved partitioning coefficient is usually abbreviated as K_d. In the present study we use R_d to take into account that the system at the WWTP may not be in equilibrium.

$$R_d = \frac{c_{\mathrm{particles}}}{c_{\mathrm{dissolved}}(\mathrm{total})} \quad (2)$$

$c_{\mathrm{particles}}$ is the concentration measured in the aqueous particle phase, and can be expressed in units of either ng L^{-1} (based on the volume of filtered water in L, which can also be converted to ng cm^{-3} based on the density of water i.e. by dividing by 1000 cm L^{-1}) or in units of ng g^{-1} based on the weight of particles

Table 2
Reported pK_a values (n = number of reported values) and calculated Q_{AW} values for PFSAs, PFCAs and HFOSA. Q_{AW} are reported as an average over all samples from the aeration tank and the secondary clarifier (n = 3 respectively, except for PFPA where n = 2 and PFDoDA at the secondary clarifier where n = 1). For each sample, the concentration of neutral acid in the dissolved aqueous phase was calculated using the minimum pK_a and the maximum pK_a.

	Reported pK_a (n)[a]	Aeration tank		Secondary clarifier	
		Q_{AW} (min reported pK_a)	Q_{AW} (max reported pK_a)	Q_{AW} (min reported pK_a)	Q_{AW} (max reported pK_a)
PFHxSA	−5.5 to 0.14 (3)	$6.5 \times 10^5 \pm 5.2 \times 10^5$	1.5 ± 1.2	$2.7 \times 10^5 \pm 5.5 \times 10^4$	0.63 ± 0.1
PFOSA	−5.5 to 0.14 (3)	$2.1 \times 10^4 \pm 9.7 \times 10^3$	$4.8 \times 10^{-2} \pm 2.3 \times 10^{-2}$	$5.3 \times 10^4 \pm 5.6 \times 10^4$	0.12 ± 0.1
PFBA	0.08 to 0.7 (6)	34 ± 32	8.1 ± 7.8	24 ± 12	5.8 ± 2.9
PFPA	−0.1 to 0.64 (4)	24 ± 18	4.4 ± 3.4	43 ± 35	7.8 ± 6.5
PFHxA	−0.16 to 0.9 (4)	57 ± 23	5.6 ± 2.3	3.6 ± 0.6	0.35 ± 0.1
PFHpA	−0.19 to −0.15 (2)	91 ± 45	83 ± 41	2.7 ± 2.0	2.5 ± 1.8
PFOA	−0.2 to 3.8 (13)	46 ± 21	$4.6 \times 10^{-3} \pm 2.1 \times 10^{-3}$	9.2 ± 4.0	$9.2 \times 10^{-4} \pm 4.0 \times 10^{-4}$
PFNA	−0.21 to −0.17 (2)	3.2 ± 29	29 ± 26	8.2 ± 4.5	7.5 ± 4.1
PFDA	−0.42 to 2.6 (5)	7.1 ± 1	$1.2 \times 10^{-2} \pm 1.6 \times 10^{-3}$	3.6 ± 2.0	$5.9 \times 10^{-3} \pm 3.3 \times 10^{-3}$
PFUnDA	−0.39 to 2.7 (5)	4.2 ± 0.2	$6.4 \times 10^{-3} \pm 3.2 \times 10^{-4}$	–	–
PFDoDA	−0.87 to 3.2 (7)	5.0 ± 4.6	$2.3 \times 10^{-3} \pm 2.1 \times 10^{-3}$	1.7	7.6×10^{-4}
HFOSA	6.24–6.52 (2)	$7.9 \times 10^{-5} \pm 5.5 \times 10^{-5}$	$4.3 \times 10^{-5} \pm 3.0 \times 10^{-5}$	$1.9 \times 10^{-4} \pm 1.5 \times 10^{-4}$	$1.9 \times 10^2 \pm 3.3 \times 10^2$

[a] (Henne and Fox, 1951; Brace, 1962; Ylinen et al., 1990; Igarashi and Yotsuyanagi, 1992; Moroi et al., 2001; Brooke et al., 2004; López-Fontán et al., 2005; Burns et al., 2008; Steinle-Darling and Reinhard, 2008; Goss, 2008a; Goss, 2008b; Rayne et al., 2009a; Rayne et al., 2009b; US Department of Health and Human Services, 2009; Wang et al., 2011).

(g) on the filter after filtration. $c_{dissolved}$(total) is the concentration of all species measured in the dissolved phase in ng L^{-1}. Here the units used are such that R_d is dimensionless or has the unit $cm^{-3}\ g^{-1}$. To account for dependence of the partitioning of PFC(A)s and PFS(A)s to organic carbon in the solids as shown by different studies (Higgins and Luthy, 2006; Ahrens et al., 2010) R_d was normalized to the organic carbon fraction by multiplying R_d with 100 divided by the percentage of organic carbon to obtain R_{OC}. If only the acid is considered to partition into the organic phase, Q_{OC} is calculated by inserting $c_{dissolved}$(HA) instead of $c_{dissolved}$(total) in Eq. (2) (Schwarzenbach et al., 2003). For each analyte two Q_{OC} have been calculated, representing the results when the minimum and maximum reported pK_a values are used to calculate $c_{dissolved}$(HA) (see Section 2.6).

Recently it was shown that under environmental conditions the role of the partitioning of anionic base is negligible and observed distributions are calculable from the properties of HA alone (Webster and Ellis, 2011). Thus, in the present field-based study, the physicochemical properties of HA are used for calculating the single species concentration ratios.

2.8. Calculations of air–water partitioning

According to theory, the vapor pressure of the anionic conjugate base of PFOA, PFO^-, and also of other anionic conjugate bases of PFCAs and PFSAs is zero (Schwarzenbach et al., 2003; Barton et al., 2007). Hence it is reasonable to assume that if PFCAs or PFSAs are detected in the gas phase of the atmosphere it must be the neutral species.

Therefore single species Q_{AW} refer to the acids (Eq. (3)). In the present study we refer to the field-derived concentrations ratios using the constant Q_{AW} to take into account that the air–water system at the WWTP may not be in equilibrium.

$$Q_{AW} = \frac{c_{air}}{c_{dissolved}(HA)} \quad (3)$$

c_{air} is the concentration in the gas phase of the atmosphere and $c_{dissolved}$(HA) is the concentration of the acids in the dissolved phase in water. $c_{dissolved}$(HA) was calculated in the same way as for Q_{OC} by inserting the minimum and maximum in the range of pK_a values in Eq. (1). Therefore two concentration ratios were obtained for each analyte.

3. Results and discussion

3.1. Quality control

IDLs for water samples ranged from 0.01 to 0.5 ng L^{-1} in the dissolved phase and 0.001–0.3 ng L^{-1} in the particle phase (Table SM5). Dissolved phase blank concentrations were below the IDLs, except for PFB(A) (0.3 ng L^{-1}). Particle phase blank concentrations ranged from 0.01 to 1.4 ng L^{-1} (Table SM6). Average recovery rates of mass-labeled internal standards in water samples were 77% in the dissolved phase and 79% in the particle phase (Table SM7).

3.2. Concentrations in the atmosphere

Gas phase concentrations of PFCAs, PFSAs and HFOSA ranged from <IDL to 50 pg m^{-3} at the aeration tank and from <IDL to 25 pg m^{-3} at the secondary clarifier (Table SM8) (Vierke et al., 2011). PFBSA, PFDSA and PFTDA were not detected in any samples (Vierke et al., 2011). Arp and Goss (2008) have shown that gas-phase PFCAs can adsorb to filters, i.e. GFFs as used in the present study. However, by the comparison of different sampling techniques in our previous study we were able to conclude that this artifact has a relatively minor influence on the gas-phase concentrations in the current study (Vierke et al., 2011).

3.3. Concentrations in water

Of the target compounds, PFOS(A) had the highest concentrations in the dissolved phase (1100 ± 170 ng L^{-1} at the primary clarifier, 1800 ± 590 ng L^{-1} at the aeration tank and 680 ± 110 ng L^{-1} at the secondary clarifier, respectively; n = 3 for each). The average of the sum of all other PFC(A)s and PFS(A)s in the dissolved phase was 100 ± 15 ng L^{-1} at the primary clarifier, 140 ± 40 ng L^{-1} at the aeration tank and 130 ± 20 ng L^{-1} at the secondary clarifier (n = 3 for each) (Tables SM9 and SM10 for concentrations of acids). The concentrations are not significantly different (p = 0.1) and demonstrate general uniformity in dissolved-phase concentrations throughout the WWTP. PFDS(A) was not detected in the dissolved phase of the primary and secondary clarifier and PFTD(A) was not detected in two samples of the secondary clarifier.

In the particle phase, PFOS(A) again exhibited the highest concentration (70 ± 14 ng L^{-1} (110 ± 40 ng g^{-1}), 2300 ± 220 ng L^{-1}

(402 ± 250 ng g^{-1}) and 22 ± 10 ng L^{-1} (56 ± 39 ng g^{-1}) at the primary clarifier, aeration tank and secondary clarifier, respectively; n = 3 for each). The sum of all other PFC(A)s and PFS(A)s in the particle phase was 6.2 ± 2.3 ng L^{-1} (11 ± 6.9 ng g^{-1}) at the primary clarifier, 170 ± 20 ng L^{-1} (27 ± 12 ng g^{-1}) at the aeration tank and 2.1 ± 1.1 ng L^{-1} (6.3 ± 6.9 ng g^{-1}) at the secondary clarifier (n = 3 respectively) (Table SM11). Due to high tap water blank concentrations for the particle phase, the concentrations of (H)FOSA, PFHp(A), PFO(A) and PFTD(A) at the primary and secondary clarifier were not reported. PFBS(A) was detected in two of three samples at the secondary clarifier and was not detected in all other samples. Higher concentrations in the aeration tank compared to the clarifiers is caused by the mixing of this tank and the expression of concentrations in weight per volume of water (ng L^{-1}). In the clarifiers, particles settle to the bottom of the tanks with few particles near the water surface (where the water samples are collected).

The degradation of precursors could have an influence on concentrations and distribution of PFC(A)s and PFS(A)s in WWTPs. Previous studies have raised the possibility that particularly during the aeration process, polyfluorinated chemicals are degraded to form PFC(A)s and PFS(A)s (Sinclair and Kannan, 2006; Loganathan et al., 2007). For example biodegradation of fluoroteleomeralcohols (FTOHs) was shown to lead to the formation of PFCAs (Dinglasen et al., 2004). If such degradation is occurring in the WWTP in the present study, it may explain the higher concentrations of PFCAs and PFSAs in the aeration tank water compared to the primary clarifier, but not in the secondary clarifier. Concentrations of precursors, i.e. FTOHs, were shown to be elevated in the atmosphere above the aeration tank compared to sites outside of the WWTP (Ahrens et al., 2011; Vierke et al., 2011) indicating their abundance in the water phase.

3.4. Particle-dissolved partitioning in water

The measured particle phase organic carbon percentages were 19% at the primary clarifier, 0.27% at the aeration tank and 2.7% at the secondary clarifier. Log R_d for PFS(A)s and PFC(A)s were highest for the aeration tank compared to the clarifiers (Fig. 1, Tables SM12 and SM13 for details, also for R_{OC} and Q_{OC}). The greatly enhanced particle-dissolved concentration ratios for PFS(A)s and PFC(A)s in the aeration tank (more than one order of magnitude higher compared to the clarifiers) is not explained by the OC-contents of the particles. Differences in particles sampled at the different tanks may contribute to differences in the concentration ratios. For instance, as discussed previously the clarifiers are relatively calm and larger particles settle to the bottom. The samples collected near the surface of the water will therefore reflect the finer and more buoyant particles; whereas aeration tanks are turbulent with a well-mixed particle phase.

Log R_d values increased for PFS(A)s with increasing chain length with approximately one log unit per C-atom. For PFC(A)s this trend was not as obvious but still the overall trend of log R_d values with chain length was increasing, except for PFB(A). Compared to log R_d values for C_{6-9} PFC(A)s, the log R_d for PFB(A) was remarkably high (i.e. 0.4). This could be due to differences in partitioning mechanisms, however, more data are necessary to explore this further. To the best of our knowledge this is the first study quantifying sorption of PFB(A). Higgins and Luthy (2006) also observed an increasing trend of K_{OC} with increasing chain length for PFOA to PFUnDA. However, other studies did not observe such a clear trend for PFHxA to PFUnDA (Kwadijk et al., 2010; Li et al., 2011).

For PFOS(A) R_{OC} (Table SM12) estimates at the secondary and primary clarifier were 0.2–0.7 log units higher compared to the carboxylic acid with the same fluorinated chain length, i.e. PFN(A). Similar results were observed for PFDS(A) and PFUnD(A) where concentration ratios at the aeration tank were one log unit higher for PFDS(A). Higher partition coefficients for PFS(A)s compared to PFC(A)s (of about 0.2 log units) have also been observed in other studies (Higgins and Luthy, 2006).

Higgins and Luthy (2006) performed sorption experiments with different freshwater sediments under equilibrium conditions in centrifuge tubes. They report K_{OC} for PFOS(A), PFDS(A), PFO(A), PFN(A), PFD(A) and PFUnD(A) (Table SM14), which in most cases are in the same range as the results from the primary and secondary clarifier. The agreement indicates that the particle–water partitioning at the clarifiers is at or near equilibrium. R_{OC} from the aeration tank are higher compared to K_{OC} from the laboratory study (Higgins and Luthy, 2006). K_d from another sorption study using a batch set-up under laboratory conditions are lower for all PFCAs compared to the results from the WWTP (Enevoldsen and Juhler, 2010) (Table SM14). For PFBS(A) and PFOS(A) measured at the secondary clarifiers, R_d shows good agreement with K_d from the batch study by Enevoldsen and Juhler (2010). As properties of the solid material can have an influence on sorption, a comparison with results obtained with sludge from a WWTP is most

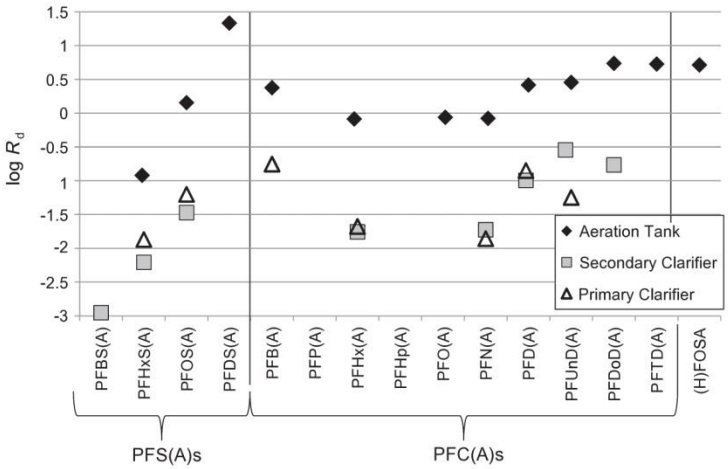


Fig. 1. Particle-dissolved concentration ratios (R_d) for PFS(A)s, PFC(A)s and (H)FOSA at the aeration tank, the secondary and primary clarifiers. Missing data are due to poor detection in either dissolved phase, particle phase or both.

appropriate. Sorption coefficients under equilibrium conditions for sludge are up to now, to the best of our knowledge, reported for PFOS(A) only (Ochoa-Herrera and Sierra-Alvarez, 2008). Log K_d ranged from 1.9 to 2.4 for anaerobic digested sewage sludge and anaerobic granular sludge (Ochoa-Herrera and Sierra-Alvarez, 2008), which is in very good agreement with R_d for PFOS(A) from our study (log R_d = 1.9–2.3) and provides further support that the equilibrium conditions were achieved at the WWTP.

Furthermore, Yu et al. (2009) report log K_d values for PFO(A) ranging from 2.3 to 2.7 $cm^3\ g^{-1}$ in two sewage treatment plants (Table SM14). These results agree with log R_d = 2.1 $cm^3\ g^{-1}$ (log R_d = −0.5) observed for PFO(A) in the aeration tank during the present study. For PFOS(A), Yu et al. (2009) reported a log K_d = 2.9–3.4 $cm^3\ g^{-1}$, which is slightly higher compared to the results for PFOS(A) from the present study at the various tanks (log R_d = 2.0 $cm^3\ g^{-1}$ (log R_d = −1.2), 2.4 $cm^3\ g^{-1}$ (log R_d = 0.15) and 1.9 $cm^3\ g^{-1}$ (log R_d = −1.5) at the primary clarifier, aeration tank and secondary clarifier, respectively). Arvaniti et al. (2012) calculated K_d values for different samples from two WWTPs whereby results from mixed liquor samples from aeration tanks might be most appropriate for comparison with results of the present study. R_d values from the aeration tank were in the lower range of K_d values reported by Arvaniti et al. (log K_d = 2.5–4.0 $cm^3\ g^{-1}$ for PFHx(A) to PFUnD(A) and log K_d = 2.0–4.0 $cm^3\ g^{-1}$ for PFHxS(A) and PFOS(A) in mixed liquor Arvaniti et al., 2012). Also Arvaniti et al. (2012) observed variations in partition coefficients for different sludge samples.

The preceding discussion of particle-dissolved partitioning of PFCAs and PFSAs and the discussion in the literature do not address the identity of the species sorbed to the particles. In addition, the present study reports the concentration ratio of the neutral species, Q_{OC} (Table SM13). Q_{OC} for PFSAs showed an increasing trend with chain length, whereas the trend for Q_{OC} of PFCAs was not as clear.

3.5. Air–water partitioning

Average calculated Q_{AW} values for PFCAs, PFSAs and HFOSA are shown in Table 2 and Fig. 2, and complete results are given in the Table SM15. Missing data for some analytes, i.e. PFBSA, PFDSA and PFTDA (and PFUnDA at the secondary clarifier), should not be interpreted as an inability of these chemicals to partition between air and water but rather as a limitation of the detection system. We note that differences in air temperature (7–12 °C) during the sampling campaign were too small to observe any correlations between partitioning behavior and temperature.

The wide variation in the calculated Q_{AW} (Table 2 and Fig. 2) are attributed to the wide range of pK_a values applied in the calculations, which can vary by up to two orders of magnitude. Another source of uncertainty is offsets or differences in the time and duration of water and air sampling. However, the variability associated with this aspect is expected to be much smaller and probably within a factor of about two. Water concentrations in the samples collected within this study shows variations of usually much less than a factor of two. Results from air samples collected above the tanks were also consistent with time and indicate that underlying water concentrations do not vary considerably over time (Vierke et al., 2011).

3.5.1. Comparison with measured air–water equilibrium partition coefficient (K_{AW}) for PFOA

Measured K_{AW} values for PFOA have been reported from two laboratory studies. Li et al. (2007) measured the air–water partitioning of different organic acids, including PFOA, by inducing evaporation from a water surface. Kutsuna and Hori (2008) used an inter-gas stripping method with a helicate plate to investigate air–water partitioning of PFOA.

The reported K_{AW} values for PFOA are 0.001 (Li et al., 2007) and 0.004 (assuming a pK_a of 2.8) and 0.007 (assuming a pK_a of 1.3) (Kutsuna and Hori, 2008). These are consistent measurements that vary by less than an order of magnitude. In the experimental setup used by Li et al. (2007), the pH was adjusted to 0.6 whereas Kutsuna and Hori (2008) operated at a pH < 0.6. Low pH ensures that most of the PFO(A) is in the protonated, i.e. PFOA, form.

The Q_{AW} from both the aeration and clarifier tanks most closely matches the laboratory K_{AW} measurements when the maximum reported pK_a is used (Fig. 2, Tables SM15 and SM16) but are three and four orders of magnitude higher when the minimum reported pK_a is used. Precursor degradation into PFO(A) in the tank at a suf-

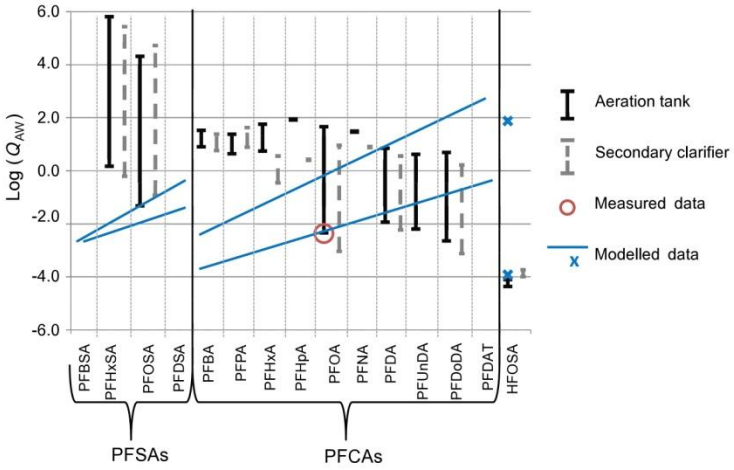


Fig. 2. Log Q_{AW} for PFSAs, PFCAs and HFOSA calculated with minimum (top of range bars) and maximum (bottom of range bars) reported pK_a values, for the aeration tank (solid black vertical bars) and the secondary clarifier (dashed grey vertical bars). The average of the measured K_{AW} values for PFOA reported in the literature are indicated with a circle (Li et al., 2007; Kutsuna and Hori, 2008) and solid blue lines indicate minimum and maximum reported K_{AW} from model predictions (for HFOSA, model values are indicated with an ×) (Arp et al., 2006; Armitage et al., 2009; Rayne and Forest, 2009a; Rayne and Forest, 2009b; Wang et al., 2011). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ficient rate to impact the relative air–water concentrations would result in $Q_{AW} < K_{AW}$. As this has not been observed for any of the calculated Q_{AW} *in situ* production of PFOA must be occurring much more slowly than the rate of approach to equilibrium (i.e. partitioning kinetics) between the aqueous and gas phases. A $Q_{AW} > K_{AW}$ could occur if PFOA is actively transported out of the water into the air via spray generation at the aeration tank, in exceedance of its equilibrium concentration. In other words, if passive diffusion of the acid is not the only transport process occurring. At the clarifier tank where the water surface is calm, no process is known to exist that could explain $Q_{AW} > K_{AW}$. It suggests that the upper range of reported pK_a best represents actual conditions.

3.5.2. Dependence of Q_{AW} with chain length

The reported estimated pK_a values for PFHpA and PFNA are between three and four log units lower than highest pK_a values reported for PFOA. If a pK_a of 2.9 (estimated for PFOA; Wang et al., 2011) is applied to all three compounds as the highest pK_a, the recalculated Q_{AW} values for PFHpA, PFNA and PFOA imply for PFCAs an overall tendency of decreasing Q_{AW} with increasing chain length. Similarly, for the PFSAs, calculations always give a lower Q_{AW} for PFOSA than for PFHxSA (i.e. decreasing Q_{AW} with increasing chain length). However, when the minimum reported values for the pK_a of the PFCAs is applied, the results give Q_{AW} values that are all within two orders of magnitude. This variation in Q_{AW} is much less than the previous prediction of approximately 0.5 log units per CF_2 unit (Arp et al., 2006).

The K_{AW} is proportional to the vapor pressure of a chemical divided by its aqueous solubility. For the longer chain PFCAs, Kaiser et al. (2005) measured a decreasing vapor pressure with increasing chain length. Similarly, a decreasing aqueous solubility with increasing chain length has been predicted (Rayne and Forest, 2009b). Because both terms decrease with increasing chain length, it is the relative rate of decrease with chain length that will determine whether the K_{AW} will decrease or increase with chain length. Wang et al. (2011) suggested that the molecular volume of a chemical influences the free energy cost of cavity formation. A longer chain length results in a higher molar volume and raises the energy costs for cavity formation in the aqueous phase, whereas energy cost is lower for the gaseous phase. Therefore partitioning to the gaseous phase is expected to increases with chain length, as this results in a lower energy requirement. Air–water partitioning measurements are available for FTOHs and show conflicting results in terms of how K_{AW} changes with increasing chain length. A study, which considered both measured values and estimated values, reports an increasing trend for K_{AW} with increasing chain length (Goss et al., 2006). Another experimental study showed a decreasing trend of K_{AW} with increasing chain length for FTOHs (Lei et al., 2004). The latest laboratory studies on air–water partitioning for FTOHs shows again a decrease in K_{AW} with chain length for 6:2 and 8:2 FTOH, which is explained by the change in conformation of the molecules with chain length (Wu and Chang, 2011). Arp et al. (2006) showed that the formation of different conformations due to intramolecular electrostatic interaction have an influence on partitioning behavior of highly fluorinated compounds compared to stretched confirmations. Intramolecular interactions also influence the pK_a values. Rayne et al. (2009b) reported an increasing pK_a with increasing chain length (>C_5) for PFCAs, which was explained by formation of cyclic structures by intramolecular hydrogen bonding between the carboxylic group and the terminal CF_3-group. This increasing pK_a with increasing chain length would also have an influence on the trend of Q_{AW} with chain length. However, the exact influence of the varying chain length of PFCAs and PFSAs on the K_{AW} is still under discussion (Arp et al., 2006; Wang et al., 2011).

When considering literature data for homolog series of other compound classes, i.e. chloroalkanes, chloroalkenes, bromoalkanes, iodoalkanes and "mixed halides", there is also no definite trend of increasing or decreasing Henrýs Law values with chain length (Mackay et al., 2006).

4. Conclusions

The present study delivers the first field-derived air–water concentration ratio (Q_{AW}) for PFCAs, PFSAs and HFOSA from *in situ* measurements at a WWTP. These values agree well with measured K_{AW} for PFOA from laboratory experiments. There remains, however, a need for reliable pK_a values that can be applied to assess the environmental partitioning for PFCAs, PFSAs and HFOSA. These measurements provide insight to the environmental partitioning and fate of these chemicals in air–water systems which is key to predicting their long-range transport, multi-media distribution and long-term environmental fate.

In situ measurement at the WWTP were also used to investigate partitioning between the particle and dissolved phase for PFC(A)s, PFS(A)s and (H)FOSA. The results agree well with data reported in the literature.

The relatively good agreement between the results from this study and reported partition coefficients from laboratory studies suggests that despite the dynamic nature of the WWTP, equilibrium partitioning is approached between the various phases that were investigated (i.e. air, water and particles).

The use of a WWTP for investigating multimedia partitioning of PFCAs and PFSAs in a real environment is advantageous compared to lab-based studies in that some of the experimental artifacts (e.g. sorption effects) can be avoided. The elevated concentrations at WWTPs also simplify analytical/detection issues compared to measurements in natural environments. The higher concentration in air at the WWTP are also an advantage to overcoming potential sampling artifacts and blank issues for gas-phase samples (Vierke et al., 2011). Lastly, the study revealed several sources of uncertainty that could be improved upon in future investigations. For instance, it may be advantageous to coordinate air and water sampling to minimize the affect of fluctuating concentrations of target compounds in these media. These fluctuations could be better quantified with additional sample collection. However, the greatest source of uncertainty is in the reported pK_a values. This uncertainty needs to be resolved by improved experimental measurement techniques.

Disclaimer

This paper does not necessarily reflect the opinion or the policies of the German Federal Environment Agency.

Acknowledgements

The authors are grateful for scholarship funding support for E.M. Webster received from the Natural Science and Engineering Research Council of Canada, from Trent University, and from the Edwin and Irene Curtin scholarship fund.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.02.067.

References

Ahrens, L., 2011. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurence and fate. J. Environ. Monitor. 13, 20–31.

Ahrens, L., Shoeib, M., Harner, T., Lee, S.C., Guo, R., Reiner, E., 2011. Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. Environ. Sci. Technol. 45, 8098–8105.

Ahrens, L., Taniyasu, S., Yeung, L.W., Yamashita, N., Lam, P.K., Ebinghaus, R., 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 79, 266–272.

Armitage, J.M., Macleod, M., Cousins, I.T., 2009. Response to comment on comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources. Environ. Sci. Technol. 43, 7153–7154.

Arp, H.P.H., Goss, K.-U., 2008. Irreversible sorption of trace concentrations of perfluorocarboxylic acids to fiber filters used for air sampling. Atmos. Environ. 42, 6869–6872.

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

Arvaniti, O.S., Ventouro, E.I., Stasinakis, A.S., Thomaidis, N.S., 2012. Occurrence of different classes of perfluorinated compounds in greek wastewater treatment plants and determination of their solid–water distribution coefficients. J. Hazard. Mater. 239–240, 24–31.

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

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

Brooke, D., Footitt, A., Nwaogu, T.A., 2004. Environmental Risk Evaluation Report: Perfluorooctanesulphonate (PFOS). Building Research Establishment Ltd., Risk and Policy Analysts Ltd., Watford, Norfolk.

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

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

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

Enevoldsen, R., Juhler, R.K., 2010. Perfluorinated compounds (PFCs) in groundwater and aqueous soil extracts: using inline SPE-LC-MS/MS for screening and sorption characterization of perfluorooctane sulphonate and related compounds. Anal. Bioanal. Chem. 398, 1161–1172.

Goss, K.-U., 2008a. The pKa values of PFOA and other highly fluorinated carboxylic acids. Environ. Sci. Technol. 42, 456–458.

Goss, K.-U., 2008b. Additions and correction 2008, 42, 456–458. Environ. Sci. Technol. 42, 5032.

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

Henne, A.L., Fox, C.J., 1951. Ionization constants of fluorinated acids. J. Am. Chem. Soc. 73, 2323–2325.

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

Houde, M., Martin, J.W., Letcher, R.J., Solomon, K.R., Muir, D.C.G., 2006. Biological monitoring of polyfluoroalkyl substances: a review. Environ. Sci. Technol. 40, 3463–3473.

Igarashi, S., Yotsuyanagi, T., 1992. Homogeneous liquid-liquid extraction by pH dependent phase separation with a fluorocarbon ionic surfactant and its application to the preconcentration of porphyrin compounds. Mikrochim. Acta 106, 37–44.

Jafvert, C.T., Westall, J.C., Grieder, E., Schwarzenbach, R.P., 1990. Distribution of hydrophobic ionogenic organic compounds between octanol and water: organic acids. Environ. Sci. Technol. 24, 1795–1796.

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

Kutsuna, S., Hori, H.H., 2008. Experimental determination of Henry's law constant of perfluorooctanoic acid (PFOA) at 298K by means of an inert-gas stripping method with a helical plate. Atmos. Environ. 42, 8883–8892.

Kwadijk, C.J.A.F., Korytar, P., Koelmans, A.A., 2010. Distribution of perfluorinated compounds in aquatic systems in The Netherlands. Environ. Sci. Technol. 44, 3746–3751.

Labadie, P., Chevreuile, M., 2011. Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Orge River (nearby Paris, France). Environ. Pollut. 159, 391–397.

Lei, Y.D., Wania, F., Mathers, D., Mabury, S.A., 2004. Determination of vapor pressures, octanol-air, and water-air partitioning coefficients for polyfluorinated sulfonamide, sulfonamidoethanols, and telomer alcohols. J. Chem. Eng. Data 49, 1013–1022.

Li, F., Sun, H., Hao, Z., He, N., Zhao, L., Zhang, T., Sun, T., 2011. Perfluorinated compounds in Haihe River and dagu drainage canal in Tianjin, China. Chemosphere 84, 265–271.

Li, H., Ellis, D.A., Mackay, D., 2007. Measurement of low air–water partition coefficients of organic acids by evaporation from a water surface. J. Chem. Eng. Data 52, 1580–1584.

Loganathan, B.G., Sajwan, K.S., Sinclair, E., Senthil Kumar, K., Kannan, K., 2007. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in kentucky and georgia. Water Res. 41, 4611–4620.

López-Fontán, J.L., Sarmiento, F., Schulz, P.C., 2005. The aggregation of sodium perfluorooctanoate in water. Colloid Polym Sci 283, 862–871.

Mackay, D., Shiu, W.Y., Ma, K.-C., Lee, S.C., 2006. Handbook for Physical Physical–Chemical Properties and Environmental Fate for Organic Chemicals. CRC Press, Boca Raton.

Moroi, Y., Yano, H., Shibata, S., Yonemitsu, T., 2001. Determination of acidity constants of perfluoroalkanoic acids. Bull. Chem. Soc. Jpn. 74, 667–672.

Ochoa-Herrera, V., Sierra-Alvarez, R., 2008. Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. Chemosphere 72, 1588–1593.

Pan, G., Jia, C., Zhao, D., You, C., Chen, H., Jiang, G., 2009. Effect of cationic and anionic surfactants on the sorption and desorption of perfluorooctane sulfonate (PFOS) on natural sediments. Environ. Pollut. 157, 325–330.

Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. Environ. Sci. Technol. 40, 32–44.

Rayne, S. K.J.F., Forest, K., Friesen, K.J., 2009a. Extending the semi-empirical PM6 method for carbon oxyacid pKa prediction to sulfonic acids: Application towards congener-specific estimates for the environmentally and toxicologically relevant C1 through C8 perfluoroalkyl derivatives. hdl.handle.net/10101/npre.2009.2922.1 (14.04.11).

Rayne, S., Forest, K., 2009a. Comment on comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources. Environ. Sci. Technol. 43, 7155–7156.

Rayne, S., Forest, K., 2009b. Perfluoroalkyl sulfonic and carboxylic acids: a critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. J. Environ. Sci. Heal. A 44, 1145–1199.

Rayne, S., Forest, K., Friesen, K.J., 2009b. Computational approches may underestimated pK_a values of longer-chain perfluorinated carboxylic acids: implication for assessing environmental and biological effects. J. Environ. Sci. Heal. A 44, 317–326.

Schwarzenbach, R., Gschwend, P.M., Imboden, D.M., 2003. Environmental Organic Chemistry. Wiley-Interscience, Hoboken, New Jersey.

Sinclair, E., Kannan, K., 2006. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environ. Sci. Technol. 40, 1408–1414.

Steinle-Darling, E., Reinhard, M., 2008. Nanofiltration for trace organic contaminant removal: structure, solution, and membrane fouling effects on the rejection of perfluorochemicals. Environ. Sci. Technol. 42, 5292–5297.

US Department of Health and Human Services, 2009. Draft Toxicological Profile for Perfluoroalkyls. Agency for Toxic Substances and Disease Registry, Atlanta.

Vierke, L., Ahrens, L., Shoeib, M., Reiner, E.J., Guo, R., Palm, W.-U., Ebinghaus, R., Harner, T., 2011. Air concentrations and particle-gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant. Environ. Chem. 8, 363–371.

Wang, Z., Macleod, M., Cousins, I.T., Scheringer, M., Hungerbühler, K., 2011. Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs). Environ. Chem. 8, 389–398.

Webster, E.M., Ellis, D.A., 2011. Equilibrium modeling: a pathway to understanding observed perfluorocarboxylic and perfluorosulfonic acid behavior. Environ. Toxicol. Chem. 10, 2229–2236.

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

Wu, Y., Chang, V.W.-C., 2011. The effect of surface adsorption and molecular geometry on the determination of Henry's law constants for fluorotelomer alcohols. J. Chem. Eng. Data 56, 3442–3448.

Ylinen, M., Koji, A., Hanhijarvi, H., Peura, P., 1990. Disposition of perfluorooctanoic acid in the rat after single and subchronic administration. Bull. Environ. Contam. Toxicol. 44, 46–53.

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

Supplementary Material

In situ Air-Water and Particle-Water Partitioning of Perfluorocarboxylic acids, Perfluorosulfonic acids and Perfluorooctyl sulfonamide at a Wastewater Treatment Plant

Lena Vierke, Lutz Ahrens, Mahiba Shoeib, Wolf-Ulrich Palm, Eva M. Webster, David A. Ellis, Ralf Ebinghaus, Tom Harner

Tables

1. Chemicals

Methanol (LC-MS grade, OmniSolv >99.99%), water (OmniSolv) and ammonium acetate (min. 97%) were purchased from EMD. Anhydrous sodium sulfate were purchased from Fischer Scientific, Supelclean EnviCab from Supelco and glacial acetic acid (>99.7+%) from Alfa Aesar. The water (OmniSolv) was cleaned using Oasis WAX cartridges (Waters) to remove possible contaminations. Nitrogen was purchased from Linde.

Table SM 1 Target compounds with abbreviation, chemical formula, precursor and product ion, supplier, purity and internal standard (IS).

Analyte	Acronym	Chemical Formula	Precursor/ product ion	Supplier (purity)	IS
Perfluorooctane sulfonamide	HFOSA	$C_8F_{17}SO_2NH_2$	498/78	Wellington Laboratories (>98%)	$^{13}C_4$-PFOS
Perfluorobutane sulfonate	$PFBS^-$	$C_4F_9SO_2O$-	299/80	Wellington Laboratories (>98%)	$^{18}O_2$-PFHxS
Perfluorohexane sulfonate	$PFHxS^-$	$C_6F_{13}SO_2O^-$	399/80	Wellington Laboratories (>98%)	$^{18}O_2$-PFHxS
Perfluorooctane sufonate	$PFOS^-$	$C_8F_{17}SO_2O^-$	499/80	Aldrich (98%)	$^{13}C_4$-PFOS
Perfluorodecane sulfonate	$PFDS^-$	$C_{10}F_{21}SO_2O^-$	599/99	Wellington Laboratories (>98%)	$^{13}C_4$-PFOS
Perfluorobutanoate	PFB^-	$C_3F_7COO^-$	213/169	Wellington Laboratories (>98%)	$^{13}C_4$-PFBA
Perfluoropentanoate	PFP^-	$C_4F_9COO^-$	263/219	Wellington Laboratories (>98%)	$^{13}C_2$-PFHxA
Perfluorohexanoate	$PFHx^-$	$C_5F_{11}COO^-$	313/269	Wellington Laboratories (>98%)	$^{13}C_2$-PFHxA
Perfluorohepantoate	$PFHp^-$	$C_6F_{12}COO^-$	363/319	Aldrich (98%)	$^{13}C_4$-PFOA
Perfluorooctanoate	PFO^-	$C_7F_{15}COO^-$	413/369	Aldrich (98%)	$^{13}C_4$-PFOA
Perfluorononanoate	PFN^-	$C_8F_{17}COO^-$	463/419	Aldrich (98%)	$^{13}C_5$-PFNA
Perfluorodecanoate	PFD^-	$C_9F_{19}COO^-$	513/469	Aldrich (98%)	$^{13}C_2$-PFDA
Perfluoroundecanoate	$PFUnD^-$	$C_{10}F_{21}COO$-	563/519	Aldrich (98%)	$^{13}C_2$-PFUnDA
Perfluorododecanoate	$PFDoD^-$	$C_{11}F2_3COO^-$	613/569	Aldrich (98%)	$^{13}C_2$-PFDoA
Perfuorotetradecanoate	$PFTD^-$	$C_{13}F_{25}COO^-$	713/669	Aldrich (98%)	$^{13}C_2$-PFDoA

Table SM 2 Internal standards with abbreviation, chemical formula, precursor and product ion, supplier and purity.

Analyte	Acronym	Chemical formula	Precursor/ product ion	Supplier (purity)
Perfluoro-1-hexane-($^{18}O_2$) sulfonate	$^{18}O_2$-PFHxS$^-$	$C_6F_{13}S[^{18}O_2]O^-$	403/103	Wellington Laboratories (>98%)
Perfluoro-1-($^{13}C_4$)-octane sulfonate	$^{13}C_4$- PFOS$^-$	$C_4F_9[1,2,3,4\text{-}^{13}C_4]\text{-}F_8SO_2O^-$	503/99	Wellington Laboratories (>98%)
Perfluoro-n-($^{13}C_4$)-butanoate	$^{13}C_4$- PFB$^-$	$2,3,4\text{-}^{13}CF_7{}^{13}COO^-$	217/172	Wellington Laboratories (>98%)
Perfluoro-n-($^{13}C_4$)-octanoate	$^{13}C_4$-PFO$^-$	$C_4F_9[2,3,4\text{-}^{13}C_3]\text{-}F_6{}^{13}COO^-$	417/372	Wellington Laboratories (>98%)
Perfluoro-n-($^{13}C_5$)-nonanoate	$^{13}C_5$-PFN$^-$	$C_4F_9[2,3,4,5\text{-}^{13}C_4]\text{-}F_8{}^{13}COO^-$	468/423	Wellington Laboratories (>98%)
Perfluoro-n-($^{13}C_2$)-decanoate	$^{13}C_2$-PFD$^-$	$C_8F_{17}{}^{13}CF_2{}^{13}COO^-$	515/470	Wellington Laboratories (>98%)
Perfluoro-n-($^{13}C_2$)-undecanoate	$^{13}C_2$-PFUnD$^-$	$C_9F_{19}{}^{13}CF_2{}^{13}COO^-$	565/520	Wellington Laboratories (>98%)
Perfluoro-n-($^{13}C_2$)-dodecanoate	$^{13}C_2$-PFDo$^-$	$C_{10}F_{21}{}^{13}CF_2{}^{13}COO^-$	615/570	Wellington Laboratories (>98%)
Perfluoro-n-($^{13}C_2$)-hexanoate	$^{13}C_2$-PFHx$^-$	$C_4F_9{}^{13}CF_2{}^{13}COO^-$	315/270	Wellington Laboratories (>98%)
Perfluoro-1-($^{13}C_4$)-octane sulfonate	$^{13}C_8$-PFOS$^-$	$C_4F_9[1,2,3,4\text{-}^{13}C_4]\text{-}F_8SO_2O^-$	507/80	Wellington Laboratories (>98%)
Perfluoro-n-($^{13}C_4$)-octanoate	$^{13}C_8$-PFO$^-$	$C_4F_9[2,3,4\text{-}^{13}C_3]\text{-}F_6{}^{13}COO^-$	421/376	Wellington Laboratories (>98%)

2. Extraction and Instrumental Analysis

After sampling the GFFs and the PUF/XAD/PUF cartridges from air sampling were wrapped in aluminum foil and stored at 6 °C in a fridge until extraction. The bottles with the water samples were stored at -12 °C until extraction.

Extraction of PUF/XAD/PUF cartridges from air samples is described in Vierke et al. (Vierke et al., 2011). Briefly PUF/XAD/PUF cartridges were Soxhlet extracted using methanol for 10 – 14 h (note: this followed a first extraction with petroleum ether targeting fluorotelomer alcohols (FTOHs) and methyl and ethyl polyfluorinated sulfonamides and sulfonamidoethanols, which are not among the target chemicals in the present study). Prior to extraction, mass-labeled standards (100 µL of 100 pg μL^{-1}) were spiked on the cartridges. The extracts were concentrated to 1 mL by rotary evaporation and nitrogen blow down. For clean-up 50 µL acetic acid and 0.35 mg EnviCarb were added to the samples. The sample was then mixed using a vortex mixer

and centrifuged to separate the aqueous layer. Finally, the cleaned extract (organic layer) was transferred into PP-vials and the injection standards $^{13}C_8$-PFOS$^-$ and $^{13}C_8$-PFO$^-$ and OmniSolv® water (EMD, resulting in a water content of 49 %) were added.

Water samples were first filtered by loading 140 ml to 160 mL sample on glass microfiber filters (mGFFs; Whatmann, 4.7 cm diameter, baked at 250 °C for 12 h and weighed). The loaded mGFFs were dried at room temperature, weighed and then spiked with 100 µL PFC$^-$/PFS$^-$ internal standard solution (500 pg µL^{-1}). The mGFFs were inserted in PP-tubes and extracted by sonnication using dichloromethane (3 times for 20 min. ∑36 mL) and then methanol (5 times for 20 min. ∑60 mL). Extracts were concentrated by rotary evaporation (iso-octane was added as keeper solvent to dichloromethane extracts) and nitrogen blow down. Sodium sulfate was used for cleanup of the iso-octane fraction and a part of this fraction was combined with the methanol extract prior to concentration. For the methanol fraction, cleanup was performed using EnviCarb in the same way as for air samples.

The dissolved phase, obtained after filtration of water samples, was spiked with 100 µL PFC$^-$ and PFS$^-$ mass-labeled internal standard solution (500 pg µL^{-1}) and was extracted using solid phase extraction (SPE) with a SPE-manifold (Supelco) and WAX-cartridges (OASIS WAX 6 cc 150 mg 30 µm) as described by Ahrens et al. (Ahrens et al., 2010). Briefly, WAX-cartridges were conditioned using 5 mL methanol and 4 mL water (OmniSolv®). Water was precleaned using WAX-cartridges. 100 mL filtered water samples were run over the cartridges at an approximate rate of 1 drop per second. The cartridges were washed afterwards with 5 mL of 0.1 % ammonium hydroxide (NH_4OH) in OmniSolv® water. The target compounds were eluted with 5 mL methanol and 5 mL of 0.1 % NH_4OH in methanol. The solvents were collected in PP-test tubes and concentrated by nitrogen blow down to 1 mL. 200 µL of the sample was transferred into a PP-vial for LC-MS/MS analysis and 10 µL injection standard (400 pg µL^{-1} of $^{13}C_8$PFOS$^-$ $^{13}C_8$PFO$^-$) was added. Samples were diluted with OmniSolv® water (49 %) before injection.

Instrumental analysis was performed using high pressure liquid chromatography (Agilent, Mississauga, ON, Canada, 1100 Series) tandem mass spectrometry (HPLC-MS/MS) (Applied Biosystems, Toronto, ON, Canada, 4000 QTRAP) in electrospray negative ionisation mode at atmospheric pressure. For separation, a pre-column (C_8, 4-mm length, 2-mm diameter, Phenomenex, Torrance, CA, USA) and a Luna 3µ column (C_8 (2), 50-mm length, 2-mm diameter, Phenomenex, Torrance, CA, USA) was used. Methanol and OmniSolv® water, each

with 10-mM ammonium acetate, were used as mobile phase. The flow was set to 0.25 µL min^{-1} and the gradient is given in Table S3. The injection volume was 25 µL.

Organic carbon was determined in one mGFF from each water sampling site using Thermal Optical Transmission box (Sunset Laboratory, Tigard, OR, USA).

Table SM 3 Eluent gradient for LC-MS/MS.

Time (min)	H_2O + 10mM NH_4OAc (%)	MeOH + 10mM NH_4OAc (%)
0.01	50	50
1.0	45	55
2.0	40	60
3.0	25	75
4.0	20	80
5.0	15	85
10.0	15	85
10.1	5	95
15.0	5	95
15.1	25	75
15.6	50	50
20.0	50	50

3. pK_a values for PFCAs, PFSAs and HFOSA from the literature

The pK_a value is influencing the dissolved phase concentrations of the neutral acids of PFCAs, PFSAs and HFOSA. In the literature different pK_a values for linear PFCAs and PFSAs are reported and discussed (see table below). To the best of our knowledge only six experimental determinations of pK_a values are available, most of them for PFOA.

The pK_a of 1.3 for PFOA was determined by pH measurements (López-Fontán et al., 2005). Potential titration done by Igarashi et al. (1992) resulted in a pK_a of 1.01 for PFOA. Also a pK_a of 2.8 (Brace, 1962) and 3.8 (Burns et al., 2008) was reported for PFOA determined by experimental set-ups. Kutsuna and Hori (2008) conclude that a pK_a of 1.3 for PFOA is most accurately based on their experimental finding, which focused on the determination of the Henry's law constant. Moroi et al. (2001) used different method to experimentally determine pK_a values for PFCAs with one to five (PFHxA) and nine (PFDA) to eleven (PFUnDA) C-atoms. pK_a values for longer chain PFCAs were determined with a solubility method. These results might not be directly comparable to the results for short chain PFCAs because the pK_a is for an

oligomeric instead of monomeric acid (Moroi et al., 2001). They observed increasing pK_a values from one to three C-atoms followed by a decrease from three to five C-atoms. No explanation could be delivered for this observation. Furthermore Rayne et al. (2009) summarized experimental pK_a values for different PFCAs. Together with results from Morio et al. (2001) they stated an increasing pK_a with increasing chain length (from higher then C_5 on). Rayne and Forest (2009b) suggest the formation of cyclic structures which can explain increasing pK_a with increasing chain length. The undissociated acid will be stabilized because of intramolecular hydrogen bonding between the carboxylic group and the terminal CF_3-group. But this would only be possible for longer chain PFCAs (i.e. >C_5).

The experimental determination of pK_a values for PFOA and other PFCAs is difficult because of their surface active properties (Goss, 2008b). Goss (2008a) recommended a pK_a of 0 for PFOA based on analogy considerations. Furthermore models were used to estimate pK_a values ranging from -0.2 to 2.9 for PFOA. The software SPARC is considered to be most appropriate for estimation (Goss, 2008b).

Based on comparison with measured values, Rayne et al. (2009) argued that computer models underestimate pK_a values. The lack of considering conformations might play a role in the underestimation (Wang et al., 2011). Exceptions to this observation are pK_a values for C_4 to C_6 PFCAs from Moroi et al. (2001).

S. 8

Table SM 4 pK_a values reported in the literature.

Reference	(Brace, 1962)	(Goss, 2008b, Goss, 2008a)			(Burns et al., 2008)	(Ylinen et al., 1990)	(Igarashi and Yotsuyanagi, 1992)	(López-Fontán et al., 2005)	(Henne and Fox, 1951)	(Rayne et al., 2009)	(Rayne et al., 20092009)	(U.S. Department of Health and Human Services, 20092009)	(Steinle-Darling and Reinhard, 2008)	(Moroi et al., 2001)	(Brooke et al., 2004)	(Wang et al., 2011)
Method	measured in 50/50 v/v ethanol/water	SPARC	COSMO-RS	estimation	experimental with aggregation, experimental without	no details provided	experimental, potentiometric titration	Experimental, pH measurements	Experimental, limiting conducting	estimations PM6	estimations PM6	for PFOA from Kissa, others SPARC	SPARC	experimental Titration and solubility (for longer chain)	No details mentioned	COSMOTHERM
PFBSA											-5.5	0.14	0.14			-3.94
PFHxSA											-5.5	0.14	0.14			-3.45
PFOSA											-5.5	0.14	0.14		-3.27	-3.41
PFDSA													0.14			-2.86
PFBA		0.4							0.2	0.1		0.08		0.32		0.85
PFPA										-0.1			-0.1	0.64		0.81
PFHxA										-0.1			-0.16	0.85		0.84
PFHpA												-0.15	-0.19			0.82
PFOA	2.8	-0.1	0.7	0	2.3 3.8	2.5	1.01	1.3		-0.1		2.8	-0.2			2.90 0.90
PFNA												-0.17	-0.21			0.82
PFDA										-0.1		-0.17	-0.21	2.58		
PFUnDA										-0.1		-0.17	-0.21	2.61		
PFDoDA		-0.2								-0.1		-0.17	-0.21	3.13		
PFTDA													-0.21			
HFOSA												6.24	6.52			

4. Instrumental detection limits, blank concentrations and recoveries

Table SM 5 Instrumental detection limit (IDL) for water samples (in ng). Calculated by extrapolating instrument response in a tap water sample to a concentration that would give a S/N value of three. IDL in ng/L is derived based on a sample volume of 100 ml for the dissolved phase and an average sample volume of 279 ml for the particle phase.

	Dissolved phase		Particle phase	
	IDL (ng)	IDL (ng L^{-1})	IDL (ng)	IDL (ng L^{-1})
PFBS(A)	0.03	0.29	0.01	0.02
PFHxS(A)	0.002	0.02	0.0004	0.002
PFOS(A)	0.01	0.09	0.001	0.002
PFDS(A)	0.004	0.04	0.003	0.01
(H)FOSA	0.001	0.01	0.0003	0.001
PFB(A)	0.02	0.15	0.03	0.11
PFP(A)	0.05	0.46	0.08	0.29
PFHx(A)	0.003	0.03	0.001	0.01
PFHp(A)	0.003	0.03	0.001	0.01
PFO(A)	0.003	0.03	0.002	0.01
PFN(A)	0.003	0.03	0.002	0.01
PFD(A)	0.002	0.02	0.0001	0.0001
PFUnD(A)	0.02	0.24	0.001	0.01
PFDoD(A)	0.02	0.23	0.002	0.01
PFTD(A)	0.004	0.04	0.004	0.01

Table SM 6 Concentrations in blank samples from the water phase (in ng L^{-1}; nd = not detected).

	Dissolved phase (ng L^{-1}) (n = 3)	Particle phase (ng L^{-1})
PFBS(A)	nd	nd
PFHxS(A)	<IDL	0.15
PFOS(A)	nd	0.75
PFDS(A)	nd	0.05
(H)FOSA	nd	0.27
PFB(A)	0.30	0.73
PFP(A)	<IDL	nd
PFHx(A)	<IDL	0.33
PFHp(A)	nd	0.74
PFO(A)	nd	1.35
PFN(A)	<IDL	0.34
PFD(A)	nd	0.01
PFUnD(A)	nd	0.84
PFDoD(A)	<IDL	0.72
PFTD(A)	nd	0.13

Table SM 7 Average recovery rates of internal standards in water samples (in % ± standard deviation).

	Dissolved phase	Particle phase
$^{18}O_2$PFHxS(A)	122 ± 18	110 ± 25
^{13}CPFOS(A)	80 ± 2	76 ± 5
^{13}CPFB(A)	29 ± 3	63 ± 21
^{13}CPFHx(A)	111 ± 9	105 ± 12
^{13}CPFO(A)	87 ± 4	82 ± 5
^{13}CPFN(A)	77 ± 8	68 ± 4
^{13}CPFD(A)	83 ± 6	83 ± 7
^{13}CPFUD(A)	69 ± 11	78 ± 9
^{13}CPFDo(A)	30 ± 12	61 ± 12

5. Concentrations in samples

Table SM 8 Concentrations in the atmospheric gas phase (in pg m^{-3}). Concentrations below the IDL or below blank concentrations are reported as <IDL and <blank, respectively; nd = not detected.

	Aeration tank (pg m^{-3})			Secondary clarifier (pg m^{-3})		
PFBSA	nd	nd	nd	nd	nd	nd
PFHxSA	0.94	0.61	2.1	0.51	0.62	0.41
PFOSA	3.3	1.9	6.2	9.5	0.94	1.6
PFDSA	nd	nd	nd	nd	nd	nd
PFBA	11	9.6	30	23	9.1	25
PFPA	7.0	1.7	0.00	3.6	0.00	9.4
PFHxA	50	16.0	14	1.9	1.6	1.5
PFHpA	13	4.7	11	0.04	0.35	0.43
PFOA	25	8.2	21	4.9	2.8	1.9
PFNA	3.1	1.7	9.3	0.76	0.52	1.4
PFDA	2.6	1.2	1.7	0.65	0.57	0.14
PFUnDA	<blank	0.27	0.25	<blank	<blank	<blank
PFDoDA	0.5	0.1	nd	<blank	0.06	<blank
PFTeDA	nd	nd	nd	nd	nd	nd
HFOSA	2.6	2.9	<blank	1.6	3.0	5.3

Table SM 9 Concentrations in the dissolved phase of water samples (in ng L^{-1}). Concentrations below the IDL or below blank concentrations are reported as <IDL and <blank, respectively, nd means not detected.

	Primary clarifier (ng L^{-1})			Aeration tank (ng L^{-1})			Secondary clarifier (ng L^{-1})		
PFBS(A)	21	20	15	26	22	14	27	20	21
PFHxS(A)	21	14	21	27	18	16	21	18	18
PFOS(A)	1100	950	1300	2300	1200	1900	810	620	610
PFDS(A)	nd	nd	nd	2.4	1.3	1.5	nd	nd	nd
(H)FOSA	0.35	0.32	0.25	1.2	0.47	0.63	0.61	0.36	0.30
PFB(A)	16	20	16	19	17	11	23	21	18
PFP(A)	5.9	4.0	3.4	7.5	6.0	2.5	8.4	5.6	5.5
PFHx(A)	19	11	7	27	18	12	29	20	16
PFHp(A)	5.1	3.6	3.0	6.6	5.3	4.0	5.5	4.5	5.3
PFO(A)	12	10	8.0	26	17	16	18	16	17
PFN(A)	5.3	7.1	4.1	9.4	6.7	7.3	5.9	5.6	5.3
PFD(A)	6.1	5.7	4.2	16	9.8	13	7.2	5.8	5.6
PFUnD(A)	2.8	3.4	2.2	3.5	3.5	2.9	3.2	2.5	2.4
PFDoD(A)	3.4	3.7	2.1	3.2	3.1	2.1	2.5	1.9	1.9
PFTD(A)	0.13	0.25	0.13	<IDL	0.23	0.15	nd	0.06	nd

Table SM 10 Concentrations of neutral acids in the aqueous phase (in pg m^{-3}). Concentrations were calculated from measured concentrations of neutral and anionic acids in water (Table S 9) using the minimum and maximum pK_a values reported in the literature. Therefore for one sample two concentrations are available. In total there were three samples per sampling site.

	Aeration tank		Secondary clarifier	
Sample 1	pg m^{-3} (min pK_a)	pg m^{-3} (max pK_a)	pg m^{-3} (min pK_a)	pg m^{-3} (max pK_a)
PFBSA	$2.6 * 10^{-6}$	1.1	$2.67 * 10^{-6}$	1.17
PFHxSA	$2.7 * 10^{-6}$	1.2	$2.08 * 10^{-6}$	9.08 * 10-1
PFOSA	$2.3 * 10^{-4}$	$1.0 * 10^{2}$	$8.10 * 10^{-5}$	35.4
PFDSA	$1.0 * 10^{-1}$	$1.0 * 10^{-1}$	-	-
PFBA	$7.2 * 10^{-1}$	3.0	$8.74 * 10^{-1}$	3.64
PFPA	$1.9 * 10^{-1}$	1.0	$2.11 * 10^{-1}$	1.15
PFHxA	$6.0 * 10^{-1}$	6.2	$6.30 * 10^{-1}$	6.50
PFHpA	$1.4 * 10^{-1}$	$1.5 * 10^{-1}$	$1.12 * 10^{-1}$	$1.23 * 10^{-1}$
PFOA	$5.2 * 10^{-1}$	$5.2 * 10^{3}$	$3.63 * 10^{-1}$	$3.63 * 10^{3}$
PFNA	$1.8 * 10^{-1}$	$2.0 * 10^{-1}$	$1.15 * 10^{-1}$	$1.26 * 10^{-1}$
PFDA	$3.2 * 10^{-1}$	$2.0 * 10^{2}$	$1.40 * 10^{-1}$	85.5
PFUnDA	$6.8 * 10^{-2}$	$4.5 * 10^{1}$	$6.28 * 10^{-2}$	41.1
PFDoDA	$6.2 * 10^{-2}$	$1.3 * 10^{2}$	$4.81 * 10^{-2}$	$1.05 * 10^{2}$
PFTeDA	0.00	0.00	-	-
HFOSA	$6.4 * 10^{4}$	$1.2 * 10^{5}$	$3.17 * 10^{4}$	$5.76 * 10^{4}$
Sample 2				
PFBSA	$2.2 * 10^{-6}$	$9.4 * 10^{-1}$	$2.02 * 10^{-6}$	$8.82 * 10^{-1}$
PFHxSA	$1.8 * 10^{-6}$	$7.7 * 10^{-1}$	$1.83 * 10^{-6}$	$7.99 * 10^{-1}$
PFOSA	$1.2 * 10^{-4}$	$5.1 * 10^{1}$	$6.18 * 10^{-5}$	27.0
PFDSA	$5.9 * 10^{-2}$	$5.9 * 10^{-2}$	-	-
PFBA	$6.4 * 10^{-1}$	2.7	$8.02 * 10^{-1}$	3.34
PFPA	$1.5 * 10^{-1}$	$8.2 * 10^{-1}$	$1.39 * 10^{-1}$	$7.63 * 10^{-1}$
PFHxA	$4.0 * 10^{-1}$	4.1	$4.27 * 10^{-1}$	4.40
PFHpA	$1.1 * 10^{-1}$	$1.2 * 10^{-1}$	$9.17 * 10^{-2}$	$1.01 * 10^{-1}$
PFOA	$3.5 * 10^{-1}$	$3.5 * 10^{3}$	$3.27 * 10^{-1}$	$3.27 * 10^{3}$
PFNA	$1.3 * 10^{-1}$	$1.4 * 10^{-1}$	$1.09 * 10^{-1}$	$1.20 * 10^{-1}$
PFDA	$1.9 * 10^{-1}$	$1.2 * 10^{2}$	$1.14 * 10^{-1}$	69.3
PFUnDA	$6.8 * 10^{-2}$	$4.4 * 10^{1}$	$4.78 * 10^{-2}$	31.2
PFDoDA	$6.1 * 10^{-2}$	$1.3 * 10^{2}$	$3.74 * 10^{-2}$	81.4
PFTeDA	$4.5 * 10^{-3}$	$4.5 * 10^{-3}$	$1.15 * 10^{-3}$	$1.15 * 10^{-3}$
HFOSA	$2.5 * 10^{4}$	$4.5 * 10^{4}$	$1.86 * 10^{4}$	$3.38 * 10^{4}$
Sample 3				
PFBSA	$1.4 * 10^{-6}$	$6.1 * 10^{-1}$	$2.08 * 10^{-6}$	$9.08 * 10^{-1}$
PFHxSA	$1.6 * 10^{-6}$	$7.2 * 10^{-1}$	$1.75 * 10^{-6}$	$7.64 * 10^{-1}$
PFOSA	$1.9 * 10^{-4}$	$8.5 * 10^{1}$	$6.10 * 10^{-5}$	26.6
PFDSA	$6.4 * 10^{-2}$	$6.4 * 10^{-2}$	-	-
PFBA	$4.2 * 10^{-1}$	1.7	$6.99 * 10^{-1}$	29.2
PFPA	$6.4 * 10^{-2}$	$3.5 * 10^{-1}$	$1.37 * 10^{-1}$	$7.52 * 10^{-1}$
PFHxA	$2.7 * 10^{-1}$	2.8	$3.54 * 10^{-1}$	3.66

S. 12

PFHpA	$8.2 * 10^{-2}$	$9.0 * 10^{-2}$	$1.08 * 10^{-1}$	$1.19 * 10^{-1}$
PFOA	$3.2 * 10^{-1}$	$3.2 * 10^{3}$	$3.41 * 10^{-1}$	$3.41 * 10^{3}$
PFNA	$1.4 * 10^{-1}$	$1.6 * 10^{-1}$	$1.04 * 10^{-1}$	$1.14 * 10^{-1}$
PFDA	$2.6 * 10^{-1}$	$1.6 * 10^{2}$	$1.10 * 10^{-1}$	67.0
PFUnDA	$5.7 * 10^{-2}$	$3.7 * 10^{1}$	$4.76 * 10^{-2}$	31.1
PFDoDA	$4.1 * 10^{-2}$	$8.9 * 10^{1}$	$3.76 * 10^{-2}$	81.9
PFTeDA	$2.8 * 10^{-3}$	$2.8 * 10^{-3}$	-	-
HFOSA	$3.3 * 10^{4}$	$6.0 * 10^{4}$	$1.54 * 10^{4}$	$2.81 * 10^{4}$

Table SM 11 Concentrations in the particulate phase of water samples (top part of the table in ng L^{-1}, bottom part of the table in ng g^{-1}). Concentrations below the IDL or below blank concentrations are reported as <IDL and <blank, respectively, nd means not detected.

	Primary clarifier (ng L^{-1})			Aeration tank (ng L^{-1})			Secondary clarifier (ng L^{-1})		
PFBS(A)	nd	nd	nd	nd	nd	nd	0.02	0.03	nd
PFHxS(A)	0.22	0.26	0.25	1.8	3.0	2.0	0.08	0.16	0.11
PFOS(A)	69	55	84	2500	2500	2100	13	32	20
PFDS(A)	1.5	1.3	1.7	30	25	48	<blank	<blank	0.01
(H)FOSA	<blank	<blank	<blank	2.8	3.9	3.1	<blank	<blank	<blank
PFB(A)	3.5	5.4	0.58	35	38	34	<blank	<IDL	<blank
PFP(A)	<IDL	<blank	<IDL	<IDL	<IDL	<IDL	<blank	<blank	<blank
PFHx(A)	0.28	0.29	0.16	9.3	15	18	0.19	0.40	0.41
PFHp(A)	<blank	<blank	<blank	<blank	<blank	<blank	<blank	0.06	<blank
PFO(A)	<blank	<blank	<blank	12	18	18	<blank	<blank	<blank
PFN(A)	0.04	0.15	<blank	5.0	7.4	6.8	<blank	0.12	0.08
PFD(A)	0.78	0.77	0.91	30	33	30	<blank	0.88	0.45
PFUnD(A)	0.3	0.02	<blank	7.0	9.4	10	0.54	0.25	1.7
PFDoD(A)	0.14	<blank	<blank	13	14	16	<blank	0.57	0.09
PFTD(A)	0.02	<blank	<blank	1.5	0.79	1.0	<blank	<blank	<blank
	Primary clarifier (ng g^{-1})			Aeration tank (ng g^{-1})			Secondary clarifier (ng g^{-1})		
PFBS(A)	nd	nd	nd	nd	nd	nd	0.06	0.03	nd
PFHxS(A)	0.50	0.48	0.22	0.50	0.36	0.21	0.20	0.17	0.55
PFOS(A)	150	100	74	690	300	220	34	33	100
PFDS(A)	3.2	2.4	1.5	8.4	3.1	5.1	<blank	<blank	0.04
(H)FOSA	<blank	<blank	<blank	0.78	0.47	0.33	<blank	<blank	<blank
PFB(A)	7.71	10.15	0.51	9.69	4.55	3.56	<blank	<IDL	<blank
PFP(A)	<IDL	<blank	<IDL	<IDL	<IDL	<IDL	<blank	<blank	<blank
PFHx(A)	0.61	0.54	0.14	2.6	1.8	1.9	0.48	0.42	2.1
PFHp(A)	<blank	<blank	<blank	<blank	<blank	<blank	<blank	0.07	<blank
PFO(A)	<blank	<blank	<blank	3.4	2.2	1.9	<blank	<blank	<blank
PFN(A)	0.08	0.28	0.00	1.4	0.9	0.72	<blank	0.13	0.42
PFD(A)	1.7	1.5	0.80	8.5	4.0	3.1	<blank	0.91	2.3
PFUnD(A)	0.67	0.04	<blank	2.0	1.1	1.07	1.36	0.26	8.4
PFDoD(A)	0.31	<blank	<blank	3.56	1.7	1.7	<blank	0.59	0.45
PFTD(A)	0.03	<blank	<blank	0.41	0.10	0.11	<blank	<blank	<blank

S. 13

6. Particle-dissolved partition coefficients

Table SM 12 Average particle-dissolved partition coefficients (n = 3 respectively, if indicated with an asterisk n=2, no data reported when concentration nd, <blank or <IDL in one of the samples).

	R_d (no dim)	Stdev	ρ (%)	Stdev	R_d ($cm^3\ g^{-1}$)	Stdev	R_{OC} ($cm^3\ g^{-1}$)	Stdev	*R*oc (no dim)	Stdev
Primary clarifier										
PFHxS(A)	0.01	0.004	1.3	0.37	23	12	120	62	0.07	0.02
PFOS(A)	0.06	0.004	5.9	0.35	100	43	550	230	0.33	0.02
PFB(A)	0.18	0.12	14	9.5	350	270	1800	1400	0.94	0.66
PFHx(A)	0.02	0.01	2.1	0.57	34	16	180	82	0.11	0.03
PFN(A)*	0.01	0.01	1.4	0.96	27	20	150	90	0.07	0.05
PFD(A)	0.16	0.05	14	3.6	240	48	1300	250	0.85	0.26
PFUnD(A)*	0.06	0.07	5.1	6.4	120	130	660	840	0.30	0.38
PFDoD(A)	-	-	-	-	-	-	-	-	0.07	0.13
PFTeD(A)	-	-	-	-	-	-	-	-	0.20	0.35
Aeration tank										
PFHxS(A)	0.12	0.05	11	4.2	18	4.1	6600	1600	45	19
PFOS(A)	1.4	0.63	57	9.6	220	98	84000	37000	540	240
PFDS(A)	22	11	95	2.2	3100	710	1200000	270000	8100	3900
PFB(A)	2.4	0.64	70	5.5	370	130	140000	47000	890	240
PFHx(A)	0.85	0.55	43	17	110	32	43000	12000	320	210
PFO(A)	0.89	0.36	46	12	130	6.3	48000	2400	330	140
PFN(A)	0.86	0.30	45	9.4	130	27	48000	9900	320	110
PFD(A)	2.5	0.81	71	6.3	390	140	150000	53000	940	300
PFUnD(A)	2.7	0.74	73	5.5	420	130	160000	48000	1000	280
PFDoD(A)	5.5	1.98	84	4.4	830	290	310000	110000	2000	740
PFTeD(A)*	5.3	2.67	83	7.3	590	240	220000	91000	2000	1000
(H)FOSA	5.2	3.02	81	10	720	250	270000	94000	1900	1100

Secondary Clarifier										
PFBS(A)*	0.001	0.001	0.07	0.04	1.8	0.50	66	18	0.04	0.01
PFHxS(A)	0.01	0.003	0.62	0.25	17	13	610	470	0.23	0.09
PFOS(A)	0.03	0.02	3.3	1.7	88	69	3200	2500	1.2	0.65
PFHx(A)	0.02	0.01	1.7	0.94	56	63	2100	2300	0.64	0.36
PFHp(A)	-	-	-	-	-	-	-	310	0.17	0.30
PFN(A)*	0.02	0.01	1.9	0.45	51	40	1900	1500	0.46	0.17
PFD(A)*	0.12	0.05	10	4.1	280	170	10000	6400	4.2	1.9
PFUnD(A)	0.32	0.32	21	17	1300	1900	49000	68000	12	12
PFDoD(A)*	0.17	0.18	14	13	270	53	9900	2000	6.3	6.6

Table SM 13 Average organic carbon normalized particle-dissolved partition coefficients for neutral acids ($Q_{OC;}$ n = 3 respectively, if indicated with an asterisk n = 2, no data reported when concentration nd, <blank or <IDL in one of the samples). Concentrations of neutral acids in the aqueous phase were calculated with minimum and maximum pK_a values reported in the literature (Table S10).

	Aeration tank		Secondary clarifier		Primary clarifier	
	Log Q_{OC} minimum pK_a	Log Q_{OC} maximum pK_a	Log Q_{OC} minimum pK_a	Log Q_{OC} maximum pK_a	Log Q_{OC} minimum pK_a	Log Q_{OC} maximum pK_a
PFBSA	-	-	11.44	5.80	-	-
PFHxSA	14.65	9.01	12.36	6.72	11.86	6.22
PFOSA	15.73	10.09	13.09	7.45	12.52	6.88
PFDSA	11.27	11.27	-	-	-	-
PFBA	10.37	9.75	-	-	7.39	6.77
PFPA	-	-	-	-	-	-
PFHxA	10.16	9.15	7.47	6.45	6.71	5.70
PFHpA	-	-	6.93	6.89	-	-
PFOA	10.22	6.22	-	-	-	-
PFNA	10.22	10.18	7.37	7.33	6.40	6.36
PFDA	10.68	7.90	8.16	5.37	7.64	4.86
PFUnDA	10.72	7.90	8.77	5.96	7.01	4.20
PFDoDA	11.02	7.68	8.33	5.00	6.58	3.24
PFTDA	-	-	-	-	7.02	7.02
HFOSA	4.57	4.31	-	-	-	-

Table SM 14 log K_d and log K_{OC} values reported in the literature (L kg^{-1}).

	Reference	details	PFHp(A)	PFO(A)	PFN(A)	PFD(A)	PFUnD(A)	PFDoD(A)	PFBS(A)	PFHxS(A)	PFHpS(A)	PFOS(A)	PFDS(A)	(H)FOSA
log K_d														
infield sediment-water	(Ahrens et al., 2010)	Sediment, pH 7.1 - 7.4, f(OC) 1.5 - 1.7 %			0.6	1.8	3.0			1.8		2.1		2.5
		SPM	1.9	2.4	2.9	3.5	4.2			2.6		3.7		3.4
infield sediment-water	(Kwadijk et al., 2010)	no details		1.8	1.8	2.9			1.4	2.4		2.5		
infield sediment-water	(Labadie and Chevreuile, 2011)	4.8 % OC	0.8		1.5	2.4	3.4	4.3		0.9	1.6	2.4		
infield sediment-water	(Li et al., 2011)	2.1 - 11 % OC	2.4	2.5	2.5	3.0	3.1					3.2		
			1.7	1.8	2.1	2.9						3.1		
batch sediment-water	(Pan et al., 2009)	0.75 % OC, pH 7.18										0.9		
												1.3		
batch soil-water	(Enevoldsen and Juhler, 2010)	sandy	-0.2	0.04	0.6	1.5			-0.4			1.2		
WWTP	(Yu et al., 2009)	primary sludge		2.3								3.0		
				2.7								3.3		
		activated sludge		2.3								2.9		
				2.7								3.4		
batch sludge - water	(Ochoa-Herrera and Sierra-Alvarez, 2008)	anaerobically digested sewage sludge										1.9		
												2.4		
		anaerobic granular sludge										2.2		
												2.3		
log K_{OC}														
Batch sediment-water	(Higgins and Luthy, 2006)	0.6 – 9 % OC		2.1	2.5	2.9	3.5					2.7	3.7	

7. Air-water partition coefficients

Table SM 15 Air-water partition coefficients (Q_{AW})

	Aeration Tank		Secondary Clarifier	
	(min pK_a)	(max pK_a)	(min pK_a)	(max pK_a)
Sample 1				
PFHxSA	$3.57 * 10^{5}$	$8.17 * 10^{-1}$	$2.46 * 10^{5}$	$5.65 * 10^{-1}$
PFOSA	$1.41 * 10^{4}$	$3.23 * 10^{-2}$	$1.17 * 10^{5}$	$2.69 * 10^{-1}$
PFBA	14.7	3.52	25.7	6.17
PFPA	37.2	6.79	17.1	3.12
PFHxA	82.8	8.02	3.02	$2.92 * 10^{-1}$
PFHpA	93.3	85.1	$3.97 * 10^{-1}$	$3.62 * 10^{-1}$
PFOA	48.6	$4.86 * 10^{-3}$	13.5	$1.35 * 10^{-3}$
PFNA	17.0	15.5	6.64	6.06
PFDA	8.17	$1.34 * 10^{-2}$	4.60	$7.55 * 10^{-3}$
PFDoDA	8.19	$3.76 * 10^{-3}$	-	-
HFOSA	$4.06 * 10^{-5}$	$2.23 * 10^{-5}$	$5.07 * 10^{-5}$	$2.78 * 10^{-5}$
Sample 2				
PFHxSA	$3.45 * 10^{5}$	$7.91 * 10^{-1}$	$3.36 * 10^{5}$	$7.71 * 10^{-1}$
PFOSA	$1.65 * 10^{4}$	$3.79 * 10^{-2}$	$1.53 * 10^{4}$	$3.50 * 10^{-2}$
PFBA	15.0	3.61	11.3	2.71
PFPA	11.0	2.01	-	-
PFHxA	39.7	3.84	3.75	$3.63 * 10^{-1}$
PFHpA	43.9	40.0	3.79	3.46
PFOA	23.9	$2.39 * 10^{-3}$	8.50	$8.50 * 10^{-4}$
PFNA	12.8	11.6	4.73	4.32
PFDA	6.30	$1.03 * 10^{-2}$	4.99	$8.19 * 10^{-3}$
PFUnDA	4.05	$6.19 * 10^{-3}$	-	-
PFDoDA	1.71	$7.85 * 10^{-4}$	1.66	$7.61 * 10^{-4}$
HFOSA	$1.18 * 10^{-4}$	$6.47 * 10^{-5}$	$1.63 * 10^{-4}$	$8.94 * 10^{-5}$
Sample 3				
PFHxSA	$1.25 * 10^{6}$	2.86	$2.36 * 10^{5}$	$5.41 * 10^{-1}$
PFOSA	$3.19 * 10^{4}$	$7.32 * 10^{-2}$	$2.68 * 10^{4}$	$6.13 * 10^{-2}$
PFDSA	-	-	-	-
PFBA	71.0	17.0	35.6	8.54
PFPA	-	-	68.3	12.5
PFHxA	49.8	4.82	4.13	$4.00 * 10^{-1}$
PFHpA	$1.35 * 10^{2}$	$1.23 * 10^{2}$	3.96	3.61
PFOA	65.5	$6.55 * 10^{-3}$	5.55	$5.55 * 10^{-4}$
PFNA	64.9	59.2	13.3	12.1
PFDA	6.79	$1.11 * 10^{-2}$	1.28	$2.10 * 10^{-3}$
PFUnDA	4.34	$6.64 * 10^{-3}$	-	-
HFOSA	-	-	$3.42 * 10^{-4}$	$1.88 * 10^{-4}$

S. 18

Table SM 16 K_{AW} values reported in the literature

Reference	(Li et al., 2007)	(Kutsuna and Hori, 2008)		(Rayne and Forest, 2009b)	(Arp et al., 2006)			(Rayne and Forest, 2009a)	(Armitage et al., 2009)	(Wang et al., 2011)
Method	experimental (pH 0.6)	experimental pK_a = 2.8	experimental pK_a = 1.3	SPARC 2007	COSMO-therm	New Sparc 2006	EPI Suite 2006	Sparc 2007	COSMO-therm 2009	COSMO-therm
PFBSA										0.003
PFHxSA										0.004
PFOSA				0.045	0.004	0.087	0.447			0.022
PFDSA										0.071
PFBA										0.001
PFPA										0.001
PFHxA				0.003	0.001	0.003	0.135		0.002	0.003
PFHpA				0.009	0.002	0.007	0.708		0.003	0.006
PFOA	0.001	0.004	0.008		0.004	0.020	3.715	0.044	0.007	0.012
PFNA				0.263	0.009	0.076	19.498		0.015	0.026
PFDA				1.995	0.016	0.355	102.329			0.054
PFUnDA				19.498	0.030	2.138	537.032			0.120
PFDoDA								245.47	0.120	0.263
PFTDA										1.072
HFOSA					0.000	51.286	75.858			0.011

8. References

Ahrens, L., Taniyasu, S., Yeung, L. W., Yamashita, N., Lam, P. K., Ebinghaus, R., 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 79, 266–272.

Armitage, J. M., Macleod, M., Cousins, I. T., 2009. Response to comment on comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources. Environ. Sci. Technol. 43, 7153–7154.

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

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

Brooke, D., Footitt, A., Nwaogu, T. A., 2004. Environmental risk evaluation report: Perfluorooctanesulphonate (PFOS). Environment Agency UK. Wallingford.

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

Enevoldsen, R., Juhler, R. K., 2010. Perfluorinated compounds (PFCs) in groundwater and aqueous soil extracts: using inline SPE-LC-MS/MS for screening and sorption characterisation of perfluorooctane sulphonate and related compounds. Anal. Bioanal. Chem. 398, 1161–1172.

Goss, K.-U., 2008a. Additions and correction 2008, Volume 42, pages 456-458. Environ. Sci. Technol. 42, 5032.

Goss, K.-U., 2008b. The pKa Values of PFOA and other highly fluorinated carboxylic acids. Environ. Sci. Technol. 42, 456–458.

Henne, A. L., Fox, C. J., 1951. Ionization constants of fluorinated acids. J. Amer. Chem. Soc. 73, 2323–2325.

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

Igarashi, S., Yotsuyanagi, T., 1992. Homogeneous liquid-liquid extraction by pH dependent phase separation with a fluorocarbon ionic surfactant and its application to the preconcentration of porphyrin compounds. Mikrochim. Acta 106, 37–44.

Kutsuna, S., Hori, H. H., 2008. Experimental determination of Henry's law constant of perfluorooctanoic acid (PFOA) at 298K by means of an inert-gas stripping method with a helical plate. Atmospheric Environment 42, 8883–8892.

Kwadijk, C. J. A. F., Korytar, P., Koelmans, A. A., 2010. Distribution of perfluorinated compounds in aquatic systems in The Netherlands. Environ. Sci. Technol. 44, 3746–3751.

Labadie, P., Chevreuile, M., 2011. Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Orge River (nearby Paris, France). Environmental Pollution 159, 391–397.

Li, F., Sun, H., Hao, Z., He, N., Zhao, L., Zhang, T., Sun, T., 2011. Perfluorinated compounds in Haihe River and Dagu Drainage Canal in Tianjin, China. Chemosphere 84, 265–271.

Li, H., Ellis, D. A., Mackay, D., 2007. Measurement of low air-water partition coefficients of organic acids by evaporation from a water surface. J. Chem. Eng. Data 52, 1580–1584.

López-Fontán, J. L., Sarmiento, F., Schulz, P. C., 2005. The aggregation of sodium perfluorooctanoate in water. Colloid. Polym. Sci 283, 862–871.

Moroi, Y., Yano, H., Shibata, S., Yonemitsu, T., 2001. Determination of acidity constants of perfluoroalkanoic acids. Bull. Chem. Soc. Jpn. 74, 667–672.

Ochoa-Herrera, V., Sierra-Alvarez, R., 2008. Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. Chemosphere 72, 1588–1593.

Pan, G., Jia, C., Zhao, D., You, C., Chen, H., Jiang, G., 2009. Effect of cationic and anionic surfactants on the sorption and desorption of perfluorooctane sulfonate (PFOS) on natural sediments. Environ. Pollut. 157, 325–330.

Rayne, S. K. J. F., Forest, K., Friesen, K. J., 2009. Extending the semi-empirical PM6 method for carbon oxyacid pKa prediction to sulfonic acids: Application towards congener-specific estimates for the environmentally and toxicologically relevant C1 through C8 perfluoroalkyl derivatives. (Nature Precedings). hdl.handle.net/10101/npre.2009.2922.1, last access14/04/2011.

Rayne, S., Forest, K., 2009a. Comment on “comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources”. Environ. Sci. Technol. 43, 7155–7156.

Rayne, S., Forest, K., 2009b. Perfluoroalkyl sulfonic and carboxylic acids: A critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. J. Environ. Sci. and Heal. A 44, 1145–1199.

Rayne, S., Forest, K., Friesen, K. J., 2009. Computational approches may underestimated pKa values of longer-chain perfluorinated carboxylic acids: Implication for assessing environmental and biological effects. J. Environ. Sci. and Heal. A 44, 317–326.

Steinle-Darling, E., Reinhard, M., 2008. Nanofiltration for trace organic contaminant removal: Structure, solution, and membrane fouling effects on the rejection of perfluorochemicals. Environ. Sci. Technol. 42, 5292–5297.

U.S. Department of Health and Human Services, 2009. Draft toxicological profile for perfluoroalkyls, last access 14/04/2011.

Vierke, L., Ahrens, L., Shoeib, M., Reiner, E. J., Guo, R., Palm, W.-U., Ebinghaus, R., Harner, T., 2011. Air concentrations and particle-gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant. Environ. Chem. 8, 363–371.

Wang, Z., Macleod, M., Cousins, I. T., Scheringer, M., Hungerbühler, K., 2011. Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs). Environ. Chem. 8, 389–398.

Ylinen, M., Koji, A., Hanhijarvi, H., Peura, P., 1990. Disposition of perfluorooctanoic acid in the rat after single and subchronic administration. Bull. Environ. Contam. Toxicol. 44, 46–53.

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

Additional material paper 1

Chemosphere 93 (2013) 2207

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Discussion

Response to comment on "*In situ* air–water and particle–water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant"

Lena Vierke [a,b,*], Lutz Ahrens [c,1], Mahiba Shoeib [c], Wolf-Ulrich Palm [b], Eva M. Webster [d], David A. Ellis [d], Ralf Ebinghaus [e], Tom Harner [c]

[a] Federal Environment Agency (UBA), Section Chemicals, Wörlitzer Platz 1, Dessau-Roßlau, Germany
[b] Leuphana University of Lüneburg, Institute of Sustainable and Environmental Chemistry, Scharnhorststr. 1, Lüneburg, Germany
[c] Environment Canada, Air Quality Processes Research Section, 4905 Dufferin Street, Toronto, ON, Canada
[d] Trent University, Centre for Environmental Modelling and Chemistry, 1600 West Bank Drive, Peterborough, ON, Canada
[e] Helmholtz-Zentrum Geesthacht, Institute for Coastal Research, Max-Planck Str. 1, Geesthacht, Germany

We thank Rayne (2013) for examining our paper in detail and are grateful for the comments.

In our study, we conducted field measurements of perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs) and perfluorooctyl sulfonamide (HFOSA) and their conjugate bases in different media at a wastewater treatment plant. Using reported physical chemical properties, such as the acid dissociation constants (pK_a), we calculated partitioning ratios and compared our field observations on partitioning behavior with data and theories presented in the literature. Comments made by Rayne (2013) are related to studies which we cite in our paper, i.e., regarding the pK_a of n-perfluorooctanoic acid (n-PFOA).

We acknowledge the comment from Rayne (2013) that there is a continued debate over the physical chemical properties of the perfluoroalkyl acids and their conjugate bases, however, a consensus has not yet been reached. Field measurement data such as ours are useful for gaining insight into mechanisms of partitioning and for discussing and testing ideas and theories. The studies and theories cited by Rayne (2013) further contribute to these discussions, focusing on the pK_a and K_{AW} of PFCAs, conformer formation of PFCAs and fluortelomeralcohols and species dependent partitioning behavior. In our opinion more work is required to better constrain and understand the physical properties of PFCAs and how they govern the partitioning and fate in the environment.

Reference

Rayne, S., 2013. Comment on "In situ air–water and particle–water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant" by Vierke, L., Ahrens, L., Shoeib, M., Palm, W.-U., Webster, E.M., Ellis, D.A., Ebinghaus, R., Harner, T. (Chemosphere, 2013. http://dx.doi.org/10.1016/j.chemosphere.2013.02.067) Chemosphere.

* Corresponding author. Address: Federal Environment Agency (UBA), Wörlitzer Platz 1, Dessau-Roßlau, Germany. Tel.: +49 34021036620; fax: +49 34021046620.
E-mail address: Lena.Vierke@uba.de (L. Vierke).
[1] Present address: Swedish University of Agricultural Sciences, Department of Aquatic Sciences and Assessment, Lennart Hjelms väg 9, 750 07 Uppsala, Sweden.

0045-6535/$ - see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.chemosphere.2013.05.008

A2 Paper 2 sediment-water partitioning enclosure

A2 Paper 2 sediment-water partitioning enclosure

Environmental Pollution 186 (2014) 7–13

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Transport of perfluoroalkyl acids in a water-saturated sediment column investigated under near-natural conditions

Lena Vierke [a,b,*], Axel Möller [c,1], Sondra Klitzke [d]

[a] Federal Environment Agency, Wörlitzer Platz 1, 06844 Dessau-Roßlau, Germany
[b] Leuphana University of Lüneburg, Scharnhorststr. 1, 21335 Lüneburg, Germany
[c] Helmholtz-Zentrum Geesthacht, Max-Planck Str. 1, 21502 Geesthacht, Germany
[d] Federal Environment Agency, Schichauweg 58, 12307 Berlin, Germany

ARTICLE INFO

Article history:
Received 23 May 2013
Received in revised form
14 October 2013
Accepted 15 November 2013

Keywords:
Riverbank filtration
PFOA
PFCAs
PFSAs
Sediment–water partition coefficient
Column study

ABSTRACT

The aim of this study was to gain an understanding of the transport of C_{4-10} perfluoroalkyl carboxylic acids (PFCAs) and $C_{4,6,8}$ perfluoroalkyl sulfonic acids (PFSAs) in a water-saturated sediment column representing a riverbank filtration scenario under near-natural conditions. Short-chain PFCAs and PFSAs with up to six C-atoms showed complete tracer-like breakthrough. Longer chain ones were retarded due to sorption to the sediment or due to other processes in the aqueous phase. The study reports the first column derived sediment–water partition coefficients ranging from 0.01 $cm^3\ g^{-1}$ to 0.41 $cm^3\ g^{-1}$ for $C_{4,6}$ PFSAs and from 0.0 $cm^3\ g^{-1}$ to 6.5 $cm^3\ g^{-1}$ for $C_{4,5,6,8,9}$ PFCAs. The results clearly indicate that short-chain PFCAs and PFSAs may pose a problem if contaminated surface waters are used for drinking water production via riverbank filtration.

1. Introduction

Recently, research on per- and polyfluoroalkyl compounds has highly improved our understanding of the risk occurring from the presence of these compounds in the environment (Kannan, 2011). In the beginning, focus of this research has mainly been on C_8 perfluoroalkyl carboxylic acid (C_8 PFCA; perfluorooctanoic acid, PFOA) and C_8 perfluoroalkyl sulfonic acid (C_8 PFSA; perfluorooctane sulfonic acid, PFOS), which was mostly motivated by the high production volumes of these two chemicals in the past 60 years (Lindstrom et al., 2011; Paul et al., 2009; Prevedouros et al., 2006). Today we know that PFOA and PFOS are persistent, bioaccumulative and toxic as defined in international regulations (Vierke et al., 2012; Wang et al., 2009b). Therefore exposure of humans and the environment should be minimised (Vierke et al., 2012; Wang et al., 2009b; Zushi et al., 2012).

Manufacturers are shifting to shorter-chain per- and polyfluorinated chemicals with four and six C-atoms (Buck et al., 2011). Not only PFCAs and PFSAs are part of this short-chain chemistry but also their polyfluorinated precursors. Research is increasingly investigating shorter-chain PFCAs and PFSAs as well as precursors of PFCAs and PFSAs. One example are fluorotelomer alcohols (FTOHs), which were already globally detected in the atmosphere (Dreyer et al., 2009). Degradation intermediates of FTOHs are i.e. fluorotelomer acids (FTCAs) or fluorotelomer unsaturated acids (FTUCAs). These degradation intermediates have already been found in the environment, i.e. in rivers (Li et al., 2011). In contradiction to PFOS and PFOA shorter-chain PFCAs and PFSAs are less toxic and less bioaccumulative (Conder et al., 2008; Ding et al., 2012). Nevertheless, they are still persistent and have already been detected in surface waters and drinking water (Möller et al., 2010; Eschauzier et al., 2010), with wastewater treatment plants and surface runoff being potential sources for these compounds (Furl et al., 2011).

Due to their higher solubility (Rayne and Forest, 2009) these short-chain PFCAs and PFSAs are more mobile, especially in the aqueous environment, than their longer chain homologues. This higher mobility has a direct impact on human and environmental exposure, for instance through drinking water. In many regions drinking water is obtained from surface waters following riverbank

* Corresponding author.
E-mail addresses: Lena.Vierke@uba.de (L. Vierke), a.moeller@gba-laborgruppe.de (A. Möller), Sondra.Klitzke@uba.de (S. Klitzke).
[1] Current address: GBA Gesellschaft für Bioanalytik mbH, Goldtschmidtstraße 5, 21073 Hamburg, Germany.

0269-7491/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envpol.2013.11.011

filtration. In Germany, water from riverbank filtration is the second major source for drinking water after ground water (Kuehn and Mueller, 2000). Riverbank filtration is capable of eliminating a wide range of substances through sorption and degradation or at least diluting peak concentrations (Verstraeten et al., 2003). However, PFCAs and PFSAs with eight and less C-atoms have been detected in riverbank filtrate (Lange et al., 2007) or dune infiltrate (Eschauzier et al., 2010).

Sandy sediments are common substrates in riverbank filtration sites. Sorption of PFCAs and PFSAs on sandy soil quantified within a batch experiment showed that this soil had a capacity to bind the analytes ($K_d = 0.63$ L kg^{-1} to 33 L kg^{-1} for perfluoroheptanoic acid (C_6 PFCA or PFHpA) to perfluorodecanoic acids (C_{10} PFCA or PFDA) and $K_d = 0.07$ L kg^{-1} and 17 L kg^{-1} for perfluorobutane sulfonic acid (C_4 PFSA or PFBS) and PFOS, Enevoldsen and Juhler 2010) and the authors concluded that sandy substrates may therefore be able to protect groundwater (Enevoldsen and Juhler, 2010). So far, the fate of PFCAs, PFSAs and precursors in columns has only been investigated by three laboratory studies, all of them conducted under water-unsaturated conditions using loamy soil (Murakami et al., 2009, 2008) and loamy sandy soil (Gellrich et al., 2012). These studies showed partly competitive sorption between the different analytes and only limited elimination of analytes during soil infiltration, with removal depending on chain length. Furthermore, leaching of PFCAs and PFSAs was investigated in a lysimeter experiment also under water-unsaturated conditions (Stahl et al., 2013), but the fate of chemicals tends to differ between water-saturated and water-unsaturated conditions. So far and to the best of our knowledge, no column study has been conducted under water-saturated conditions in sandy substrates. Besides, available findings from infield studies (Eschauzier et al., 2010; Lange et al., 2007) don't allow for a quantification of the transport of PFCAs and PFSAs during riverbank filtration. Water-saturated conditions are important because they are characteristic for riverbank filtration schemes used as a source for the production of drinking water. The aim of our experiment was to gain an understanding of the transport of C_{4-10} PFCAs and $C_{4,6-8}$ PFSAs in a water-saturated sediment system representing a riverbank filtration scenario and to quantify possible attenuation through the determination of sorption parameters. Furthermore, though not the primary focus, some precursors were also investigated. The results of this study help to assess the potential risk of breakthrough of PFCAs and PFSAs in riverbank filtrate occurring from the presence of these substances in surface waters.

2. Material and methods

Riverbank filtration was simulated under near-natural conditions in a water-saturated sediment column fed with surface water and by applying environmentally relevant concentrations of the analytes. To quantify the sorption of analytes during infiltration, breakthrough was compared to a tracer.

2.1. Chemicals

Table 1 shows the names and abbreviations of analytes which were in the focus of the present study.

Furthermore, methylperfluoro butanesulfonamid (MeFBSA), methylperfluoro butanesulfonamidoethanol (MeFBSE), 2-Perfluorohexyl ethanoic acid (6:2 FTCA), 2-Perfluorooxyl ethanoic acid (8:2 FTCA), 2-Perfluorodexyl ethanoic acid (10:2 FTCA), 2H-Perfluoro-2-octenoic acid (6:2 FTUCA) and 2H-Perfluoro-2-decenoic acid (8:2 FTUCA) were spiked onto the column. Tables S1 and S2 of the supplementary content list all native as well as mass labelled standards, their acronyms, suppliers, mass transitions and the matching of mass labelled and native standards.

In aqueous media per- and polyfluorinated acids are in equilibrium with their conjugate bases. The fraction of each depends on the pK_a of the acid and the pH value of the media. We analytically detected both the acids and their conjugate bases, whereby the fraction of the base is expected to be higher compared to the fraction of the acids due to the low pK_as of PFCAs, PFSAs and their precursors (Goss, 2008; Vierke et al., 2013b). Therefore, where we name the species as the acids in this study, this always includes both species.

2.2. Water-saturated sediment column

The experiment was conducted on the Federal Environment Agency's facility for the simulation of riverbank and slow sand filtration (SIMULAF) in Berlin, Germany (for details of the site see Grützmacher et al., 2005). The water-saturated column (termed as 'enclosure' in the following; length 1 m, surface area 1 m^2) was embedded in a natural slow sand filter basin and fed by surrounding surface water. The water was pumped continuously through the sediment column at a filter velocity of 1.1 m d^{-1}, which was checked daily. This velocity is in the range of values often encountered in riverbank filtration scenarios (Hijnen et al., 2005; Weiss et al., 2005). Water samples were collected from the supernatant and at a sediment depth of 40 cm and 80 cm depth. A pump was plugged to the sampling ports in 40 cm and 80 cm depth to collect the samples. Grab sampling with a bucket on a stick was used for supernatant sampling. Sample volume was approximately 1 L measured in polypropylen(PP)-bottles. At a flow rate of 0.74 L min^{-1} it was not expected that the removal of 1 L samples would disturb the system. The supernatant was adjusted to a height of 15.5 cm, resulting in a final volume of 155 L. The turbidity of the water in the supernatant amounted to 3 FNU. The pH value of the water in the supernatant, 40 cm and 80 cm depth ranged from 7.4 to 7.9 and water temperature was 14.8 °C–24.9 °C. The oxygen concentration in the columns effluent ranged from 4.7 mg L^{-1} to 8.7 mg L^{-1} during the experiment. Concentrations of dissolved organic carbon (DOC) were highest in the supernatant (3.5 ± 0.3 mg L^{-1}, $n = 4$) and ranged from 2.5 mg L^{-1} to 3.1 mg L^{-1} in the various depths. Ionic strength amounted to 17.5 mmol L^{-1} with a calcium concentration of 4.3 mmol L^{-1}. The column was filled with coarse-grained medium sand (grain size distribution is given in Table S3) followed by 30 cm gravel (Fig. 1). The sand had a content of 0.02% N, 0.07% organic carbon (OC), 0.3% carbonate C and a C/N-ratio of 16.1. The bulk density (ρ_B) of the sediment amounted to 1.57 g cm^{-3}. From the density of the raw material ($\rho_F = 2.65$ g cm^{-3} for quartz sand, Scheffer and Schachtschabel, 1998) a porosity (n) of 0.41 and a void ratio (ε) of 0.7 was calculated. The enclosure and the surrounding pond were located outside and were therefore influenced by natural conditions (i.e. natural microbial community and day–night temperature fluctuations). The experiment was conducted for three weeks in the beginning of September 2011 under environmental conditions.

2.3. Experimental design

Prior to the experiment background concentrations in the enclosure were determined once. Therefore 1 L water samples were collected from the supernatant, from 40 cm and 80 cm depth, respectively.

The supernatant of the enclosure was then spiked with 5 μg of each C_{4-10} PFCAs, $C_{4,6-8}$ PFSAs, MeFBSA, MeFBSE, 6:2, 8:2, 10:2 FTCAs and 6:2 and 8:2 FTUCAs (in total 1.85 ml methanol solution of standards), yielding a target concentration of 32.3 ng L^{-1} for each analyte. 136 ml 25% NaCl solution was added as a tracer and the supernatant was mixed with a stick. Mixing was evaluated by conductivity measurements. As soon as (after approximately 5 min) conductivity changes in the supernatant were minimal (1350 ± 5 μS cm^{-1}) two 1 L samples were taken to determine analyte concentrations right after spiking. One litre water samples were collected from the supernatant and after 40 cm and 80 cm of sediment passage during the following sampling period (in total 53 sampling events at three sampling points of which 70 were analysed). Sampling frequency was reduced in the course of the experiment because high concentration variations were expected mainly in the beginning. At the beginning of the experiment, samples were collected more frequently, i.e. six times per day for the first five days, three times per day in the second week and only once a day in the third week.

Water samples from the supernatant were filtered using glassfiber filters (GFF, Macherey–Nagel, Ø 45 mm, 0.7 μm, heated at 450 °C for 10 h) right after sampling and all samples were stored at 4 °C in PP-bottles until extraction. The effect of filtration on concentrations of analytes was tested with spiked MilliQ water. An aliquot of the water was filtered. Compared to unfiltered water the difference in recovered concentrations were <10% (except for 20% in the case of PFHxA).

Table 1
Name and abbreviations of PFCAs and PFSAs in the focus of the present study.

Name	Abbreviation
Perfluoro-1-butanesulfonicacid	PFBS, C_4 PFSA
Perfluoro-1-hexanesulfonicacid	PFHxS, C_6 PFSA
Perfluoro-1-heptanesulfonicacid	PFHpS, C_7 PFSA
Perfluoro-1-octanesulfonicacid	PFOS, C_8 PFSA
Perfluoro-*n*-butanoic acid	PFBA, C_4 PFCA
Perfluoro-*n*-pentanoic acid	PFPA, C_5 PFCA
Perfluoro-*n*-hexanoic acid	PFHxA, C_6 PFCA
Perfluoro-*n*-heptanoic acid	PFHpA, C_7 PFCA
Perfluoro-*n*-octanoic acid	PFOA, C_8 PFCA
Perfluoro-*n*-nonanoic acid	PFNA, C_9 PFCA
Perfluoro-*n*-decanoic acid	PFDA, C_{10} PFCA

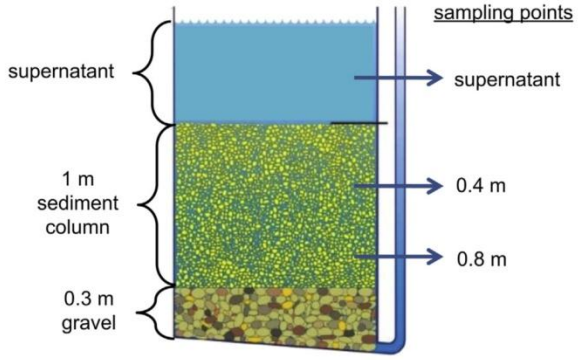


Fig. 1. Cross-sectional view of the enclosure.

2.4. Preparation and analysis of water samples

For solid-phase extraction (OASIS® WAX 6cc, 150 mg, 30 μm cartridges) of water samples the method from Ahrens et al. (2007) was used with slight modifications: Prior to sample application, cartridges were conditioned with 5 ml 0.1% NH_4OH (suprapur, 25%, GC Standards GmbH) in methanol (MeOH, Picograde, >99.0%, LGC Standards GmbH), 5 ml MeOH and 5 ml MilliQ water. 400 ml of each sample were spiked with mass-labelled internal standards (IS) (80 μl at 100 ng ml^{-1} mass-labelled $C_{6,8}$ PFSAs, C_{4-10} PFCAs, MeFOSA, MeFOSE, 6:2 FTCA, 8:2 FTCA, 10:2 FTCA, 6:2 FTUCA and 8:2 FTUCA, for details see Table S1) and were loaded on a preconditioned cartridge at a rate of 1 drop per second. After loading of samples, cartridges were washed with 0.1% NH_4OH in MilliQ and were dried 30 min under vacuum. Elution was achieved with 10 ml 0.1% NH_4OH in methanol. A gentle flow of nitrogen was used to concentrate the samples to a final volume of 150 μl at room temperature (measured with a photo sensor in standardised vials, flowtherm optocontrol Barkey). 2-(N-deuterioethylperfluro-1-octane-sufonamido)-1,1,2,3-tetradeuterioethanol (D9-NEtFOSE, 10 μl out of 0.8 μg ml^{-1}, 8 ng) was added. Before instrumental analysis with LC-ESI-MS/MS (Hewlett Packard Series 1100, API 3000) a 50 μl aliquot of the final extract was combined with 20 μl of MilliQ water and perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfinate (MPFOSi, 10 μl at 0.9 μg ml^{-1}, 9 ng) was added as injection standard. Methanol and MilliQ water each with a concentration of 10 mM NH_4OAc (fractopur, >99.0%, Merck) were used as eluent in liquid chromatography.

One analytical blank sample was extracted within one batch consisting of seven samples. Analytical blank samples were treated in the same way as samples but without the addition of water to the cartridges. Concentrations in analytical blanks were subtracted from samples in the specific batch. Analytical blank concentrations were frequently detected for PFOS (3.6 ± 2.2 ng L^{-1}, $n = 9$), PFBA (0.2 ± 0.3 ng L^{-1}, $n = 12$), PFPA (0.2 ± 0.3 ng L^{-1}, $n = 12$), PFHxA (0.1 ± 0.1 ng L^{-1}, $n = 12$), PFHpA (3.6 ± 3.3 ng L^{-1}, $n = 12$) and PFOA (0.1 ± 0.1 ng L^{-1}, $n = 12$). The limit of detection (LOD) were derived from blank concentrations or instrumental detection limits and ranged from 0.02 ng L^{-1} to 3.3 ng L^{-1} (Table S4). As for PFOS and PFHpA the concentrations in blank samples were too high, these two analytes were excluded from further evaluation.

For quantification, ten point (single measurement) calibration curves ($r^2 > 0.98$) ranging from 200 ng ml^{-1} to 0.125 ng ml^{-1} were used. Average recoveries of mass-labelled IS ranged from 72% to 87% for PFSAs, from 83% to 102% for PFCAs, from 27% to 32% for MeFBSA and MeFBSEs and from 65% to 84% for *n*:2 FTCAs and *n*:2 FTUCAs. Due to low recoveries of MeFBSA and MeFBSE results are only qualitatively. All concentrations were corrected for recovery of IS. For the quantification of the tracer a calibration curve was used to convert the conductivity measurement (in μS cm^{-1}) in concentrations (g L^{-1}).

2.5. Quantification of the transport of analytes in the sediment column

On the basis of the obtained breakthrough curves of tracer and analytes, (i) recoveries, (ii) retardation factors (R) and (iii) sediment-dissolved partition coefficients (K_d) were calculated.

(i) For recovery calculations, the quantity of tracer and analytes broken through in the different depths was compared to their quantity detected in the supernatant right after spiking. Polynoms which best described the breakthrough curves of tracer or analyte were used to calculate the respective quantities in the different depths by linear interpolation.

(ii) To quantify sorption processes R was calculated for every analyte as shown in Equation (1), with t_{50} (min) being the time at which half of the detected quantity of the tracer or analyte has passed the respective sampling point.

$$R = \frac{t_{50\ (\text{analyte})}}{t_{50\ (\text{tracer})}} \quad (1)$$

(iii) The sediment-dissolved partition coefficient (K_d) takes sediment characteristics into account (Equation (2)), acknowledging that partitioning in the sediment column is not expected to be at equilibrium (Benker et al., 1998).

$$K_d = \frac{n_e}{\rho_B} * (R - 1) \quad (2)$$

In Equation (2) ρ_B (in g cm^3) denotes the density of the sediment and n_e the effective porosity (dimensionless), which was calculated by using the linear flow velocity (v_a, in m d^{-1}) and the filter velocity (v_f, in m d^{-1}; Equation (3) and Table 2). In addition, a one dimensional model was used to fit the measured breakthrough curve of the tracer by adjusting n_e and D. Input data for the model were column length (40 cm and 80 cm), column radius (56.5 cm), flow rate (0.74 L min^{-1}), input mass of the tracer (34 g) and input tracer concentration (0.34 g L^{-1}). Modelled values for n_e were in good agreement with results obtained from Equation (3) (Table 2).

$$n_e = \frac{v_f}{v_a} \quad (3)$$

To describe the relation between partition coefficients and OC content of the sediment OC normalised partition coefficients (K_{OC}) were calculated as shown in Equation (4), with f_{OC} being the fraction of OC in the sediment.

$$K_{OC} = K_d * \frac{100}{f_{OC}} \quad (4)$$

3. Results and discussion

3.1. Background concentrations in the enclosure

In samples prior to spiking the enclosure the following analytes were found at concentrations in the low nanogram per litre range (in supernatant, 40 cm depth, 80 cm depth): PFBS (1.2 ng L^{-1}, 1.2 ng L^{-1}, 1.1 ng L^{-1}), PFHxS (0.3 ng L^{-1}, 0.4 ng L^{-1}, 0.4 ng L^{-1}), PFBA (1.2 ng L^{-1}, 1.6 ng L^{-1}, 1.6 ng L^{-1}), PFPA (1.0 ng L^{-1}, <LOD, <LOD), PFHxA (0.3 ng L^{-1}, 0.3 ng L^{-1}, 0.4 ng L^{-1}), PFOA (1.1 ng L^{-1}, 0.6 ng L^{-1}, 0.8 ng L^{-1}) and PFNA (0.2 ng L^{-1}, 0.1 ng L^{-1}, <LOD). These background concentrations were subtracted from the concentrations measured following spiking for each sampling point. This correction was applied to each analyte in every sample. Therefore, this shifted breakthrough curves only vertically but did not change their shape. A vertical shift does not influence parameters relevant for the quantification of contaminant breakthrough. Furthermore, the background concentrations proved very similar for the different sampling points, i.e. variation was low.

3.2. Fate of PFCAs, PFSAs and precursors in the water of the supernatant

The supernatant concentrations right after spiking ranged from 1.0 ng L^{-1} (6:2 FTUCA) to 15.9 ng L^{-1} (PFOA) (Table S5). These concentrations were at least a factor of two lower than the expected target concentrations (32 ng L^{-1}), while the tracer showed the expected concentrations (0.2 g L^{-1}). No pattern or trend with respect to chain length was observed for the difference between

Table 2
Linear flow velocity (v_a), filter velocity (v_f) and effective porosity (n_e) in 40 cm, 80 cm and in the effluent based on Equation (3) and on model calculations.

	v_a (m d^{-1})	v_f (m d^{-1})	n_e (−) (calculated according to Equation (3))	n_e (−) (calculated with a one dimensional model)	D (dm) (calculated with a one dimensional model)
40 cm	3.8	1.0	0.28	0.3	0.4
80 cm	3.3		0.33	0.3	0.5

target and measured concentrations. 6:2 FTCA, 8:2 FTCA, 10:2 FTCA and 8:2 FTUCA were not detected at all.

Several processes are conceivable to explain the observed discrepancies between theoretical target concentrations and measured concentrations after spiking the supernatant. While in theory analytes associated with suspended matter could be removed from the aqueous phase by the filtration of the supernatant samples (pore size 0.7 μm), this appears unlikely, as the turbidity of the supernatant was very low (3 FNU). PFCAs and PFSAs may enrich at the air–water interface (Psillakis et al., 2009), possibly leading to lower concentrations in the dissolved phase of the supernatant. However, sampling of the supernatant included the upper layer of the water, thus including PFCAs and PFSAs enriched at the air–water interface and excluding this mechanism. A further possibility for the loss of analytes from the dissolved phase in the supernatant right after spiking could be precipitation as calcium complexes. Concentration of calcium was 4.3 mmol L^{-1} in the inflowing water (see material and methods). So far and to the best of our knowledge, the formation of Ca^{2+} complexes with PFCAs or PFSAs has not been reported in the literature. However linear alkylbenzenesulfonates (LAS; Westall et al., 1999) have a similar structure and for these the equilibrium of calcium complex formation was reported to be achieved after 10 min (Matheson et al., 1985). Therefore it appears that the hypothesis of a loss of PFCAs and PFSAs through the precipitation of such complexes (leading to their accumulation on the sediment surface) merits further testing in future studies.

Mechanisms explaining the fate of analytes can be gleaned from comparing the dilution curves of the tracer to those of the analytes in the supernatant. Dilution in the supernatant took place through inflowing water. Dilution of most analytes was in accordance with the tracer suggesting no losses due to decomposition, volatilisation or sorption to enclosure material within the time frame investigated (Fig. 2). Only MeFBSA and 6:2 FTUCA diluted faster than the tracer. This may indicate volatilisation as their vapour pressures are higher compared to the vapour pressure of the other analytes (16.6 Pa for MeFBSA and 18.2 Pa for 6:2 FTUCA, Wang et al., 2011). Furthermore, while MeFBSE and 6:2 FTUCA may have been subject to (photo)degradation (Gauthier and Mabury, 2005; Lange, 2001), this is likely to be negligible within the 10 min elapsed until the first sampling, because another study showed that 70 h were needed to achieve a 28% decrease of 8:2 FTUCA due to photo-degradation in aqueous solution (Gauthier and Mabury, 2005). This demonstrates differences of several orders of magnitude with respect to time required for the degradation of the respective substances.

3.3. Transport of analytes in the sediment column

6:2 FTUCA, MeFBSA, PFHpS and PFDA were detected in the supernatant (with concentrations right after spiking of 1.0 ng L^{-1} for 6:2 FTUCA, 12.5 ng L^{-1} for MeFBSA, 5.4 ng L^{-1} for PFHpS and 6.6 ng L^{-1} for PFDA) but were not detected in any of the samples from 40 cm and 80 cm depth. For 6:2 FTUCA and MeFBSA degradation (Buck et al., 2011) or slow volatilisation (Wang et al., 2011) may have been responsible for the loss. Furthermore, concentrations of 6:2 FTUCA (1.0 ng L^{-1}) were very low right after spiking and dilution could have led to concentrations below the LOD. Conclusions on the fate of 6:2 FTUCA in the sediment were therefore not possible. In contrast, PFHpS and PFDA are more persistent and their vapour pressure is low (Kaiser et al., 2005; Wang et al., 2011); therefore degradation and volatilisation were not expected to occur and thus their fate is unknown.

PFPA and MeFBSE were detected only in a few samples in 40 cm depth but not in 80 cm depth (Tables S6 and S7), and thus only qualitative analysis was possible.

Quantitative analysis of the concentrations of PFBS, PFHxS, PFBA, PFHxA, PFOA and PFNA, in 40 cm showed tracer-like breakthrough especially for PFBA, PFBS and PFHxS but also for PFHxA (Fig. 3). PFOA and PFNA were retarded compared to the tracer (Fig. 4).

3.4. Quantification of transport – recoveries in 40 cm and 80 cm depth

Recoveries of PFBS, PFHxS, PFBA, PFPA and PFHxA in 40 cm were in the same range as the tracer indicating complete breakthrough (Fig. 5).

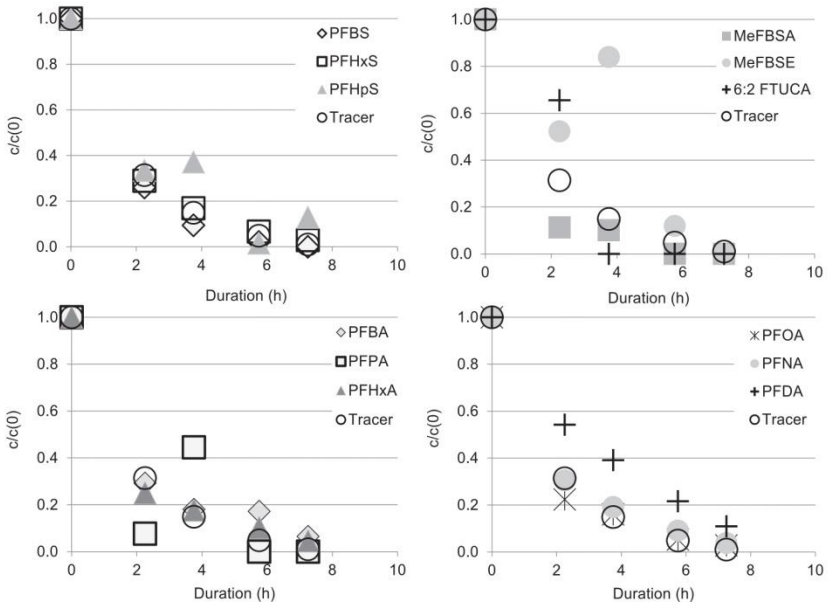


Fig. 2. Dilution curves in the supernatant for different analytes in comparison to the tracer.

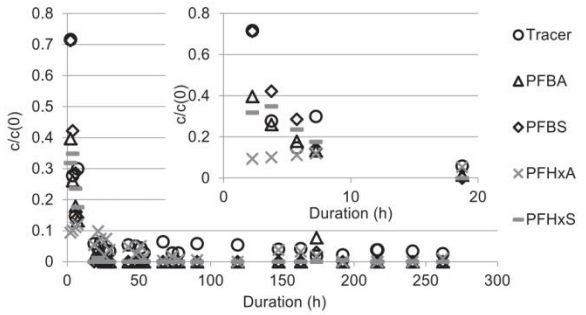


Fig. 3. Breakthrough curves of short-chain PFCAs and PFSAs compared to the tracer in 40 cm. The upper graph is an excerpt of the lower one showing a higher resolution of the time scale in the first 20 h.

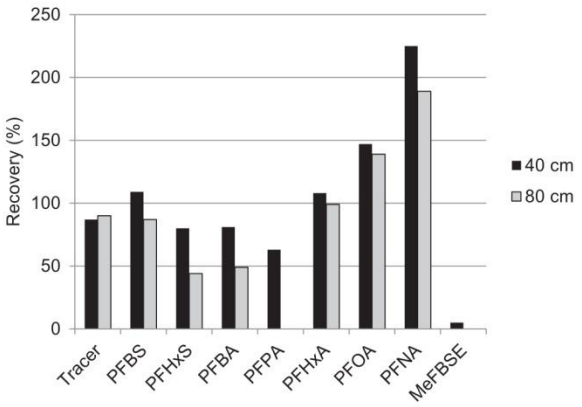


Fig. 5. Recoveries (in %) of tracer and analytes in 40 cm and 80 cm based on measured concentrations in the supernatant after spiking. PFPA and MeFBSE were not detected in 80 cm.

For all of these analytes, recoveries were higher in 40 cm compared to 80 cm. This observation was in line with higher retardation in 80 cm compared to 40 cm (see below). Furthermore, recoveries increased with increasing chain length for PFCAs (except of PFPA). Recoveries of PFOA and PFNA reached up to 150% and 225% indicating a higher quantity found in 40 cm and 80 cm, respectively, compared to the initial quantity in the supernatant. Breakthrough curves for PFOA and PFNA were tailing and did not reach the baseline within the duration of the experiment indicating that the total amount has not yet been eluted from the column. Low concentrations may add some uncertainties to the quantification of recoveries.

High recoveries of PFOA and PFNA might be caused by sorption to suspended matter. Sorbed PFCAs and PFSAs would not have been captured in the analysis of supernatant samples but were still available for sediment passage if they desorbed for instance due to a decrease in aqueous concentrations caused by dilution. Anyhow, the removal of analytes associated to suspended matter through sample filtration is not expected to be a significant mechanism, as discussed above for the discrepancy between initial target and measured concentration in the supernatant.

Furthermore the precipitation of PFOA and PFNA as calcium complexes could, if proved by future studies, explain high recoveries of PFOA and PFNA. The constant input of fresh water (i.e. dilution of the supernatant) continuously could have re-adjusted the equilibrium between dissolved analytes and precipitated complexes in favour of the dissolved phase, and the re-dissolution of the analytes in the water renders them available for transport. Hence, they are subsequently captured in the different depths of the enclosure resulting in increased recoveries. As longer chain PFCAs showed higher recoveries than short-chain PFCAs we presume longer chain PFCAs to precipitate with Ca^{2+} to a greater extent than short-chain PFCAs.

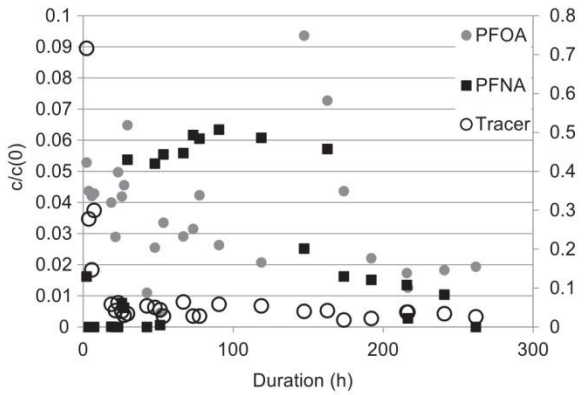


Fig. 4. Breakthrough curves of longer chain PFCAs (left axis) compared to the tracer (right axis) in 40 cm depth.

Also (bio)degradation of precursors resulting in PFCAs and PFSAs (Dinglasen et al., 2004; Liu et al., 2010; Wang et al., 2009a; Lange, 2000; 2001) may have contributed to increased concentrations in 40 cm and 80 cm. In our study we detected 6:2 FTUCA, MeFBSE and MeFBSA. Degradation of these precursors could not have lead to increased recoveries of PFOA and PFNA because all these precursors have shorter chain length compared to PFOA and PFNA and degradation would lead to shorter chain PFCAs or PFSAs. Furthermore, yields of PFCAs and PFSAs during precursor degradation were reported to be <10% during study times of several days to weeks (Liu et al., 2007, 2010; Wang et al., 2005). As the concentrations of precursors in the enclosure's supernatant were low compared to PFCAs or even below the limit of quantifications, these would not have been sufficient to produce the concentrations found for PFCAs and PFSAs.

In conclusion for PFOA and PFNA, our data suggest that interactions in the aqueous phase of the supernatant seemed to control their availability in the water resulting in a gradual and retarded release into the sediment and hence leading to the observed higher recoveries in 40 cm and 80 cm depth. Further studies are needed to understand the underlying processes.

3.5. Quantification of the transport – retardation factors and partition coefficients

For the analytes showing sufficiently clear breakthrough curves, the retardation factors and partition coefficients shown in Table 3 were calculated. For most of the analytes peaks were obvious, indicating that concentrations in the samples decreased after reaching a maximum until they were no longer detectable (Fig. 3). For other analytes, especially PFOA, the end of the peaks were not as clear because concentrations did not reach the baselines (Fig. 4). The resulting tailing of peaks added uncertainties to the quantification of retardation factors (Table S8).

Retardation factors and partition coefficients were higher in 80 cm compared to 40 cm for all analytes except of PFOA and PFNA

Table 3
Retardation factors R, partition coefficients ($cm^3\ g^{-1}$) and organic carbon normalised partition coefficients K_{OC}.

	R		log K_d		log K_{OC}	
	40 cm	80 cm	40 cm	80 cm	40 cm	80 cm
PFBS	[b]	2.6	–	−0.47	–	2.7
PFHxS	1.1	3.0	−2.0	−0.39	1.2	2.8
PFBA	1.0	2.8	−2.4	−0.43	0.8	2.7
PFPA	1.3	[b]	−1.4	[a]	1.8	[a]
PFHxA	4.7	15	−0.18	0.46	3.0	3.6
PFOA	38	25	0.82	0.69	4.0	3.9
PFNA	26	21	0.65	0.62	3.8	3.8
MeFBSE	[b]	[a]	–	[a]	–	[a]

[a] Not detected.
[b] Timely resolution of data points not sufficient.

(Table 3). The observed higher sorption in 80 cm compared to 40 cm might be attributed to changes in biofilm composition (i.e. extracellular polymer substances (EPS) were released by microorganisms onto sediment grains serving as a potential surface for sorption) caused by a relative depletion of dissolved oxygen with depth. An analysis of the biofilms would have been necessary to further evaluate this assumption.

An increasing trend of partition coefficients with increasing chain length was found for PFSAs and PFCAs in this study, except of PFOA and/or PFNA. Partition coefficients were slightly higher for PFOA compared to PFNA, but due to the tailing peak of PFOA it seems likely that results for PFOA were slightly overestimated, particularly as lower values for PFOA are to be expected from the results of Higgins and Luthy (2006). For PFBA to PFOA partition coefficients increased by approximately 1.0 log unit per each additional CF_2 moiety. This was a stronger increase in sorption compared to what is reported in the literature, i.e. 0.5–0.6 log units increase of partition coefficients with each CF_2 unit (Higgins and Luthy, 2006). Differences in sediment texture and water chemistry could have been a reason for the higher increase in our study compared to what is reported in the literature.

Results for PFBS and PFBA, which have the same number of C-atoms, showed similar log K_d in 80 cm (Table 3). PFHxS had clearly lower partitioning coefficients than PFHxA (Table 3). In other studies, i.e. batch studies and studies where water and sediment from rivers and oceans were sampled (infield studies), stronger partitioning of PFSAs to different sediments has been observed compared to PFCAs with the same number of perfluorinated C-atoms (Ahrens et al., 2010; Higgins and Luthy, 2006; Labadie and Chevreuile, 2011), but these publications do not give information on the texture of the sediments investigated. A comparison of partition coefficients of PFSAs and PFCAs with the same number of perfluorinated C-atoms was not possible within our study, because one part of these pairs was either not spiked or was not detected. Nevertheless, PFSAs did not show clearly stronger partitioning in the water-saturated sediment column compared to PFCAs. This is supported by another column study: In a column with loamy sandy soil PFBS eluted close to 100% whereas in the same column PFBA was not fully recovered (no other PFCAs or PFSAs were spiked) indicating also higher sorption of PFBA compared to PFBS (Gellrich et al., 2012). Furthermore Gellrich et al. (2012) found for parts of their experiments no leaching differences between PFCAs and PFSAs. Therefore, the authors stated a leaching behaviour which mainly depends on the chain length.

To the best of our knowledge, we report the first column-derived partition coefficients of PFCAs and PFSAs. Therefore, a direct comparison with results from similar experimental set-ups was not possible as only data from infield-studies or batch-studies were available (Table S9). Results of batch studies might have overestimated sorption due to lower solid:water ratios and because of break-up of aggregates resulting in lager surface areas accessible for sorption (Benker et al., 1998). While in a study by Enevoldsen and Juhler (2010), who used sandy soil, the ratio of soil to water was 3:14 and 12:25, the ratio in our study amounted to 2.5:1 (sandy sediment). Nevertheless, results for PFOA, PFNA and PFBS (PFOA log K_d = 0.0, PFNA log K_d = 0.6, PFBS log K_d = −0.4; Enevoldsen and Juhler, 2010; Table S9) showed good agreement with partition coefficients in our study (no other analytes were in the scope of both studies). From this observation it could be assumed that the solid:water ratio did not significantly affect sorption, but further investigations are necessary. From infield studies, where surface waters and the underlying sediments were investigated, Ahrens et al. (2010) report log K_d = 0.6 for PFNA and Labadie and Chevreuile (2011) found log K_d = 0.8 for PFHxA, which again showed good agreement with our study. For PFBA, to the best of our knowledge, the only partition coefficients available so far were reported from a wastewater treatment plant. The results were based on concentrations in suspended matter and aqueous phase of the primary clarifier (log K_d = −0.7; Vierke et al., 2013a) and were similar to ours.

Competitive binding was found to influence transport. Gellrich et al. (2012) found in their column study, that PFBA could be displaced from bindings sites in the soil if longer chain PFCAs were present. While their concentrations were similar to the ones in our study, their column had a length of 50 cm and their column diameter was 20 times smaller than our column, hence providing much fewer bindings sites than our study. Therefore, we did not presume competitive sorption to play a major role in our study.

3.6. Conclusions – relevance for the production of drinking water using riverbank filtration

Breakthrough curves, recoveries and partition coefficients showed that short-chain PFCAs and PFSAs (i.e. with up to six C-atoms) are only slightly retarded in the water-saturated sediment column (as shown by log K_d < 0.5). The shortest chain length analytes, PFBA and PFBS, were attenuated only by 50% and 25% in 40 cm depth of the sediment column. Even though longer chain PFCAs, i.e. PFOA and PFNA, yielded higher sorption coefficients compared to the shorter-chain PFCAs, breakthrough was still observed during the experimental period. Highest concentrations in 40 cm depth were attenuated by more than 90% in relation to peak concentrations in the supernatant.

Furthermore, our results indicate that precursors were also able to pass a water-saturated sediment column. Their contribution to the occurrence of PFCAs and PFSAs in riverbank filtrate warrants future research.

In consequence, if contaminated surface waters are used as a resource for drinking water production via sediment passage short-chain PFCAs and PFSAs will not be subject to attenuation whilst longer chain PFCAs will be diluted as a result of the retardation by the sediment, but nevertheless, a fraction of these may also eventually be able to pass the sediment. The data presented here are relevant to such settings because they were obtained under near-natural conditions with low, i.e. environmentally relevant concentrations of analytes. Therefore, contaminated riverbank filtrate used for drinking water production is likely to require further treatment to prevent human exposure to these substances.

Acknowledgement

We thank Silke Meier, Stefan Heise and Lothar Beetz (all from the Federal Environment Agency) for technical assistance and their support during sampling, Jürgen Gandraß (Helmholtz-Zentrum Geesthacht) for his help during instrumental analysis, Ralf

Ebinghaus (Helmholtz-Zentrum Geesthacht) for providing the lab and materials for sample analysis and Ingrid Chorus (Federal Environment Agency) for proofreading the manuscript.

Disclaimer

This paper does not necessarily reflect the opinion or the policies of the German Federal Environment Agency.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.11.011.

References

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

Ahrens, L., Taniyasu, S., Yeung, L.W., Yamashita, N., Lam, P.K., Ebinghaus, R., 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 79, 266–272.

Benker, E., Davis, G.B., Barry, Y., 1998. Estimating the retardation coefficients of trichloroethene for a sand aquifer low in sediment organic carbon – a comparison of methods. J. Contam. Hydrol. 30, 157–178.

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

Conder, J.M., Hoke, R.A., Wolf, W., de Russell, M.H., Buck, R.C., 2008. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. Environ. Sci. Technol. 4, 995–1003.

Ding, G.-H., Frömel, T., van den Brandhof, E.-J., Baerselman, R., Peijnenburg, W.J., 2012. Acute toxicity of poly- and perfluorinated compounds to two cladocerans, *Daphnia magna* and *Chydorus sphaericus*. Environ. Toxicol. Chem. 31, 605–610.

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

Dreyer, A., Weinberg, I., Temme, C., Ebinghaus, E., 2009. Polyfluorinated compounds in the atmosphere of the Atlantic and Southern Oceans: evidence for a global distribution. Environ. Sci. Technol. 43, 6507–6514.

Enevoldsen, R., Juhler, R.K., 2010. Perfluorinated compounds (PFCs) in groundwater and aqueous soil extracts: using inline SPE-LC-MS/MS for screening and sorption characterisation of perfluorooctane sulphonate and related compounds. Anal. Bioanal. Chem. 398, 1161–1172.

Eschauzier, C., Haftka, J., Stuyfzand, P.J., Voogt, P. de, 2010. Perfluorinated compounds in infiltrated River Rhine water and infiltrated rainwater in Coastal Dunes. Environ. Sci. Technol. 44, 7450–7455.

Furl, C.V., Meredith, C.A., Strynar, M.J., Nakayama, S.F., 2011. Relative importance of wastewater treatment plants and non-point sources of perfluorinated compounds to Washington State rivers. Sci. Total Environ. 409, 2902–2907.

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

Gellrich, V., Stahl, T., Knepper, T.P., 2012. Behavior of perfluorinated compounds in soils during leaching experiments. Chemosphere 87, 1052–1056.

Goss, K.-U., 2008. The pKa values of PFOA and other highly fluorinated carboxylic acids. Environ. Sci. Technol. 42, 456–458.

Grützmacher, G., Wessel, G., Chorus, I., Bartel, H., 2005. Are There Limits to Cyanobacterial Toxin (Microcystin) Elimination by Sand Passage? ISMAR.

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

Hijnen, W.A.M., Brouwer-Hanzens, A.J., Charles, K.J., Charles, K., Medema, G.J., 2005. Transport of S2 phage, *Escherichia coli*, *Clostridium perfringens*, *Cryptosporidium parvum*, and *Giardia intestinalis* in a gravel and a sandy soil. Environ. Sci. Technol. 39, 7860–7868.

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

Kannan, K., 2011. Perfluoroalkyl and polyfluoroalkyl substances: current and future perspectives. Environ. Chem. 8, 333–338.

Kuehn, W., Mueller, U., 2000. Riverbank filtration an overview. J. AWWA 92, 60–69.

Labadie, P., Chevreuile, M., 2011. Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Orge River (nearby Paris, France). Environ. Pollut. 159, 391–397.

Lange, C.C., 2000. The Aerobic Biodegradation of N-EtFOSE Alcohol by the Microbial Activity Present in Municipal Wastewater Treatment Sludge, Minnesota.

Lange, C.C., 2001. The 18-Day Aerobic Biodegradation Study of Perfluorooctanesulfonyl-based Chemistries, Minnesota.

Lange, F.T., Wenz, M., Schmidt, C.K., Brauch, H.J., 2007. Occurrence of perfluoroalkyl sulfonates and carboxylates in German drinking water sources compared to other countries. Water Sci. Technol. 56, 151–158.

Li, F., Sun, H., Hao, Z., He, N., Zhao, L., Zhang, T., Sun, T., 2011. Perfluorinated compounds in Haihe River and Dagu Drainage Canal in Tianjin, China. Chemosphere 84, 265–271.

Lindstrom, A.B., Strynar, M.J., Libelo, L.E., 2011. Polyfluorinated compounds: past, present, and future. Environ. Sci. Technol. 45, 7954–7961.

Liu, J., Lee, L.S., Nies, L.F., Nakatasu, C.H., Turco, R.F., 2007. Biotransformation of 8:2 fluorotelomer alcohol in soil and by soil bacteria isolates. Environ. Sci. Technol. 41, 8024–8030.

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

Matheson, K.L., Cox, M.F., Smith, D.L., 1985. Interactions between linear alkylbenzene sulfonates and water hardness ions. I. Effect of calcium ion on surfactant solubility and implications for detergency performance. J. Am. Oil Chem. Soc., 1391–1396.

Möller, A., Ahrens, L., Sturm, R., Westerveld, J., van der Wielen, F., Ebinghaus, R., Voogt, P. de, 2010. Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. Environ. Pollut. 158, 3243–3250.

Murakami, M., Kuroda, K., Sato, N., Fukushi, T., Takizawa, S., Takada, H., 2009. Groundwater pollution by perfluorinated surfactants in Tokyo. Environ. Sci. Technol. 43, 3480–3486.

Murakami, M., Nobuyuki, S., Anegawa, A., Nakada, N., Harada, A., Komatsu, T., Takada, H., Tanaka, H., Ono, Y., Furumai, H., 2008. Multiple evaluations of the removal of pollutants in road runoff by soil infiltration. Water Res. 42, 2745–2755.

Paul, A.G., Jones, K.C., Sweetman, A., 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environ. Sci. Technol. 43, 386–392.

Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. Environ. Sci. Technol. 40, 32–44.

Psillakis, E., Cheng, J., Hoffmann, M.R., Colussi, A.J., 2009. Enrichment factors of perfluoroalkyl oxoanions at the air/water interface. J. Phys. Chem. A, 8826–8829.

Rayne, S., Forest, K., 2009. Perfluoroalkyl sulfonic and carboxylic acids: a critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. J. Environ. Sci. Health Part A 44, 1145–1199.

Scheffer, F., Schachtschabel, P., 1998. Lehrbuch der Bodenkunde. Enke, Spektrum Akademischer Verlag.

Stahl, T., Riebe, R.A., Falk, S., Failing, K., Brunn, H., 2013. Long-term lysimeter experiment to investigate the leaching of Perfluoroalkyl Substances (PFASs) and the carry-over from soil to plants: results of a pilot study. J. Agric. Food Chem. 61, 1784–1793.

Verstraeten, I.M., Heberer, T., Scheytt, T., 2003. Occurrence, characteristics, transport, and fate of pesticides, pharmaceuticals, industrial products, and personal care products at riverbank filtration sites. In: Ray, C., Melin, G., Linsky, R.B. (Eds.), Riverbank Filtration. Improving Source-Water Quality. Kluwer Academic Publishers, Dordrecht, Boston, London, pp. 175–228.

Vierke, L., Staude, C., Biegel-Engler, A., Drost, W., Schulte, C., 2012. Perfluorooctanoic acid (PFOA) – main concerns and regulatory development in Europe from an environmental point of view. Environ. Sci. Eur. 24, 16.

Vierke, L., Ahrens, L., Shoeib, M., Palm, W.-U., Webster, E.M., Eliis, D.A., Ebinghaus, R., Harner, T., 2013a. In situ air–water and particle–water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant. Chemosphere 92, 941–948.

Vierke, L., Berger, U., Cousins, I.T., 2013b. Estimation of the acids dissociation constant of perfluoroalkyl carboxylic acids through an experimental investigation of their water-to-air transport. Environ. Sci. Technol. 47, 11032–11039.

Wang, N., Szostek, B., Buck, R.C., Folsom, P.W., Sulecki, L.M., Capka, V., Berti, W.R., Gannon, J.T., 2005. Fluorotelomer alcohol biodegradations – direct evidence that perfluorinated carbon chains breakdown. Environ. Sci. Technol. 39, 7516–7528.

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

Wang, T., Wang, Y., Liao, C., Cai, Y., Jiang, G., 2009b. Perspectives on the inclusion of perfluorooctane sulfonate into the Stockholm convention on persistent organic pollutants. Environ. Sci. Technol. 43, 5171–5175.

Wang, Z., Macleod, M., Cousins, I.T., Scheringer, M., Hungerbühler, K., 2011. Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs). Environ. Chem. 8, 389–398.

Weiss, W.J., Bouwer, E.J., Aboytes, R., LeChevallier, M.W., O'Melia, C.R., Le, B.T., Schwab, K.J., 2005. Riverbank filtration for control of microorganisms: results from field monitoring. Water Res. 39, 1990–2001.

Westall, J.C., Chen, H., Zhang, W., Brownawell, B.J., 1999. Sorption of linear alkylbenzenesulfonates on sediment materials. Environ. Sci. Technol. 33, 3110–3118.

Zushi, Y., Hogarh, J.N., Masunaga, S., 2012. Progress and perspective of perfluorinated compound risk assessment and management in various countries and institutes. Clean Technol. Environ. Policy 14, 9–20.

Supplementary Content

Transport of perfluoroalkyl compounds in a water-saturated sediment column investigated under near-natural conditions

Lena Vierke[a, b, *], Axel Möller[c, 1], Sondra Klitzke[d]

[a]Federal Environment Agency, Wörlitzer Platz 1, 06844 Dessau-Roßlau, Germany, Lena.Vierke@uba.de

[b]Leuphana University of Lüneburg, Scharnhorststr.1, 21335 Lüneburg, Germany

[c]Helmholtz-Zentrum Geesthacht, Max-Planck Str.1, 21502 Geesthacht, Germany, Axel.Moeller@hzg.de

[d]Federal Environment Agency, Schichauweg 58, 12307 Berlin, Germany, Sondra.Klitzke@uba.de

*corresponding author: Tel 0049 340 2103 6620, Fax 0049 340 2104 6620

[1] Current address: GBA Gesellschaft für Bioanalytik mbH, Goldtschmidtstraße 5, 21073 Hamburg, Germany

1. Analytes

Table S 1: List of analytes with their abbreviations and suppliers of standards.

Name	Abbreviation	Supplier	Name of standard
Perfluoro-1-butanesulfonicacid	PFBS	Wellington Laboratories	PFAC-MXA
Perfluoro-1-hexanesulfonicacid	PFHxS	Wellington Laboratories	PFAC-MXA
Perfluoro-1-heptanesulfonicacid	PFHpS	Wellington Laboratories	L-PFHpS
Perfluoro-1-octanesulfonicacid	PFOS	Wellington Laboratories	PFAC-MXA
Perfluoro-n-butanoic acid	PFBA	Wellington Laboratories	PFAC-MXA
Perfluoro-n-pentanoic acid	PFPA	Wellington Laboratories	PFAC-MXA
Perfluoro-n-hexanoic acid	PFHxA	Wellington Laboratories	PFAC-MXA
Perfluoro-n-heptanoic acid	PFHpA	Wellington Laboratories	PFAC-MXA
Perfluoro-n-octanoic acid	PFOA	Wellington Laboratories	PFAC-MXA
Perfluoro-n-nonanoic acid	PFNA	Wellington Laboratories	PFAC-MXA
Perfluoro-n-decanoic acid	PFDA	Wellington Laboratories	PFAC-MXA
N-methylperfluoro-1-butanesulfonamide	MeFBSA	present from 3M	-
N-methylperfluro-1-butanesufonamidoethanol	MeFBSE	present from 3M	-
2-Perfluorohexyl ethanoic acid (6:2)	6:2 FTCA o. FHEA	Wellington Laboratories	FTA MXA
2-Perfluoroocxyl ethanoic acid (8:2)	8:2 FTCA o. FOEA	Wellington Laboratories	FTA MXA
2-Perfluorodexyl ethanoic acid (10:2)	10:2 FTCA o. FDEA	Wellington Laboratories	FTA MXA
2H-Perfluoro-2-octenoic acid (6:2)	6:2 FTUCA o. FHUEA	Wellington Laboratories	FHUEA
2H-Perfluoro-2-decenoic acid (8:2)	8:2 FTUCA o. FOUEA	Wellington Laboratories	FHOEA
Perfluoro-1-hexane[$^{18}O_2$]sulfonicacid	$^{18}O_2$PFHxS	Wellington Laboratories	MPFAC-MXA
Perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonicacid	$^{13}C_4$PFOS	Wellington Laboratories	MPFAC-MXA
Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	$^{13}C_4$PFBA	Wellington Laboratories	MPFAC-MXA

Perfluoro-n-[1,2,-$^{13}C_2$]hexanoic acid	$^{13}C_2$PFHxA	Wellington Laboratories	MPFAC-MXA
Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	$^{13}C_4$PFOA	Wellington Laboratories	MPFAC-MXA
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	$^{13}C_5$PFNA	Wellington Laboratories	MPFAC-MXA
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	$^{13}C_2$PFDA	Wellington Laboratories	MPFAC-MXA
N-methyl-d3-perfluoro-1-octanesulfonamide	D3-MeFOSA	Wellington Laboratories	d-N-MeFOSA-M
2-(N-deuteriomethylperfluro-1-octane-sufonamido)-1,1,2,3-tetradeuterioethanol	D7-MeFOSE	Wellington Laboratories	d7-N-MeFOSE-M
2-Perfluorohexyl-[1,2-$^{13}C_2$]-ethanoic acid (6:2)	^{13}CFHEA	Wellington Laboratories	MFTA-MXA
2-Perfluoroocxyl-[1,2-$^{13}C_2$]-ethanoic acid (8:2)	^{13}CFOEA	Wellington Laboratories	MFTA-MXA
2-Perfluorodexyl-[1,2-$^{13}C_2$]-ethanoic acid (10:2)	^{13}CFDEA	Wellington Laboratories	MFTA-MXA
2H-Perfluoro-[1,2-$^{13}C_2$]-2-octenoic acid (6:2)	^{13}CFHUEA	Wellington Laboratories	MFHUEA
2H-Perfluoro-[1,2-$^{13}C_2$]-2-decenoic acid (8:2)	^{13}CFOUEA	Wellington Laboratories	MFOUEA
2-(N-deuterioethylperfluro-1-octane-sufonamido)-1,1,2,3-tetradeuterioethanol	D9-EtFOSE	Wellington Laboratories	d9-N-EtFOSE-M
Perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfinate	MPFOSi	Wellington Laboratories	MPFOSi

Table S 2: Masstransfer of analytes and corresponding masslabelled internal standards (IS)

Name	Masstransfer	IS	Masstransfer
PFBA	213 / 169	$^{13}C_4$PFBA	217 / 172
PFPA	263 / 219		
PFHxA	313 / 269	$^{13}C_2$PFHxA	315 / 270
PFHpA	363 / 319		
PFOA	413 / 369	$^{13}C_4$PFOA	417 / 372
PFNA	463 / 419	$^{13}C_5$PFNA	468 / 423
PFDA	513 / 469	$^{13}C_2$PFDA	515 / 470
PFBS	299 / 80		
PFHxS	399 / 80	$^{18}O_2$PFHxS	403 / 84
PFHpS	449 / 79		
PFOS	499 / 80	$^{13}C_4$PFOS	503 / 80
MeFBSA	312/219	d3-N-MeFOSA-M	515/169
MeFBSE	416/59	d7-N-MeFOSE-M	623/59
FHEA	377/293	$^{13}C_2$FHEA	379/294
FOEA	477/393	$^{13}C_2$FOEA	479/394
FDEA	577/493	$^{13}C_2$FDEA	579/494
FHUEA	357/293	$^{13}C_2$FHUEA	359/294
FOUEA	457/393	$^{13}C_2$FOUEA	459/394
d9-N-EtFOSE	640/59	-	
PFOSi	487/423	-	

2. Grain Size distribution

Table S 3: Grain size distribution of the coarse-grained medium sand in the enclosure.

Grain size (mm)	< 0.002	0.002 - 0.0063	0.0063 - 0.02	0.02 - 0.063	0.063 - 0.2	0.2 - 0.63	0.63 - 2.0
Fraction (%)	0.0	0.0	0.1	0.4	14.8	73.8	10.9

3. Limits of detection

Table S 4: Limits of detection (LOD) in ng L^{-1} for analytes in water samples. For analytes were blank concentrations were frequently detected the standard deviation of the blank concentrations was defined as LOD. The instrumental detection limit, determined as the concentrations in the lowest calibration points which corresponds to a signal of noise ratio of three, was used as LOD for compounds were no blank concentrations were found.

	LOD (in ng L^{-1})
PFBS	0.05
PFHxS	0.02
PFHpS	0.17
PFOS	2.2
PFBA	0.28
PFPA	0.3
PFHxA	0.1
PFHpA	3.3
PFOA	0.12
PFNA	0.04
PFDA	0.04
MeFBSA	0.36
MeFBSE	0.04
FHEA	0.27
FOEA	0.96
FDEA	0.66
FHUEA	0.13
FOUEA	0.13

4. Concentrations of analytes in samples

Table S 5: Concentrations in samples from the supernatant (nd = not detected, *set to LOD/2).

Dura-tion	PFBS	PFHxS	PFHpS	PFBA	PFPA	PFHxA	PFOA	PFNA	PFDA	MeFBSA	MeFBSE	FHUEA
min	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}
System blank	1.1	0.31	nd	1.2	0.97	0.29	1.1	0.18	nd	nd	nd	nd
0	8.3	8.4	5.4	11	3.7	10	16	7.9	6.6	13	7.9	1.0
135	3.0	2.7	1.8	4.1	1.2	3.0	4.4	2.5	3.6	1.4	4.1	0.68
225	1.8	1.7	2.0	3.0	2.2	2.2	3.5	1.7	2.6	1.3	6.7	nd
345	1.3	0.85	0.09*	2.9	0.15*	1.4	1.9	0.88	1.4	nd	0.95	nd
435	1.1	0.55	0.70	1.8	0.15*	0.78	1.5	0.47	0.72	nd	nd	nd
1125	0.42	nd	0.09*	2.1	0.15*	0.55	0.74	0.04	0.01	nd	nd	nd
1290	0.60	nd	0.09*	2.6	0.15*	0.38	0.92	0.12	0.04	nd	nd	nd
1545	0.12	0.41	nd	0.14*	0.15*	0.33	0.99	0.19	nd	nd	nd	nd
1635	1.3	0.45	nd	0.66	0.15*	0.13	0.86	0.11	0.02*	nd	nd	nd
2865	0.09	nd	nd	0.38	0.15*	0.43	1.1	0.56	0.16	nd	nd	nd
5430	0.10	0.14	nd	0.66	0.15*	0.38	1.0	0.52	nd	nd	nd	nd
14445	0.19	0.29	nd	0.14*	0.15*	0.26	0.94	0.15	nd	nd	nd	nd

Table S 6: Concentrations in samples from 40 cm (nd = not detected, *set to LOD/2).

Duration	PFBS	PFHxS	PFBA	PFPA	PFHxA	PFOA	PFNA	MeFBSE
min	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}
System blank	1.2	0.4	1.6	0.15*	0.32	0.56	0.06	nd
135	6.3	3.0	5.5	0.15*	1.3	1.3	0.19	0.41
225	4.2	3.2	4.2	0.96	1.4	1.2	0.02*	0.18
345	3.2	2.3	3.4	0.15*	1.5	1.2	0.02	nd
435	2.2	1.8	2.9	1.0	1.6	1.2	0.02	nd
1125	0.79	0.26	1.8	0.15*	0.89	1.1	0.06	nd
1290	0.91	0.49	1.8	0.15*	1.4	0.98	0.04	nd
1395	0.93	0.37	1.9	0.15*	1.1	1.3	0.02*	nd
1545	0.13	0.38	0.5	0.44	0.54	1.2	0.12	nd
1635	0.69	0.37	1.5	0.15*	1.1	1.2	0.11	nd
1770	0.23	0.16	0.34	0.15*	0.72	1.5	0.48	nd
2550	0.48	0.33	0.14*	0.15*	0.83	0.72	0.02*	nd
2865	0.03*	0.19	0.28	0.15*	0.57	0.93	0.47	nd
3075	0.40	0.34	0.44	0.15*	0.85	0.62	0.07	nd
3210	0.03*	0.14	0.56	0.15*	0.47	1.1	0.49	nd
4005	0.03*	0.19	0.42	0.15*	0.35	0.98	0.49	nd
4395	0.16	0.23	0.58	0.15*	0.49	1.0	0.54	nd
4650	0.05	0.19	0.61	0.15*	0.38	1.2	0.53	nd
5430	0.03*	0.08	0.55	0.15*	0.37	0.94	0.55	nd
7125	0.08	0.24	0.72	0.15*	0.30	0.86	0.53	nd
8835	0.98	0.21	3.9	0.15*	0.72	1.9	0.26	nd
9765	1.2	0.13	0.61	0.15*	0.66	1.6	0.50	nd
10425	1.4	0.22	2.4	0.15*	0.51	1.2	0.19	nd
11520	0.09	0.43	0.14*	0.15*	0.28	0.88	0.18	nd
12945	0.07	0.39	0.14*	0.15*	0.30	0.81	0.17	nd
12985	0.88	0.09	0.51	0.15*	0.28	0.74	0.08	nd
14445	0.05	0.34	0.72	0.15*	0.11	0.82	0.14	nd
15705	0.41	0.15	1.3	0.15*	0.42	0.84	0.05	nd
20220	1.1	0.10	1.5	0.15*	0.38	1.3	0.25	nd
21480	1.3	0.12	3.4	0.15*	0.62	0.94	0.11	nd

Table S 7: Concentrations in samples from 80 cm (nd = not detected, *set to LOD/2).

Duration	PFBS	PFHxS	PFBA	PFHxA	PFOA	PFNA
min	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}
System blank	1.1	0.36	1.6	0.37	0.77	nd
135	0.94	0.41	1.4	0.05*	0.64	0.02*
225	0.38	0.14	1.4	0.34	0.98	Nd
345	0.38	0.52	0.14*	0.23	0.88	0.05
435	1.6	0.50	0.50	0.24	0.99	0.02*
1125	1.9	1.2	2.7	0.38	0.93	Nd
1290	1.5	1.0	2.9	0.39	0.96	Nd
1395	0.63	1.1	1.8	0.29	0.85	0.05
1545	0.43	0.76	1.5	0.42	0.86	0.02*
1635	1.8	0.93	3.0	0.05*	1.1	0.06
1770	0.68	0.44	1.6	0.42	1.2	nd
2550	1.4	0.44	1.3	0.22	0.9	0.06
2865	0.18	0.18	1.2	0.64	1.1	nd
3075	1.6	0.58	0.93	0.22	0.80	nd
3210	0.19	0.16	0.96	0.56	1.1	nd
4005	0.21	0.19	1.1	0.64	1.2	nd
4395	0.12	0.22	0.78	0.76	1.1	nd
4650	0.22	0.13	0.47	0.69	0.94	nd
5430	0.03*	0.16	0.78	0.69	0.88	0.42
7125	0.03*	0.15	0.58	0.57	1.0	0.41
9765	0.03*	0.18	0.49	0.53	1.0	0.45
11520	0.03	0.36	0.35	0.47	1.2	0.13
12945	0.11	0.40	0.31	0.44	1.2	0.13
14445	0.21	nd	0.90	0.68	1.1	0.10
15705	0.42	0.21	1.4	0.83	1.5	0.07
20220	3.6	1.4	13	15	17	0.91
21480	0.48	0.19	1.3	0.14	1.1	0.11

5. Sediment-dissolved partition coefficients and organic carbon normalized sediment-dissolved partitioning coefficients

Table S 8: Sediment-dissolved partition coefficients (K_d in $cm^3\ g^{-1}$ and log R_d) and organic carbon normalized sediment-dissolved partitioning coefficients (K_{OC} in $cm^3\ g^{-1}$ and log K_{OC}).

	R		K_d ($cm^3\ g^{-1}$)		log K_d		K_{OC} ($cm^3\ g^{-1}$)		log K_{OC}		Comment	
	40 cm	80 cm	40 cm	80 cm	40 cm	80 cm	40 cm	80 cm	40 cm	80 cm	40 cm	80 cm
PFBS	0.42	2.6	[2]	0.34	-	-0.47	-	490	-	3.0	timely resolution of data points not sufficient	Peak with scattered data points
PFHxS	1.1	3.0	0.01	0.41	-2.00	-0.39	14	590	1.2	2.8	Clear Peak	Clear peak
PFBA	1.0	2.8	0.004	0.37	-2.4	-0.43	6.3	530	0.8	2.7	Clear Peak	Peak with scattered data points
PFPA	1.3	[1]	0.04	[1]	-1.4	[1]	64	0.00	1.8	-	Peak with very few data points	[1]
PFHxA	4.7	15	0.66	2.9	-0.18	0.46	940	4100	3.0	3.6	slightly tailing peak	slightly tailing peak
PFOA	38	25	6.5	4.9	0.82	0.69	9300	7020	4.0	3.9	No clear peak but high concentration for the entire experiment	No clear peak and concentrations shortly above the detection limit for the entire experiment
PFNA	26	21	4.5	4.1	0.65	0.62	6400	5900	3.8	3.8	clear peak	Clear peak
MeFBSE	0.53	[1]	[2]	-	[2]	-	[2]	-	[2]	-	Detected in two samples only	[1]

[1] not detected

[2] a negative R would result in a negative K_d and K_{OC}

6. Sediment-dissolved partition coefficients reported in the literature

Table S 9: Log K_d values ($cm^3\ g^{-1}$ or $L\ Kg^{-1}$) reported in the literature.

	Reference	details	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFHpS	PFOS	PFOSA	8:2 FTUCA
infield sediment-water	(Ahrens et al., 2010)	sediment pH 7.1 - 7.4, 1.5 - 1.7 % OC			0.0	0.6	1.8		1.8		2.1	2.5	
		SPM		1.9	2.4	2.9	3.5		2.6		3.7	3.4	
infield sediment-water	(Kwadijk et al., 2010)	no details			1.8	1.8	2.9	1.4	2.4		2.5		
infield sediment-water	(Labadie and Chevreuile, 2011)	4.8 % OC	0.8	0.8		1.5	2.4		0.9	1.6	2.4		
infield sediment-water	(Li et al., 2011)	2.1 - 11 % OC	2.5	2.4	2.5	2.5	3.0				3.2		2.8
			1.8	1.7	1.8	2.1	2.9				3.1		2.6
batch sediment-water	(Pan et al., 2009)	0.75 % OC, pH 7.18									0.9		
											1.3		
batch soil-water	(Enevoldsen and Juhler, 2010)	sandy		*-0.2*	*0.0*	*0.6*	*1.5*	*-0.4*			*1.2*		
WWTP	(Yu et al., 2009)	primary sludge			2.3						3.0		
		primary sludge			2.7						3.3		
		activated sludge			2.3						2.9		
		activated sludge			2.7						3.4		
batch sludge - water	(Ochoa-Herrera and Sierra-Alvarez, 2008)	anaerobically sewage sludge									1.9		
		anaerobically sewage sludge									2.4		
		anaerobic slduge									2.2		
		anaerobic slduge									2.3		

7. References

Ahrens, L.,Taniyasu, S.,Yeung, L. W.,Yamashita, N.,Lam, P. K.,Ebinghaus, R., 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 79, 266–272.

Enevoldsen, R.,Juhler, R. K., 2010. Perfluorinated compounds (PFCs) in groundwater and aqueous soil extracts: using inline SPE-LC-MS/MS for screening and sorption characterisation of perfluorooctane sulphonate and related compounds. Anal. Bioanal. Chem. 398, 1161–1172.

Kwadijk, C. J. A. F.,Korytar, P.,Koelmans, A. A., 2010. Distribution of Perfluorinated Compounds in Aquatic Systems in The Netherlands. Environ. Sci. Technol. 44, 3746–3751.

Labadie, P.,Chevreuile, M., 2011. Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Orge River (nearby Paris, France). Environmental Pollution 159, 391–397.

Li, F.,Sun, H.,Hao, Z.,He, N.,Zhao, L.,Zhang, T.,Sun, T., 2011. Perfluorinated compounds in Haihe River and Dagu Drainage Canal in Tianjin, China. Chemosphere 84, 265–271.

Ochoa-Herrera, V.,Sierra-Alvarez, R., 2008. Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. Chemosphere 72, 1588–1593.

Pan, G.,Jia, C.,Zhao, D.,You, C.,Chen, H.,Jiang, G., 2009. Effect of Cationic and Anionic Surfactants on the Sorption and Desorption of Perfluorooctane Sulfonate (PFOS) on Natural Sediments. Environmental Pollution 157, 325–330.

Yu, Q.,Zhang, R.,Deng, S.,Huang, J.,Yu, G., 2009. Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study. Water Research 43 (4), 1150–1158.

A3 Paper 3 particle-gas partitioning WWTP

RESEARCH FRONT

CSIRO PUBLISHING

Research Paper

www.publish.csiro.au/journals/env L. Vierke et al., *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133

Air concentrations and particle–gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant

Lena Vierke,[A,B] *Lutz Ahrens*,[A] *Mahiba Shoeib*,[A,F] *Eric J. Reiner*,[C,D] *Rui Guo*,[D,C] *Wolf-Ulrich Palm*,[B] *Ralf Ebinghaus*[E] *and Tom Harner*[A]

[A]Environment Canada, Science and Technology Branch, 4905 Dufferin Street, Toronto, ON, M3H 5T4, Canada.

[B]Leuphana University of Lüneburg, Institute for Environmental Chemistry, Scharnhorststrasse 1, D-21335 Lüneburg, Germany.

[C]Ontario Ministry of the Environment, 125 Resources Road, Toronto, ON, M9P 3V6, Canada.

[D]University of Toronto, Department of Chemistry, Toronto, ON, M5S 3H6, Canada.

[E]Helmholtz-Zentrum Geesthacht, Institute for Coastal Research, Max-Planck Strasse, 1, D-21502 Geesthacht, Germany.

[F]Corresponding author. Email: mahiba.shoeib@ec.gc.ca

Environmental context. Polyfluoroalkyl compounds, widely used chemicals in consumer and industrial products, are global pollutants in the environment. Transport mechanisms and environmental pathways of these compounds, however, are not yet fully understood. We show that a wastewater treatment plant can be an important source for polyfluoroalkyl compounds to the atmosphere where they have the potential to be transported long distances.

Abstract. An air sampling campaign was conducted at a wastewater treatment plant (WWTP) to investigate air concentrations and particle–gas partitioning of polyfluoroalkyl compounds (PFCs). Samples were collected at an aeration tank and a secondary clarifier using both active high volume samplers and passive samplers comprising sorbent-impregnated polyurethane foam (SIP) disks. Water to air transport of PFCs was believed to be enhanced at the aeration tank owing to aerosol-mediated transport caused by surface turbulence induced by aeration. Mean air concentrations of target PFCs at the aeration tank were enriched relative to the secondary clarifier by factors of ~19, ~4 and ~3 for ∑fluorotelomer alcohols (FTOHs) (11 000 *v.* 590 pg m^{-3}), ∑perfluorooctane sulfonamides & perfluorooctane sulfonamidoethanols (FOSAs & FOSEs) (120 *v.* 30 pg m^{-3}) and ∑perfluoroalkyl carboxylates & perfluoroalkyl sulfonates (PFCAs & PFSAs) (4000 *v.* 1300 pg m^{-3}) respectively. The particle associated fraction in the atmosphere increased with increasing chain length for PFCAs (from 60 to 100%) and PFSAs were predominantly bound to particles (~98%). Lower fractions on particles were found for FTOHs (~3%), FOSAs (~30%) and FOSEs (~40%). The comparison of the active and passive air sampling showed good agreement.

Additional keywords: atmosphere, passive air sampler, PFC, PFOA, PFOS, WWTP.

Introduction

Polyfluoroalkyl compounds (PFCs), such as perfluorooalkyl carboxylates (PFCAs) and perfluorooalkyl sulfonates (PFSAs), have been detected in a variety of environmental media and also in remote regions[1]; including rivers,[2] oceans,[3] the atmosphere,[4] wildlife,[1] and in humans.[5] PFCAs and PFSAs are persistent, bioaccumulative and toxic.[6–8] Fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs) and perfluorooctane sulfonamidoethanols (FOSEs) are precursors for PFCAs and PFSAs.[9–11] These precursors are volatile and can be transported in the atmosphere.[12–14]

There is still uncertainty about the origin of PFCs in the environment and the transport pathways of PFCAs and PFSAs are still under discussion. Wastewater treatment plants (WWTPs) are known to be point sources for PFCAs and PFSAs in rivers.[15,16] PFCs can be further transported via ocean currents to remote regions.[3] In terms of atmospheric pathways, the long-range transport of precursors can contribute to the occurrence of PFCs in remote regions.[17,18] However, the amounts from transport of PFCAs and PFSAs in ocean currents or from their precursor compounds in the atmosphere are not sufficient to fully explain the levels detected in remote regions.[13,17] Additionally, atmospheric PFCA and PFSA concentrations in urban areas cannot be explained by only considering the degradation of precursors.[19]

Recently, a laboratory experiment and a model have shown the transport of perfluorooctanoic acid (PFOA) in the gas-phase in its neutral form.[20,21] It was suggested that PFOA originated

1448-2517/11/040363

from aerosol-mediated transport from a water body into the atmosphere.[20] PFCAs and PFSAs have been detected in the particle-phase in the atmosphere; however, only a few studies have reported their presence in the gas-phase.[19,22]

The aim of this study was to generate more information on aerosol-mediated sources of PFCs by investigating the air concentrations and particle–gas partitioning of PFCs emitted at two locations in a WWTP – the aeration tank and the secondary clarifier. A secondary aim was to compare measurements conducted using the active high volume air sampler with time-integrated measurements using a sorbent-impregnated polyurethane foam (SIP) disk passive air sampler.

Experimental methods

Chemicals

The target analytes included 10 PFCAs (C_4–C_{12}, C_{14}), 4 PFSAs (C_4, C_6, C_8, C_{10}), 3 FTOHs (6 : 2, 8 : 2, 10 : 2 FTOH), 3 FOSAs, 2 FOSEs, 1 PFOSEA and 19 mass-labelled internal standards (see Tables A1 and A2 in the Accessory publication, available at http://www.publish.csiro.au/?act=view_file&file_id=EN10133_AC.pdf).

Sampling

Sampling took place at a WWTP in Ontario, Canada, during spring 2010. At this sampling site two sampling locations were chosen: one at the aeration tank, where activated sludge is added to the wastewater to remove organic materials; and the other at the secondary clarifier, where the sludge is allowed to settle, to be separated from the water. The main difference between the two sampling sites is that air is blown into the wastewater at the aeration tank, to create an aerobic environment for the microbes. This generates a turbulent and bubbling surface at the aeration tank whereas the surface of the secondary clarifier is relatively calm.

High volume air samples (~140 m^3 per sample) were collected for 24 h, twice per week over a period of 6 weeks at an aeration tank and a secondary clarifier at a WWTP. Glass fibre filters (GFFs) (Pall Corporation, Quebec, QC, Canada, Type A/E Glass 102-mm diameter baked at 250°C before sampling) were used to collect the particle-phase, whereas PUF/XAD/PUF cartridges (precleaned large PUF plug, Supelco, Oakville, ON, Canada, 7.6-cm length, 6-cm diameter, 15 g of XAD-2 (SupelcoTM-2), Supelco) were used for trapping gas-phase compounds. In addition, SIP disks were deployed in duplicate for 37 days during the same time period at both sampling sites to provide a time-integrated sample. To prepare SIP disks, precleaned PUF disks (diameter 14 cm, thickness 1.35 cm, surface area 365 cm^2, mass 4.4 g, volume 207 cm^3, density 0.0231 g cm^{-3}, Tisch Environmental, Cleves, OH, USA) were coated by dipping in a hexane and ground Amberlite XAD-4 slurry (styrene-divenylbenzene, Supelco) and then drying, according to the method described in Shoeib et al.[23]

The effective air volume (V_{air}) for passive samples was calculated using[24]:

$$V_{air} = K_{SIP-air} \times V_{SIP}\left[1 - \exp\left(-\frac{d \times k_a}{K_{SIP-air} \times D_{film}}\right)\right] \quad (1)$$

V_{SIP} is the volume of the SIP disks (2.10×10^{-4} m^3), d the deployment time (37 days), D_{film} the thickness of the SIP disks (5.67×10^{-3} m) and k_a the air-side mass-transfer coefficient (108 m day^{-1}) calculated as the ratio of the sampling rate and the area of the SIP disks (3.7×10^{-2} m^2). The sampling rate was determined during another study ($r = 4$ m^3 day^{-1}).[24] SIP–air partitioning coefficients ($K_{SIP-air}$) and the slope of octanol–air partitioning coefficients (K_{OA}) from the literature[23,25,26] were used for the determination of temperature dependent $K_{SIP-air}$ values (average temperature during sampling period 9°C). The sample volume for FTOHs, FOSAs and FOSEs ranged from 120 to 140 m^3.

For PFCAs and PFSAs, an effective air volume of 150 m^3 was calculated based on the duration of 37 days and a SIP disk sampling rate of 4 m^3 day^{-1} according to Genualdi et al.[24]

Field blank samples for all sample media were collected by exposing them for 1 min at the sampling site and then treated them like real samples. Total suspended particles (TSPs) were determined gravimetrically by weighing the GFFs before and after sampling and dividing the mass by the air sample volumes. Furthermore air temperature was measured at the sampling sites.

Extraction and analysis

The extraction method and analysis was similar to methods used elsewhere.[23,24] All samples were spiked with mass-labelled internal standards before extraction. The PUF/XAD/PUF cartridges and the SIP-disks were extracted using Soxhlet apparatus with petroleum ether (6 h, 240 mL, ~20–40 cycles) for FTOHs, FOSAs and FOSEs and thereafter with methanol (10–14 h, 240 mL, ~50–70 cycles) for PFCAs and PFSAs. The GFFs were extracted by sonication using dichloromethane for FTOHs, FOSAs and FOSEs (three times using 12 mL for 20 min and then combining extracts) and methanol for PFCAs and PFSAs (five times using 12 mL for 20 min and then combining extracts). The two fractions for each sample media were treated separately. All fractions were concentrated by rotary evaporation (Büchi, Flawil, Switzerland) and nitrogen blow down. The methanol fractions were cleaned with ENVI-Carb.[27] The petroleum ether and dichloromethane fractions were applied to sodium sulfate columns for removing moisture. After clean up, 80% of the dichloromethane extract was combined with the corresponding methanol extract, because PFCAs and PFSAs were found to be partially extracted into dichloromethane. The methanol fractions were treated by adding 50% water and injections standards $^{13}C_8$-PFOS and $^{13}C_8$-PFOA, whereas Me_2FOSA was added as the injection standard to the other fractions.

Gas chromatography mass spectrometry (GC-MS) in positive chemical ionisation mode (PCI) (Agilent Technologies, Mississauga, ON, Canada, 7890 A GC system) was used for analysis of FTOHs, FOSAs and FOSEs (except for PFOSA). The separation of target compounds was performed on a DB-WAX column (30 m, 0.25-mm inner diameter, 0.25-μm film, J&W Scientific, Folsom, CA, USA). The injection volume was 2 μL and using splitless injection (200°C). The oven temperature program is given in the Accessory publication (Table A3). Helium was used as carrier gas at a flow rate of 1.3 mL min^{-1}. Methane was used as the reaction gas.

Instrumental analysis of PFCAs and PFSAs (including PFOSA) was performed using high pressure liquid chromatography (Agilent 1100 Series) tandem mass spectrometry (HPLC-MS/MS) (Applied Biosystems, Toronto, ON, Canada, 4000 QTRAP) in the electrospray negative ionisation mode at atmospheric pressure. For separation, a pre-column (C_8, 4-mm length, 2-mm diameter, Phenomenex, Torrance, CA, USA) and a Luna column (C_8 (2), 50-mm length, 2-mm

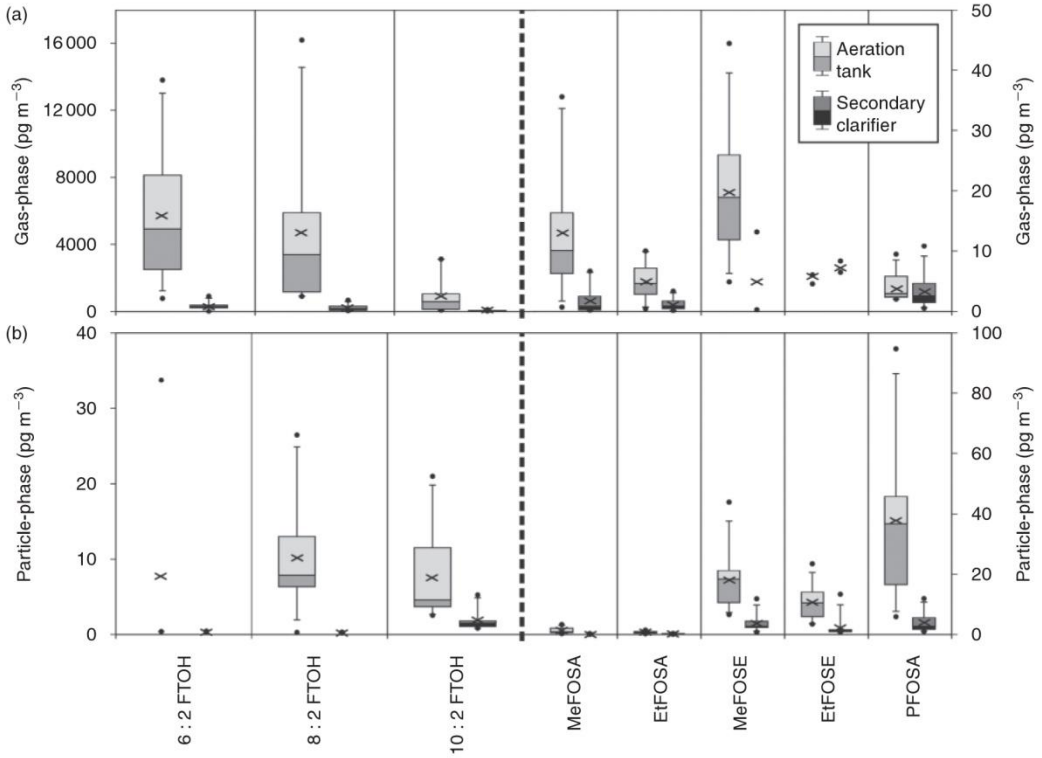


Fig. 1. Box-whisker plots for FTOH, FOSA and FOSE concentrations in the gas (a) and particle-phase (b) at the aeration tank and the secondary clarifier. The boxes show median concentrations and the 25th and 75th percentiles; 10th and 90th percentiles are indicated by the whiskers and the dots represent the minimum and maximum concentrations. The mean concentrations are indicated with an ×. If more then 25% of the data for one compound were below the IDL only minimum, maximum and mean values are shown.

diameter, 3-µm particle size, Phenomenex) was used. Methanol and water, each with 10-mM ammonium acetate, were used as the mobile phase. The flow was set to 0.25 µL min^{-1} and the gradient is given in the Accessory publication (Table A4). The injection volume was 25 µL.

Quantification was performed based on response factors of the target compounds and their corresponding internal standards. The ratio of both response factors was used for recovery correction. The calibration curves included eleven points for FTOHs (0.3–3800 ng mL^{-1}), seven points for FOSAs and FOSEs (0.12–115 ng mL^{-1}) and eight points for PFCAs and PFSAs (0.005–5.0 ng mL^{-1}). Instrument detection limits (IDLs) were calculated by extrapolating instrument response in blank samples to a concentration that would give a S/N value of three. A further limit of detection (LOD) calculated as three times the standard deviation (s.d.) of the blanks was used. Concentrations below the blank levels and below the IDL were set to half of the LOD for statistical analysis. In cases where the substitution for a particular chemical was required for more than 25% of the data set, only the mean value was presented in Figs 1 and 2 as the other statistical parameters are subject to bias by substituting a constant value.[28] Compounds not detected above the IDL in any of the samples were excluded from further investigations.

Prior to extraction, small punches (0.7 cm^2) of seven GFFs from each sampling site were analysed for organic carbon using a Thermal Optical Transmission box (Sunset Laboratory, Tigard, OR, USA). PFC concentrations for the relevant GFFs were corrected based on the punched area.

Results and discussion

Quality control

Concentrations in blank samples ranged from <IDL to 7 pg m^{-3} in PUF/XAD/PUF cartridges and GFFs and from <IDL to 10 pg m^{-3} in SIP disks. All results were corrected for blanks. Details of IDLs and the blank levels for individual compounds are given in Tables A5 and A6 in the Accessory publication.

LODs ranged from 0.4 to 13 pg m^{-3} for FTOHs, FOSAs and FOSEs and from 0.01 to 39 pg m^{-3} for PFCAs and PFSAs (see Table A6 in the Accessory publication).

Recoveries for internal standards of target PFCs in PUF/XAD/PUF cartridges ranged from 5.9 ± 1.8% for ^{13}C-6 : 2 FTOH to 100 ± 18% for ^{13}C-10 : 2 FTOH; from 72 ± 13% for d_3-MeFOSA to 230 ± 37% for d_9-EtFOSE and from 21 ± 11% for $^{13}C_2$-PFDoDA to 180 ± 96% for $^{13}C_2$-PFBA. The low recoveries for ^{13}C-6 : 2 FTOH are associated with the high volatility of this compound and the resulting evaporative losses during Soxhlet extraction and concentration. Signal enhancement caused by solvent or interfering compounds might be responsible for high recoveries, i.e. for d_9-EtFOSE. For GFFs, the recoveries ranged from 9.4 ± 2.8% for ^{13}C-6 : 2 FTOH to 150 ± 25% for d_9-EtFOSE and from 36 ± 8.5% for $^{13}C_2$-PFBA to 67 ± 16% for $^{13}C_2$-PFHxA. For the SIP disks recoveries ranged from 6.4 ± 1.0% for ^{13}C-6 : 2 FTOH to 310 ± 40% for $^{18}O_2$-PFHxS. All samples (including blanks) were recovery corrected using appropriate factors based on recoveries presented above and summarised in Table A7. The poor recoveries

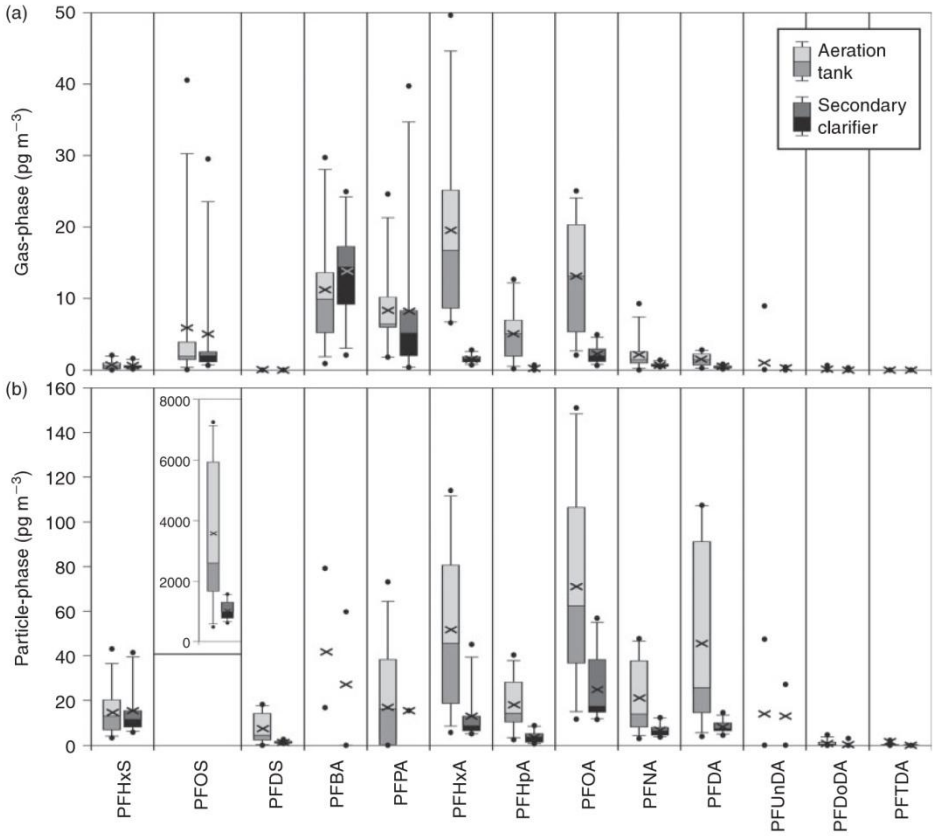


Fig. 2. Box-whisker plots for PFCA and PFSA concentrations in the gas (a) and particle-phase (b) at the aeration tank and the secondary clarifier. The boxes show median concentrations and the 25th and 75th percentiles; 10th and 90th percentiles are indicated by the whiskers and the dots represent the minimum and maximum concentrations. The mean concentrations are indicated with an ×. If more then 25% of the data for one compound were below the IDL only minimum, maximum and mean values are shown.

for 6 : 2 FTOH cause greater uncertainty in the derived air concentration for this compound.

FTOH, FOSA and FOSE air concentrations

Gas- and particle-phase air concentrations for FTOH, FOSA and FOSE are shown in Fig. 1 and are summarised with results from passive samples in Table 1. Detailed results are in Tables A8–A11 in the Accessory publication. PFOSEA was not detected above the IDL in any sample and was therefore excluded from further investigations.

Gas-phase samples were dominated by FTOHs with a mean concentration of 11 000 pg m^{-3} at the aeration tank and 590 pg m^{-3} at the secondary clarifier. Mean ∑FOSA & FOSE concentrations were 43 pg m^{-3} at the aeration tank and 16 pg m^{-3} at the secondary clarifier. Conversely, ∑FTOH exhibited the lowest particle-phase concentrations (25 pg m^{-3} at the aeration tank and 1.9 pg m^{-3} at the secondary clarifier), whereas for ∑FOSA & FOSE particle-phase concentrations were higher at 69 and 11 pg m^{-3} respectively. The mean ∑FTOH concentrations at the aeration tank were 18 times higher for the gas-phase and 13 times higher for the particle-phase compared with the secondary clarifier (*t*-test, $P < 0.001$ and $P < 0.005$ respectively). Mean ∑FOSA & FOSE concentrations were approximately a factor of three to six higher at the aeration tank compared with the secondary clarifier (*t*-test, $P < 0.001$ for gas- and particle-phase respectively). These results point to the important role of the aeration process in emitting high concentrations of PFCs to the atmosphere.

Composition

The composition of FTOHs, FOSAs and FOSEs in each sample is shown in Figs A1 and A2 in the Accessory publication. The profile of FTOHs in the gas-phase was dominated by 6 : 2 FTOH (54%) > 8 : 2 FTOH (38%) > 10 : 2 FTOH (8%) and was similar at both sampling sites. In the particle-phase at the aeration tank, all of the FTOHs were detected (8 : 2 FTOH (47%) > 10 : 2 FTOH (35%) > 6 : 2 FTOH (18%)) whereas at the secondary clarifier only 10 : 2 FTOH was detected above the IDL. For FOSAs and FOSEs the gas-phase profile was different at the two sites. The aeration tank samples were dominated by MeFOSE (47%) and MeFOSA (27%), whereas the secondary clarifier samples were dominated by PFOSA (39%) and MeFOSA (24%). FOSAs and FOSEs in the particle-phase showed a similar pattern at the aeration tank and the secondary

Table 1. Individual PFC concentrations in the gas-phase and particle-phase and from SIP disk passive air samplers at the aeration tank and secondary clarifier in picograms per cubic metre (minimum–maximum and average in parentheses)

	Aeration tank			Secondary clarifier		
	Gas-phase	Particle-phase	SIP disk passive air samples	Gas-phase	Particle-phase	SIP disk passive air samples
6 : 2 FTOH	780–14 000 (5700)	0.36–34 (7.7)	11 000–12 000 (12 000)	0.31–910 (330)	0.36–0.36 (0.36)	670–910 (790)
8 : 2 FTOH	900–16 000 (4700)	0.250–27 (10)	5700–5800 (5800)	27–670 (220)	0.25–0.25 (0.25)	310–350 (330)
10 : 2 FTOH	72–3100 (920)	2.5–21 (7.5)	780–860 (820)	6.2–110 (41)	0.82–5.2 (1.9)	41–48 (45)
∑FTOH	3300–33 000 (11 000)	4.5–79 (25)	18 000–19 000 (18 000)	34–1700 (590)	1.4–5.8 (2.5)	1100–1300 (1200)
MeFOSA	0.71–36 (13)	0.27–3.3 (1.4)	13–14 (14)	0.23–6.7 (1.9)	0.1–0.66 (0.4)	0.79–1.0 (0.90)
EtFOSA	0.46–10 (4.9)	0.25–1.5 (0.8)	5.7–5.9 (5.8)	0.19–3.4 (1.2)	0.1–0.32 (0.23)	1.2–1.6 (1.4)
MeFOSE	4.9–44 (20)	6.6–44 (18)	16–18 (17)	0.54–13 (5.6)	0.77–12 (3.7)	4.5–4.9 (4.7)
EtFOSE	4.1–7.0 (6.5)	3.4–24 (11)	8.5–9.4 (8.9)	<6.96–8.3 (7.1)	0.81–13 (2.2)	1.8–2.3 (2.0)
PFOSA	2.3–9.5 (4.3)	5.9–95 (38)	4.9–10 (7.7)	0.54–11 (3.3)	0.97–12 (4.0)	0.0–0.0 (0.0)
∑FOSA & FOSE	11–100 (43)	23–120 (69)	52–55 (54)	11–31 (16)	4.9–31 (11)	6.9–9.3 (8.1)
PFHxS	0.06–2.1 (0.78)	3.3–43 (15)	0.62–0.87 (0.74)	0.12–1.6 (0.59)	5.8–41 (15)	0.65–0.91 (0.75)
PFOS	1.1–41 (5.8)	480–7200 (3900)	220–260 (240)	0.65–30 (4.7)	620–1600 (1100)	21–38 (30)
PFDS	0.01–0.01 (0.01)	0.04–18 (7.4)	0.01–0.01 (0.01)	0.01–0.01 (0.01)	0.84–2.6 (1.4)	0.01–0.01 (0.01)
PFBA	0.9–30 (11)	9.3–79 (42)	13–15 (14)	2.1–25 (14)	1.4–62 (31)	6.7–13 (9.9)
PFPA	1.7–25 (8.7)	0.99–73 (22)	6.1–6.7 (6.4)	0.42–40 (8.8)	19–19 (19)	0.34–2.4 (1.4)
PFHxA	6.6–50 (20)	5.7–110 (52)	18–20 (19)	0.7–2.8 (1.6)	5.0–45 (13)	1.2–1.7 (1.4)
PFHpA	0.16–13 (5.1)	2.5–40 (18)	5.2–6.0 (5.6)	0.04 –0.81 (0.54)	0.66–8.8 (3.8)	0.85–1.0 (0.94)
PFOA	2.1–25 (13)	12–150 (71)	8.1–11 (9.7)	0.63–4.9 (2.3)	12–57 (25)	2.0–3.1 (2.5)
PFNA	0.69–9.3 (2.1)	3.0–48 (21)	1.1–1.2 (1.1)	0.45–1.4 (0.72)	3.7–12 (6.8)	0.41–0.66 (0.54)
PFDA	0.25–2.8 (1.4)	4.0–110 (46)	2.0–2.2 (2.1)	0.14–0.81 (0.42)	4.5–15 (8.3)	0.28–0.38 (0.33)
PFUnDA	0.03–9.0 (1.2)	0.59–47 (14)	1.2–1.2 (1.2)	0.06–0.41 (0.33)	2.0–27 (15)	012–0.35 (0.24)
PFDoDA	0.09–0.64 (0.24)	0.09–4.7 (1.1)	0.15–0.21 (0.18)	0.06–0.31 (0.11)	0.08–3.1 (1.3)	0.02–0.05 (0.04)
PFTDA	0.004–0.004 (0.004)	0.02–2.2 (0.31)	0.01–0.01 (0.01)	0.0–0.0 (0.0)	0.03–0.36 (0.17)	0.01–0.01 (0.01)
∑PFCA & PFSA	25–120 (69)	849–7600 (3900)	280–320 (300)	17–86 (34)	760–1700 (1100)	35–61 (48)
∑PFC	3300–33 000 (11 000)	29–130 (94)	18 000–19 000 (19 000)	47–1790 (600)	6.0–36 (13)	1100–1300 (1200)

clarifier with dominant compounds being PFOSA (53 and 40% respectively), MeFOSE (27 and 38% respectively) and EtFOSE (~17% at both sites).

Comparisons with other measurements

It is interesting to compare the magnitude of air concentrations for the various PFCs measured at the WWTP to other studies. This comparison will give some sense of the importance of the WWTP as a point source to air. Air concentrations of FTOH in the urban area of Toronto ($\sum$FTOH = 81 pg m^{-3} sum of particle and gas-phase[29]) were two orders of magnitude lower than at the aeration tank and one order of magnitude lower than at the secondary clarifier. Thus WWTPs seem to be an important point source for FTOHs. Differences were less drastic for other PFCs. For instance, FOSA and FOSE concentrations were approximately six times higher at the aeration tank compared with urban areas ($\sum$FOSA & FOSE = 19 pg m^{-3} sum of particle and gas-phase[19,29]) and the FOSA & FOSE concentrations at the secondary clarifier were generally in the same range as in urban areas.[19,29] Ongoing studies at this WWTP are attempting to quantify the emission fluxes to air so that WWTPs as a whole can be assessed in terms of their contribution to the atmospheric burdens of PFCs.

PFCA and PFSA air concentrations

Gas- and particle-phase results for PFCA and PFSA in air are shown in Fig. 2 and further summarised in Table 1 and in Tables A8–A11 in the Accessory publication.

Gas-phase concentrations of PFCAs and PFSAs ($\sum$PFCA & PFSA 70 pg m^{-3} at the aeration tank and 34 pg m^{-3} at the secondary clarifier) were one to three orders of magnitude lower compared with FTOHs; however, they were two times higher than FOSAs and FOSEs. In contrast, $\sum$PFCA & PFSA concentrations in the particle-phase were 500 and 100 times higher than the $\sum$FTOH and $\sum$FOSA & FOSE concentrations respectively. PFOS was the dominant compound in the particle-phase. PFOS concentrations (average 3600 pg m^{-3} at the aeration tank and 1000 pg m^{-3} at the secondary clarifier) were one to three orders of magnitude higher than concentrations of the other PFCs. It is interesting to note that mean $\sum$PFCA & PFSA concentrations were significantly higher at the aeration tank compared with the secondary clarifier (factor of 1–4, *t*-test $P < 0.012$ for the gas-phase, $P < 0.003$ for the particle-phase). In former studies investigating other WWTPs, higher PFC concentrations were reported in treated effluent in comparison to influent wastewater, though mass flow charts from Schultz et al. indicate similar concentrations in the aeration tank and secondary clarifier.[15,30] This indicates that the observed differences in air concentrations are most likely associated with enhanced mass transfer (water to air transfer) of PFCAs and PFSAs owing to the aeration process rather than to differences in wastewater concentrations of PFCAs and PFSAs between the aeration tank and secondary clarifier.

Composition

The composition of PFCAs and PFSAs in each sample is shown in Fig. A3 in the Accessory publication. The profile of PFCAs and PFSAs in the gas-phase was different at the two sampling sites. At the aeration tank, PFHxA was dominant (29%), followed by PFOA and PFBA (both ~19%). The contributions of the remaining compounds were 10% (PFPA)

and lower. Samples from the secondary clarifier were dominated by PFBA (48%), followed by PFPA (15%) and PFOS (11%). The contributions of the remaining compounds were below 9%. These results indicate that the different treatment processes of the wastewater at the WWTP caused different air emission signatures for the PFCAs and PFSAs. However, in general, PFOS and the short chain PFCAs (C_4–C_8) were the dominant compounds in the gas-phase at both the aeration tank and the secondary clarifier, whereas the contribution of the longer chain PFCAs (C_9–C_{14}) was very low (<3%). PFOS was also dominant among the PFCAs and PFSAs in the particle-phase (~91% of ∑PFCA & PFSA) at both sites. The next dominant PFCA and PFSA after PFOS was PFOA (3% at the aeration tank and 5% at the secondary clarifier), followed by PFHxS, PFHxA and PFDA (each >0.5%). The dominance of PFOS and PFOA on atmospheric particles has been reported in the literature[19]; however, the dominance of PFOS as observed in this study was not previously observed or reported. The dominance of PFOS (and PFOA) in particles might reflect the pattern of PFCs used in industrial and consumer products.[31,32]

Comparisons with other measurements

Chemical ratios are sometimes used to compare or differentiate sources. In the current study the ratio of PFOS and PFOA, i.e. PFOS/PFOA, observed at the WWTP could be compared with other locations to gain some sense of whether the WWTP as a point source could be contributing substantially to the broader contamination of the atmosphere. The ratio PFOS/PFOA in the gas-phase from the WWTP (0.4–2.1) was in the same range as the ratio from an urban area (0.5),[19] which suggests a possible contribution of the WWTP to urban air or at least that the source for urban air is similar. However, for the particle-phase, PFOS/PFOA was more than 100 times higher at the WWTP (42–50) compared with an urban area (0.3).[19] This may indicate that the particle-phase signature at the WWTP is a localised or short-lived source.

Most literature reports of PFCAs and PFSAs focus on the particle-phase exclusively. For instance, Dreyer et al. reported ∑PFCA and ∑PFSA concentrations in the particle-phase in Germany of 1.0 and 1.3 pg m^{-3} respectively.[4,33] These concentrations are one to three orders of magnitude lower compared with concentrations at the WWTP in this study. In a study from New York State, PFCAs and PFSAs were measured in the gas and particle-phase.[19] These concentrations (i.e. ∑C_6,C_{10} PFSA & $C_{7–12}$ PFCA 8.0 and PFOS 2.3 pg m^{-3})[19] were also one to three orders of magnitude lower compared with the present study (210 and 3600 pg m^{-3} at the aeration tank and 110 and 1000 pg m^{-3} at the secondary clarifier).

In summary, the measured concentrations of PFSAs and PFCAs at the WWTP were greatly elevated compared with other studies, even for urban areas. This highlights the importance of WWTPs as point-source emitters of these compounds to the atmosphere.

Correlations of atmospheric concentrations with sampling parameters

The influence of various meteorological and particle parameters (e.g. ambient air temperature, TSP and particle OC content) on PFC air concentrations were investigated.

Air temperature, which ranged from −0.2 to 12.5°C during high volume sampling, showed a positive correlation for FOSEs and FOSAs in the gas phase, i.e. MeFOSA and MeFOSE ($P<0.05$). This is likely owing to greater evaporation of these compounds at higher temperatures. However, other PFCs did not exhibit this correlation. It is likely that evaporation from wastewater is governed more by the temperature of the wastewater (versus the air temperature) which is much less subject to variability. A positive correlation of the PFC concentration with the air temperature was found previously[34]; however, owing to a weak correlation, it was assumed that other factors may have also had an influence.[33]

The OC contents of the particles from the two sites were not significantly different (4.0 ± 1.1% OC at the aeration tank, $n=7$, and 3.3 ± 0.9% OC at the secondary clarifier, $n=7$; t-test $P=0.2$) and no correlation with atmospheric PFC concentrations were found. The TSP concentration was significantly higher at the aeration tank (120 ± 29 µg m^{-3}, $n=12$) in comparison to the secondary clarifier (75 ± 20 µg m^{-3}, $n=12$, t-test $P<0.001$) but again no correlation with atmospheric PFC concentrations were found. The higher TSP concentration above the aeration tank is likely the result of aerosol generation and the release of wastewater particulates to air.

Particle–gas partitioning

The percent on particles for the various target PFCs is summarised in Fig. 3. This was calculated as the concentrations in the particle-phase (in picograms per cubic metre) divided by the sum of concentrations in the gas and particle-phase (in picograms per cubic metre) and multiplied by 100. There was no substantial difference in particle–gas partitioning of target compounds collected at the aeration tank versus the secondary clarifier and so average values are represented in Fig. 3.

Of the target PFCs, the FTOHs showed the smallest particle-phase percentages that were typically less than 10%. Particle bound fractions for FTOHs found during ship-based measurements for 8 : 2 FTOH and 10 : 2 FTOH were higher compared with results from the present study (up to 23%,[29] 26% for 8 : 2 FTOH and 15% for 10 : 2 FTOH[35]).

Particle-phase percentages increased for MeFOSA and EtFOSA (~19 and ~15% respectively) and were even higher for MeFOSE, EtFOSE and PFOSA (38–70%). Other studies showed lower particle-phase percentages from land-based measurements (i.e. MeFOSA & EtFOSA <10%, EtFOSE 14%[4]), whereas ship-based measurements were similar to the results for the WWTP (i.e. MeFOSA & EtFOSA ~15%,[4] MeFOSE 30%,[29] EtFOSE 57%[4]).

The PFSAs had the highest particle associated fractions with almost 100% bound on particles. PFCAs were also mainly particle-associated and this increased generally according to chain length as: PFBA (~64%) ≈ PFPA (~68%) < PFHxA (~78%) < PFHpA (~80%) < PFOA (~86%) ≈ PFNA (~88%) < PFDA (~95%) > PFUnDA (~89%) > PFDoDA (~80%) < PFTDA (~100%). This pattern is likely owing to the decrease in vapour pressure (which favours the condensed state) with increasing chain length for the neutral forms of PFCAs.[36,37] Only one study is available for comparison with these results.[19] Particle-phase percentages reported for New York State were 60% for PFHpA, 40% for PFOA and PFNA and 30% for PFDA, PFDoDA and PFOS.[19] Moreover, the shorter chain PFCA, PFHpA, had the highest particle-bound fractions and the longest chain PFCA, PFDA, had the lowest particle-phase fractions.[19] At this time, we have no explanation for these contradictory results.

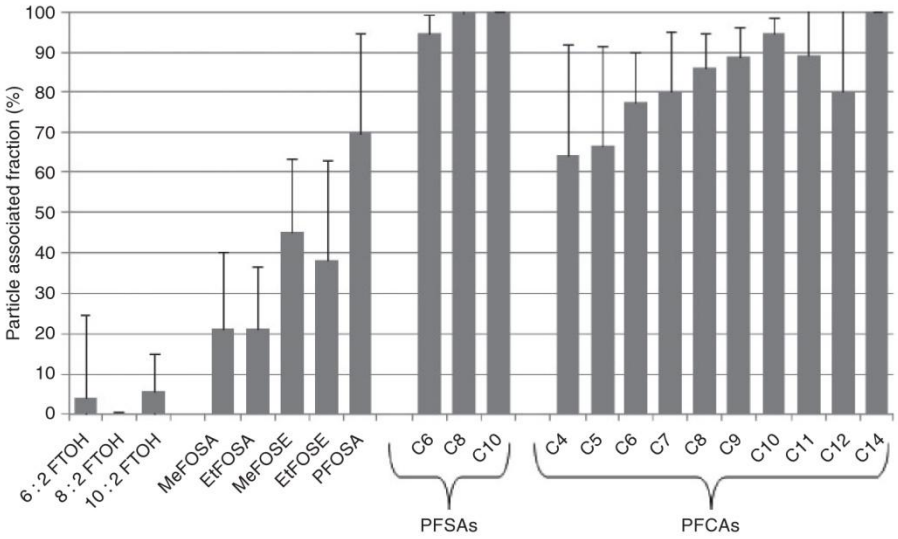


Fig. 3. Particle associated fractions (%) for individual PFCs in air at the aeration tank and secondary clarifier.

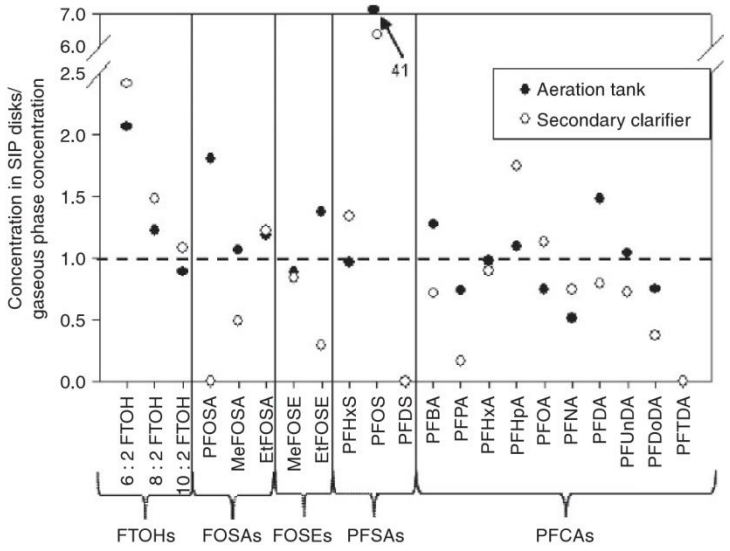


Fig. 4. Ratio between individual PFC concentrations in the SIP disks passive air samples (pg m^{-3}) ($n = 2$) and gas-phase from active air sampling (pg m^{-3}) ($n = 12$). The dashed line represents perfect agreement.

Comparison of active v. *passive sampling techniques*

It is interesting to compare the gas-phase air concentrations from the intermittent high volume samples against the time-integrated concentrations derived using the passive samples. Differences can be expected for several reasons: (i) differences in the sampling time, i.e. the high volume samples were collected on two consecutive days each week and represented ~29% of the time that was sampled by the continuous and time-integrating passive samplers. Thus, high and low air concentration episodes that could offset the true time-integrated air concentrations might not have been captured by this 29% of the time window; (ii) although passive samplers better cover the entire duration of the study, there is greater uncertainty with these derived concentrations owing to uncertainties in the sampling rates; (iii) collection of particles on the SIP disks is known to occur[38] and this may result in an overestimate of the gas-phase concentration for compounds that are particle-associated (this issue is discussed further, below); and (iv) general analytical errors that contribute to uncertainties.

Despite these potential uncertainties and confounding factors, the agreement between gas-phase concentrations derived from high volume samples *v.* SIP disk passive air samples was fairly good as shown in Fig. 4 with detailed results presented in

Table 1. The concentrations differed by a mean factor of 1.5 for FTOHs, 0.96 for FOSAs, 0.85 for FOSEs, 1.1 for PFHxS, 24 for PFOS and 0.8 for PFCAs.

Sampling artefacts

Previous laboratory investigations have shown that PFCAs may adsorb to filters (GFFs and quartz fibre filters (QFFs)) and therefore particle-phase concentrations derived from sampling techniques using GFFs and QFFs could be overestimated.[39] The results of the present study and the comparison of active versus passive samples provides some insight into this issue. PFCAs and PFSAs were found predominantly in the particle-phase. However, the presence of PFCAs in the gas-phase and the good agreement between gas-phase concentrations using high volume sampler and passive air sampler concentrations indicate that this sampling artefact has a relatively minor influence on the gas-phase concentrations. However, we acknowledge that the high concentrations of target compounds at the WWTP may not provide the best conditions for detecting this artefact. It may be more important at lower air concentrations.

Particle-phase sampling by the SIP disks is another 'artefact' that complicates the comparison of results from high volume samples and from SIP disks. It has been shown that the SIP disk sampling chamber allows ~10% of the ambient particles to be sampled and so the SIP disk is not just a gas-phase passive sampler.[38] The net effect is demonstrated well by the results for PFOS (see Fig. 4). In the high volume samples, the PFOS particle-phase air concentrations are more than two orders of magnitude larger than the gas-phase concentration. The air concentration derived from the SIP disk passive air samples, which represents mainly the gas-phase and ~10% of the particle-phase,[38] fall somewhere in between. In this case the 10% of ambient particles that are sampled by the SIP disk outweigh the gas-phase contribution. More studies are required to further elaborate and quantify particle-phase sampling by passive samplers and sorption artefact for filters.

Conclusion

This study demonstrates the importance of WWTPs as point sources of PFCs to the atmosphere. The aeration process in particular is shown to be a key emission process for both gas-phase and particle-associated PFCs. Aerosol-mediated transport is believed to account for the higher amounts of particle-associated PFCs in air near the aeration tank. This pathway is likely also to be important in open water bodies as aerosols are generated and released to air via sea spray and wave action. Passive and active samplers are shown to be complementary and comparable air sampling approaches for PFCs.

Acknowledgements

We thank the German Academic Exchange Service and the Chemicals Management Plan (Government of Canada) for partial funding. We greatly acknowledge Cathy Cheng for valuable help during sampling.

References

[1] C. M. Butt, U. Berger, R. Bossi, G. T. Tomy, Levels and trends of poly- and perfluorinated compounds in the arctic environment. *Sci. Total Environ.* **2010**, *408*, 2936. doi:10.1016/J.SCITOTENV.2010.03.015

[2] M. S. McLachlan, K. E. Holmstrom, M. Reth, U. Berger, Riverine discharge of perfluorinated carboxylates from the European continent. *Environ. Sci. Technol.* **2007**, *41*, 7260. doi:10.1021/ES071471P

[3] L. Ahrens, J. L. Barber, Z. Xie, R. Ebinghaus, Longitudinal and latitudinal distribution of perfluoroalkyl compounds in the surface water of the Atlantic Ocean. *Environ. Sci. Technol.* **2009**, *43*, 3122. doi:10.1021/ES803507P

[4] A. Dreyer, I. Weinberg, C. Temme, R. Ebinghaus, Polyfluorinated compounds in the atmosphere of the Atlantic and Southern Oceans: evidence for a global distribution. *Environ. Sci. Technol.* **2009**, *43*, 6507. doi:10.1021/ES9010465

[5] M. Houde, J. W. Martin, R. J. Letcher, K. R. Solomon, D. C. G. Muir, Biological monitoring of polyfluoroalkyl substances: a review. *Environ. Sci. Technol.* **2006**, *40*, 3463. doi:10.1021/ES052580B

[6] J. M. Conder, R. A. W. W. de Hoke, M. H. Russell, R. C. Buck, Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. *Environ. Sci. Technol.* **2008**, *42*, 995. doi:10.1021/ES070895G

[7] C. Lau, K. Anitole, C. Hodes, D. P.-H. A. Lai, J. See, Perfluoroalkyl acids: a review of monitoring and toxicological findings. *Toxicol. Sci.* **2007**, *99*, 366. doi:10.1093/TOXSCI/KFM128

[8] D. Herzke, M. Schlabach, E. Mariussen, H. Uggerud, E. Heimstad, *A literature survey on selected chemical compounds: literature survey of polyfluorinated organic compounds, phosphor containing flame retardants, 3-nitrobenzanthrone, organic tin compounds, platinum and silver* **2007**. Available at http://www.klif.no/publikasjoner/2238/ta2238.pdf [Verified 21 March 2011].

[9] D. A. Ellis, J. W. Martin, A. O. De Silva, S. A. Mabury, M. D. Hurley, M. P. S. Andersen, T. J. Wallington, Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* **2004**, *38*, 3316. doi:10.1021/ES049860W

[10] J. W. Martin, D. A. Ellis, S. A. Mabury, Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of *N*-ethyl perfluorobutanesulfonamide. *Environ. Sci. Technol.* **2006**, *40*, 864. doi:10.1021/ES051362F

[11] J. D'eon, M. D. Hurley, T. J. Wallington, S. A. Mabury, Atmospheric chemistry of *N*-methyl perfluorobutane sulfonamidoethanol, $C_4F_9SO_2N(CH_3)CH_2CH_2OH$: kinetics and mechanism of reaction with OH. *Environ. Sci. Technol.* **2006**, *40*, 1862. doi:10.1021/ES0520767

[12] Y. D. Lei, F. Wania, D. Mathers, S. A. Mabury, Determination of vapor pressure, octanol–air, and water–air partition coefficients for polyfluorinated sulfonamide, sulfonamidoethanols, and telomer alcohols. *J. Chem. Eng. Data* **2004**, *49*, 1013. doi:10.1021/JE049949H

[13] C. J. Young, V. I. Furdui, J. Franklin, R. M. Koerner, D. C. G. Muir, S. A. Mabury, Perfluorinated acids in Arctic snow: new evidence for atmospheric formation. *Environ. Sci. Technol.* **2007**, *41*, 3455. doi:10.1021/ES0626234

[14] A. Jahnke, U. Berger, R. Ebinghaus, C. Temme, Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53°N–33°S). *Environ. Sci. Technol.* **2007**, *41*, 3055. doi:10.1021/ES062389H

[15] B. G. Loganathan, K. S. Sajwan, E. Sinclari, K. S. Kumar, K. Kannan, Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. *Water Res.* **2007**, *41*, 4611. doi:10.1016/J.WATRES.2007.06.045

[16] L. Ahrens, S. Felizeter, Z. Xie, R. Sturm, R. Ebinghaus, Polyfluorinated compounds in wastewater treatment plant effluents and surface waters along the River Elbe, Germany. *Mar. Pollut. Bull.* **2009**, *58*, 1326. doi:10.1016/J.MARPOLBUL.2009.04.028

[17] U. Schenker, M. Scheringer, M. Macleod, J. W. Martin, I. T. Cousins, K. Hungerbühler, Contribution of volatile precursor substances to the flux of perfluorooctanoate to the Arctic. *Environ. Sci. Technol.* **2008**, *42*, 3710. doi:10.1021/ES703165M

[18] N. L. Stock, V. I. Furdui, D. C. G. Muir, S. A. Mabury, Perfluoroalkyl contaminants in the Canadian Arctic: evidence of atmospheric transport and local contamination. *Environ. Sci. Technol.* **2007**, *41*, 3529. doi:10.1021/ES062709X

[19] S. K. Kim, K. Kannan, Perfluorinated acids in air, rain, snow, surface runoff, and lakes: relative importance of pathways to contamination of urban lakes. *Environ. Sci. Technol.* **2007**, *41*, 8328. doi:10.1021/ES072107T

[20] C. J. McMurdo, D. A. Ellis, E. Webster, J. Butler, R. Christensen, L. K. Reid, Aerosol enrichment of the surfactant PFO and mediation of the water–air transport of gaseous PFOA. *Environ. Sci. Technol.* **2008**, *42*, 3969. doi:10.1021/ES7032026

[21] E. Webster, D. A. Ellis, L. K. Reid, Modeling the environmental fate of perfluorooctanoic acids and perfluorooctanoate: an investigation of the role of individual species partitioning. *Environ. Chem.* **2010**, *29*, 1466. doi:10.1002/ETC.181

[22] C. A. Barton, M. A. Kaiser, M. H. Russell, Partitioning and removal of perfluorooctanoate during rain events: the importance of physical-chemical properties. *J. Environ. Monit.* **2007**, *9*, 839. doi:10.1039/B703510A

[23] M. Shoeib, T. Harner, S. C. Lee, D. Z. J. Lane, Sorbent-impregnated polyurethane foam disk for passive air sampling of volatile fluorinated chemicals. *Anal. Chem.* **2008**, *80*, 675. doi:10.1021/AC701830S

[24] S. Genualdi, S. C. Lee, M. Shoeib, A. Gawor, L. Ahrens, T. Harner, Global pilot study of legacy and emerging persistent organic pollutants using sorbent-impregnated polyurethane foam disk passive air samplers. *Environ. Sci. Technol.* **2010**, *44*, 5534. doi:10.1021/ES1009696

[25] S. Thuens, A. Dreyer, R. Sturm, C. Temme, R. Ebinghaus, Determination of the octanol–air partition coefficients (KOA) of fluorotelomer alcohols. *J. Chem. Eng. Data* **2008**, *53*, 223. doi:10.1021/JE700522F

[26] A. Dreyer, V. Langer, R. Ebinghaus, Determination of octanol–air partition coefficients (KOA) of fluorotelomer acrylares, perfluoroalkyl sulfonamids, and perfluoroalkylsulfonamido ethanols. *J. Chem. Eng. Data* **2009**, *54*, 3022. doi:10.1021/JE900082G

[27] C. R. Powley, S. W. George, T. W. Ryan, R. C. Buck, Matrix effect-free analytical methods for determination of perfluorinated carboxylic acids in environmental matrixes. *Anal. Chem.* **2005**, *77*, 6353. doi:10.1021/AC0508090

[28] D. R. Helsel, M. T. Obvious, Better methods for interpreting non-detect data. *Environ. Sci. Technol.* **2005**, *39*, 419A. doi:10.1021/ES053368A

[29] M. Shoeib, T. Harner, P. Vlahos, Perfluorinated chemicals in the Arctic atmosphere. *Environ. Sci. Technol.* **2006**, *40*, 7577. doi:10.1021/ES0618999

[30] M. M. Schultz, C. P. Higgins, A. Huset, R. G. Luthy, D. F. Barofsky, J. A. Field, Fluorochemical mass flows in a municipal wastewater treatment facility. *Environ. Sci. Technol.* **2006**, *40*, 7350. doi:10.1021/ES061025M

[31] K. Prevedouros, I. T. Cousins, R. C. Buck, S. H. Korzeniowski, Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40*, 32. doi:10.1021/ES0512475

[32] A. G. Paul, K. C. Jones, A. Sweetman, A first global production, emission, and environmental inventory for perfluorooctane sulfonate. *Environ. Sci. Technol.* **2009**, *43*, 386. doi:10.1021/ES802216N

[33] A. Dreyer, V. Matthias, C. Temme, R. Ebinghaus, Annual time series of air concentrations of polyfluorinated compounds. *Environ. Sci. Technol.* **2009**, *43*, 4029. doi:10.1021/ES900257W

[34] A. Jahnke, L. Ahrens, R. Ebinghaus, C. Temme, Urban versus remote air concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany. *Environ. Sci. Technol.* **2007**, *41*, 745. doi:10.1021/ES0619861

[35] M. Shoeib, P. Vlahos, T. Harner, A. Peters, M. Graustein, J. Narayan, Survey of polyfluorinated chemicals (PFCs) in the atmosphere over the northeast Atlantic Ocean. *Atmos. Environ.* **2010**, *44*, 2887. doi:10.1016/J.ATMOSENV.2010.04.056

[36] M. A. Kaiser, B. S. Larsen, C.-P. C. Kao, R. C. Buck, Vapor pressures of perfluorooctanoic, -nonanoic, -decanoic, -undecanoic, and -dodecanoic acids. *J. Chem. Eng. Data* **2005**, *50*, 1841. doi:10.1021/JE050070R

[37] S. Rayne, K. Forest, Perfluoroalkyl sulfonic and carboxylic acids: a critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. *J. Environ. Sci. Heal. A* **2009**, *44*, 1145. doi:10.1080/10934520903139811

[38] J. Klánová, P. Eupr, J. Kohoutek, T. Harner, Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers. *Environ. Sci. Technol.* **2008**, *42*, 550. doi:10.1021/ES072098O

[39] H. P. H. Arp, K.-U. Goss, Irreversible sorption of trace concentrations of perfluorocarboxylic acids to fiber filters used for air sampling. *Atmos. Environ.* **2008**, *42*, 6869. doi:10.1016/J.ATMOSENV.2008.05.012

Manuscript received 6 December 2010, accepted 24 January 2011

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Accessory publication

Air concentrations and particle–gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant

Lena Vierke,[A,B] *Lutz Ahrens*,[A] *Mahiba Shoeib*,[A,F] *Eric J. Reiner*,[C,D] *Rui Guo*,[D,C] *Wolf-Ulrich Palm*,[B] *Ralf Ebinghaus*[E] *and Tom Harner*[A]

[A]Environment Canada, Science and Technology Branch, 4905 Dufferin Street, Toronto, ON, M3H 5T4, Canada.

[B]Leuphana University of Lüneburg, Institute for Environmental Chemistry, Scharnhorststrasse 1, D-21335 Lüneburg, Germany.

[C]Ontario Ministry of the Environment, 125 Resources Road, Toronto, ON, M9P 3V6, Canada.

[D]University of Toronto, Department of Chemistry, Toronto, ON, M5S 3H6, Canada.

[E]Helmholtz-Zentrum Geesthacht, Institute for Coastal Research, Max-Planck Strasse, 1, D-21502 Geesthacht, Germany.

[F]Corresponding author. Email: mahiba.shoeib@ec.gc.ca

Chemicals

Methanol (LC-MS grade, OmniSolv >99.99%), acetone (OmniSolv 99.84%), petroleum ether (OmniSolv), dichlormethane (OmniSolv >99.96%), iso-octane (2,2,4-Trimethylpentane Omni-Solv >99.97%), water (OmniSolv) and ammonium acetate (min. 97%) were purchased from EMD. Anhydrous sodium sulfate were purchased from Fischer Scientific, supelclean EnviCab from Supelco and glacial acetic acid (99.7+%) from Alfa Aesar. The water (OmniSolv) was cleaned using Oasis WAX cartridges (Waters) to remove possible contaminations. Methane, nitrogen and helium were purchased from Linde.

Table A1. Target compounds with abbreviation, chemical formula, precursor and product ion, supplier, purity and internal standard (IS)

Analyte	Abbreviation	Chemical formula	Precursor/ product ion	Supplier (purity)	IS
Perfluoro hexylethanol	6:2 FTOH	$C_8F_{13}H_4OH$	365/327	Wellington Laboratories (>98%)	^{13}C-6:2 FTOH
Perfluoro octylethanol	8:2 FTOH	$C_{10}F_{17}H_4OH$	465/427	Wellington Laboratories (>98%)	^{13}C-8:2 FTOH
Perfluorodecyl ethanol	10:2 FTOH	$C_{12}F_{21}H_4OH$	565/527	Wellington Laboratories (>98%)	^{13}C-10:2 FTOH
Perfluorooctane sulfonamide	PFOSA	$C_8F_{17}SO_2NH_2$	498/78	Wellington Laboratories (>98%)	$^{13}C_4$-PFOS
N-methyl perfluorooctane sulfonamide	MeFOSA	$C_8F_{17}SO_2NHCH_3$	514	Wellington Laboratories (>98%)	d_3 MeFOSA
N-ethyl perflourooctae sulfonamide	EtFOSA	$C_8F_{17}SO_2NHC_2H_5$	528	Wellington Laboratories (>98%)	d_5 EtFOSA
N-methyl perfluorooctane sulfonamido-ethanol	MeFOSE	$C_8F_{17}SO_2NCH_3C_2H_4OH$	540/558	Wellington Laboratories (>98%)	d_7 MeFOSE
N-ethyl perflourooctane sulfonamido-ethanol	EtFOSE	$C_8F_{17}SO_2NC_2H_5C_2H_4OH$	554/572	Wellington Laboratories (>98%)	d_9 EtFOSE
N-methyl perfluorooctane sulfonamide ethylacrylate	Me PFOSEA	$C_8F_{17}SO_2N(C_2H_4OH)(C_2H_4OCOC_2H_3)$	540	Wellington Laboratories (>98%)	d_7 MeFOSE
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_2O$-	299/80	Wellington Laboratories (>98%)	$^{18}O_2$-PFHxS
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_2O^-$	399/80	Wellington Laboratories (>98%)	$^{18}O_2$-PFHxS
Perfluorooctane sufonate	PFOS	$C_8F_{17}SO_2O^-$	499/80	Aldrich (98%)	$^{13}C_4$-PFOS
Perfluorodecane sulfonate	PFDS	$C_{10}F_{21}SO_2O^-$	599/99	Wellington Laboratories (>98%)	$^{13}C_4$-PFOS
Perfluorobuntanoate	PFBA	$C_3F_7COO^-$	213/169	Wellington Laboratories (>98%)	$^{13}C_4$-PFBA
Perfluoropentanoate	PFPA	$C_4F_9COO^-$	263/219	Wellington Laboratories (>98%)	$^{13}C_2$-PFHxA
Perfluorohexanoate	PFHxA	$C_5F_{11}COO^-$	313/269	Wellington Laboratories (>98%)	$^{13}C_2$-PFHxA
Perfluorohepantoate	PFHpA	$C_6F_{12}COO^-$	363/319	Aldrich (98%)	$^{13}C_4$-PFOA
Perfluorooctanoate	PFOA	$C_7F_{15}COO^-$	413/369	Aldrich (98%)	$^{13}C_4$-PFOA

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Analyte	Abbreviation	Chemical formula	Precursor/ product ion	Supplier (purity)	IS
Perfluorononanoate	PFNA	$C_8F_{17}COO^-$	463/419	Aldrich (98%)	$^{13}C_5$-PFNA
Perfluorodecanoate	PFDA	$C_9F_{19}COO^-$	513/469	Aldrich (98%)	$^{13}C_2$-PFDA
Perfluoroundecanoate	PFUnDA	$C_{10}F_{21}COO$-	563/519	Aldrich (98%)	$^{13}C_2$-PFUnDA
Perfluorododecanoate	PFDoDA	$C_{11}F2_3COO^-$	613/569	Aldrich (98%)	$^{13}C_2$-PFDoA
Perfuorotetradecanoate	PFTDA	$C_{13}F_{25}COO^-$	713/669	Aldrich (98%)	$^{13}C_2$-PFDoA

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Table A2. Internal standards with abbreviation, chemical formula, precursor and product ion, supplier and purity

Analyte	Abbreviation	Chemical formula	Precursor/ product ion	Supplier (purity)
N, *N*-dimethylperfluoro-1-octanesulfonamide	Me_2FOSA	$C_8F_{17}SO_2N(CH_3)_2$	528	Wellington Laboratories (>98%)
2-perfluorohexyl-($^{13}C_2$)-ethanol	^{13}C-6:2 FTOH	$C_6F_{13}{}^{13}CH_2{}^{13}CD_2OH$	369/331	Wellington Laboratories (>98%)
2-perfluorooctyl-($^{13}C_2$)-ethanol	^{13}C-8:2 FTOH	$C_8F_{17}{}^{13}CH_2{}^{13}CD_2OH$	469/497	Wellington Laboratories (>98%)
2-perfluorodecyl-($^{13}C_2$)-ethanol	^{13}C-10:2 FTOH	$C_{10}F_{21}{}^{13}CH_2{}^{13}CD_2OH$	569/531	Wellington Laboratories (>98%)
Methyl-d_3-perfluorooctane sulfonamide	d_3-MeFOSA	$C_8F_{17}SO_2NHCD_3$	517	Wellington Laboratories (>98%)
Ethyl-d_5-perfluorooctane sulfonamide	d_5-EtFOSA	$C_8F_{17}SO_2NHC_2D_5$	533	Wellington Laboratories (>98%)
Methyl-d_7-perfluorooctane sulfonamido ethanol	d_7-MeFOSE	$C_8F_{17}SO_2NCD_3C_2D_4$	547/565	Wellington Laboratories (>98%)
Ethyl-d_9-perflourooctane sulfonamido ethanol	d_9 EtFOSE	$C_8F_{17}SO_2NC_2D_5\,C_2D_4OH$	581	Wellington Laboratories (>98%)
Perfluoro-1-hexane-($^{18}O_2$) sulfonate	$^{18}O_2$-PFHxS	$C_6F_{13}S[^{18}O_2]O^-$	403/103	Wellington Laboratories (>98%)
Perfluoro-1-($^{13}C_4$)-octane sulfonate	$^{13}C_4$- PFOS	$C_4F_9[1,2,3,4\text{-}^{13}C_4]\text{-}F_8SO_2O^-$	503/99	Wellington Laboratories (>98%)
Perfluoro-*n*-($^{13}C_4$)-butanoate	$^{13}C_4$- PFBA	$2,3,4\text{-}^{13}CF_7{}^{13}COO^-$	217/172	Wellington Laboratories (>98%)
Perfluoro-*n*-($^{13}C_4$)-octanoate	$^{13}C_4$-PFOA	$C_4F_9[2,3,4\text{-}^{13}C_3]\text{-}F_6{}^{13}COO^-$	417/372	Wellington Laboratories (>98%)
Perfluoro-*n*-($^{13}C_5$)-nonanoate	$^{13}C_5$-PFNA	$C_4F_9[2,3,4,5\text{-}^{13}C_4]\text{-}F_8{}^{13}COO^-$	468/423	Wellington Laboratories (>98%)
Perfluoro-*n*-($^{13}C_2$)-decanoate	$^{13}C_2$-PFDA	$C_8F_{17}{}^{13}CF_2{}^{13}COO^-$	515/470	Wellington Laboratories (>98%)
Perfluoro-*n*-($^{13}C_2$)-undecanoate	$^{13}C_2$-PFUnDA	$C_9F_{19}{}^{13}CF_2{}^{13}COO^-$	565/520	Wellington Laboratories (>98%)
Perfluoro-*n*-($^{13}C_2$)-dodecanoate	$^{13}C_2$-PFDoA	$C_{10}F_{21}{}^{13}CF_2{}^{13}COO^-$	615/570	Wellington Laboratories (>98%)
Perfluoro-*n*-($^{13}C_2$)-hexanoate	$^{13}C_2$-PFHxA	$C_4F_9{}^{13}CF_2{}^{13}COO^-$	315/270	Wellington Laboratories (>98%)
Perfluoro-1-($^{13}C_4$)-octane sulfonate	$^{13}C_8$-PFOS	$C_4F_9[1,2,3,4\text{-}^{13}C_4]\text{-}F_8SO_2O^-$	507/80	Wellington Laboratories (>98%)
Perfluoro-*n*-($^{13}C_4$)-octanoate	$^{13}C_8$-PFOA	$C_4F_9[2,3,4\text{-}^{13}C_3]\text{-}F_6{}^{13}COO^-$	421/376	Wellington Laboratories (>98%)

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Instrumental analysis

Table A3. Temperature program for the GC oven

	Rate (°C min^{-1})	Value (°C)	Hold time (min)	Run time (min)
Initial	–	60	2	2.00
Ramp 1	2	70	0	7.00
Ramp 2	8	120	0	13.25
Ramp 3	10	220	0	23.25

Table A4. Eluent gradient for HPLC

Time (min)	H_2O + 10 mM NH_4OAc (%)	MeOH + 10 mM NH_4OAc (%)
0.01	50	50
1.0	45	55
2.0	40	60
3.0	25	75
4.0	20	80
5.0	15	85
10.0	15	85
10.1	5	95
15.0	5	95
15.1	25	75
15.6	50	50
20.0	50	50

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Instrumental detection limits

Table A5. Instrument detection limits (IDLs) (expressed as picograms and picograms per cubic metre) were calculated by extrapolating instrument response in blank samples to a concentration that would give a S/N value of 3

Reporting of IDLs in units of picograms per cubic metre was done using an average air volume of 142 pg m^{-3} for PUF/XAD/PUF cartridges and GFFs and compound-specific air volumes for SIP disks

Name	PUF/XAD/PUF IDL		GFFs IDL		SIP disks IDL	
	(pg)	(pg m^{-3})	(pg)	(pg m^{-3})	(pg)	(pg m^{-3})
6:2 FTOH	88	0.61	100	0.73	96	0.60
8:2 FTOH	110	0.77	72	0.51	96	0.60
10:2 FTOH	71	0.50	81	0.57	58	0.36
PFOSA	0.79	0.01	0.55	0.001	1.4	0.01
MeFOSA	59	0.42	17	0.12	110	1.2
EtFOSA	36	0.25	23	0.16	19	0.20
MeFOSE	110	0.74	96	0.67	70	1.3
MePFOSEA	58	0.41	70	0.49	63	1.2
EtFOSE	150	1.1	58	0.41	89	1.8
PFBS	11	0.08	12	0.09	20	0.14
PFHxS	2.2	0.02	0.83	0.01	1.3	0.01
PFOS	7.2	0.05	1.8	0.01	4.3	0.03
PFDS	1.6	0.01	0.89	0.01	2.7	0.02
PFBA	0.79	0.12	9.2	0.06	27	0.19
PFPA	17	0.10	11	0.08	6.8	0.05
PFHxA	15	0.04	3.1	0.02	3.6	0.03
PFHpA	5.8	0.05	8.3	0.06	4.2	0.03
PFOA	6.5	0.01	4.2	0.03	8.6	0.06
PFNA	2.1	0.01	2.2	0.02	2.7	0.02
PFDA	2.0	0.02	2.6	0.02	1.4	0.01
PFUnDA	2.6	0.02	26	0.18	5.7	0.04
PFDoDA	3.0	0.04	3.8	0.03	4.3	0.03
PFTDA	5.9	0.01	2.5	0.02	1.6	0.01

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Concentrations in blank samples and limits of detection

Table A6. Mean concentrations ± s.d. and LOD (3 s.d.) (in parentheses) in blank samples for the different air sample media (*n* = 5 for PUF/XAD/PUF cartridges, *n* = 7 for GFFs and *n* = 2 for SIP disks)

Asterisks denote where half of the instrument detection limit (IDL, see Table A5) was used for compounds not detected in blank samples. In these cases LOD could not be calculated and IDL was used instead of LOD

Compound	PUF/XAD/PUF (pg m^{-3})	GFFs (pg m^{-3})	SIP disks (pg m^{-3})
6:2 FTOH	0.3 (0.61)*	0.4 (0.73)*	0.7 ± 0.6 (1.8)
8:2 FTOH	3.1 ± 2.6 (7.8)	0.3 (0.51)*	7.1 ± 0.6 (1.8)
10:2 FTOH	4.9 ± 1.3 (3.9)	1.8 ± 1.1 (3.3)	4.3 ± 0.6 (1.8)
PFOSA	3.9 ± 2.1 (6.3)	4.5 ± 2.4 (7.2)	2.0 ± 0.1 (0.3)
MeFOSA	3.5 ± 0.5 (1.5)	3.1 ± 0.4 (1.2)	3.8 ± 0.8 (2.4)
EtFOSA	0.4 ± 0.2 (0.6)	0.2 ± 0.1 (0.3)	0.1 ± 0.1 (0.3)
MeFOSE	3.7 ± 4.2 (13)	1.6 ± 1.6 (4.8)	0.5 ± 0.4 (1.2)
MePFOSEA	0.2 (0.41)*	0.3 (0.49)	0.5 ± 0.4 (1.2)
EtFOSE	4.4 ± 4.6 (13.8)	0.6 ± 1.1 (3.3)	0.7 ± 0.5 (1.5)
PFBS	0.04 (0.08)*	0.04 (0.09)*	0.07 (0.14)*
PFHxS	1.1 ± 0.47 (1.4)	0.28 ± 0.03 (0.09)	0.30 ± 0.09 (0.27)
PFOS	4.2 ± 1.8 (5.4)	6.4 ± 5.9 (18)	7.04 ± 1.06 (3.2)
PFDS	0.01 (0.01)*	0.03 ± 0.02 (0.06)	0.01 (0.02)*
PFBA	7.1 ± 5.7 (17)	22 ± 42 (125)	14 ± 11 (33)
PFPA	3.4 ± 4.2 (13)	6.7 ± 13 (39)	1.6 ± 1.8 (5.4)
PFHxA	1.2 ± 0.3 (0.9)	0.84 ± 0.3 (0.9)	1.1 ± 0.22 (0.66)
PFHpA	1.4 ± 0.5 (1.5)	2.2 ± 2.8 (8.4)	1.2 ± 0.03 (0.09)
PFOA	5.6 ± 2.0 (6.0)	2.1 ± 0.81 (2.4)	11 ± 2.7 (8.1)
PFNA	0.95 ± 0.46 (1.4)	0.48 ± 0.10 (0.3)	0.65 ± 0.08 (0.24)
PFDA	0.86 ± 0.15 (0.45)	0.95 ± 0.34 (1.0)	0.71 ± 0.01 (0.03)
PFUnDA	1.3 ± 0.27 (0.81)	5.4 ± 9.6 (29)	1.2 ± 0.23 (0.69)
PFDoDA	0.71 ± 0.05 (0.15)	1.2 ± 0.82 (2.5)	0.63 ± 0.03 (0.09)
PFTDA	0.004 (0.01)*	0.13 ± 0.14 (0.43)	0.01 (0.01)*

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Recoveries

Table A7. Mean recoveries (%) (±s.d.) of internal standards (IS) in the different air sample media (*n* = 12 for PUF/XAD/PUF cartridges and GFFs, *n* = 4 for SIP disks)

IS	PUF/XAD/PUF Cartridges		GFFs		SIP disks (%)
	Aeration tank (%)	Secondary clarifier (%)	Aeration tank (%)	Secondary clarifier (%)	
^{13}C-6:2 FTOH	18 ± 23	5.9 ± 1.8	9.4 ± 2.8	9.7 ± 2.1	6.4 ± 1.0
^{13}C-8:2 FTOH	75 ± 8.5	67.5 ± 8.7	47 ± 12	49 ± 6.6	66 ± 8.6
^{13}C-10:2 FTOH	98 ± 14	100 ± 18	56 ± 10	58 ± 6.2	110 ± 14
d_3-MeFOSA	72 ± 13	80 ± 21	80 ± 9.2	81 ± 6.3	99 ± 11
D_5-EtFOSA	84 ± 9.4	91 ± 19	85 ± 9.6	85 ± 6.7	100 ± 12
d_7-MeFOSE	220 ± 39	200 ± 47	130 ± 24	130 ± 11	230 ± 46
D_9-EtFOSE	230 ± 37	220 ± 48	150 ± 25	130 ± 15	230 ± 61
$^{18}O_2$-PFHxS	120 ± 37	120 ± 39	62 ± 23	54 ± 14	310 ± 40
$^{13}C_4$-PFOS	78 ± 20	79 ± 20	37 ± 11	38 ± 8.3	75 ± 5.2
$^{13}C_2$-PFBA	150 ± 53	180 ± 96	36 ± 3.9	36 ± 8.5	160 ± 64
$^{13}C_2$-PFHxA	130 ± 240	140 ± 32	63 ± 1	67 ± 16	240 ± 50
$^{13}C_4$-PFOA	83 ± 220	92 ± 17	47 ± 6.9	49 ± 10	73 ± 7.1
$^{13}C_5$-PFNA	66 ± 22	67 ± 15	39 ± 7.3	44 ± 10	34 ± 0.4
$^{13}C_2$-PFDA	59 ± 27	54 ± 14	51 ± 9.0	57 ± 13	27 ± 2.3
$^{13}C_2$-PFUnDA	43 ± 25	38 ± 14	52 ± 11	62 ± 15	25 ± 6.4
$^{13}C_2$-PFDoDA	27 ± 20	21 ± 11	47 ± 9.9	55 ± 15	18 ± 4.0

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Atmospheric concentrations

Table A8. Gas-phase concentrations (blank corrected) at the aeration tank

Concentrations are given in picograms per cubic metre. Values that fell below the LOD but above the mean blank are indicated with an asterisk (*). Non-detections and cases where blank correction resulted in a negative value are replaced with ½ LOD value (Table A6) and italicised. Note: in case where more than 25% of samples for a given target chemical are replaced by ½ LOD value, the summary statistics for these compounds are not included in box and whisker plots (due to bias[1]), and only mean values are reported

Name	1	2	3	4	5	6	7
6:2 FTOH	8300	3000	5500	780	3200	1400	6300
8:2 FTOH	3200	1000	1600	3600	11000	16000	5600
10:2 FTOH	600	120	210	590	3100	3100	1100
∑FTOH	12000	4200	7300	4900	17000	33000	13000
MeFOSA	7.6	0.71*	6.5	14	16	36	29
EtFOSA	5.3	0.46*	3.1	5.8	4.8	10	9.6
MeFOSE	27	4.9*	121*	14	24	44	24
EtFOSE	4.1*	*7.0*	*7.0*	*7.0*	*7.0*	*5.4**	*7.0*
PFOSA	*3.1*	4.2*	6.3	3.0*	9.5	5.8*	2.5*
∑FOSA–FOSE	44	17	35	44	61	100	74
PFHxS	*0.70*	0.06*	0.15*	0.63*	0.76*	1.7	0.42*
PFOS	*2.7*	1.1*	1.4*	4.1*	1.5*	41	1.6*
PFDS	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*
∑PFSA	3.4	1.2	1.6	4.7	2.3	42	2.0
PFBA	8.6*	4.1*	6.2*	11*	0.9*	4.9*	10*
PFPA	25	*6.3*	5.9*	7.1*	8.2*	11*	14
PFHxA	7.1	6.6	15	18	22	22	33
PFHpA	0.16*	1.8	3.1	2.5	5.6	5.9	7.3
PFOA	2.1*	4.3*	8.6	9.6	18	18	22
PFNA	*0.69*	0.71*	1.2*	1.1*	1.0*	0.96*	2.0
PFDA	0.28*	0.25*	0.88	0.78	2.1	2.3	1.7
PFUnDA	2.5	0.13*	*0.41*	*0.41*	0.12*	*0.41*	9.0
PFDoDA	*0.09*	*0.09*	0.15*	*0.09*	0.56	0.31	0.20
PFTDA	*0.004*	*0.004*	*0.004*	*0.004*	*0.004*	*0.004*	*0.004*
∑PFCA	46	24	41	51	59	65	99

Table A8. (*Continued*)

Name	8	9	10	11	12	mean	s.d.
6:2 FTOH	11000	7600	4400	2300	2300	5700	3900
8:2 FTOH	6000	4900	1900	930	910	4700	4600
10:2 FTOH	880	900	240	97	72	920	1100
∑FTOH	18000	13000	6500	3400	3300	11000	8600
MeFOSA	16	12	8.5	6.2	4.1	13	10
EtFOSA	7.6	4.5	3.6	2.8	1.4	4.9	3.0
MeFOSE	28	22	16	12*	9.5*	20	11
EtFOSE	6.1*	*7.0*	*7.0*	*7.0*	*7.0*	7.0	1.4
PFOSA	2.6*	2.3*	2.9*	*3.1*	5.8*	3.7	2.7
∑FOSA–FOSE	61	48	38	30	28	48	23
PFHxS	0.95*	0.97*	0.61*	2.05*	0.34*	0.78	0.59
PFOS	3.3*	1.9*	1.9*	6.2	3.1*	5.8	11
PFDS	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.0*
∑PFSA	4.2	2.9	2.5	8.3	3.4	6.6	11
PFBA	11*	24	9.6*	30	14*	11	8.3
PFPA	7.0*	*6.3*	1.6*	*6.3*	*6.3*	8.7	5.8
PFHxA	50	26	16	14	7.0	20	12
PFHpA	13	5.3	4.7	11	1.3*	5.1	3.8
PFOA	25	17	8.2	21	4.0*	13	7.9
PFNA	3.1	2.7	1.7	9.3	1.7	2.2	2.4
PFDA	2.6	2.8	1.2	1.7	0.68	1.4	0.88
PFUnDA	*0.41*	0.03*	0.27*	0.25*	*0.41*	1.2	2.5
PFDoDA	0.50	0.64	0.10*	*0.09*	*0.09*	0.24	0.21
PFTDA	*0.004*	*0.004*	*0.004*	*0.004*	*0.004*	*0.004*	*0.0*
∑PFCA	110	85	43	93	36	63	28

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Table A9. Gas-phase concentrations (blank corrected) at the secondary clarifier

Concentrations are given in picograms per cubic metre. Values that fell below the LOD but above the mean blank are indicated with an asterisk (*). Non-detections and cases where blank correction resulted in a negative value are replaced with ½ LOD value (Table A6) and italicised. Note: in case where more than 25% of samples for a given target chemical are replaced by ½ LOD value, the summary statistics for these compounds are not included in box and whisker plots (due to bias [1]), and only mean values are reported

Name	1	2	3	4	5	6	7
6:2 FTOH	290	330	240	280	350	910	530
8:2 FTOH	180	83	110	170	240	670	420
10:2 FTOH	46	6.2	16	29	62	113	60
∑FTOH	510	420	360	470	650	1700	1000
MeFOSA	2.9	0.23*	0.93*	0.84*	6.1	6.7	0.58*
EtFOSA	3.4	0.45*	0.63	1.0	1.9	2.5	0.72
MeFOSE	13	0.57*	*6.3*	*6.3*	*6.3*	2.7*	*6.3*
EtFOSE	8.3*	*7.0*	*7.0*	*7.0*	*7.0*	*7.0*	*7.0*
PFOSA	2.8*	5.0*	1.5*	1.8*	0.94*	2.4*	3.6*
∑FOSA–FOSE	31	13	16	17	22	21	18
PFHxS	0.50*	0.18*	0.12*	0.31*	1.6	1.3*	0.57*
PFOS	1.9*	30	2.6*	2.4*	2.0*	2.3*	1.25*
PFDS	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*
∑PFSA	2.4	30	2.7	2.7	3.6	3.6	1.8
PFBA	9.7*	13*	14*	5.3*	2.1*	17*	16*
PFPA	5.1*	40	23	*6.3*	*6.3*	1.5*	0.42*
PFHxA	1.7	0.98	1.6	1.1	2.2	1.5	2.8
PFHpA	*0.81*	*0.81*	*0.81*	*0.81*	0.68*	0.09*	0.59*
PFOA	1.3*	0.63*	1.2*	2.0*	2.7*	1.8*	3.7*
PFNA	0.69*	0.67*	0.45*	0.59*	0.56*	0.82*	1.1*
PFDA	0.26*	0.42*	0.42*	0.15*	0.50	0.34*	0.39*
PFUnDA	*0.41*	0.06*	*0.41*	0.06*	0.40*	*0.41*	*0.41*
PFDoDA	*0.09*	*0.09*	0.11*	*0.09*	*0.09*	0.10*	0.31
PFTDA	*0.004*	*0.004*	*0.004*	*0.004*	*0.004*	*0.004*	*0.004*
∑PFCA	20	56	42	16	16	23	26

Table A9. (*Continued*)

Name	8	9	10	11	12	mean	s.d.
6:2 FTOH	390	290	230	110	*0.31*	330	230
8:2 FTOH	290	330	100	52	27	220	190
10:2 FTOH	48	74	23	9.9	7.6	41	32
∑FTOH	720	690	350	170	34	590	440
MeFOSA	0.89*	1.3*	0.47*	*0.70*	*0.70*	1.9	2.2
EtFOSA	1.0	1.1	0.77	0.19	*0.29*	1.2	0.96
MeFOSE	0.54*	*6.3*	*6.3*	*6.3*	*6.3*	5.6	3.3
EtFOSE	*7.0*	*7.0*	*7.0*	*7.0*	*7.0*	7.1	0.40
PFOSA	1.6*	0.54*	3.0*	5.3*	11	3.3	2.8
∑FOSA–FOSE	11	16	18	19	25	16	5.3
PFHxS	0.51*	0.49*	0.62*	0.41*	0.42*	0.59	0.43
PFOS	9.51	1.1*	0.94*	1.6*	0.65*	4.7	8.2
PFDS	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	0.01	0.0
∑PFSA	10	1.6	1.6	2.1	1.1	5.2	8.1
PFBA	23	18	9.1*	25	15*	14	6.6
PFPA	3.6*	2.3*	*6.3*	9.4*	1.7*	8.8	11.4
PFHxA	1.9	1.5	1.6	1.5	0.70*	1.6	0.56
PFHpA	0.04*	*0.81*	0.35*	0.43*	0.22*	0.54	0.30
PFOA	4.9*	3.0*	2.8*	1.9*	1.2*	2.3	1.2
PFNA	0.76*	0.48*	0.52*	1.4	0.67*	0.72	0.27
PFDA	0.65	0.81	0.57	0.14*	0.39*	0.42	0.20
PFUnDA	*0.41*	0.18	*0.41*	*0.41*	*0.41*	0.33	0.14
PFDoDA	*0.09*	*0.09*	0.06*	*0.09*	*0.09*	0.11	0.06
PFTDA	*0.004*	*0.004*	*0.004*	*0.004*	*0.004*	0.004	0.0
∑PFCA	35	27	22	40	20	29	12

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Table A10. Particle-phase concentrations (blank corrected) at the aeration tank

Concentrations are given in picograms per cubic metre. Values that fell below the LOD but above the mean blank are indicated with an asterisk (*). Non-detections and cases where blank correction resulted in a negative value are replaced with ½ LOD value (Table A6) and italicised. Note: in case where more than 25% of samples for a given target chemical are replaced by ½ LOD value, the summary statistics for these compounds are not included in box and whisker plots (due to bias[1]), and only mean values are reported

Name	1	2	3	4	5	6	7
6:2 FTOH	*0.36*	32	4.5	*0.36*	34	*0.36*	*0.36*
8:2 FTOH	21	27	5.8	6.8	14	7.3	8.5
10:2 FTOH	17	21	3.0*	2.5*	13	3.6	4.6
∑FTOH	39	79	13	9.7	61	11	14
MeFOSA	0.82*	0.97*	2.5	0.71*	0.81*	0.42*	3.3
EtFOSA	0.72	0.85	0.98	0.43	0.54	0.25*	1.5
MeFOSE	44	8.9	17	20	20	14	20
EtFOSE	24	3.4	6.3	9.2	13	12	14
PFOSA	5.9*	13	45	37	37	95	67
∑FOSA–FOSE	75	27	71	67	72	120	110
PFHxS	5.8	13	21	17	13	43	21
PFOS	830	1700	7200	6000	480	2300	6900
PFDS	*0.04*	2.3	18	16	1.1	4.9	15
∑PFSA	830	1700	7300	6000	500	2300	6900
PFBA	*63*	20*	9.3*	*63*	*63*	*63*	10*
PFPA	*19*	0.99*	1.3*	1.9*	73	44	31*
PFHxA	5.7	15	57	63	66	110	110
PFHpA	2.5*	5.5*	10	20	29	40	32
PFOA	12	23	60	64	76	150	110
PFNA	3.0	8.0	48	40	8.6	23	44
PFDA	4.0	15	110	93	9.5	29	110
PFUnDA	4.4*	*15*	1.1*	47	*15*	*15*	4.7*
PFDoDA	*1.2*	0.09*	0.48*	1.2*	0.20*	1.7*	0.58*
PFTDA	*0.21*	0.35*	0.25*	0.03*	0.02*	0.29*	0.13*
∑PFCA	120	100	300	390	340	470	460

Table A10. (*Continued*)

Name	8	9	10	11	12	mean	s.d.
6:2 FTOH	20	*0.36*	*0.36*	*0.36*	*0.36*	7.7	13
8:2 FTOH	9.1	6.7	6.2	9.4	*0.25*	10	7.2
10:2 FTOH	6.6	4.1	4.1	6.0	4.5	7.5	6.1
∑FTOH	35	11	11	16	5.1	25	24
MeFOSA	2.0	2.1	0.66*	1.7	0.27*	1.4	0.94
EtFOSA	1.3	0.89	0.52	0.99	0.74	0.80	0.34
MeFOSE	21	23	12	10	6.6	18	9.8
EtFOSE	14	14	8.8	5.8	4.0	11	5.6
PFOSA	46	29	42	27	12	38	25
∑FOSA–FOSE	85	68	63	45	23	69	28
PFHxS	16	6.7	7.8	8.0	3.3	15	11
PFOS	5700	1700	2900	5100	2100	3600	2400
PFDS	9.7	3.1	4.1	11	2.7	7.4	6.4
∑PFSA	5700	1700	3000	5100	2100	3600	2500
PFBA	38*	16*	*63*	21*	79*	42	26
PFPA	*19*	6.3*	3.7*	19	41	22	22
PFHxA	85	28	34	31	15	52	36
PFHpA	25	12	12	16	12	18	12
PFOA	89	45	44	35	140	71	45
PFNA	32	12	12	16	7.6	21	16
PFDA	85	21	22	39	15	46	40
PFUnDA	0.68*	2.03*	*15*	47	0.59*	14	17
PFDoDA	1.5*	0.20*	*1.2*	0.59*	4.7	1.1	1.2
PFTDA	0.03*	0.14*	0.06*	0.03*	2.2	0.31	0.62
∑PFCA	380	140	210	230	320	290	130

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Table A11. Particle-phase concentrations (blank corrected) at the secondary clarifier

Concentrations are given in picograms per cubic metre. Values that fell below the LOD but above the mean blank are indicated with an asterisk (*). Non-detections and cases where blank correction resulted in a negative value are replaced with ½ LOD value (Table A6) and italicised. Note: in case where more than 25% of samples for a given target chemical are replaced by ½ LOD value, the summary statistics for these compounds are not included in box and whisker plots (due to bias[1]), and only mean values are reported

Name	1	2	3	4	5	6	7
6:2 FTOH	*0.36*	*0.36*	*0.36*	*0.36*	*0.36*	*0.36*	*0.36*
8:2 FTOH	*0.25*	*0.25*	*0.25*	*0.25*	*0.25*	*0.25*	*0.25*
10:2 FTOH	4.0	5.2	1.4*	1.0*	1.7*	0.82*	1.3*
∑FTOH	4.6	5.8	2.0	1.6	2.3	1.4	2.0
MeFOSA	0.31*	0.13*	0.10*	*0.66*	0.10*	*0.66*	0.10*
EtFOSA	0.32*	0.29*	0.24*	0.10*	0.23*	0.30*	0.17*
MeFOSE	12	2.6*	2.5*	2.8*	3.6*	2.3*	3.5*
EtFOSE	13	0.82*	1.4*	1.0*	1.5*	1.6*	0.94*
PFOSA	5.7*	1.7*	2.3*	0.97*	8.0	12	3.8*
∑FOSA–FOSE	31	5.5	6.6	5.6	13	17	8.5
PFHxS	14	7.7	7.2	5.8	41	35	15
PFOS	770	840	800	620	760	1100	1500
PFDS	1.6	1.2	0.88	0.95	1.8	2.6	1.4
∑PFSA	790	850	810	630	800	1200	1600
PFBA	*63*	3.7*	9.0*	*63*	*63*	*63*	7.8*
PFPA	*19*	*19*	*19*	*19*	*19*	*19*	*19*
PFHxA	8.5	5.5	6.9	6.4	45	26	12
PFHpA	8.8	1.1*	0.66*	4.3*	7.7*	5.5*	3.8*
PFOA	19	12	13	16	57	44	18
PFNA	5.4	4.4	4.5	3.7	12	12	6.8
PFDA	6.7	6.3	6.8	4.5	9.8	15	11
PFUnDA	1.94*	*15*	*15*	*15*	*15*	*15*	*15*
PFDoDA	*1.2*	*1.2*	*1.2*	*1.2*	0.08*	0.41*	*1.2*
PFTDA	0.16*	0.09*	*0.21*	0.03*	0.13*	0.36*	0.05*
∑PFCA	130	68	76	130	230	200	95

Table A11. (*Continued*)

Name	8	9	10	11	12	mean	s.d.
6:2 FTOH	*0.36*	*0.36*	*0.36*	*0.36*	*0.36*	*0.36*	*0.0*
8:2 FTOH	*0.25*	*0.25*	*0.25*	*0.25*	*0.25*	*0.25*	*0.0*
10:2 FTOH	1.8*	1.7*	1.6*	1.2*	0.84*	1.9	1.3
∑FTOH	2.4	2.3	2.2	1.8	1.5	2.5	1.3
MeFOSA	*0.66*	0.17*	*0.66*	*0.66*	*0.66*	0.41	0.27
EtFOSA	0.25*	0.18*	0.27*	*0.19*	0.20*	0.23	0.06
MeFOSE	4.7	5.0	2.6*	0.77*	1.7*	3.7	2.8
EtFOSE	1.7*	1.3*	0.81*	0.94*	0.94*	2.1	3.5
PFOSA	1.5	3.1*	4.9*	2.3*	1.9*	4.0	3.2
∑FOSA–FOSE	8.7	9.8	9.2	4.9	5.5	11	7.5
PFHxS	12	13	16	9.7	10	15	11
PFOS	1100	1400	1600	1100	860	1000	320
PFDS	1.2	1.6	1.8	1.2	0.84	1.4	0.55
∑PFSA	1100	1400	1600	1100	880	1100	320
PFBA	17*	9.3*	*63*	11*	1.4*	31	28
PFPA	*19*	*19*	*19*	*19*	*19*	19	0.0
PFHxA	8.9	11	13	8.3	5.0	13	12
PFHpA	2.5*	1.1*	3.1*	3.7*	3.9*	3.8	2.5
PFOA	15	17	21	16	51	24.8	16
PFNA	6.1	7.2	8.2	6.8	4.7	6.8	2.8
PFDA	7.6	9.0	10	7.2	6.5	8.3	2.7
PFUnDA	*15*	*15*	*15*	27	*15*	15	5.4
PFDoDA	2.4*	*1.2*	*1.2*	*1.2*	3.1	1.3	0.77
PFTDA	0.22*	0.05*	*0.21*	*0.21*	0.29*	0.17	0.10
∑PFCA	93	89	150	100	110	120	50

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

Composition in air samples

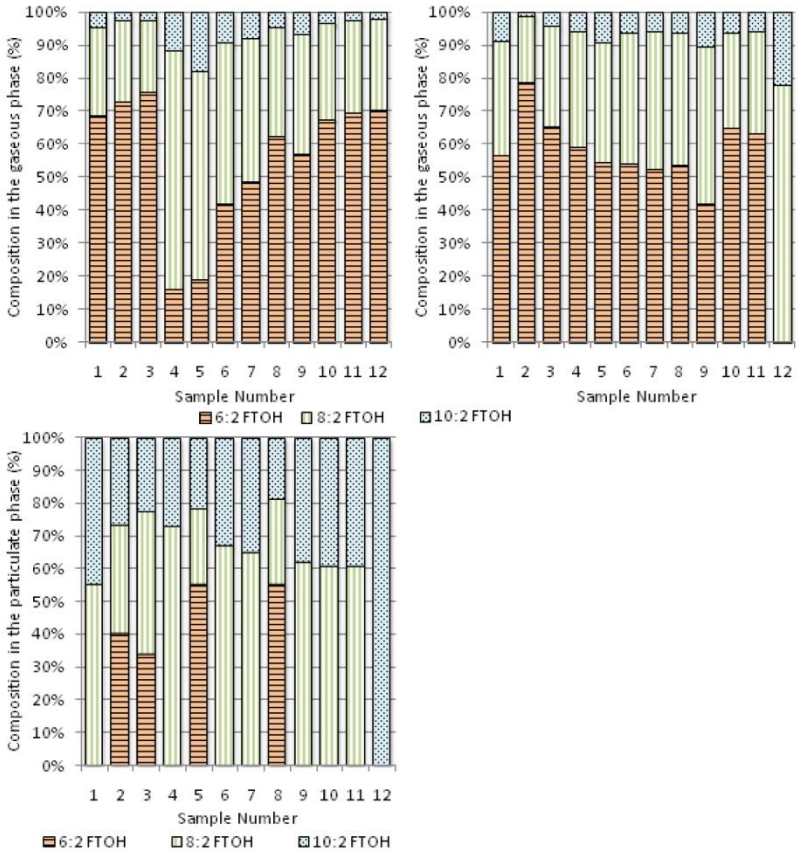


Fig. A1. Composition of FTOHs in the gas phase (top) and the particle phase (bottom) at the aeration tank (left) and the secondary clarifier (right). FTOH concentrations at the secondary clarifier were below the IDL for 6:2 FTOH and 8:2 FTOH.

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

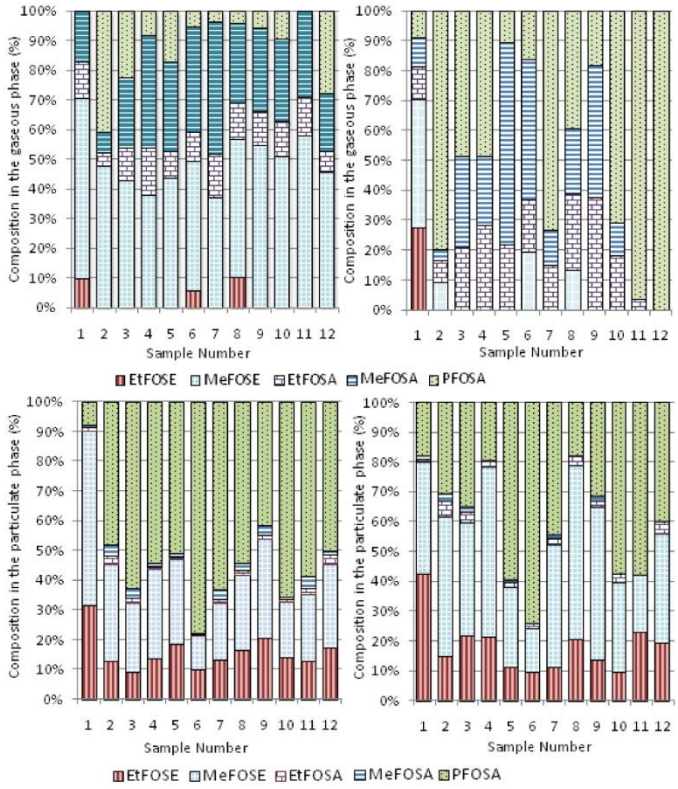


Fig. A2. Composition of FOSAs and FOSEs in the gas phase (top) and the particle phase (bottom) at the aeration tank (left) and the secondary clarifier (right). In the gas phase in sample 12 at the secondary clarifier all compound except of PFOSA were below the IDL.

©CSIRO 2011 *Environ. Chem.* **2011**, *8*, 363–371. doi:10.1071/EN10133_AC

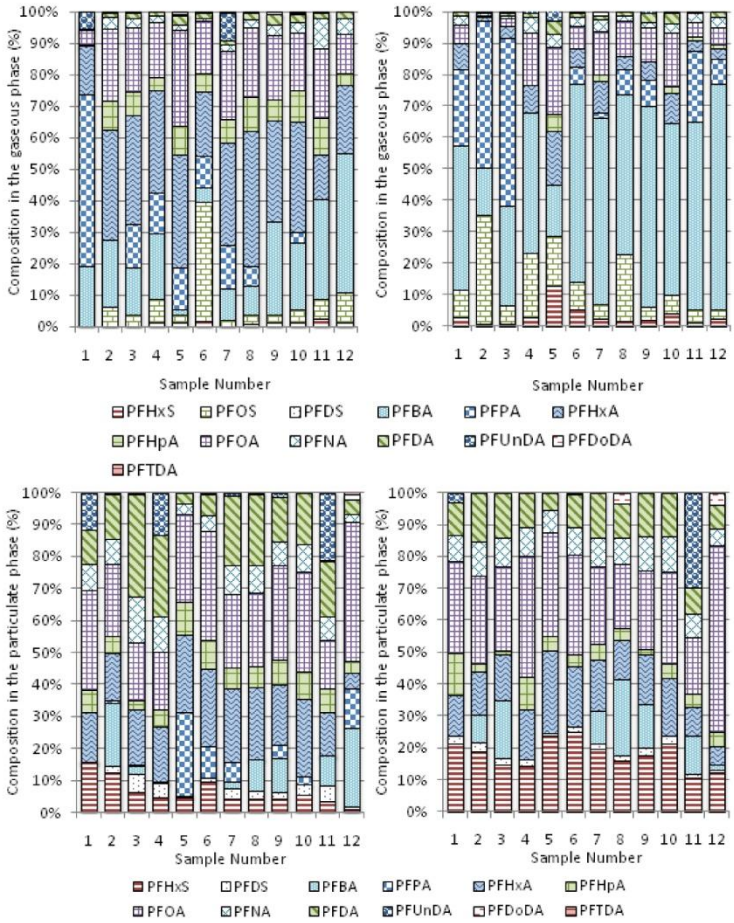


Fig. A3. Composition of PFCAs and PFSAs in the gas phase (top) and the particle phase (bottom) at the aeration tank (left) and the secondary clarifier (right). The particle phase concentrations of PFOS in each sample (~90% in average) are not shown.

References

[1] D. R. Helsel, M. T. Obvious, Better methods for interpreting nondetect data. *Environ. Sci. Technol*. **2005**, *39*, 419A. doi:10.1021/es053368a

A4 Paper 4 pK_a via water-to-air transport

On page 11036 of the paper "Assuming that 100 k_A is k_W, [...]" is incorrect. Correct is "Assuming that k_A is 100 k_W, [...]".

Environmental Science & Technology

Article

pubs.acs.org/est

Estimation of the Acid Dissociation Constant of Perfluoroalkyl Carboxylic Acids through an Experimental Investigation of their Water-to-Air Transport

Lena Vierke,*[,†,‡] Urs Berger,[§] and Ian T. Cousins[§]

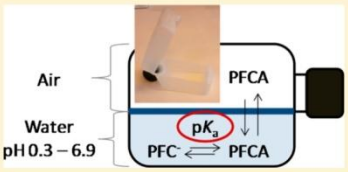
[†]Federal Environment Agency, Section for Chemicals, Wörlitzer Platz 1, Dessau-Roßlau, Germany

[‡]Institute of Sustainable and Environmental Chemistry, Leuphana University Lüneburg, Scharnhorst Str. 1, Lüneburg, Germany

[§]Department of Applied Environmental Science (ITM), Stockholm University, Svante Arrhenius väg 8, Stockholm, Sweden

Supporting Information

ABSTRACT: The acid dissociation constants (pK_as) of perfluoroalkyl carboxylic acids (PFCAs) have been the subject of discussion in the literature; for example, values from −0.2 to 3.8 have been suggested for perfluorooctanoic acid (PFOA). The dissociated anionic conjugate bases of PFCAs have negligible air−water partition coefficients (K_{AW}s) and do not volatilize from water. The neutral acids, however, have relatively high K_{AW}s and volatilization from water has been demonstrated. The extent of volatilization of PFCAs in the environment will depend on the water pH and their pK_a. Knowledge of the pK_as of PFCAs is therefore vital for understanding their environmental transport and fate. We investigated the water-to-air transfer of PFCAs in a novel experimental setup. We used ∼1 μg L^{-1} of PFCAs in water (above environmental background concentrations but below the concentration at which self-association occurs) at different water pH (pH 0.3 to pH 6.9) and sampled the PFCAs volatilized from water during a 2-day experiment. Our results suggest that the pK_as of C_{4-11} PFCAs are <1.6. For PFOA, we derived a pK_a of 0.5 from fitting the experimental measurements with a volatilization model. Perfluoroalkane sulfonic acids were not volatilized, suggesting that their pK_as are below the investigated pH range (pK_a <0.3).



INTRODUCTION

Perfluoroalkyl carboxylic acids (PFCAs with the general chemical formula $C_nF_{2n+1}COOH$) and their conjugate bases (together referred to as PFC(A)s) are characterized by a perfluorinated carbon chain connected to a carboxylic acid group. The perfluorinated carbon chain of these manmade chemicals provides unique oleophobic and hydrophobic properties as well as extraordinary stability (no observed degradation under typical environmental conditions).[1] These properties make PFC(A)s very useful for a wide range of different industrial and consumer product applications.[2,3] At the same time, their stability causes PFC(A)s to be very persistent, and once released to the environment, they will reside there for decades to centuries.[4] The widespread occurrence of PFC(A)s in the environment is proof of their ubiquitous distribution in different environmental media globally.[5−7] Furthermore, some long-chain PFC(A)s are bioaccumulative,[8] for example, enrich in food chains,[9,10] and have toxic properties, for example, perfluorooctanoic acid (PFOA) is toxic for reproduction.[11,12] PFC(A)s are found in remote regions,[13,14] but the mechanism of their long-range transport in the environment is not yet fully understood.[15] The neutral acid and its anionic conjugate base have different physical-chemical properties. The dissociated anionic form has a negligible vapor pressure, is soluble in water, and has a very low air−water partition coefficient.[16] The neutral acid has a relatively high vapor pressure[16,17] and transfer from water to air has been demonstrated.[18,19] As only the acid form is expected to volatilize, the extent of volatilization of PFC(A)s will depend on the pH value of the water phase and the acid dissociation constant (pK_a). To understand the environmental transport and fate of PFC(A)s, knowledge of the correct pK_a values is critically important.[15]

The determination of pK_as for PFCAs is a challenge and has resulted in some discussion in the literature.[20−22] The challenges in experimental pK_a determination, as well as in the measurement of other physical-chemical and environmental partitioning properties, are due to the surfactant properties of PFC(A)s,[2] which make them enrich at surfaces,[23,24] and the self-aggregation in solution (starting with the formation of premicelles at concentration below the critical micelle concentration).[25] Furthermore, at relatively high solute concentrations (1 mg L^{-1}) PFOA preferably forms dimeric clusters, which have a higher pK_a compared to individual molecules.[26] Also mixed solvent systems (e.g., water and methanol) bias the results of pK_a determinations.[27] The wide range of pK_as measured for PFOA (pK_a <1.0−3.8)[20,25,26,28,29] is a reflection of these difficulties.[20,25,26,28,29] Theoretical estimations and model calculations are similarly variable with predicted pK_as of −0.2 to 2.9 reported for PFOA.[30−34] For other PFCAs only two studies reported measured pK_as (0.2 for PFBA,[35] 0.31−0.85 for PFBA to PFHxA and 2.58−3.13 for

Received: June 18, 2013
Revised: August 13, 2013
Accepted: August 16, 2013
Published: August 16, 2013

PFDA to PFDoDA[36]). It is unclear if these measurements of other PFCAs were also biased by processes like dimerization or aggregation.

The aim of this study was to better constrain the pK_as for PFCAs by an experimental investigation of their water-to-air transport behavior at comparatively low water concentrations (above environmental background water concentrations but below the concentration at which self-association occurs) and at a range of different water pH. By better constraining the pK_a, we will be able to assess the presence of the neutral acid forms of PFCAs under environmentally relevant conditions.

MATERIALS AND METHODS

Terminology. To make a distinction between the protonated acid form and the dissociated anionic form of PFCAs, we designate PFCA anions by removing the "A" from the individual substance acronym (e.g., PFO for perfluorooctanoate), maintain the original abbreviation for the acid (e.g., PFOA for perfluorooctanoic acid), and refer to both chemical forms using a collective abbreviation involving parentheses surrounding the "A," for example, PFO(A) for combined perfluorooctanoate and perfluorooctanoic acid.[3]

Theory. To constrain the pK_as for PFCAs we exploited the relationship between the pH of an aqueous PFC(A) solution and the transfer of the neutral acid species to the gas phase. Perfluoroalkane sulfonic acids (PFSAs) were also investigated in the same experiment for comparison purposes because they are structurally similar to PFCAs but are expected to have a lower pK_a.[37] Furthermore, 8:2 fluorotelomer unsaturated acid (8:2 FTUCA) was used as a (semiquantitative) reference chemical. The pK_a of 8:2 FTUCA is expected to be higher compared to PFCAs, based on pK_as of 2.5−3.3 and 2.4−3.4 calculated with SPARC and COMO-RS for 7:2 and 11:2 FTUCA, respectively.[30]

The air−water distribution ratio of an organic acid (D_{AW}) (note we use the term "ratio" and not "partition coefficient" since there is more than one species) can be determined using eq 1 where $K_{AW,neutral}$ is the air−water partition coefficient of the neutral species, pH refers to the acidity of the aqueous solution and pK_a is the acid dissociation constant of interest.[38]

$$D_{AW} = K_{AW,neutral}(1 + 10^{pH-pKa})^{-1} \quad (1)$$

An implicit assumption of this equation is that the anionic species cannot be transported to the gas phase (i.e., K_{AW} is negligible for the anion, also suggested by Barton et al.[16]). We hypothesize that in order to get a transfer of PFCAs from the water to the air gas phase, the pH of the water must be close to or below the pK_a. We have therefore conducted laboratory volatilization experiments for PFCAs from water at a range of different water pH. We monitored the amount of PFCAs lost from the water over time and the amount transported to the overlying gas phase. It was not sufficient to only measure the loss of PFC(A)s from water at different pH because loss from water can also be due to sorption to the walls of the vessels. Knowledge of both concentrations in water and sorption to the walls was needed to monitor the overall mass-balance in the experimental system.

To describe the expected results of the experiments we used an adapted version of a model (widely used in multimedia environmental modeling[39]) based on two-film theory for estimating the air−water exchange of organic solutes.[40] The model is expressed by eq 2.[39]

$$C_{Wt} = C_{W0}e^{-k_{OW}t/Y} \quad (2)$$

Where C_{Wt} is the water concentration at time t after initial addition of the chemical (mol m^{-3}), C_{WO} is the initial water concentration of the chemical (at t_0) (mol m^{-3}), k_{OW} is the overall mass transfer coefficient for water-to-air transport (m h^{-1}), t is the time after initial addition of the chemical (h) and Y is the water depth (m). The only modification we made to the original model was in the estimation of k_{OW}, which was determined as shown in eq 3.

$$k_{OW} = \frac{1}{\frac{1}{k_W} + \frac{1}{k_A D_{AW}}} \quad (3)$$

Where k_W is the water-side mass transfer coefficient (m h^{-1}) and k_A is the air-side mass transfer coefficient (m h^{-1}). In the original model K_{AW} was used instead of D_{AW}.

We applied this model to estimate the losses of PFCAs from water over time in volatilization experiments conducted at different pH. Figure 1 illustratively shows the calculated loss of PFOA from water for different pH after 2 d (assuming that the loss is caused by volatilization from water) with the model parametrized to correspond to our experimental setup (surface area 25 cm^2, water depth 0.01 m). From Figure 1 it can be observed that the pH at the midpoint (or turning point) of the curve corresponds to the pK_a of the chemical (in Figure 1 illustratively set at both pK_a 0 and 3.8, representing the lower and upper bound of pK_as reported for PFOA).[30,31,20] Furthermore, it can be seen that the curve begins to level off two pH units to the left and to the right of this turning point because at these pH values >99% of the chemical is either in the neutral form (to the left) or anionic form (to the right). The water-to-air transfer of PFCAs should not occur at pH values of the water >2 units above the pK_a.

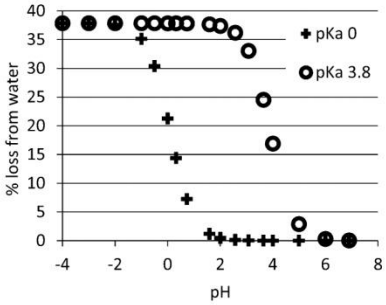


Figure 1. Calculated loss of PFOA from water after 2 d for different water pH (414 g mol^{-1} molar mass, Henrys Law constant of 2.48 Pa m^3 mol^{-1},[18] assumed pK_a for PFOA of 0[30] or 3.8,[20] air side mass transfer coefficient (k_A) 0.1 m h^{-1} and water side mass transfer coefficient (k_W) 0.001 m h^{-1}, k_A and k_W are low to represent the near stagnant conditions in the experiment[39]).

Chemicals, Reagents and Solvents. The following chemicals were selected for the experiment: perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA) and perfluorododecanoic acid (PFDoDA). Furthermore, perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), and 8:2 FTUCA were investigated for comparative purposes. Tables with full names, abbreviations and suppliers of standards for all

analytes including internal standards (IS, used for quantification in chemical analysis) can be found in the Supporting Information (Table S1 and S2). Except for 8:2 FTUCA, which was dissolved in methanol, all target compounds were available as crystalline standards and were dissolved in methanol (LiChrosolv Merck) and diluted with water; 560 μL of that dilution contained approximately 60 μL of methanol. The dilution was blown down with a stream of nitrogen at 37 °C until 120 μL of solvent had evaporated (60 μL methanol and 60 μL water, determined by weighting). As methanol has a higher vapor pressure than water and water and methanol do not form an azeotrope, it is expected that all methanol was removed from the final standard.

Bottled water was used for the experiments (HiPerSolv Chromanorm VWR) and the pH was adjusted with sulfuric acid (95−97% Sigma Aldrich). Sodium hydroxide (98.6% J. T. Baker) solutions were prepared in water (17 mol L^{-1}) and in methanol (2.5 mol L^{-1}).

Experimental Setup. In a first pilot experiment we attempted to investigate the transfer of PFCAs from a spiked water reservoir (donor solution) at a range of different pH via the gas phase to a second unspiked water reservoir at neutral pH (acceptor) within two connected polypropylene (PP) vessels. At low pH the PFC(A)s were readily lost from the donor solution but they were not recovered in the acceptor water reservoir. However, the mass balances of the PFC(A)s could be closed within the analytical uncertainties by accounting for compounds sorbed to the vessel walls (both the walls in contact with the air space above the water surfaces and the walls in contact with the donor solution below the surface) and compounds remaining in the donor solution. A simpler setup with only a spiked donor solution in a capped PP-vessel was therefore used for subsequent experiments (Figure 2). The vessel walls above the water surface in the top part of the vessel served as a passive air sampler to monitor the transfer of analytes at different pH from the water phase to the gas phase.

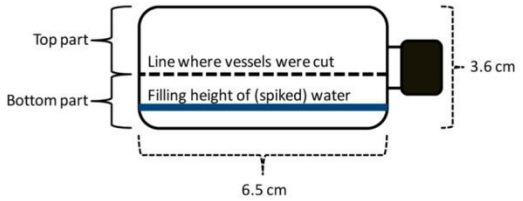


Figure 2. Diagram of the vessels used for the volatilization experiment.

A single experimental setup consisted of a rectangular PP-vessel (100 mL, bulk dimensions 6.5 × 4.0 × 3.6 cm^3) with a screw cap filled with 20 mL water (Figure 2). The water was adjusted to a certain pH with sulfuric acid and spiked with the analytes (nominally 20 ng for each PFC(A) and PFS(A) and 60 ng for 8:2 FTUC(A) in 20 mL). Formation of aggregates, which could influence the pK_a of PFCAs, has been reported to occur at concentrations >2 g L^{-1}[20,25,37] and PFOA dimers can form at ∼1 mg L^{-1}.[26] As the nominal concentrations in our experiments were approximately 1 μg L^{-1}, formation of aggregates could be excluded. Targeted pH values were 7.0, 4.5, 3.5, 3.0, 2.5, 1.5, 0.5 and 0.0, and the actual pH was determined with a pH meter (PHM210 Radiometer analytical, pH −9 to 23, ±0.2 pH units). It was not practical to investigate the water-to-air transfer with the current setup at pH values <0 because this would have required a high percentage of sulfuric acid in the water. pH-adjusted water was prepared in glass flasks and 19 mL (graduated pipettes) were transferred into the vessels, while the vessel was already lying in the final position. A 1 mL aliquot of analyte solution in water was added carefully with a pipet avoiding splashing, which resulted in a final volume of 20 mL. The vessels were kept lying on their sides during the entire duration of the experiment and water was not allowed to come in contact with the vessel's walls above the water surface. Stirring was avoided to prevent bubble formation and the possible formation of aqueous aerosols that could transfer the ionic forms of PFC(A)s and PFS(A)s into the air space.[24] Therefore stagnant water is essential for the experiment.

In a second pilot experiment, we investigated the kinetics of the transfer over 14 days with the single PP-vessel setup. The results showed that PFC(A) and PFS(A) sorption to the walls below the water surface did not increase significantly with time after one day (results not shown), but the fraction of PFC(A)s sorbed to the walls above the water surface increased up to approximately four days (Figure S1, Supporting Information). As the aim of this study was to compare the transfer of analytes from water into the gas phase at different pH, a run time of two days was chosen for further experiments and no equilibrium conditions were needed.

Five vessels were prepared for each pH value. Two vessels were analyzed right after setting-up the experiments (duplicate analysis at t_0) and two vessels were analyzed at the end of the experiment after 2 days (duplicate analysis at t_2). The fifth setup was used for pH determination.

Sample Preparation. For analysis of the water in the duplicate vessels at t_0 and t_2, the water was carefully decanted from the vessel into a 50 mL PP-tube, avoiding contact between the water and the walls in the top part of the vessels. A 1 mL aliquot of the IS solution (2 μg L^{-1} IS for each analyte except of 6 μg L^{-1} for 8:2 FTUCA) was added to the samples followed by NaOH to reach a pH >10 (controlled with pH-indicator paper). This was necessary in order to prevent further sorption or volatilization of the analytes. Subsequently 20 mL of methanol were added, the tubes were capped, ultrasonicated for 30 min at room temperature and a 200 μL aliquot was transferred into a PP-vial for instrumental analysis. For samples from experiments at pH 0.0 and pH 0.5, it was necessary to centrifuge the tubes before an aliquot was withdrawn due to the formation of a white precipitate.

To analyze the PFC(A)s and PFS(A)s sorbed to the vessel walls, the PP-vessels were cut with a knife (Figure 2). The walls of the top and bottom parts of the vessel were extracted separately by rinsing with a 1 mL aliquot of NaOH in methanol (2.5 mol L^{-1}) and with 50 μL IS (2 μg L^{-1} IS for each analyte except for 6 μg L^{-1} for 8:2 FTUCA). For instrumental analysis, 100 μL of the extract was transferred into a PP-vial containing 100 μL water. As can be seen from Figure 2, the cutting line was a little higher than the water surface to ensure that no PFC(A)s from the aqueous phase are sorbed to the top part of the vessel, representing the gaseous phase. The amount sorbed from the gaseous phase to the small surface area above the water surface and below the cutting line was expected to be relatively low and introduce only a small error to the mass balance calculations.

The cutting and rinsing of each vessel was done right after transferring the water into the tubes and adding the IS. Therefore, exposure of the vessel to air was only approximately 2 min, minimizing contamination and loss from the vessels.

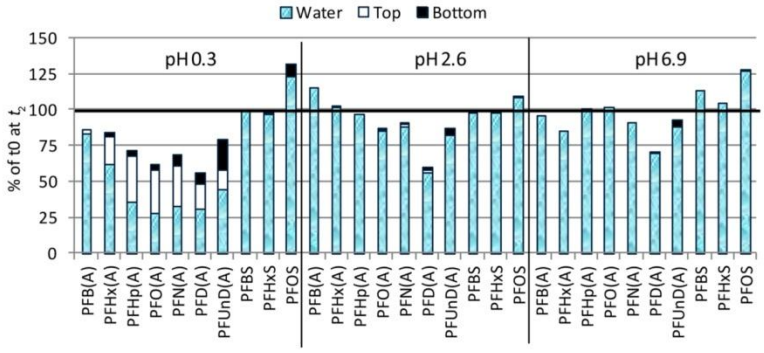


Figure 3. Percentages of the total amount remaining in the systems at t_2 (found in the water and sorbed to the top and bottom parts of the vessel) relative to t_0 for selected water pH (see Supporting Information Figure S3 for remaining pH values).

Instrumental Analysis and Quantification. Samples were analyzed on a UPLC/MS/MS system (Waters Acquity and Xevo TQ-S) using electrospray ionization. The column was a BEH C18 (1.7 μm particles, 50 mm × 2.1 mm, Waters) operated at 65 °C. Ten percent methanol in water and methanol both with 2 mmol ammonium acetate were used as mobile phase at a flow rate of 0.4 mL min^{-1}. The injection volume was 10 μL. Further details are described by Vestergren et al.[41] For quantification, an eight point external linear calibration curve was established covering a concentration range from 0.09 to 20 μg L^{-1} in methanol/2.5 mol L^{-1} NaOH in water (1:1) for all analytes but 8:2 FTUCA (r^2 > 0.99 for all curves). For 8:2 FTUCA, the calibration standards had concentrations of 0.39 to 63 μg L^{-1} (in 1:1 methanol/water). The IS concentrations in the calibration solutions were constant and corresponded to the concentrations in the sample extracts. Quantification was undertaken using the internal standard method. Relative response factors (relative to the respective IS) were derived from the calibration curve.

Quality Assurance. The lowest quantifiable concentrations in the calibration standards were defined as method quantification limits (MQLs). The MQLs were 0.09 μg L^{-1} for all analytes except for PFB(A) (0.4 μg L^{-1}), PFHx(A) (0.1 μg L^{-1}) and 8:2 FTUCA (0.3 μg L^{-1}). A MQL of 0.09 μg L^{-1} corresponded to <1% of the total amount spiked into the water. Experimental blank set-ups at pH 7.0 were run with each batch of experiments and treated in the same way as the other set-ups except that the analytes were not added to the water in the blank vessels. Concentrations in all blanks (water, rinsing of top and bottom parts of the vessels) were either not detectable or below the respective MQLs. Final results given in this study are always averages of the duplicate experiments for each pH. Deviations were <20% for all analytes in the majority of duplicates. Absolute recoveries of IS in the samples compared to the calibration standards are given in Supporting Information Table S3. Recoveries higher than 100% might reflect matrix effects caused by differences in NaOH concentrations between the calibration standards and the samples. The pH values in the different vessels were measured six times over a period of four days and remained constant for the duration of the experiment (Table S4, Supporting Information).

■ RESULTS AND DISCUSSION

The quantified amounts of all analytes in the individual water samples and in the extracts from the top and bottom parts of the vessels are given in Supporting Information Tables S5−S8. As PFDoD(A) was not detected above its MQL in the water at t_0, it was not further evaluated. It is unclear why PFDoD(A) was not detectable. We speculate that sorption could have been especially strong for this long-chain PFCA, resulting in both a lower concentration in the aqueous spiking solution than the targeted concentration and a significant sorption to the vessel walls below the water surface already at t_0. 8:2 FTUC(A) was quantifiable only in water samples due to analytical challenges. Detection of 8:2 FTUC(A) in the presence of NaOH was not possible. Results are semiquantitative and are given in the Supporting Information (Figure S2).

Mass Balances. At t_0, no analytes were found above their respective MQLs in the extracts of the top or bottom parts of the vessels. In calculating mass balances, the total amounts of the different analytes quantified in the water phase at t_0 were defined as 100% and the amounts found in the different extracts at t_2 were compared to this reference. The results of the mass balance calculations are shown in Figure 3 for selected pH values and in Supporting Information Figure S3 for the remaining pH values.

For PFS(A)s, the mass balances show a good agreement for all pH values (Figure 3), indicating that no pH dependent loss was occurring within the system. At all pH values, a small fraction of PFOS was found to be sorbed to the bottom part of the vessels, which was not observed for the other PFSAs.

Mass balances are negative for PFC(A)s at lower pH values (Figure 3). The most probable explanation for this lack of a closed mass balance is strong sorption to the vessel walls so that the mild extraction procedure of the walls used in this study (rinsing with NaOH in methanol) did not desorb them quantitatively. Small amounts of PFC(A)s that could have been present in the gas phase are not expected to account for the missing 30−40%.

The supplier of the PFCA standards reported potential formation of methylesters of PFCAs with methanol. We rule out this phenomenon as explanation for the negative mass balance, because all methanol was evaporated from the standard mixture used for spiking and because an esterification would also have occurred for the short-chain homologues.

Volatilization of PFC(A)s Evidenced by Sorption to the Top Parts of the Vessels. The fraction of the total amount found in the vessels at t_2 which is sorbed to the walls above the water surface is shown in Figure 4. PFCAs were detected in the washings from the top part of the vessels containing water of low pH, whereas PFSAs were not detected even at the lowest pH. We believe that these results are strong

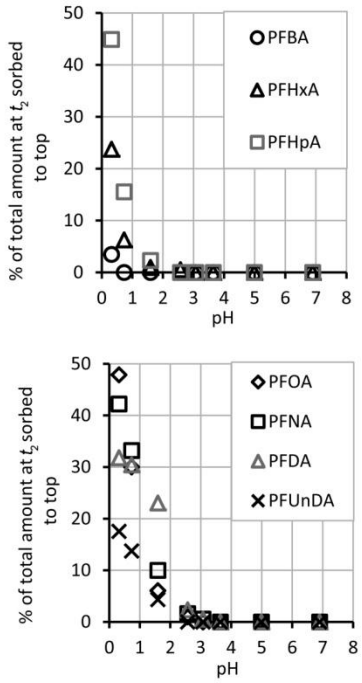


Figure 4. Percentage of the total amount in the system at t_2 sorbed to the top of the vessels at t_2 as a function of the water pH.

evidence for volatilization of PFCAs at low pH, because PFSAs are expected to have a lower pK_a and therefore volatilize at lower pH compared to PFCAs.[37]

Hydraulic transport of the PFC(A)s up the walls of the vessels could be a plausible alternate explanation for their detection above the water surface, but we can exclude this explanation for two reasons: (i) PFSAs have not been detected above the MQL in the extracts of the top parts of the vessels (even after 14 days in preliminary tests) and PFSAs would be expected to undergo hydraulic transport in the same way as PFC(A)s. (ii) The fraction sorbed to the top part of the vessels showed dependence with pH and no analytes were found in the extracts of the top parts above the MQL at pH values ≥3.6, whereas hydraulic transport would not be expected to be pH dependent.

Using Experimental Measurements to Constrain the Range of pK_as of PFCAs. It was shown (Figure 1) that the pK_a of PFCAs will be approximately 2 units below the pH at which volatilization is first observed to occur. The application of this approach to our experimental data is limited by the analytical sensitivity and by the pH-resolution of measured data points.

Due to these limitations, only upper limits of pK_as for all PFCAs were derived from experimental data. The following example explains this approach: Under an assumption of a pK_a of 0, the modeled (Figure 1) or measured curve (Figure 4) is expected to level off and approach the *X*-axis at pH 2.0. At pH 2.0, the model estimates (assuming a pK_a of 0) <1% of PFOA to be present in the gas phase. For the experiment, this would mean a concentration <MQL sorbed to the top part of the vessels. At the next lowest pH where measured data are available (in our study pH 1.6) >1% of PFOA is expected to be in the gas phase based on model results, which would lead to quantifiable amounts at the top part of the vessels in the experiment. In analogy model results for a pK_a of 3.8 (Figure 1) would result in <1% in the gas phase at pH 5.8, >1% at pH 5.0 in our experiment. On the basis of this theory, the lowest pH in our experiment where no sorption to the top part of the vessel was found minus two units was used to estimate the upper limit of the pK_a of the respective PFCA.

Within the experiment, no sorption of any of the PFC(A)s to the top of the vessels was observed for pH 6.9, 5.0, and 3.6. Therefore, the pK_as for all investigated PFCAs are estimated to be ≤1.6.

Some of the PFCA homologues showed sorption to the top part of the vessel at pH 3.1 (PFNA and PFDA), whereas others were only found at lower pH. This would theoretically allow to further constrain the upper limit of the pK_a for these homologues. However, due to some measurement uncertainties we chose a conservative approach by setting an estimated upper limit of the pK_a to 1.6 for all investigated PFC(A)s. Furthermore, it should be noted that branched isomers of PFC(A)s can be present in the system. A branching at the C-atom next to the acid group is expected to lead to a higher pK_a compared to the straight chain homologue.[42] Branching at other positions has been theoretically estimated to have no influence on the pK_a compared to straight chain PFCAs.[42]

Derivation of pK_a for PFOA by Fitting Experimental Data with a Volatilization Model. The least-squares method was used to fit data from the model described in eqs 1−3 to the experimental results for PFOA. K_{AW}, k_w and k_a were needed as input parameters. We used a $D_{AW\ eff}$ of 1.02 * 10^{-3} for PFO(A) as input to the model (pH 0.6, 20 °C).[18] For other PFCAs, only theoretical K_{AW}s of unknown accuracy were available,[34] and therefore a fit of modeled data to measurements was performed for PFO(A) only.

To compare model results (% loss from water to air) with measured data (% sorbed to top), it was assumed that in the experimental set-ups the whole amount of PFOA that was transferred from water to air was sorbed to the top part of the vessel. The fraction sorbed to the top at t_2 of the total amount in the system at t_0 can be compared to modeled data. The model does not account for sorption to the vessel walls below the water surface. As this fraction was low in our experiments the influence is expected to be negligible.

The value for k_A is typically about a hundred times higher than k_W because diffusion of chemicals in air is much faster than diffusion in water.[39] Assuming that 100 k_A is k_w, it is possible to adjust k_A until a good fit is found between the model and experimental results for PFO(A). k_A is the more sensitive of the two mass transfer coefficients as volatilization is air-side controlled.

Fitting the data of the model to the experimental data for PFOA (Figure S4, Supporting Information) resulted in a pK_a of 0.5 and a k_A of 0.12 m h^{-1}. The value of k_A is about 100 times lower than usually used to model volatilization of chemicals from lakes,[39] but a low value could be expected since the air and water in the experimental set-ups was relatively stagnant.

Comparison with pK_as Reported in the Literature. The pK_a of PFOA derived with the model fit in the present study (pK_a 0.5) is in the range of other theoretical estimates. COSMOS-RS estimated a pK_a of 0.7[30] and COSMOtherm a pK_a of 0.8[43] and 0.9[34] for PFOA. Experimentally determined pK_as for PFOA at the lower end of the reported range are between <1.0 and 1.3[25,26,29] and are therefore slightly higher than the result from our experiment, but still within reasonable

agreement. Higher pK_as for PFOA reported in the literature (2.8[28] and 3.8[20]) have been attributed to (i) the presence of methanol in the experimental systems,[27] (ii) the aggregation of hydrophobic PFOA in solution[25,26,36] (as noted by Cheng et al.,[26] PFO aggregation should have the opposite effect) and (iii) the formation of a stable $(PFO)_2H^-$ cluster.[26] Cheng et al.[26] observed no evidence for self-association or cluster formation at low, environmentally realistic PFOA concentrations (of 2 nM or ~0.8 μg L^{-1}). As the concentrations of PFOA used in this study were ~1.0 μg L^{-1} and methanol was removed from solution, it is not expected that pK_a will be subject to the previously observed experimental artifacts. In previous experiments concentrations were in the range of 400 μg L^{-1} to 40 g L^{-1}.[20,25,26,28,29] Our experimental setup could be used in future experiments to further investigate different artifacts, that is, by studying a range of water concentrations.

For the other investigated PFCAs, much less literature data are available for comparison. For PFBA, Henne and Fox[35] reported a pK_a of 0.2. A study by Moroi et al.[36] reported experimental pK_as for PFBA (0.32), PFHxA (0.85), PFDA (2.58) and PFUnDA (2.61). The results for PFBA and PFHxA are in agreement with the upper limit derived in our study (pK_a ≤1.6), whereas published results for PFDA and PFUnDA are clearly higher. This discrepancy between our estimates and those reported by Moroi et al.[36] for PFDA and PFUnDA might be a results of self-association in the solubility method at concentrations of approximately 40 mg L^{-1} used for the longer chain PFCAs (note that they used a titration method at concentrations of 2−40 g L^{-1} for determining the pK_as of the short-chain PFCAs).[36]

Implication for the Environmental Fate of PFC(A)s. Under neutral conditions (pH 7.0), 3×10^{-5}% of total species would be present in the protonated form for an acid with a pK_a of 0.5 and 4×10^{-4}% for a pK_a of 1.6. At lower pH (e.g., pH 5.0), which will be relevant under some environmental conditions, the fractions would be 0.003% (pK_a 0.5, pH 5.0) and 0.04% (pK_a 1.6, pH 5.0). Fractions of the protonated acids in aqueous media under typical environmental conditions are therefore <0.1% for the pK_as estimated in this study. The pK_as derived are therefore so low that the uncertainty in their precise values does not make much difference for the fraction of the acid in aqueous phases under environmental relevant conditions.

PFC(A)s, and also PFS(A)s, were previously detected in sample media which reportedly represented the atmospheric gas phase using different sampling techniques at different locations.[44−48] Possible sampling artifacts were investigated and discussed in several of these studies.[46,48] The strong sorption of PFCAs from the gas phase to (PP-)surfaces in our experiment is in line with the sorption of gaseous PFCAs to glass fiber filters during air sampling as shown by Arp and Goss.[49] Whereby for the glass fiber filters the sorption mechanism was suggested to be adsorption,[49] sorption to the PP-vessels is likely a combination of ad- and absorption. The relative importance of the two sorption mechanisms for sorption of PFCAs to the PP-vessels is unknown. Furthermore, crystalline PFOA in a glass bottle has also been shown to be transferred from the solid phase to the gas phase (sublimed) followed by resublimation on the walls of the bottle.[50] This sublimation and resublimation indicates an equilibrium process between solid and gaseous PFOA and such an equilibrium process between gaseous and sorbed PFCAs can be expected in our study and in the environment as well.

Our results did not show any transfer of PFSAs from water to the gas phase. Sampling of ultrafine particles on passive samplers,[46] on gas-phase sample media in high volume samplers after passing through the filter (e.g., <1 μm) or enriched in denuders[48] could be responsible for findings of gas phase PFSAs in other studies and also bias the results of real gas phase PFCAs. Even if PFCAs and PFSAs are not present in the gas phase, it does not preclude long-range transport in the atmosphere. Particles in the so-called "accumulation mode" (0.1−2.5 μm) have a relatively long atmospheric lifetime[51] and thus PFC(A)s (and PFSAs) sorbed to these ultrafine particles would be transported long distances.

Previous studies have also investigated the water to air transfer of PFC(A)s and PFSAs. Kaiser et al.[17] reported transfer of PFOA from stirred water into a stream of nitrogen at pH much higher than in our experiment (pH 7.0 and 5.6). Even if turbulence was minimized during stirring[17] aerosol mediated transfer from water to air[24,52] could be an explanation for these observations. In our experimental set-ups the vessels were stationary, the water was not stirred and therefore liquid aerosol formation was not expected to occur. Under natural conditions, however, including in wastewater treatment plants or also by stirring water in a laboratory experiment, formation of liquid aerosols can be expected and has been demonstrated.[24]

Further investigations of potential sources of atmospheric PFCA, such as direct atmospheric release from manufacturing sites and waste incineration, resuspension of aerosol associated PFCAs and precursor degradation, are needed. Atmospheric degradation of fluorotelomer alcohols (FTOHs),[53] perfluoroalkane sulfonamides,[54] perfluoroalkane sulfamidoethanols[55] and fluorotelomer iodides (FTIs)[56] was shown to lead to the formation of gaseous PFCAs. Levels of PFC(A)s in precipitation could not be explained by atmospheric degradation of a few well-known precursors in a model calculation, but there are likely many other precursors present in the atmosphere that can degrade to form PFCAs.[6,57] Understanding the mass balance of PFCAs (sources and sinks) in the atmosphere is an important ongoing area of research.

■ ASSOCIATED CONTENT

Supporting Information

Details on chemical standards, data on quantified amounts in each sample, figures showing additional experimental data and the results for 8:2 FTUCA. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Lena.Vierke@uba.de; fax: +49 340 2104 6620; tel: +49 340 2103 6620.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Jana Johansson, Anne-Sofie Kärsrud, Tomas Alsberg and Michael McLachlan from Stockholm University, Department of Applied Environmental Science (ITM), for their

support. This paper does not necessarily reflect the opinion or the policies of the German Federal Environment Agency.

REFERENCES

(1) Frömel, T.; Knepper, T. P. In *Reviews of Environmental Contamination and Toxicology*; Whitacre, D. M., de Voogt, P., Eds.; Springer: New York, 2010; pp 161−178.

(2) Kissa, E. *Fluorinated surfactants and repellents*; Marcel Dekker: New York, 2001.

(3) Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; Voogt, P. de; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integr. Environ. Assess. Manage.* **2011**, *7*, 513−541.

(4) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40*, 32−44.

(5) Houde, M.; De Silva, A. O.; Muir, D. C. G.; Letcher, R. Monitoring of perfluorinated compounds in aquatic biota: an updated review. *Environ. Sci. Technol.* **2011**, *45*, 7962−7973.

(6) Cousins, I. T.; Kong, D.; Vestergren, R. Reconciling measurement and modelling studies of the sources and fate of perfluorinated carboxylates. *Environ. Chem.* **2011**, *8*, 339−354.

(7) Ahrens, L. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *J. Environ. Monit.* **2011**, *13*, 20−31.

(8) Conder, J. M.; Hoke, R. A.; Wolf, W. de; Russell, M. H.; Buck, R. C. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. *Environ. Sci. Technol.* **2008**, *4*, 995−1003.

(9) Müller, C. E.; De Silva, A. O.; Small, J.; Williamson, M.; Wang, X.; Morris, A.; Katz, S.; Gamberg, M.; Muir, D. C. G. Biomagnification of perfluorinated compounds in a remote terrestrial food chain: Lichen-caribou-wolf. *Environ. Sci. Technol.* **2011**, *45*, 8665−8673.

(10) Houde, M.; Trevor, B. D.; Small, J.; Wells, R. S.; Fair, P. A.; Brossart, G.; Solomon, K. R.; Muir, D. C. G. Biomagnification of perfluoroalkyl compounds in the bottlenose dolphin (Tursiops truncatus) food web. *Environ. Sci. Technol.* **2006**, *40*, 4138−4144.

(11) European Chemicals Agency. Background document to the Opinion proposing harmonised classification and labelling at Community level of Perfluorooctanoic acid (PFOA), 2011.

(12) Vierke, L.; Staude, C.; Biegel-Engler, A.; Drost, W.; Schulte, C. Perfluorooctanoic acid (PFOA) - main concerns and regulatory development in Europe from an environmental point of view. *Environ. Sci. Eur.* **2012**, *24*, 16.

(13) Braune, B. M.; Letcher, R. J. Perfluorinated sulfonate and carboxylate compounds in eggs of seabirds breeding in the Canadian arctic: Temporal trends (1975−2011) and interspecies comparison. *Environ. Sci. Technol.* **2013**, *47*, 616−624.

(14) Butt, C. M.; Berger, U.; Bossi, R.; Tomy, G. T. Levels and trends of poly- and perfluorinated compounds in the arctic environment. *Sci. Total Environ.* **2010**, *408*, 2936−2965.

(15) Armitage, J. M.; Macleod, M.; Cousins, I. T. Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model. *Environ. Sci. Technol.* **2009**, *43*, 1134−1140.

(16) Barton, C. A.; Kaiser, M. A.; Russell, M. H. Partitioning and removal of perfluorooctanoate during rain events: The importance of physical-chemical properties. *J. Environ. Monit.* **2007**, *9*, 839−846.

(17) Kaiser, M. A.; Dawson, B. J.; Barton, C. A.; Botelho, M. A. Understanding potential exposure sources of perfluorinated carboxylic acids in the workplace. *Ann. Occup. Hyg.* **2010**, *54*, 915−922.

(18) Li, H.; Ellis, D. A.; Mackay, D. Measurement of low air-water partition coefficients of organic acids by evaporation from a water surface. *J. Chem. Eng. Data* **2007**, *52*, 1580−1584.

(19) Kutsuna, S.; Hori, H. Experimental determination of Henry's law constant of perfluorooctanoic acid (PFOA) at 298 K by means of an inert-gas stripping method with a helical plate. *Atmos. Environ.* **2008**, *42*, 8883−8892.

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

(21) Goss, K.-U.; Arp, H. P. H. Comment on "Experimental pK_a determination for perfluorooctanoic acid (PFOA) and the potential impact of pK_a concentration dependence on laboratory-measured partitioning phenomena and environmental modeling. *Environ. Sci. Technol.* **2009**, *43*, 5150−5151.

(22) Burns, D. C.; Ellis, D. A.; Webster, E. M.; McMurdo, C. J. Response to comment on "Experimental pK_a determination for perfluorooctanoic acid (PFOA) and the potential impact of pK_a concentration dependence on laboratory-measured partitioning phenomena and environmental modeling. *Environ. Sci. Technol.* **2009**, *43*, 5152−5154.

(23) Ju, X.; Jin, Y.; Sasaki, K.; Saiti, M. Perfluorinated surfactants in surface, subsurface water and microlayer from Dalian coastal waters in China. *Environ. Sci. Technol.* **2008**, *42*, 3538−3542.

(24) Reth, M.; Berger, U.; Broman, D.; Cousins, I. T.; Nilsson, E. D.; McLachlan, M. S. Water-to-air transfer of perfluorinated carboxylates and sulfonates in a sea spray simulator. *Environ. Chem.* **2011**, *8*, 381−388.

(25) López-Fontán, J. L.; Sarmiento, F.; Schulz, P. C. The aggregation of sodium perfluorooctanoate in water. *Colloid Polym. Sci.* **2005**, *283*, 862−871.

(26) Cheng, J.; Psillakis, E.; Hoffmann, M. R.; Colussi, A. J. Acid dissociation versus molecular association of perfluoroalkyl oxoacids: environmental implications. *J. Phys. Chem. A* **2009**, *113*, 8152−8156.

(27) Kutsuna, S.; Hori, H.; Sonoda, T.; Iwakami, T.; Wakisaka, A. Preferential solvation of perfluorooctanoic acid (PFOA) by methanol in methanol-water mixtures: A potential overestimation of the dissociation constant of PFOA using a Yasuda-Shedlovsky plot. *Atmos. Environ.* **2012**, *49*, 411−414.

(28) Brace, N. O. Long chain alkanoic and alkenoic acids with perfluoroalkyl terminal segments. *J. Org. Chem.* **1962**, *27*, 4491−4498.

(29) Igarashi, S.; Yotsuyanagi, T. Homogeneous liquid-liquid extraction by pH dependent phase separation with a fluorocarbon ionic surfactant and its application to the preconcentration of porphyrin compounds. *Mikrochim. Acta* **1992**, *106*, 37−44.

(30) Goss, K.-U. The pK_a values of PFOA and other highly fluorinated carboxylic acids. *Environ. Sci. Technol.* **2008**, *42*, 456−458.

(31) Goss, K.-U. Additions and Correction 2008, Volume *42*, pages 456-458. *Environ. Sci. Technol.* **2008**, *42*, 5032.

(32) Rayne, S.; Forest, K.; Friesen, K. J. Computational approaches may underestimate pK_a values of longer-chain perfluorinated carboxylic acids: Implication for assessing environmental and biological effects. *J. Environ. Sci. Health, Part A* **2009**, *44*, 317−326.

(33) Steinle-Darling, E.; Reinhard, M. Nanofiltration for trace organic contaminant removal: structure, solution, and membrane fouling effects on the rejection of perfluorochemicals. *Environ. Sci. Technol.* **2008**, *42*, 5292−5297.

(34) Wang, Z.; Macleod, M.; Cousins, I. T.; Scheringer, M.; Hungerbühler, K. Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs). *Environ. Chem.* **2011**, *8*, 389−398.

(35) Henne, A. L.; Fox, C. J. Ionization constants of fluorinated acids. *J. Am. Chem. Soc.* **1951**, *73*, 2323−2325.

(36) Moroi, Y.; Yano, H.; Shibata, S.; Yonemitsu, T. Determination of acidity constants of perfluoroalkanoic acids. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 667−672.

(37) Rayne, S.; Forest, K. Perfluoroalkyl sulfonic and carboxylic acids: A critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. *J. Environ. Sci. Health, Part A* **2009**, *44*, 1145−1199.

(38) Schwarzenbach, R.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; Wiley-Interscience: Hoboken, NJ, 2003.

(39) Mackay, D. *Multimedia Environmental Models*; Lewis Publishers: Boca Raton, FL, 2001.
(40) Mackay, D.; Leinonen, P. J. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. *Environ. Sci. Technol.* **1975**, *9*, 1178−1180.
(41) Vestergren, R.; Ullah, S.; Cousins, I. T.; Urs, B. A matrix effect-free method for reliable quantification of perfluoroalkyl carboxylic acids and perfluoroalkane sulfonic acids at low parts per trillion levels in dietary samples. *J. Chromatogr., A* **2012**, *1237*, 64−71.
(42) Rayne, S.; Forest, K. Theoretical studies on the pK_a values of perfluoroalkyl carboxylic acids. *J. Mol. Struct.: THEOCHEM* **2010**, *949*, 60−69.
(43) COSMOlogic. pKa prediction of n-PFCA, ny. http://www.cosmologic.de/data/engineering/Perfluoroalkylcarboxylicacids_COSMOtherm_links.pdf.
(44) Weinberg, I.; Dreyer, A.; Ebinghaus, R. Waste water treatment plants as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air. *Environ. Pollut.* **2011**, *159*, 125−132.
(45) Ahrens, L.; Shoeib, M.; Harner, T.; Lee, S. C.; Guo, R.; Reiner, E. Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. *Environ. Sci. Technol.* **2011**, *45*, 8098−8105.
(46) Vierke, L.; Ahrens, L.; Shoeib, M.; Reiner, E. J.; Guo, R.; Palm, W.-U.; Ebinghaus, R.; Harner, T. Air concentrations and particle-gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant. *Environ. Chem.* **2011**, *8*, 363−371.
(47) Weinberg, I.; Dreyer, A.; Ebinghaus, R. Landfills as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air. *Atmos. Environ.* **2011**, *45*, 935−941.
(48) Ahrens, L.; Shoeib, M.; Harner, T.; Lane, D. A.; Guo, R.; Reiner, E. J. Comparison of annular diffusion denuder and high volume air samplers for measuring per- and polyfluoroalkyl substances in the atmosphere. *Anal. Chem.* **2011**, *83*, 9622−9628.
(49) Arp, H. P. H.; Goss, K.-U. Irreversible sorption of trace concentrations of perfluorocarboxylic acids to fiber filtres used for air sampling. *Atmos. Environ.* **2008**, *42*,
(50) Kaiser, M. A.; Larsen, B. S.; Kao, C.-P. C.; Buck, R. C. Vapor pressures of perfluorooctanoic, -nonanoic, -decanoic, -undecanoic, and -dodecanoic acids. *J. Chem. Eng. Data* **2005**, *50*, 1841−1843.
(51) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics*; John Wiley & Sons, Inc.: New York, 1998.
(52) McMurdo, C. J.; Ellis, D. A.; Webster, E.; Butler, J.; Christensen, R.; Reid, L. K. Aerosol enrichment of the surfactant PFO and mediation of the water-air transport of gaseous PFOA. *Environ. Sci. Technol.* **2008**, *42*, 3969−3974.
(53) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* **2004**, *38*, 3316−3321.
(54) Martin, J. W.; Ellis, D. A.; Mabury, S. A. Atmospheric chemistry of perfluoroalkanesulfonamides: Kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. *Environ. Sci. Technol.* **2006**, *40*, 864−872.
(55) Ďeon, J.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, $C_4F_9SO_2N(CH_3)CH_2CH_2OH$: Kinetics and mechanism of reaction with OH. *Environ. Sci. Technol.* **2006**, *40*, 1862−1868.
(56) Young, C. J.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. Atmospheric chemistry of 4:2 fluorotelomer iodides (n-$C_4C_9CH_2CH_2I$): Kinetics and products of photolysis and reaction with OH radicals and Cl atoms. *J. Phys. Chem. A* **2008**, *112*, 13542−13548.
(57) Schenker, U.; Scheringer, M.; Macleod, M.; Martin, J. W.; Cousins, I. T.; Hungerbühler, K. Contribution of volatile precursor substances to the flux of perfluorooctanoate to the arctic. *Environ. Sci. Technol.* **2008**, *42*, 3710−3716.

Supporting Information

Estimation of the acid dissociation constant of perfluoroalkyl carboxylic acids through an experimental investigation of their water-to-air transport

Vierke, Lena[1,2]*; *Berger, Urs*[3]; *Cousins, Ian T.*[3]

[1]Federal Environment Agency, Section for Chemicals, Wörlitzer Platz 1, Dessau-Roßlau, Germany; [2]Leuphana University Lüneburg, Institute of Sustainable and Environmental Chemistry, Scharnhorst Str. 1, Lüneburg, Germany; [3]Stockholm University, Department of Applied Environmental Science (ITM), Svante Arrhenius väg 8, Stockholm, Sweden

Corresponding Author

*Lena.Vierke@uba.de, Fax. +49 340 2104 6620 Tel. +49 340 2103 6620

1. Names and abbreviations of standards and internal standards

Table S 1: Abbreviations and names of analytes including the suppliers and purity for crystalline standards. 8:2 FTUCA was dissolved in methanol.

Abbreviation	Name	Supplier	Purity
PFBA	Perfluorobutanoic acid	Aldrich	99 %
PFHxA	Perfluorohexanoic acid	ABCR	98 %
PFHpA	Perfluoroheptanoic acid	Aldrich	99 %
PFOA	Perfluorooctanoic acid	ABCR	98 %
PFNA	Perfluorononanoic acid	Aldrich	97 %
PFDA	Perfluorodecanoic acid	Fluka	≥ 97 %
PFUnDA	Perfluoroundecanoic acid	Aldrich	95 %
PFDoDA	Perfluorododecanoic acid	Aldrich	95 %
PFBS	Perfluorobutane sulfonic acid	Dyneon (potassium salt)	unknown
PFHxS	Perfluorohexane sulfonic acid	Interchim (potassium salt)	98 %
PFOS	Perfluorooctane sulfonic acid	Fluka (potassium salt)	≥ 98 %
8:2 FTUCA	2H-Perfluorodecanoic acid	Wellington Laboratories	unknown

Table S 2: Names, abbreviations and suppliers of mass-labeled internal standards (IS).

Abbreviation	Name	Supplier
MPFHxS[1]	Perfluoro-1-hexane-[$^{18}O_2$]sulfonic acid	Wellington Laboratories (MPFAC-MXA)
MPFOS	Perfluoro-1-[1,2,3,4-$^{13}C_4$]octane sulfonic acid	
MPFBA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	
MPFHxA	Perfluoro-n-[1,2,-$^{13}C_2$]hexanoic acid	
MPFOA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	
MPFNA	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	
MPFDA	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	
MPFUnDA	Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	
MPFDoDA	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	
MPFHpA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	Wellington Laboratories
M8:2 FTUCA	2H-Perfluorooctyl-[1,2-$^{13}C_2$]-decanoic acid	Wellington Laboratories

[1] MPFHxS has also been used as IS for PFBS.

2. Quality assurance

Table S 3: Absolute recoveries of IS in different samples compared to the calibration standards (averages ± standard deviation, in %, n = 35).

Name	Water	Top	Bottom
PFBA	184 ± 42	122 ± 26	125 ± 26
PFHxA	128 ± 27	124 ± 45	127 ± 36
PFHpA	132 ± 25	128 ± 30	129 ± 30
PFOA	123 ± 27	126 ± 34	124 ± 35
PFNA	137 ± 25	135 ± 30	133 ± 29
PFDA	116 ± 21	116 ± 24	113 ± 25
PFUnDA	133 ± 32	124 ± 35	111 ± 36
PFDoDA	182 ± 53	158 ± 46	143 ± 50
PFHxS	117 ± 13	115 ± 13	101 ± 17
PFOS	117 ± 19	111 ± 20	95 ± 22
8:2 FTUCA	51 ± 90	not analyzed	not analyzed

Table S 4: Nominal and measured pH over an experimental period of four days.

Nominal	Measured (± standard dev.; n = 6)
0	0.32 ± 0.01
0.5	0.73 ± 0.01
1.5	1.59 ± 0.01
2.5	2.57 ± 0.01
3	3.07 ± 0.01
3.5	3.64 ± 0.01
4.5	4.99 ± 0.04
neutral	6.90 ± 0.05

3. 14-days time series for sorption to top part of vessel at pH 0

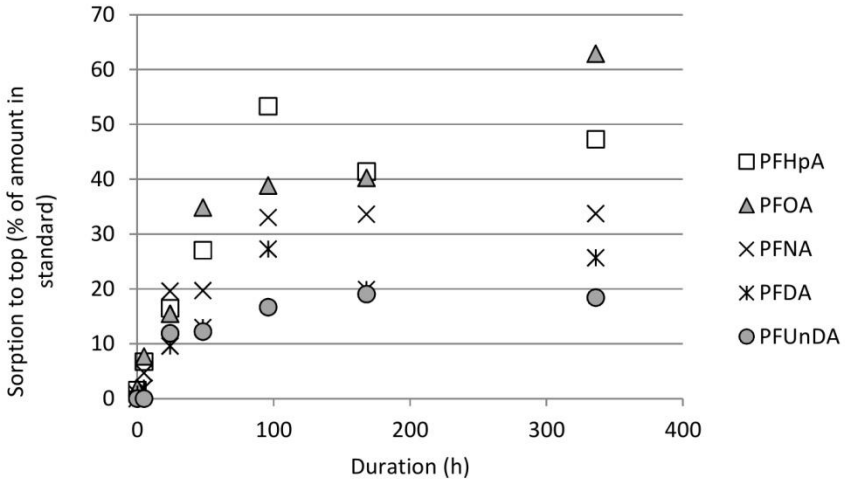


Figure S 1: Fraction (in % of amount in the standard used for spiking) sorbed to the top part of the vessel at certain time points at pH 0 (semi-quantitative, analytical method not fully optimized).

5. Quantified amounts of target compounds

Table S 5: Amounts (in ng) in 1 mL water for duplicates of each setup at t0 (to be multiplied with a factor 20 to calculate the whole amount in the water of the system).

Nominal pH	Blank	neutral		4.5		3.5		3		2.5		1.5		0.5		0	
PFBA	n.d.	1.1	1.1	1.0	0.98	1.7	1.3	0.9	1.1	0.97	0.88	1.1	1.4	1.4	0.97	2.1	1.0
PFHxA	n.d.	1.9	2.4	1.6	1.7	1.6	1.5	1.6	1.7	1.5	1.6	1.6	1.6	1.8	1.8	7.0	1.7
PFHpA	n.d.	0.82	0.87	0.89	0.85	0.96	0.93	0.82	0.89	0.89	0.90	0.93	0.91	0.83	0.9	0.91	0.85
PFOA	n.d.	1.1	0.99	1.3	1.2	1.1	0.99	1.1	1.1	1.2	1.1	1.3	1.1	1.1	1.3	1.3	1.0
PFNA	n.d.	1.0	0.96	0.93	0.96	1.1	0.9	1.0	0.91	1.2	1.0	1.1	1.1	1.1	1.1	0.86	1.0
PFDA	n.d.	1.0	0.94	0.98	1.1	0.92	0.95	0.83	1.1	1.1	1.0	1.0	0.94	1.2	0.96	0.94	0.98
PFUnDA	n.d.	0.24	0.41	0.19	0.3	0.28	0.21	0.27	0.18	0.29	0.20	0.22	0.22	0.24	0.36	0.24	0.3
PFDoDA	n.d.	0.06	0.07	0.09	0.06	0.14	0.11	0.06	0.05	0.07	0.09	0.09	0.08	0.03	0.06	0.06	0.06
PFTeDA	n.d.	0.35	0.31	0.19	0.22	0.68	0.24	0.33	0.34	0.14	0.45	0.33	0.19	n.d.	n.d.	n.d.	n.d.
PFBS	n.d.	0.96	1.2	1.1	1.1	1.2	1.1	1.0	1.2	1.2	1.1	1.1	1.2	1.1	1.2	1.2	1.3
PFHxS	n.d.	0.98	1.1	1.0	1.1	1.1	1.1	1.0	1.2	1.1	1.0	0.94	1.1	0.86	1.0	1.0	1.1
PFOS	n.d.	0.84	0.89	0.86	0.98	0.76	0.94	0.77	1.1	0.75	1.0	0.56	0.74	0.91	0.92	0.9	0.93
8:2 FTUCA	n.d.	1.9	1.9	2.7	2.9	2.1	1.7	1.7	2.1	1.7	1.9	2.2	1.8	2.2	1.8	2.3	2.1

Table S 6: Amounts (in ng) in 1 mL water for duplicates of each setup at t2 (to be multiplied with a factor 20 to calculate the whole amount in the water of the system).

Nominal pH	Blank		neutral		4.5		3.5		3		2.5		1.5		0.5		0	
PFBA	n.d.	n.d.	0.97	1.1	1.3	1.4	1.5	1.1	1.0	0.93	1.1	1.0	1.5	2.0	1.1	1.2	1.1	1.4
PFHxA	n.d.	n.d.	1.8	1.8	1.7	1.7	1.7	1.8	1.8	1.8	1.7	1.5	1.7	1.8	1.7	1.5	1.0	1.1
PFHpA	n.d.	n.d.	0.83	0.88	0.83	0.92	0.89	0.9	0.82	0.83	0.86	0.88	0.77	0.92	0.68	0.61	0.33	0.31
PFOA	n.d.	n.d.	1.1	0.97	1.1	1.4	1.1	1.1	1.0	0.96	0.99	0.96	0.95	0.9	0.49	0.50	0.32	0.34
PFNA	n.d.	n.d.	0.9	0.9	0.96	0.95	0.91	0.91	0.86	0.93	1.0	0.93	0.6	0.71	0.35	0.38	0.31	0.31
PFDA	n.d.	n.d.	0.44	0.91	0.76	0.85	1.1	1.2	1.0	0.75	0.67	0.5	0.36	n.d.	0.35	0.31	0.35	0.24
PFUnDA	n.d.	n.d.	0.26	0.31	0.19	0.3	0.27	0.27	0.28	0.24	0.16	0.25	0.20	0.26	0.12	0.14	<MQL	0.12
PFDoDA	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL
PFTeDA	n.d.	n.d.	0.22	0.27	1.2	0.24	0.2	0.39	0.26	0.24	0.56	0.30	<MQL	0.58	n.d.	n.d.	n.d.	n.d.
PFBS	n.d.	n.d.	1.2	1.2	1.4	1.3	1.3	1.2	1.1	1.2	1.4	0.93	1.1	1.3	1.0	1.1	1.2	1.2
PFHxS	n.d.	n.d.	1.1	1.1	1.3	1.2	1.1	1.0	0.95	1.1	1.2	0.92	1.1	1.1	0.88	0.97	1.0	1.0
PFOS	n.d.	n.d.	1.1	1.1	1.5	1.1	0.96	1.2	1.5	0.91	1.0	0.93	0.72	1.2	0.99	1.0	1.3	0.98
8:2 FTUCA	n.d.	n.d.	2.0	2.2	2.1	1.9	0.52	0.59	0.26	0.14	0.23	0.19	0.28	0.19	0.38	0.61	0.14	0.07

9 **Table S 7: Amounts (in ng) extracted from the top part of the vessels for duplicates of each setup at t2.**

Nominal pH	Blank		neutral		4.5		3.5		3		2.5		1.5		0.5		0	
PFBA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	0.7	1.2
PFHxA	<MQL	<MQL	<MQL	n.d.	n.d.	<MQL	<MQL	n.d.	<MQL	<MQL	0.17	<MQL	0.28	0.42	2.3	2.2	6.8	7.0
PFHpA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	0.38	0.42	2.5	2.5	5.6	5.9
PFOA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	0.20	0.19	1.1	1.3	4.9	5.0	6.4	7.7
PFNA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	0.1	<MQL	0.33	0.33	1.5	1.6	4.0	5.3	4.6	6.2
PFDA	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	<MQL	<MQL	0.1	0.1	0.3	0.29	1.2	1.5	2.7	5.1	3.6	3.3
PFUnDA	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	<MQL	0.17	0.29	0.52	0.64	0.77	0.73
PFDoDA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL
PFTeDA	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.
PFHxS	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	<MQL	n.d.	<MQL
PFOS	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

10

11 **Table S 8**: Amounts (in ng) extracted from the bottom part of the vessels for duplicates of each setup at t2.

Nominal pH	Blank		neutral		4.5		3.5		3		2.5		1.5		0.5		0	
PFBA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL
PFHxA	<MQL	<MQL	n.d.	n.d.	<MQL	<MQL	<MQL	0.4	n.d.	<MQL	<MQL	<MQL	0.31	<MQL	0.89	0.82	0.84	1.0
PFHpA	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	n.d.	0.17	n.d.	<MQL	<MQL	<MQL	0.17	<MQL	0.64	0.84	0.68	0.75
PFOA	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	0.23	<MQL	<MQL	0.15	0.12	0.48	0.17	1.5	1.8	1.2	0.91
PFNA	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	<MQL	0.29	0.13	0.23	0.30	0.3	0.86	0.32	2.0	2.2	1.5	1.1
PFDA	n.d.	n.d.	0.16	0.25	0.26	0.14	0.33	0.38	0.21	0.53	0.54	0.53	1.4	0.61	2.3	2.4	1.6	1.4
PFUnDA	n.d.	n.d.	0.23	0.33	0.16	<MQL	0.17	0.17	0.12	0.16	0.32	0.18	0.59	0.32	0.84	1.2	0.88	1.4
PFDoDA	n.d.	n.d.	<MQL	<MQL	<MQL	n.d.	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	0.12	0.1	0.33	0.27	0.25	0.21
PFTeDA	n.d.	n.d.	0.11	<MQL	0.27	n.d.	<MQL	n.d.	0.1	0.24	0.19	0.12	<MQL	0.18	n.d.	n.d.	0.23	0.19
PFBS	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	n.d.	0.2	n.d.	<MQL	<MQL	n.d.	<MQL	<MQL	0.23	0.13	<MQL	<MQL
PFHxS	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	0.21	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	0.46	0.29	0.2	0.15
PFOS	n.d.	n.d.	0.1	0.1	0.23	<MQL	0.20	0.35	<MQL	0.30	0.26	0.14	0.58	0.33	3.3	2.5	1.9	1.3

12

5. 8:2 FTUC(A) as a reference chemical

Figure 4 shows the fraction of the total amount found in the vessels at t0 that was found in water at t2 for 8:2 FTUC(A) compared to PFC(A)s. The loss of 8:2 FTUC(A) from water compared to the loss of PFC(A)s from water shows that 8:2 FTUC(A) is already lost from water at higher pHs (3.5 - 5) and that the loss is leveling off at lower pHs (<3). It can be concluded that the system is showing different results for chemicals with different pK_a's indicating that the results are influenced by the pK_a.

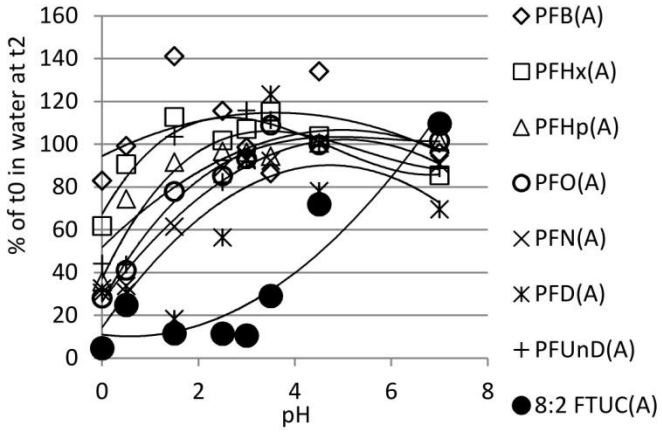


Figure S 2: Percentage of 8:2 FTUC(A) (semi-quantitative) and PFC(A)s remaining at t2 (relative to the total amount in the system at t0) plotted as a function of the water pH. Lines represent a polynomical fit for the data point of each analyte.

6. Mass balances

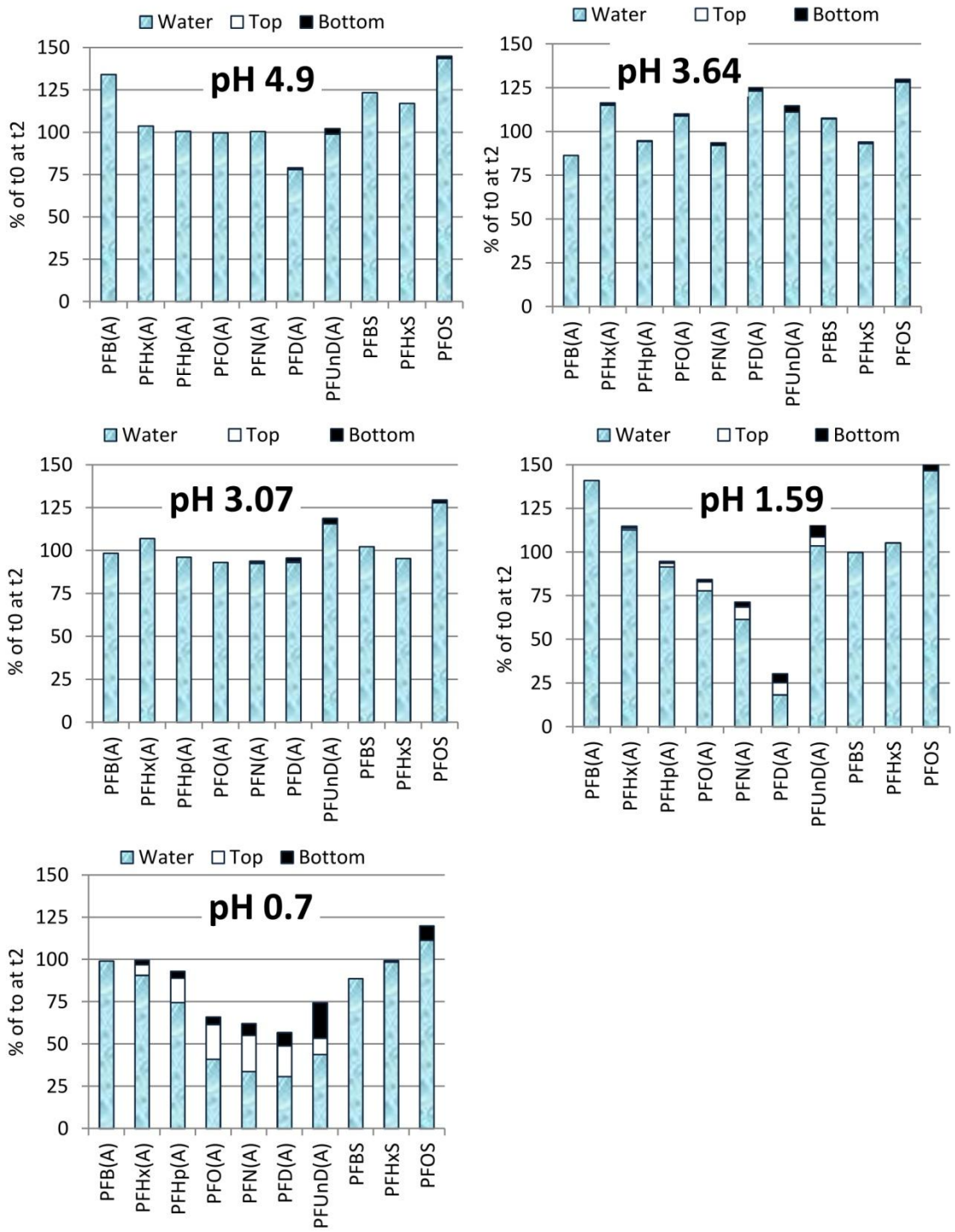


Figure S 3: Percentages of the total amount remaining in the systems at t2 (found in the water and sorbed to the top and bottom parts of the vessel) relative to the amount at t0 for selected water pHs.

7. Model fit for PFOA

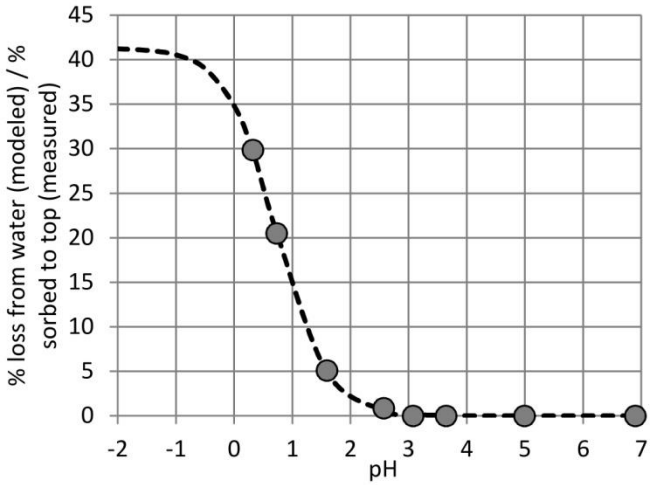


Figure S 4: Least square fit of modeled results to measured data for PFOA. Calculated loss from water after two days (dashed line, in %) and measured fraction sorbed to the top part after two days (dots, in % of amount found at t0) plotted against the pH of the water.

A5 Paper 5 PFOA concerns and regulatory developments

Published as open access article.

Vierke et al. Environmental Sciences Europe 2012, 24:16
http://www.enveurope.com/content/24/1/16

Environmental Sciences Europe
a SpringerOpen Journal

RESEARCH Open Access

Perfluorooctanoic acid (PFOA) — main concerns and regulatory developments in Europe from an environmental point of view

Lena Vierke[1,2*], Claudia Staude[1], Annegret Biegel-Engler[1], Wiebke Drost[1] and Christoph Schulte[1]

Abstract

Background: Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most investigated substances of the group of per- and polyfluorinated chemicals (PFCs). Whereas for PFOS regulatory measures are already in force on international level (inclusion in Stockholm Convention on Persistent Organic Pollutants) such activities are missing for PFOA. The environmental concerns of PFOA, which are summarized in the present study, underline the necessity of regulatory measures on an international level for PFOA. Since it seems more likely to agree on a regulation within the European Union first, a regulatory strategy based on the European chemicals regulation REACH (EC No. 1907/2006), is discussed in the present study.

Results: PFOA is persistent in the environment, ubiquitous present in surface waters, and subject to long-range transport. It accumulates in biota, especially in top predators. PFOA is increasingly analyzed in food items, and in drinking water. PFOA's intrinsic properties such as its persistency (P), its potential for bioaccumulation (B) and its toxicity (T) suggest that PFOA is a promising candidate for being identified as a Substance of Very High Concern (SVHC) under REACH. Because of the dispersive occurrence of PFOA in the environment, the presence in imported products, and the use of PFCs, which can degrade to PFOA in various consumer products, a restriction under REACH seems to be the most effective regulatory measure to minimize human and environmental exposure to PFOA in the European Union.

Conclusion: Due to its intrinsic properties, PFOA fulfills the REACH PBT-criteria. The next regulatory step will be the identification of PFOA and its ammonium salt (APFO) as SVHC according to REACH and the addition to the REACH Candidate List. As a second step, a restriction proposal will be prepared to include both substances and precursors into REACH Annex XVII.

Keywords: PFCs, PFCAs, PFO, PFOA, APFO, REACH, SVHC, Candidate List, Restriction, Regulation, Per- and polyfluorinated chemicals

Background

Per- and polyfluorinated chemicals (PFCs) are emerging pollutants of the 21st century. These man-made chemicals have been produced since the 1950s. Due to their outstanding properties – they provide water, oil, and grease repellency and are very stable – certain PFCs have been used in a variety of consumer products. A number of studies are available reporting the occurrence of these chemicals in all environmental media as well as in humans [1-4]. In total, according to an OECD survey, the group of produced and used PFCs consists of more than 600 compounds [5]. They are characterized by a fully (per-) or partly (poly-) fluorinated carbon chain in connection with different functional groups. Two compounds from the PFC family are well known: Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). PFOS has recently been identified as a persistent organic pollutant (POP) and was included into Annex B of the Stockholm Convention on Persistent Organic Pollutants [6]. For PFOA only some national measures exist worldwide for the time being. For example, the Environmental Protection

* Correspondence: Lena.Vierke@uba.de
[1]Federal Environment Agency, Wörlitzer Platz 1, Dessau-Roßlau 06844, Germany
[2]Leuphana University of Lüneburg, Scharnhorststr. 1, Lüneburg 21335, Germany

Agency of the United States (US-EPA) agreed with eight fluoropolymer and -telomere manufacturers on a PFOA-stewardship program in 2006 [7]. The first goal of the agreement was a 95 % emission reduction of PFOA, its precursors, and related higher homologue chemicals until 2010 using the emission data of the year 2000 as a baseline. The second goal is the elimination of these chemicals by 2015 [7]. Canada prepared a risk management scope for PFOA and long chain PFCs in 2010 [8] and a draft screening assessment for PFOA, its salts, and its precursors [9]. The scope is currently under revision. Canada has an agreement with industry to work on the elimination of PFOA residuals from products sold in Canada [10]. In Europe some national regulatory activities are present for PFOA, i.e. the ban of PFOA from consumer products in Norway from 2013 on [11]. In Germany recommended maximum concentrations for drinking water are available [12,13]. A Europe-wide regulation is missing so far.

The aim of this paper is (i) to summarize the concerns of PFOA from an environmental point of view, (ii) to assess whether PFOA is a persistent, bioaccumulative and toxic (PBT) substance according to the European Chemicals Regulation (REACH EC No. 1907/2006), and (iii) to illustrate a strategy to phase out PFOA in the EU using REACH. It is not the aim of this paper to be a review. In parts only selected studies and exemplary studies are mentioned, which are helpful to support the intention of the study. Additionally, further information needs are formulated.

In the following the abbreviation PFOA (CAS. No. 335-67-1) refers to the acid PFOA (Figure 1) as well as to the conjugate base perfluorooctanoate (PFO). Both species are in equilibrium, whereas the fraction of each species depends on the pH of the environmental media and the pK_a of PFOA. The general relationship of pH and pK_a is given by the Henderson-Hasselbalch equation [14]. In the literature pK_a values in the range of −0.2 to 3.8 are discussed for PFOA [15,16]. Therefore, under normal environmental conditions (i.e. pH 7) more than 99 % is present as conjugate base PFO. In environmental and human samples, generally, PFO is measured. However, in most cases PFOA is documented for these samples in the literature. Only in cases where it is important to distinguish between both of the PFOA-species and where species specific knowledge is available it is clearly indicated that either the acid PFOA or the conjugate base PFO is meant in the following.

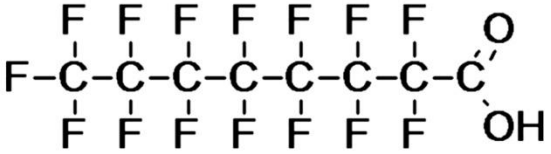


Figure 1 Structure of PFOA.

Furthermore, PFOA is used and produced as ammonium salt (APFO) (CAS. No. 3825-26-1). APFO is highly soluble and dissociates in the environment under the formation of PFO. Again, when analyzing samples concerning their APFO content usually PFO is measured. In the literature the concentrations are referred to as PFOA or APFO in most cases. For a better understanding of the present study, the term PFOA stands for APFO and PFO as well.

There are other salts of PFOA available as well, i.e. sodium salt, potassium salt and silver salt. These salts are not included in the present paper due to a lack of physico-chemical data and other studies up to the present.

Results and discussion

Uses and sources of environmental exposure

PFOA has been mainly used as polymerization aid in the manufacturing of fluoropolymers and in aqueous fluoropolymer dispersions, which are used for paints, photographic film additives and in the textile finishing industry [17,18]. Furthermore, PFOA has been used in aqueous fire fighting foams [17,18].

Telomerization and electrochemical fluorination (ECF) are procedures which have been applied to produce PFOA as well as other PFCs [19]. With a radical reaction all hydrogen atoms are replaced with fluorine in the ECF process. The more common production process nowadays is the telomerization. Here, perfluorinated iodides (PFIs) are used as starting point for the formation of PFOA. Since other PFCs are also produced by applying the telomerization process, PFOA might be present in the final product as an unintended by-product or a residue [19]. Whereas the ECF process results in both linear and branched isomers the telomerization process results in linear isomers only.

From 1951 to 2004 the estimated total global production of PFOA and APFO was 3600 – 5700 t [18]. Latest data on production volumes are rare. As a result from the US-EPA stewardship program and further activities to substitute the substance in many uses, production of PFOA decreased significantly at least in Europe and North America. Partly, this is documented in annual progress reports of the US EPA stewardship program [7]. For the time period from 2005 to 2050 480 – 950 t of total PFOA emissions are estimated [20]. Results of an OECD survey, which was, however, not answered by all PFOA manufacturers and users, showed that PFOA as well as its ammonium salt was manufactured in four countries in 2008, whereas masses in products are <5.5 t [17].

Although the production volume of PFOA is relatively low in industrialized countries, it is still detected in a number of consumer products. Especially in products

with water, dirt, and grease repellent properties like treated carpets (0.2 to 6 mg kg^{-1} PFOA [21]), outdoor jackets (0.08 to 0.6 mg kg^{-1} PFOA [19]), and impregnating agents (up to 3.6 μg mL^{-1} PFOA [22]) PFOA was found. For example in Norway the import of articles was figured out as main source since there is no manufacturing and use of PFOA itself. Carpets, coated and impregnated paper, textiles, paint and lacquer (12 kg, 1.3 kg, 0.5 kg and 1 kg annual maximal PFOA emission in Norway, respectively) have been identified as a potential source for PFOA in Norway [19].

Some PFCs can degrade to PFOA under environmental conditions. Those precursor compounds are within this study defined by a carbon chain of at least seven perfluorinated C-atoms connected to different functional groups. Examples for those precursors are fluorotelomer alcohols (FTOHs) [23], Polyfluoroalkyl Phosphoric Acid (PAPs) [24] and polyfluorinated iodides (PFIs) [25]. These compounds are also present in consumer products, i.e. up to 52 μg mL^{-1} 8:2 FTOH in impregnating agents [22].

The fact that PFOA and its precursors are present in numerous consumer products indicates wide and dispersive sources of the compounds into the environment. Moreover, during the production of fluoropolymers and fluoroelastomers, PFCs can be released into the environment [18]. During the whole life cycle of products containing these compounds, starting with the manufacturing, including the use and ending with the disposal, PFOA and its precursors might be emitted into the environment. Detection of PFOA and precursors in wastewater treatment plant (WWTP) effluents [26] as well as in air emitted from WWTPs [27-29] give further evidence for the wide dispersive use of PFOA and precursors. Households are one possible source for PFOA and its precursors in municipal WWTPs. Additionally, landfills emit PFOA with their leachates [30] or release these substances into the atmosphere [29,31].

Concerns about PFOA from an environmental point of view

There are different reasons which show that the releases of PFOA and APFO into the environment are of concern (Table 1). Most of the concerns are related to the environmental persistence of PFOA. PFOA is not expected to undergo biotic or abiotic degradation in the environment. Tests under laboratory conditions prove the suspected environmental persistence as no degradation was observed [32]. Besides these laboratory tests also monitoring data confirm the persistence of PFOA. For example, PFOA was found in groundwater close to a former fire-training area years after the last use of PFOA containing fire fighting foams on this area [33]. Additionally, its high water-solubility (especially of the conjugate base PFO) characterizes the fate of PFOA in the environment: the aqueous phase is one major pathway for the occurrence and the distribution of PFOA in the environment. Various measurements and studies showed that PFOA is ubiquitously present in oceans and other surface waters [2,34-36]. The formation of deep ocean water is discussed as a potential sink for PFOA [2]. Sources of PFOA into oceans are rivers and atmospheric deposition. The distribution of PFOA in aqueous media is also of concern when the long-range transport potential of the substance is examined. For example, findings of PFOA in remote areas like the Arctic or the Antarctic give evidence for the long- range transport potential, because PFOA is not known to be used or produced in these regions. Mainly two transport pathways are discussed: (a) Transport of PFOA in ocean currents and (b) transport of precursors in the atmosphere. Precursors are then degraded to PFOA [18]. The contribution of these two transport pathways to the occurrence of PFOA in remote regions is still under discussion [20,56,57]. Furthermore, transport of PFOA bound on particles, i.e. directly emitted from industrial facilities [58] or emitted from oceans is possible as well [18]. Even the transfer of PFOA from particles into the gas phase [59] and the detection of PFOA in the gas phase [28] were shown. Because of the low vapor pressure of the conjugate base PFO only the acid PFOA is expected to be present in the gaseous phase [59,60].

The occurrence of PFOA in biota of remote regions is another topic of concern. It was shown that PFOA accumulates in food webs and findings in top predators are reported [4]. PFOA is toxic for reproduction (Cat 1B) and has carcinogenic potential (in accordance with opinion of Risk Assessment Committee of the European Chemicals Agency (ECHA), [61,62]). Furthermore, PFOA has a long residence time of 3.5 years in human blood and is present in breast milk [63,64]. One exposure pathway for humans is nutrition [65]. For example in fish, meat, and vegetables PFOA has been found in low levels [46,66]. The PFOA load of these food items results most probably from environmental concentrations in water and biota. Also the transfer of PFOA from soil into plants [67], i.e. after application of PFOA contaminated sewage sludge on fields, or the migration from food packages can be a source for PFOA in food [46]. Another potential human exposure pathway is the occurrence of PFOA in drinking water [48,68]. In cases where surface waters are used for the production of drinking water, PFOA is not effectively removed by common purification methods [69]. Therefore, the occurrence in surface waters is of concern from a human health point of view as well.

It has to be kept in mind that the precursors contribute to the exposure of PFOA to humans and the environment, additionally [24,25,54]. Biotic as well as abiotic degradation of those precursors does occur and partly results in the formation of PFOA [70]. Especially indoor air contains up

Table 1 Summary of concerns about PFOA under environmental aspects

Concern	Exemplary data from the literature which prove the concern	Ref.
Environmental persistence	no degradation observed	[32]
Findings and distributions in surface waters	n.d. – 3640 ng L^{-1} PFOA in river water	[2]
	0. 4 – 16 ng L^{-1} PFOA in lake water	
	two orders of magnitude higher concentrations in coastal areas compared to open ocean waters	
	15 – 192000 pg L^{-1} PFOA in oceans	[35]
	flux of 14 t PFOA per year from rivers into oceans in Europe	[37]
	1.2 g PFOA daily mass load from a WWTP (Germany) into a river	[38]
	< MDL – 204 ng L^{-1} PFOA in a river (USA)	[39]
	< LOD – 10.7 ng L^{-1} PFOA in a river (China)	[40]
Long-range transport and findings in remote regions	up to 3.4 ng g^{-1} ww PFOA in polar bears	[1]
	<LOD – 1.2 PFOA ng g^{-1} ww in fish from the Arctic	
	n.d. – 0.14 ng g^{-1} ww PFOA in seabirds from the Arctic	
	n.d. – 1.6 ng g^{-1} ww PFOA in whales from the Arctic	
	0.44 – 1.4 pg m^{-3} in atmospheric particles from the Arctic	
	13.1 – 520 pg L^{-1} in snow of ice caps from the Arctic	[41]
	<30 – 182 pg L^{-1} in surface waters from the Arctic	
Findings and accumulation in food webs and top predators	1.3 – 2.7 ng g^{-1} ww PFOA in waterbird liver	[42]
	increasing concentrations in polar bears, 0.6 – 14 µg kg^{-1} in 1990 and 11.8 – 17.6 µg kg^{-1} in 2006	[43]
	43 ng g^{-1} ww in blood plasma of dolphins	[4]
	up to 6.2 ng g^{-1} ww in arctic ringed seal liver	[44]
	<LOQ – 45 µg kg^{-1} PFOA in liver and < LOQ – 7.4 µg kg^{-1} PFOA in muscle tissue of wild boars	[45]
Findings in food	2.6 ng g^{-1} PFOA in roast beef	[46]
	0.74 ng g^{-1} PFOA in pizza	
	3.6 ng g^{-1} PFOA in microwave pop corn	
	<0.25 – 4.4 ng g^{-1} ww PFOA in edible fish	[47]
Findings in drinking water	up to 519 ng L^{-1} PFOA (Germany, after use of contaminated soil improver)	[48]
	0.3 – 6.3 ng L^{-1} PFOA in tap-water (Spain)	[49]
	<0.2 – 0.7 ng L^{-1} PFOA in bottled water	
	1.0 – 2.9 ng L^{-1} PFOA (Italy)	[50]
	0.65 – 2.5 ng L^{-1} PFOA (Norway)	[51]
	mean 23 ng L^{-1} PFOA (Germany)	[13]
	up to 13.3 µg L^{-1} PFOA in wells close to a fluoropolymer production facility	[52]
	<0.5 – 9.7 ng L^{-1} PFOA (Australia)	[53]
Precursors in the environment	27 pg m^{-3} 8:2 FTOH in the atmosphere of the Northern Hemisphere	[54]
	7.8 pg m^{-3} 8:2 FTOH in the atmosphere of the Southern Hemisphere	
	8.1 – 17.4 pg m^{-3} 8:2 FTOH in indoor air of residential houses	[55]
	79 – 209 pg m^{-3} 8:2 FTOH in stores selling outdoor equipment	
	47 – 200 ng g^{-1} PAPs in wastewater treatment plant sludge	[24]
	3 – 82 pg L^{-1} perfluorooctyl iodide (PFOI) in ambient air	[25]

to 10 – 20 times higher concentrations of these substances than outdoor air, i.e. FTOHs [55,71-73].

In conclusion, the described concerns about PFOA circumstantiate the impact of the exposure of humans via the environment, which is known as man via environment exposure. From a regulatory point of view these concerns raise the question whether PFOA is a Substance of Very High Concern (SVHC) under REACH. SVHC are substances which for example have persistent (P), bioaccumulative (B) and toxic (T) properties. The available data on PFOA need to be compared with the PBT-criteria defined in REACH.

Assessment of PFOA and APFO fulfilling the PBT-criteria for Substances of Very High Concern under REACH

In Annex XIII of the REACH regulation criteria for the identification of PBT-substances are defined. These criteria will be used in the following to assess whether PFOA is a PBT-substance. The relevant criteria and the corresponding PFOA properties are summarized in Table 2.

Assessment of persistence

In general, persistence is defined by measured half-lives for the environmental compartments water, sediment, and soil. The numerical values for minimum half-lives in water are 60 days in marine waters, and 40 days in freshwater, 180 days in marine sediment, and 120 days in freshwater sediment, as well as 120 days for the soil compartment. At least one of these values must be exceeded to fulfill the criteria for persistent substances under REACH.

Due to the stability of PFOA it is, in general, challenging or even impossible to measure its half-life. Nevertheless, some studies are available showing that no abiotic or biotic degradation was observed [74-78]. The atmospheric half-life of PFOA derived by analogy from short-chain perfluorinated carboxylic acids is 130 days [90]. For hydrolysis a half-life greater than 92 years is reported based on observations of the APFO concentration in buffered aqueous solutions [32]. Taking all the information together, PFOA does not undergo abiotic or biotic degradation under environmental conditions. Therefore, PFOA is considered to fullfil the persistence criteria of REACH.

Assessment of the bioaccumulation potential

The numerical criterion under REACH defining that a substance is bioaccumulative is a bioconcentration factor (BCF) in aquatic species higher than 2000. For PFOA only BCFs far below 2000 were measured in bioconcentration studies using fish and other aquatic species and an exposure route via the surrounding water [32]. Bioaccumulation factors (BAFs) were determined from field measurements. Compared to BCFs, BAFs take all possible routes of exposure into consideration, whereas the BCF excludes dietary uptake. Reported BAFs were also

Table 2 PBT-assessment of PFOA

	Relevant criteria for the identification of PFOA as PBT-substances (Extract of Annex XIII of the REACH regulation)	Concerns of PFOA	Reference
P	DT50 (marine water) > 60 d DT50 (fresh or estuarine water) > 40 d DT50 (marine sediment) > 180 d DT50 (fresh or estuarine sediment) > 120 d DT50 (soil) > 120 d	No measurable half-lives available because of the high persistence	[74-78]
B	BCF > 2000	BCF 1.8 – 27	[79,80]
	Bioaccumulation in terrestrial and aquatic species Biomagnification in the food chain, i.e. biomagnification or trophic magnification factors (BMF, TMF)	BAF 0.04 - 29 2BMF (marine) 0.02 – 125 BMF (terrestrial) 0.9 – 11 TMF (marine) 0.3 – 13 TMF (terrestrial) 1.1 – 2.4	[9,42,81-88]
	Analysis of human body fluids or tissues, such as blood, milk, or fat	< 0.15 – 0.25 μg L^{-1} in breast milk	[89]
	Elevated levels in biota, in particular in endangered species or in vulnerable populations	up to 3.4 ng g^{-1} ww in polar bear livers	[1]
T	Long-term no-observed effect concentration (NOEC)< 0.01 mg L^{-1} Classification as carcinogenic (category 1A or 1B), germ cell mutagenic (category 1A or 1B), or toxic for reproduction (category 1A, 1B, or 2) (according to EC No 1272/2008)	chronic toxicity, i.e. 30 d-NOEC = 100 mg L^{-1} for *Pimephales promelas* Repr. 1B	[32,61]
	Other evidence of chronic toxicity, i.e. specific target organ toxicity after repeated exposure (STOT RE category 1 or 2) (according to EC No 1272/2008)	STOT RE 1	

far below 2000 [42,81-83]. There is no defined threshold value for BAFs in Annex XIII of REACH, but taking into account the BCF threshold, again the numerical criterion for bioaccumulation of Annex XIII is not fulfilled.

For assessing the bioconcentration data the high water solubility of PFOA could be the reason for the effective excretion of PFOA by fish via gill permeation, facilitated by high water throughput. Therefore, it is not surprising that no BCF > 2000 is reported in the literature for PFOA and it is also the reason, why several authors came to the conclusion that PFOA does not bioaccumulate in aquatic organisms [79]. However, this possible excretion pathway does not exist for air breathing animals [91,92] and therefore bioconcentration values in fish may not be the most relevant endpoint to consider.

Also, octanol-water partition coefficients (K_{OW}) can be taken into consideration under REACH to assess the bioaccumulation potential of a chemical. To the best of our knowledge there are no measured K_{OW} values available for PFOA. Only estimates for the neutral PFOA acid are reported [93,94]. However, if this K_{OW} for the neutral PFOA is applied to environmental conditions, where also PFO is present, the pK_a is needed [95]. As the pK_a is, as already outlined above, subject to broad discussion, it should be avoided to assess the bioaccumulation potential of PFOA in the environment based on not yet assured properties.

Annex XIII of the REACH regulation was revised in March 2011 (Commission Regulation (EU) No. 253/2011). For assessing the bioaccumulation potential of a substance the criteria were expanded to include more recent findings with respect to biomagnification, bioaccumulation in terrestrial species, concentrations in human body fluids, etc. [96]. However, this weight of evidence evaluation needs expert judgment, since there are no hard, i.e. quantitative, definitions of these new criteria. To the best of our knowledge the new criteria were up to now not used for the assessment of chemicals under REACH.

Information that PFOA bioaccumulates can be drawn from biomagnifications factors (BMFs) and trophic magnification factors (TMFs). Both of them are related to concentrations in predator/prey relationships, whereas TMFs take into consideration a food web. Generally, factors higher than one indicate accumulation. Studies report TMFs or BMFs greater than one, indicating bioaccumulation of PFOA. For example studies on dolphins [97] and caribou [84] clearly show that PFOA is bioaccumulative to a certain degree. Moreover, for the food chains walrus (liver)/clam, narwhal (liver)/Arctic cod, and celuga (liver)/Arctic cod the BMFs are above one, respectively, indicating bioaccumulation [98]. Also for a Canadian Arctic marine food web (sediment and different organisms (macroalgae, bivalves, fish, seaducks, and marine mammals)) a TMF larger than one was reported. Even after protein-normalization, the TMF value was greater than one [97].

BMFs between 0.9 and 11 were calculated in the terrestrial food chain of lichen, caribou, and wolf, living in the remote Canadian environment, indicating bioaccumulation. Furthermore, calculated TMFs were greater than one, indicating trophic magnification, too [84].

Field studies are complex and therefore difficult to judge concerning their reliability. Each of the field studies has its drawbacks due to sample collection in different years, the sampling of body tissues and fluids instead of whole body or uncertainty of prey constitution etc. and may not be considered as a standalone proof for the bioaccumulation potential of PFOA. Nevertheless taken together all studies their results can be considered overall conclusive. The weight of evidence of these studies suggests that PFOA can biomagnify in the food chain as indicated by biomagnifications factors and trophic magnification factors larger than one.

Also the detection of PFOA in human body fluids, such as blood, milk and fat, can be used as additional information to assess whether PFOA is a bioaccumulating substance as defined in Annex XIII of the REACH regulation. PFOA has been found in human blood from all around the world [99]. In addition the following observations are of relevance: Five to eight times higher levels have been found at locations, where people had been exposed to PFOA contaminated drinking water indicating accumulation in the blood compartment [100,101]. Time trend studies show that PFOA levels are significantly associated with the time being exposed to PFOA, i.e. during work as a ski waxer [102-104]. And recent studies strongly indicate that PFOA levels increase with age [105,106]. Elimination half-lives of PFOA in humans of 3.5 [64] or 3.26 [107] years indicate the bioaccumulation potential of PFOA.

Occurrence of PFOA in endangered species and in vulnerable populations can be used in accordance with Annex XIII of the REACH regulation to assess the bioaccumulation properties of a substance as well. Because polar bears live in remote regions where no direct PFOA source is known, detection of PFOA in polar bears indicates the uptake from the surrounding environment [1].

In conclusion, a number of data are available demonstrating the bioaccumulation potential of PFOA especially in air breathing animals. Moreover, the detection in human body fluids of the general population together with long elimination half-lives is of very high concern. Additionally, it is of special concern that PFOA biomagnifies in endangered species or vulnerable populations as shown by the findings of PFOA in polar bears. Thus, it can be concluded that PFOA is a bioaccumulative substance in accordance with Annex XIII of the REACH regulation.

Assessment of toxic and eco-toxic effects

Toxic substances under REACH are those with no-observed effect concentrations (NOECs) below 0.01 mg L^{-1} or substances classified as being carcinogenic, mutagenic or toxic for reproduction for humans according to regulation EC No 1272/2008. These criteria for toxic substances are defined in Annex XIII of the REACH regulation.

The acute and toxic effects of PFOA to fathead minnow (*Pimephales promela)* have been analyzed [32]. The threshold value of Annex XIII is not met. The same was observed for aquatic invertebrates [32].

In March 2010 Norway submitted a proposal for the harmonized classification and labeling of PFOA and APFO in the EU. In December 2011 the Risk Assessment Committee of the ECHA came to the conclusion that classification according to regulation EC No. 1272/2008 for PFOA is Repr. 1B and STOT RE 1 [61]. In agreement with the Annex XIII of the REACH regulation the category for reproduction toxicity and specific organ toxicity after repeated dose fulfill the toxicity criteria.

Conclusion on PBT-assessment

PFOA clearly fulfills the P and T criteria of REACH Annex XIII. For the B-criterium a weight of evidence approach mainly based on field studies investigating the accumulation of PFOA in different food webs results in the conclusion that PFOA is a bioaccumulative substance in agreement with REACH Annex XIII. Therefore, PFOA is considered to fulfill the PBT-criteria as defined in REACH. Because of the dissociation of PFOA as well as APFO under environmental conditions the results for PFOA can be transferred to APFO. Hence, APFO fulfills the REACH PBT-criteria, too.

Strategy for regulation of PFOA under REACH

The REACH regulation provides different options for regulatory measures [108]. The PBT-properties of PFOA and APFO in combination with its different source are exceptionally of the PFOA case. (Figure 2) needs to consider both parts to protect the environment.

Identification as substance of very high concern (SVHC) and addition to the REACH-Candidate List

PFOA and APFO fulfill the PBT-criteria under REACH, which is one possible requirement for a substance to be identified as a SVHC according to REACH, Art. 57d. The identification of SVHC is based on the intrinsic properties of the substances mainly. From a human health point of view PFOA and APFO also fulfill the criteria for the classification as toxic for reproduction (Art. 57c). The next step is to identify the SVHC-properties of PFOA and APFO according to a formal process defined in REACH. Therefore, Germany and Norway are preparing a proposal assessing the PBT-properties of PFOA and APFO in detail. Subsequently to the submission to ECHA this proposal is open for public consultation. Finally, the Member State Committee, which is established with the ECHA, needs to identify the SVHC-properties of PFOA according to Art. 59. Once PFOA and APFO are identified as SVHC ECHA will include the substances into the Candidate List – the list of substances proposed for authorization. This process will start in 2013.

The identification of PFOA and APFO as SVHC in the EU might indicate to states outside of the EU the need to minimize risks, and might also be a starting point for other regulatory measures on national or international level. Furthermore, this might be a strong signal to manufacturers and downstream users to replace PFOA and APFO. Authorization is the foreseen instrument in the REACH regulation to control the risks of SVHC. Once PFOA and APFO are included in the Candidate List they could be included into Annex XIV of the REACH regulation. Following inclusion into this Annex, manufacturers, importers and downstream users would not be allowed to use or to place these substances as such on the European market without an authorization of any single use. Risk control, good functioning of the internal market, and the replacement of SVHC by substitutes are aims of the authorization. Assuring the safe use of the substances, manufacturers, importers and downstream users can apply for authorization using the substances on its own, in a mixture or in an article.

The following three reasons make the instrument of authorization ineffective to control the emissions of PFOA in the environment and the environmental exposure: (i) PFOA and APFO themselves are produced and imported into the EU in decreasing amounts. (ii) Consumer articles containing PFOA, i.e. textiles, are partly imported into the EU and authorization does not apply for imported articles. (iii) Also precursors contribute to the presence of PFOA into the environment. However, precursors of SVHC are not included in the substance definition and therefore won't be included into Annex XIV. Therefore, the contribution of precursors and residues in (imported) articles to the environmental exposure of PFOA is not addressed by the authorization instrument. If an authorization based on the intrinsic properties of a substance is coming into effect, a restriction based on the same risk will not be possible.

Restriction

An option to regulate manufacturing, placing on the market or use of a substance on its own, in a mixture or in an article is the inclusion into Annex XVII of the REACH regulation (Restriction, Art. 67). A restriction

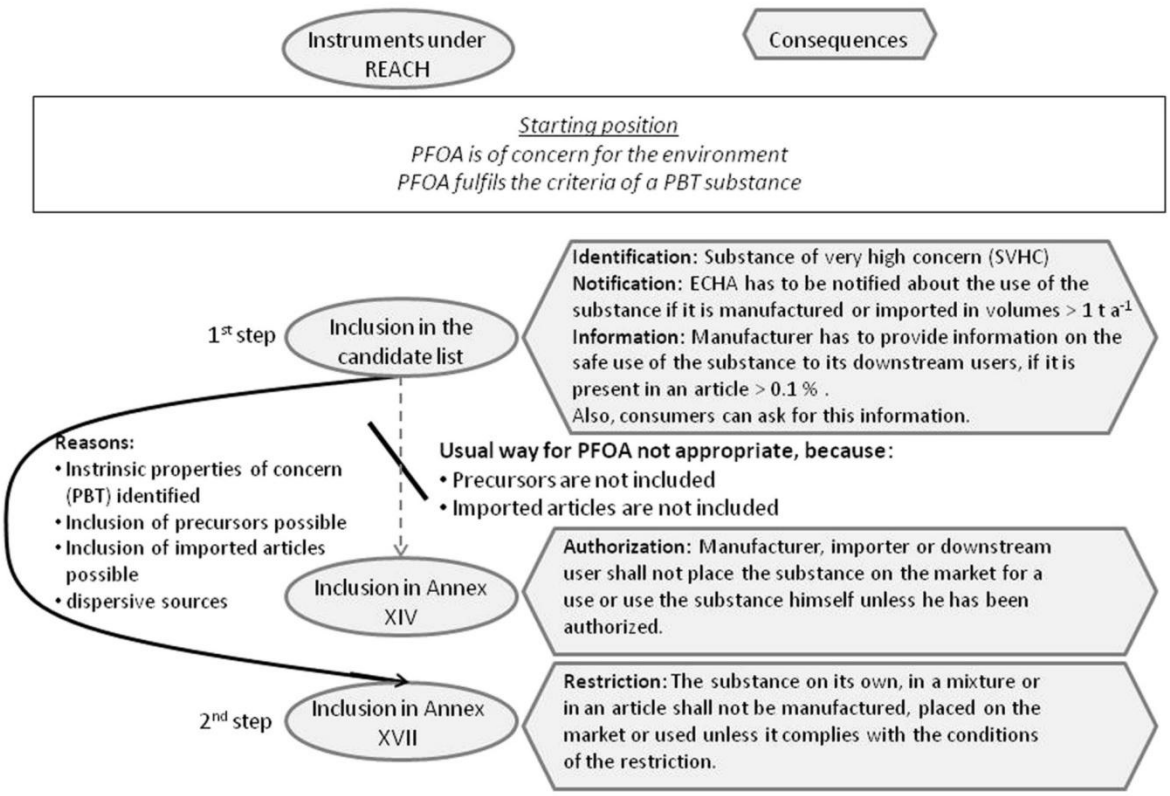


Figure 2 Strategy for regulation of PFOA under REACH.

might also include residue limits for PFOA and its precursors in articles. For PFOA and APFO as PBT-substances this seems to be appropriate to reduce the environmental PFOA concentrations effectively, because especially the residues in articles need to be controlled successfully. As also precursor compounds contribute to the environmental exposure with PFOA, these compounds need to be included in the restriction as well. To decide how an effective restriction needs to be designed more information about the residues of PFOA in articles and mixtures are necessary. Furthermore, relevant precursors need to be identified and included in the restriction. When suggesting a restriction, information about possible substitutes is essential: Some substitutes are already known but not much is known about their properties and their long-term effects. A restriction of PFOA, its salts, and its precursors under REACH is envisaged by Germany and Norway and will be initiated in 2013.

Conclusion

This study demonstrates that PFOA and APFO are PBT-substances and promising SVHC candidates according to REACH. Hence, PFOA and APFO need to be added to the REACH Candidate List. This step alone does not minimize exposure effectively and does not address the concerns of PFOA appropriately. A restriction for production, placing on the market and/or use of PFOA and APFO in certain articles and mixtures is, therefore, necessary as a follow-up. For the future a regulatory process beyond the European level is required to achieve a global protection of humans and the environment from PFOA exposure. Since there are numerous different PFCs manufactured and used worldwide, the intrinsic properties of other PFCs need to be evaluated in future, too. Especially, their fate and behavior in the environment has to be monitored to find out if further regulatory measures are needed.

Methods

Literature review and analysis of data obtained in the review were performed to achieve the aim of the study. Furthermore, interpretation of the REACH regulation was necessary. For that reason, also a workshop with experts from different EU-member states, the EU-Commission and the ECHA was hosted in Dessau-Roßlau (Germany) in November 2011.

Abbreviations
APFO: Perfluorooctanoic acid ammonium salt; BAFs: Bioaccumulation factor; BCF: Bioconcentration factor; BMFs: Biomagnifications factor; DT50: Degradation half-life; ECHA: European Chemicals Agency; ECF: Electrochemical fluorination; FTOHs: Fluorotelomer alcohols; K_{OW}: Octanol-water partition coefficient; NOEC: No-observed effect concentration; PAPs: PAPs: Polyfluoroalkyl Phosphoric Acid; PBT: Persistent, bioaccumulative and toxic; PFCs: Per- and polyfluorinated chemicals; PFIs: Per and polyfluorinated iodides; PFO: Perfluorooctanoat; PFOA: Perfluorooctanoic acid; PFOS: Perfluorooctane sulfonic acid; POP: Persistent organic pollutant; REACH: European Chemicals Regulation, EC No. 1907/2006, Registration, Evaluation and Authorization of Chemicals; SVHC: Substance of Very High Concern; TMFs: Trophic magnification factor; WWTP: Wastewater treatment plant.

Competing interests
The authors declare that they have no competing interests.

Acknowledgements
We thank the participants of the workshop on "Regulatory issues of PFCs" hosted by the Federal Environment Agency in Germany for their valuable input in assessing the bioaccumulation properties of PFOA, especially Greg Hammond from Environment Canada. We acknowledge the cooperation with our colleagues, Heidi Morka, Ingunn Correll Myhre, Stine Husa and Marit Kopangen from the Norwegian Climate and Pollution Agency for the work on regulation of PFOA under REACH. Furthermore, we thank the anonymous reviewers for their helpful comments on our manuscript.

Authors' contributions
All authors contributed in equal parts to this publication. All authors read and approved the final manuscript. This paper does not necessarily reflect the opinion or the policies if the German Federal Environment Agency.

Received: 11 January 2012 Accepted: 7 May 2012
Published: 7 May 2012

References

1. Butt CM, Berger U, Bossi R, Tomy GT: **Levels and trends of poly- and perfluorinated compounds in the arctic environment.** *Sci Total Environ* 2010, **408:**2936–2965.
2. Ahrens L: **Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate.** *J Environ Monit* 2011, **13:**20–31.
3. Sturm R, Ahrens L: **Trends of polyfluoroalkyl compounds in marine biota and in humans.** *Environ Chem* 2010, **7:**457–484.
4. Houde M, Martin JW, Letcher RJ, Solomon KR, Muir DC: **Biological monitoring of polyfluoroalkyl substances: A review.** *Environ Sci Technol* 2006, **40:**3463–3473.
5. OECD: *Lists of PFOS, PFAS, PFCA, Related compounds and chemicals that may degrade to PFCA.*: ENV/JM/MONO(2006)15. 2007. [http://www.oecd.org/LongAbstract/0,3425,en_2649_34375_39160347_119666_1_1_1,00.html].
6. Secretariat of the Stockholm Convention: *The new POPs under the Stockholm Convention.*: ; 2011. [http://chm.pops.int/Implementation/NewPOPs/ThenewPOPs/tabid/672/Default.aspx].
7. U.S. Environmental Protection Agency: *2010/2015 PFOA Stewardship Program.* 2012. [http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html].
8. Environment Canada, Health Canada: *Risk management scope for Perfluorooctanoic Acid (PFOA), its Salts, and its Precursors, and Long-Chain (C9-C20) Perfluorocarboxylic Acids (PFCAs), their Salts, and their Precursors.* 2010. [http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=6B9B6B28-1&xml=F68CBFF1-B480-4348-903D-24DFF9D623DC].
9. Environment Canada Health Canada: ***Draft screening assessment perfluorooctanoic acid, its salts, and its precursors***. 2010. [http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=6B9B6B28-1&xml=F68CBFF1-B480-4348-903D-24DFF9D623DC].
10. Environment Canada: *Environmental Performance Agreement ("Agreement") Respecting Perfluorinated Carboxylic Acids (PFCAs) and their Precursors in Perfluorochemical Products Sold in Canada.* 2010. [http://www.ec.gc.ca/epe-epa/default.asp?lang=En&n=81AE80CE-1#X-2010073015020613].
11. European Commission: *Notification Number: 2010/9019/N.*: ; 2011. [http://ec.europa.eu/enterprise/tris/pisa/app/search/index.cfm?fuseaction=pisa_notif_overview&iYear=2010&inum=9019&lang=EN&sNLang=EN]
12. Drinking Water Commission of the German Ministry of Health at the Federal Environment Agency: *Provisional evaluation of PFT in drinking water with the guide substances perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) as examples.*: ; 2011. [http://www.umweltbundesamt.de/wasser-e/themen/downloads/trinkwasser/pft-in-drinking-water.pdf].
13. Wilhelm M, Bergmann S, Dieter HH: **Occurrence of perfluorinated compounds (PFCs) in drinking water of North Rhine-Westphalia, Germany and new approach to assess drinking water contamination by shorter-chained C4-C7 PFCs.** *Int J Hyg Environ Health* 2010, **213:**224–232.
14. Schwarzenbach RP, Gschwend PM, Imboden DM: *Environmental Organic Chemistry*. 2nd edition. New Jersey: John Wiley & Sons; 2003.
15. Steinle-Darling E, Reinhard M: **Nanofiltration for trace organic contaminant removal: structure, solution, and membrane fouling effects on the rejection of perfluorochemicals.** *Environ Sci Technol* 2008, **42:**5292–5297.
16. Burns DC, Ellis DA, Li H, McMurdo CJ, Webster E: **Experimental pKa determination for perfluorooctanoic acid (PFOA) and the potential impact of pKa concentration dependence on laboratory-measured partitioning phenomena and environmental modeling.** *Environ Sci Technol* 2008, **42:**9283–9288.
17. OECD PFC Steering Group: *Survey on the production, use and release of PFOS, PFAS, PFOA, PFCA, their related substances and products/mixtures containing these substances (2009 survey)*. 2010. [http://www.oecd.org/document/58/0,3343,en_2649_34375_2384378_1_1_1_1,00.html].
18. Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH: **Sources, fate and transport of perfluorocarboxylates.** *Environ Sci Technol* 2006, **40:**32–44.
19. Norwegian Pollution Control Agency. *PFOA in Norway*. 2354/2007. [www.klif.no/publikasjoner/2354/ta2354.pdf].
20. Armitage JM, MacLeod M, Cousins IT: **Modeling the global fate and transport of perfluorooctanic acid and perfluorooctanoate emitted from direct sources using a multipsecies mass balance model.** *Environ Sci Technol* 2009, **43:**1134–1140.
21. Washburn ST, Bingman TS, Braithwaite SK, Buck RC, Buxton LW, Clewell HJ, Haroun LA, Kester JE, Rickard RW, Shipp AM: **Exposure assessment and risk characterization for perfluorooctanoate in selected consumer articles.** *Environ Sci Technol* 2005, **39:**3904–3910.
22. Fiedler S, Pfister G, Schramm K-W: **Poly- and perfluorinated compounds in household consumer products.** *Toxicol Environ Chem* 2011, **92:**1801–1811.
23. Ellis DA, Martin JW, De Silva AO, Mabury SA, Hurley MD: **Sulbaek Andersen MP, Wallington TJ: Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids.** *Environ Sci Technol* 2004, **38:**3316–3321.
24. D'eon JC, Crozier PW, Furdui VI, Reiner EJ, Libelo EL, Mabury SA: **Observation of a Commercial Fluorinated Material, the Polyfluoroalkyl Phosphoric Acid Diesters, in Human Sera, Wastewater Treatment Plant Sludge, and Paper Fibers.** *Environmental Science & Technology* 2009, **43:**4589–4594.
25. Ruan T, Wang Y, Wang T, Zhang Q, Ding L, Liu J, *et al*: **Presence and partitioning behavior of polyfluorinated iodine alkanes in environmental matrices around a fluorochemical manufacturing plant: another possible source for perfluorinated carboxylic acids?** *Environ Sci Technol* 2010, **44:**5755–5761.
26. Loganathan BG, Sajwan KS, Sinclair E, Senthil KK, Kannan K: **Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia.** *Water Res* 2007, **41:**4611–4620.
27. Weinberg I, Dreyer A, Ebinghaus R: **Waste water treatment plants as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air.** *Environ Pollut* 2011, **159:**125–132.
28. Vierke L, Ahrens L, Shoeib M, Reiner EJ, Guo R, Palm W-U, Ebinghaus R, Harner T: **Air concentrations and particle-gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant.** *Environ Chem* 2011, **8:**363–371.
29. Ahrens L, Shoeib M, Harner T, Lee SC, Guo R, Reiner EJ: **Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere.** *Environ Sci Technol* 2011, **45:**80980–88105.
30. Busch J, Ahrens L, Sturm R, Ebinghaus R: **Polyfluoroalkyl compounds in landfill leachates.** *Environ Pollut* 2010, **158:**1467–1471.
31. Weinberg I, Dreyer A, Ebinghaus R: **Landfills as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air.** *Atmos Environ* 2011, **45:**935–941.

32. OECD. SIDS Initial Assessment Report after SIAM 22—Ammonium Perfluorooctanoate & Perfluorooctanic Acid. 1–210. 2006.
33. Moody CA, Field JA: **Determination of perfluorocarboxylates in groundwater impacted by fire- fighting activity.** *Environ Sci Technol* 1999, **33:**2800–2806.
34. Yamashita N, Kannan K, Taniyasu S, Horii Y, Okazawa T, Petrick G, Gamo T: **Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-tandem mass spectrometry.** *Environ Sci Technol* 2004, **38:**5522–5528.
35. Yamashita N, Kannan K, Taniyasu S, Horii Y, Petrick G, Gamo T: **A global survey of perfluorinated acids in oceans.** *Mar Pollut Bull* 2005, **51:**658–668.
36. Busch J, Ahrens L, Xie Z, Sturm R, Ebinghaus R: **Polyfluoroalkyl compounds in the East Greenland Arctic Ocean.** *J Environ Monit* 2010, **12:**1242–1246.
37. McLachlan MS, Holmstrom KE, Reth M, Berger U: **Riverine discharge of perfluorinated carboxylates from the European continent.** *Environ Sci Technol* 2007, **41:**7260–7265.
38. Becker AM, Suchan M, Gerstmann S, Frank H: **Perfluorooctanoic acid and perfluorooctane sulfonate released from a waste water treatment plant in Bavaria, Germany.** *Environ Sci Pollut Res Int* 2010, **17:**1502–1507.
39. Lasier PJ, Washington JW, Hassan SM, Jenkins TM: **Perfluorinated chemicals in surface waters and sediments from northwest Georgia, USA, and their bioaccumulation in Lumbriculus variegatus.** *Environ Toxicol Chem* 2011, **30:**2194–2201.
40. Sun H, Li F, Zhang T, Zhang X, He N, Song Q, Zhao L, Sun L, Sun T: **Perfluorinated compounds in surface waters and WWTPs in Shenyang, China: mass flows and source analysis.** *Water Res* 2011, **45:**4483–4490.
41. Stock NL, Furdui VI, Muir DC, Mabury SA: **Perfluoroalkyl contaminants in the Canadian Arctic: evidence of atmospheric transport and local contamination.** *Environ Sci Technol* 2007, **41:**3529–3536.
42. Loi EI, Yeung LW, Taniyasu S, Lam PK, Kannan K, Yamashita N: **Trophic magnification of poly- and perfluorinated compounds in a subtropical food web.** *Environ Sci Technol* 2011, **45:**5506–5513.
43. Dietz R, Bossi R, Rigét FF, Sonne C, Born EW: **Increasing Perfluoroalkyl Contaminants in East Greenland Polar Bears (Ursus maritimus): a new toxic threat to the Arctic Bears.** *Environ Sci Technol* 2008, **42:**2701–2707.
44. Butt CM, Muir DC, Stirling I, Kwan M, Mabury SA: **Rapid response of Arctic ringed seals to changes in perfluoroalkyl production.** *Environ Sci Technol* 2007, **41:**42–49.
45. Stahl T, Falk S, Failing K, Berger J, Georgii S, Brunn H: **Perfluorooctanoic Acid and Perfluorooctane Sulfonate in Liver and Muscle Tissue from Wild Boar in Hesse, Germany.** *Arch Environ Contam Toxicol* 2011. In Press.
46. Picó Y, Farré M, Llorca M, Barceló D: **Perfluorinated compounds in food: a global perspective.** *Crit Rev Food Sci Nutr* 2011, **51:**605–625.
47. D'Hollander W, De VP, De CW, Bervoets L: **Perfluorinated substances in human food and other sources of human exposure.** *Rev Environ Contam Toxicol* 2010, **208:**179–215.
48. Skutlarek D, Exner M, Farber H: **Perfluorinated surfactants in surface and drinking waters.** *Environ Sci Pollut Res Int* 2006, **13:**299–307.
49. Ericson I, Nadal M, Van BB, Lindstrom G, Domingo JL: **Levels of perfluorochemicals in water samples from Catalonia, Spain: is drinking water a significant contribution to human exposure?** *Environ Sci Pollut Res Int* 2008, **15:**614–619.
50. Loos R, Wollgast J, Huber T, Hanke G: **Polar herbicides, pharmaceutical products, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and nonylphenol and its carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in Northern Italy.** *Anal Bioanal Chem* 2007, **387:**1469–1478.
51. Haug LS, Salihovic S, Jogsten IE, Thomsen C, Van BB, Lindstrom G, Becher G: **Levels in food and beverages and daily intake of perfluorinated compounds in Norway.** *Chemosphere* 2010, **80:**1137–1143.
52. Hoffmann K, Webster TF, Bartell SM, Weisskopf MG, Fletcher T: **Private drinking water wells as a source of exposure to perfluorooctanoic acid (PFOA) in communities surrounding a fluoropolymer production facility.** *Environ Health Perspect* 2011, **119:**92–97.
53. Thompson J, Eaglesham G, Mueller J: **Concentrations of PFOS, PFOA and other perfluorinated alkyl acids in Australian drinking water.** *Chemosphere* 2011, **83:**1320–1325.
54. Dreyer A, Weinberg I, Temme C, Ebinghaus R: **Polyfluorinated compounds in the atmosphere of the atlantic and southern oceans: evidence for a global distribution.** *Environ Sci Technol* 2009, **43:**6507–6514.
55. Langer V, Dreyer A, Ebinghaus R: **Polyfluorinated compounds in residential and nonresidential indoor air.** *Environ Sci Technol* 2010, **44:**8075–8081.
56. Armitage J, Cousins IT, Buck RC, Prevedouros K, Russell MH, MacLeod M, Korzeniowski SH: **Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources.** *Environ Sci Technol* 2006, **40:**6969–6975.
57. Schenker U, Scheringer M, MacLeod M, Martin JW, Cousins IT, Hungerbühler K: **Contribution of volatile precursor substances to the flux of perfluorooctanoate to the arctic.** *Environ Sci Technol* 2008, **42:**3710–3716.
58. Barton CA, Butler LE, Zarzecki CJ, Laherty JM: **aiser MA: Characterizing perfluorooctanoate in ambient air near the fence line of a manufacturing facility: comparing modeled and monitored values.** *J Air Waste Manage Assoc* 2006, **56:**48–55.
59. McMurdo CJ, Ellis DA, Webster E, Butler J, Christensen RD, Reid LK: **Aerosol enrichment of the surfactant PFO and mediation of the water-air transport of gaseous PFOA.** *Environ Sci Technol* 2008, **42:**3969–3974.
60. Barton CA, Kaiser MA, Russell MH: **Partitioning and removal of perfluorooctanoate during rain events: the importance of physical-chemical properties.** *J Environ Monit* 2007, **9:**839–846.
61. European Chemicals Agency: *Opinions of the Committee for Risk Assessment on proposals for harmonised classification and labelling*. 2012. [http://echa.europa.eu/web/guest/opinions-of-the-committee-for-risk-assessment-on-proposals-for-harmonised-classification-and-labelling].
62. European Chemicals Agency: *RAC adopts 13 scientific opinions on the harmonised classification and labelling of industrial chemicals and pesticide active substances*. 2011. [http://echa.europa.eu/en/web/guest/view-article/-/journal_content/4709c09f-6dde-4aab-8d8c-4991b7622f45].
63. Fromme H, Tittlemier SA, Volkel W, Wilhelm M, Twardella D: **Perfluorinated compounds—exposure assessment for the general population in western countries.** *Int J Hyg Environ Health* 2009, **212:**239–270.
64. Olsen GW, Burris JM, Ehresman DJ, Froehlich JW, Seacat AM, Butenhoff JL, *et al*: **Half-life of serum elimination of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in retired fluorochemical production workers.** *Environ Health Perspect* 2007, **115:**1298–1305.
65. Trudel D, Horowitz L, Wormuth M, Scheringer M, Cousins IT, Hungerbuhler K: **Estimating consumer exposure to PFOS and PFOA.** *Risk Anal* 2008, **28:**251–269.
66. European Food Safety Authority: **Results of the monitoring of perfluoroalkylated substances in food in the period 2000–2009.** *EFSA Jounal* 2011, **09:**2016–2040.
67. Stahl T, Heyn J, Thiele H, Huther J, Failing K, Georgii S, Brunn H: **Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plants.** *Arch Environ Contam Toxicol* 2009, **57:**289–298.
68. Vestergren R, Cousins IT: **Tracking the pathways of human exposure to perfluorocarboxylates.** *Environ Sci Technol* 2009, **43:**5565–5575.
69. Lange FT, Wenz M, Schmidt CK, Brauch HJ: **Occurrence of perfluoroalkyl sulfonates and carboxylates in German drinking water sources compared to other countries.** *Water Sci Technol* 2007, **56:**151–158.
70. Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, De Voogt P, Jensen AA, Kannan K, Mabury SA, van Leeuwen SP: **Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins.** *Integr Environ Assess Manag* 2011, **7:**513–541.
71. Shoeib M, Harner T, Wilford BH, Jones KC, Zhu J: **Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: occurrence, partitioning, and human exposure.** *Environ Sci Technol* 2005, **39:**6599–6606.
72. Haug LS, Huber S, Schlabach M, Becher G, Thomsen C: **Investigation on per- and polyfluorinated compounds in paired samples of house dust and indoor air from norwegian homes.** *Environ Sci Technol* 2011, **45:**7991–7998.
73. Ericson Jogsten I, Nadal M, Van Bavel B, Lindström G, Domingo JL: **Per- and polyfluorinated compounds (PFCs) in house dust and indoor air in Catalonia, Spain: Implications for human exposure.** *Environ Int* 2012, **39:**172–180.
74. Hanson M, Small J, Sibley P, Boudreau T, Brain R, Mabury S, Solomon K: **Microcosm Evaluation of the Fate, Toxicity, and Risk to Aquatic Macrophytes from Perfluorooctanoic Acid (PFOA).** *aect* 2005, **49:**307–316.
75. Wang N, Szostek B, Buck RC, Folsom PW, Sulecki LM, Capka V, Berti WR, Gannon JT: **Fluorotelomer alcohol biodegradation-direct evidence that perfluorinated carbon chains breakdown.** *Environ Sci Technol* 2005, **39:**7516–7528.

76. Meesters RJ, Schroeder HF: **Perfluorooctane sulfonate—a quite mobile anionic anthropogenic surfactant, ubiquitously found in the environment.** *Water Sci Technol* 2004, **50:**235–242.
77. Schröder HF: **Determination of fluorinated surfactants and their metabolites in sewage sludge samples by liquid chromatography with mass spectrometry and tandem mass spectrometry after pressurised liquid extraction and separation on fluorine-modified reversed-phase sorbents.** *J Chromatogr A* 2003, **1020:**131–151.
78. Liou JS, Szostek B, Derito CM, Madsen EL: **Investigating the biodegradability of perfluorooctanoic acid.** *Chemosphere* 2010, **80:**176–183.
79. Conder JM, Hoke RA, De WW, Russell MH, Buck RC: **Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds.** *Environ Sci Technol* 2008, **42:**995–1003.
80. Martin JW, Mabury SA, Solomon KR, Muir DC: **Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (Oncorhynchus mykiss).** *Environ Toxicol Chem* 2003, **22:**196–204.
81. Martin JW, Mabury SA, Solomon KR, Muir DC: **Dietary accumulation of perfluorinated acids in juvenile rainbow trout (Oncorhynchus mykiss).** *Environ Toxicol Chem* 2003, **22:**189–195.
82. Quinete N, Wu Q, Zhang T, Yun SH, Moreira I, Kannan K: **Specific profiles of perfluorinated compounds in surface and drinking waters and accumulation in mussels, fish, and dolphins from southeastern Brazil.** *Chemosphere* 2009, **77:**863–869.
83. Morikawa A, Kamei N, Harada K, Inoue K, Yoshinaga T, Saito N, Koizumi A: **The bioconcentration factor of perfluorooctane sulfonate is significantly larger than that of perfluorooctanoate in wild turtles (Trachemys scripta elegans and Chinemys reevesii): an Ai river ecological study in Japan.** *Ecotoxicol Environ Saf* 2005, **65:**14–21.
84. Müller CE, De Silva AO, Small J, Williamson M, Wang X, Morris A, Katz S, Gamberg M, Muir DC: **Biomagnification of perfluorinated compounds in a remote terrestrial food chain: Lichen-Caribou-Wolf.** *Environ Sci Technol* 2011, **45:**8665–8673.
85. Houde M, Bujas TA, Small J, Wells RS, Fair PA, Bossart GD, Solomon KR, Muir DC: **Biomagnification of perfluoroalkyl compounds in the bottlenose dolphin (Tursiops truncatus) food web.** *Environ Sci Technol* 2006, **40:**4138–4144.
86. Butt CM, Mabury SA, Kwan M, Wang X, Muir DC: **Spatial trends of perfluoroalkyl compounds in ringed seals (Phoca hispida) from the Canadian Arctic.** *Environ Toxicol Chem* 2008, **27:**542–553.
87. Martin JW, Whittle DM, Muir DC, Mabury SA: **Perfluoroalkyl contaminants in a food web from Lake Ontario.** *Environ Sci Technol* 2004, **38:**5379–5385.
88. Tomy GT, Pleskach K, Ferguson SH, Hare J, Stern G, Macinnis G, Marvin CH, Loseto L: **Trophodynamics of some PFCs and BFRs in a western Canadian Arctic marine food web.** *Environ Sci Technol* 2009, **43:**4076–4081.
89. Fromme H, Mosch C, Morovitz M, Alba-Alejandre I, Boehmer S, Kiranoglu M, Faber F, Hannibal I, Genzel-Boroviczeny O, Koletzko B: **Volkel W*I*: Pre- and postnatal exposure to perfluorinated compounds (PFCs).** *Environ Sci Technol* 2010, **44:**7123–7129.
90. Hurley MD, Andersen MPS, Wallington TJ, Ellis DA, Martin JW, Mabury SA: **Atmospheric chemistry of perfluorinated carboxylic acids: reaction with OH radicals and atmospheric lifetimes.** *J Phys Chem A* 2004, **108:**615–620.
91. Kelly BC, Gobas FAPC, McLachlan MS: **Intestinal absorption and biomagnification of organic contaminants in fish, wildlife, and humans.** *Environ Toxicol Chem* 2004, **23:**2324–2336.
92. Kelly BC, Ikonomou MG, Blair JD, Morin AE, Gobas FAPC: **Food web-specific biomagnification of persistent organic pollutants.** *Science* 2007, **317:**236–239.
93. Arp HP, Niederer C, Goss KU: **Predicting the partitioning behavior of various highly fluorinated compounds.** *Environ Sci Technol* 2006, **40:**7298–7304.
94. Wang Z, MacLeod M, Cousins IT, Scheringer M, Hungerbühler K: **Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs).** *Environ Chem* 2011, **8:**389–398.
95. Webster E, Ellis DA: **Equilibrium modeling: A pathway to understanding observed perfluorocarboxylic and perfluorosulfonic acid behavior.** *Environ Toxicol Chem* 2011, **30:**2229–2236.
96. Gobas FAPC, de Wolf W, Burkhard LP, Verbruggen E, Plotzke K: **Revisiting bioaccumulation criteria for POPs and PBT assessments.** *Integr Environ Assess Manag* 2009, **5:**624–637.
97. Kelly BC, Ikonomou MG, Blair JD, Surridge B, Hoover D, Grace R, Gobas FAPC: **Perfluoroalkyl contaminants in an Arctic marine food web: trophic magnification and wildlife exposure.** *Environ Sci Technol* 2009, **43:**4037–4043.
98. Tomy GT, Budakowski W, Halldorson T, Helm PA, Stern GA, Friesen K, Pepper K, Tittlemier SA, Fisk AT: **Fluorinated organic compounds in an eastern Arctic marine food web.** *Environ Sci Technol* 2004, **38:**6475–6481.
99. Lau C, Anitole K, Hodes C, Lai D, Pfahles-Hutchens A, Seed J: **Perfluoroalkyl acids: a review of monitoring and toxicological findings.** *Toxicol Sci* 2007, **99:**366–394.
100. Emmet EA, Shofer FS, Zhang H, Freemann D, Desai C, Shaw LM: **Community exposure to perfluorooctanoate: relationships between serum concentrations and exposure sources.** *J Occup Environ Med* 2006, **48:**759–770.
101. Wilhelm M, Kraft M, Rauchfuss K, Hölzer J: **Assessment and management of the first German case of a contaminatoon with perfluorinated compounds (PFC) in the REgion Sauerland, North Rhine-Westphalia.** *J Toxicol Environ Health A* 2008, **71:**725–733.
102. Freberg BI, Haug LS, Olsen R, Daae HL, Hersson M, Thomsen C, Thorud S, Becher G, Molander P, Ellingsen DG: **Occupational exposure to airborne perfluorinated compounds during professional ski waxing.** *Environ Sci Technol* 2010, **44:**7723–7728.
103. Nilsson H, Karrman A, Westberg H, Rotander A, Van BB, Lindstrom G: **A time trend study of significantly elevated perfluorocarboxylate levels in humans after using fluorinated ski wax.** *Environ Sci Technol* 2010, **44:**2150–2155.
104. Nilsson H, Karrman A, Rotander A, Van BB, Lindstrom G, Westberg H: **Inhalation exposure to fluorotelomer alcohols yield perfluorocarboxylates in human blood?** *Environ Sci Technol* 2010, **44:**7717–7722.
105. Haug LS, Thomsen C, Becher G: **Time trends and the influence of age and gender on serum concentrations of perfluorinated compounds in archived human samples.** *Environ Sci Technol* 2009, **43:**2131–2136.
106. Haug LS, Huber S, Becher G, Thomsen C: **Characterisation of human exposure pathways to perfluorinated compounds—Comparing exposure estimates with biomarkers of exposure.** *Environ Int* 2011, **37:**687–693.
107. Brede E, Wilhelm M, Göen T, Müller J, Rauchfuss K, Kraft M, Hölzer J: **Two-year follow-up biomonitoring pilot study of residents'and controls' PFC plasma levels after PFOA reduction in public water system in Arnsberg, Germany.** *Int J Hyg Environ Health* 2010, **213:**217–223.
108. Lahl U, Hawxwell KA: **REACH–the new European chemicals law.** *Environ Sci Technol* 2006, **40:**7115–7121.

doi:10.1186/2190-4715-24-16
Cite this article as: Vierke *et al.*: Perfluorooctanoic acid (PFOA) — main concerns and regulatory developments in Europe from an environmental point of view. *Environmental Sciences Europe* 2012 **24**:16.

Appendix B - Overview of articles included in this cumulative Ph.D. thesis

(in accordance with the guideline for cumulative dissertations in Sustainability Science [January 2012], in the following termed "the guideline")

Title of Ph.D. thesis:

Environmental Mobility of Short Chain Perfluoroalkyl Carboxylic Acids – Partition Behaviour and Resulting Environmental Concern

Papers included:

[1] Lena Vierke, Lutz Ahrens, Mahiba Shoeib, Wolf-Ulrich Palm, Eva M. Webster, David A. Ellis, Ralf Ebinghaus, Tom Harner (2013): *In situ* air-water and particle-water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant. Chemosphere 92, 941–948. DOI: 10.1016/j.chemosphere.2013.02.067.

Additional material

Lena Vierke, Lutz Ahrens, Mahiba Shoeib, Wolf-Ulrich Palm, Eva M. Webster, David A. Ellis, Ralf Ebinghaus, Tom Harner (2013): Response to comment "*In situ* air-water and particle-water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant". Chemosphere 93, 2007, DOI: 10.1016/j.chemosphere.2013.05.008.

[2] Lena Vierke, Axel Möller, Sondra Klitzke (2013): Fate of per- and polyfluoralkyl compounds in a water-saturated sediment column investigated under near-natural conditions. Environmental Pollution 186, 7–13. http://dx.doi.org/10.1016/j.envpol.2013.11.011.

[3] Lena Vierke, Lutz Ahrens, Mahiba Shoeib, Eric J. Reiner, Rui Guo, Wolf-Ulrich Palm, Ralf Ebinghaus, Tom Harner (2011): Air concentrations and particle-gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant. Environmental Chemistry 8, 363–371. DOI: 10.1071/EN10133.

[4] Lena Vierke, Urs Berger, Ian T. Cousins (2013): Estimation of the acid dissociation constant of perfluoroalkyl carboxylic acids through an experimental investigation of their water-to-air transport. Environmental Science and Technology 47, 11032–11039. DOI: 10.1021/es402691z.

[5] Lena Vierke, Claudia Staude, Annegret Biegel-Engler, Wiebke Drost, Christoph Schulte (2012): Perfluorooctanoic acid (PFOA) - main concerns and regulatory developments in Europe from an environmental point of view. Environmental Sciences Europe 24, 16–27. www.enveurope.com/content/24/1/16.

Authors' contributions to the articles and articles publication status (according to §16 of the guideline):

#	Short title	Specific contributions of all authors	Author status	Weighting factor	Publication status	Conference contributions
[1]	Air-water and particle-water partitioning WWTP	LV, TH, DE, EW, WUP: idea LV, TH, LA: conception of the study LV, LA, MS: sampling LV, LA, MS: sample extraction and analysis LV, LA, TH, DE, EW, WUP, RE evaluation of results LV: manuscript preparation and writing LA, TH, DE, EW, WUP, RE, MS: comments on manuscript	Co-author with predominant contribution	1.0	Published in Chemosphere (IF 3.137, SJR 1.554)	DIOXIN 2011*
[2]	Sediment-water partitioning enclosure	LV, SK: idea LV, SK, AM: conception LV, SK: sampling LV, AM: sample extraction and analysis LV, SK: evaluation and interpretation of data LV: manuscript preparation and writing SK, AM: comments on manuscript	Co-author with predominant contribution	1.0	Published in Environmental Pollution (IF 3.730, SJR 1.763)	YES 2013 SETAC World 2012

[3]	Particle-gas partitioning WWTP	LV, MH, TH, LA: Idea LV, TH, LA, RE, WUP: Conception of the study LV, MH, LA: sampling LV, MH, LA: sample extraction LV, MH, LA, ER, RG: sample analysis LV, LA, TH, WUP, RE, ER: data evaluation LV: manuscript preparation and writing LA, MS, RG,TH, WUP, RE, ER: comments on manuscript	Co-author with predominant contribution	1.0	Published in Environmental Chemistry (IF 2.652, SJR 1.060)	GDCH 2010 PFASs Workshop 2011 SETAC NA 2010[†]
[4]	pK_a via water-to-air transport	LV, UB, IC: idea and conception of study LV, UB: sampling and analysis LV, UB, IC: evaluation of results LV, IC: modelling of results LV: manuscript preparation and writing UB, IC: comments on manuscript	Co-author with predominant contribution	1.0	Published in Environmental Science and Technology (IF 5.257, SJR 2.665)	DIOXIN 2013 PFASs Workshop 2013

[5]	PFOA concerns and regulatory develop-ments	LV, ABE, CS: conception of the study LV, ABE, CSt: literature review LV, ABE, CS: regulatory strategy LV, ABE, CSt, WD: assessment LV: manuscript preparation and writing ABE, CSt, WD, CS: comments on manuscript	Co-author with equal contribution	1.0	Published in Environmental Sciences Europe (IF not available, SJR 0.234)	ICCE 2011[†] PFASs Workshop 2012 PFASs Workshop 2013
Sum:				5.0		

Explanations

Specific contributions of all authors

ABE = Annegret Biegel-Engler
AM = Axel Möller
CS = Christoph Schulte
CSt = Claudia Staude
DE = David A. Ellis
ER = Eric Reiner
EW = Eva M. Webster
IC = Ian T. Cousins
LA = Lutz Ahrens
LV = Lena Vierke
MS = Mahiba Shoeib
RE = Ralf Ebinghaus
RG = Rui Guo
SK = Sondra Klitzke
TH = Tom Harner
UB = Urs Berger
WD = Wiebke Drost
WUP = Wolf-Ulrich Palm

Author status

according to §12b of the guideline:
Single author [Allein-Autorenschaft] = Own contribution amounts to 100%.
Co-author with predominant contribution [Überwiegender Anteil] = Own contribution is greater than the individual share of all other co-authors and is at least 35%.
Co-author with equal contribution [Gleicher Anteil] = (1) own contribution is as high as the share of other co-authors, (2) no other co-author has a contribution higher than the own contribution, and (3) the own contribution is at least 25%.
Co-author with important contribution [Wichtiger Anteil] = own contribution is at least 25%, but is insufficient to qualify as single authorship, predominant or equal contribution.
Co-author with small contribution [Geringer Anteil] = own contribution is less than 20%.

Appendix B – Overview of articles included in this cumulative Ph.D. thesis

Weighting factor

according to §14 of the guideline:

Single author [Allein-Autorenschaft]	1.0
Co-author with predominant contribution [Überwiegender Anteil]	1.0
Co-author with equal contribution [Gleicher Anteil]	1.0
Co-author with important contribution [Wichtiger Anteil]	0.5
Co-author with small contribution [Geringer Anteil]	0

Publication status

IF = Impact Factor 2012, published by Thomson Reuters

SJR = SCImago Journal Rank 2012, Scopus Journal Analyzer

Conference contributions (acronym, society, date, venue, website)

DIOXIN 2011* — 31st International Symposium on Halogenated Persistent Organic Pollutants, August 21-15, 2011, Brussels (Belgium), www.dioxin2011.org, e-poster presentation.

DIOXIN 2013 — 33rd International Symposium on Halogenated Persistent Organic Pollutants, August 25-30, 2013, Daegu (Korea), www.dioxin2013.org, oral presentation.

GDCH 2010 — Gemeinsame Jahrestagung 2010 der GDCh-Fachgruppe Umweltchemie und Ökotoxikologie und SETAC German-Language Branch e.V., September 6-9, 2010, Dessau-Roßlau (Germany), oral presentation.

ICCE 2011† — International Conference on Chemistry and the Environment, September 11-15, Zurich (Switzerland), www.icce2011.org, oral presentation by co-author.

PFASs Workshop 2011 — 3rd International Workshop Anthropogenic Perfluorinated Compounds, June 15-17, 2011, Amsterdam (The Netherlands), www.perfood.eu/Internationalworkshopperfluoros.html, poster presentation.

PFASs Workshop 2012 — 4th International Workshop Per- and Polyfluorinated Alkyl Substance, November 7-9, 2012, Idstein (Germany), www.hs-fresenius.de/die-hochschule/forschung/institute-for-analytical-research-ifar/pfas-workshops, oral presentation.

PFASs Workshop 2013 — 5th International Workshop Per- and Polyfluorinated Alkyl Substance, October 27-29, 2013, Helsingør (Denmark), www.nordfluoro-workshop-2013.de, poster presentations.

SETAC NA 2010† — SETAC North America 31st Annual Meeting, November 7-11, 2010, Portland (Oregon), www.portland.setac.org, oral presentation by co-author.

SETAC World 2012	6th SETAC World Congress / SETAC Europe 22nd Annual Meeting, May 20-24, Berlin (Germany), www.berlin.setac.eu, poster presentation.
YES 2013	3rd Young Environmental Scientist Meeting, February 11-13, 2013, Krakow (Poland), www.sac-online.eu/yes2013, oral presentation.

* Otto-Hutzinger Student Award

† Presentation by co-author

Declaration (according to § 16 of the guideline)

I avouch that all information given in this appendix is true in each instance and overall.

[Lena Vierke]