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Polyfluorinated compounds in effluents of waste water treatment plants and surface water along the River Elbe, Germany

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Abstract

Polyfluorinated compounds (PFCs) were investigated in WWTP effluents and surface water along the River Elbe collected in 2007. Concentrations of various PFCs, including C_4-C_8 perfluorinated sulfonates (PFSAs), C_6 and C_8 perfluorinated sulfinates, 6:2 fluorotelomer sulfonate, C_5-C_{13} perfluorinated carboxylic acids (PFCAs), C_4 and C_8 perfluoroalkyl sulfonamides and 6:2, 8:2 and 10:2 unsaturated fluorotelomercarboxylic acids were quantified. $\sum$PFC concentrations of the river water ranged from 7.6 to 26.4 ng L^{-1}, whereas $\sum$PFC concentrations of WWTP effluents were about five to ten times higher (30.5 to 266.3 ng L^{-1}), indicating that WWTPs are potential sources of PFCs into the marine environment. PFC patterns of different WWTP effluents varied depending on the origin of the waste water, whereas the PFC composition profile of the river water was relatively constant. In both kinds of water samples, perfluorooctanoic acid (PFOA) was the major PFC, whereas perfluorobutane sulfonate (PFBS) was the predominant PFSA.

1. Introduction

Recently scientific interest focussed on a new group of chemical substances, the polyfluorinated compounds (PFCs). The production of PFCs started in the 1950s, whereas substantial quantities of PFCs for commercial purposes have been produced in the last 20 years (Renner, 2001). PFCs are used in numerous products, for example in coatings on paper or textiles, or as fluoropolymer additives (Kissa, 2001). During production processes or after usage PFCs can be released into the environment (Prevedouros et al., 2006), where they have been found ubiquitously like in water (Yamashita et al., 2005), sediment (Higgins and Luthy, 2006), air (Jahnke et al., 2007) and organisms (Martin et al., 2003). Furthermore, the contamination of drinking water with PFCs can lead to a higher contamination of the surrounding population (Skutlarek et al., 2006; Hölzer et al., 2008). In the environment PFCs are persistent, bioaccumulative and have possibly adverse effects on humans and wildlife (Goecke-Flora and Reo, 1996; Austin et al., 2003; Martin et al., 2003; Joensen et al., 2009). Volatile precursors are able to undergo long-range transport via the atmosphere whereas ionic PFCs can be transported by ocean currents (Yamashita et al., 2005; Jahnke et al., 2007; Yamashita et al., 2008). As a result of these characteristics PFOS and precursor compounds are discussed as the first PFC group to be listed and banned as persistent organic pollutants (POPs) in the Stockholm Convention.

In general, neutral PFCs like perfluoroalkyl sulfonamides and fluorotelomer alcohols are less water-soluble and more volatile than perfluorinated acids. In the atmosphere as well as under aerobic conditions, e.g. in activated sludge, they can be degraded to perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonates (PFSAs) (Ellis et al., 2004; Martin et al., 2006; Rhoads et al., 2008). As final degradation products, PFCAs and PFSAs are very persistent in the environment (Kissa, 2001). Waste water treatment plants (WWTPs) seem to be not effective to remove PFCs from waste water, hence they are potential sources into the

river system and consequently the marine environment act as a sink for these compounds (Schultz et al., 2006b; Huset et al., 2008).

In 2001, the major producer of PFCs, the 3M Company, agreed to phase out production of perfluorooctyl sulfonyl fluoride (POSF), which is a major precursor of several PFCs like perfluorooctane sulfonate (PFOS) (Prevedouros et al., 2006). In addition, the European Union (EU) formed a directive in December 2006, which prohibits the general use of PFOS in June 2008 (European Parliament and Council). But there is still a growing demand on substances with the unique properties of PFCs, thus other PFCs are replacing PFOS.

The aim of the present study was the investigation of waste water treatment plant effluents and surface water along the River Elbe, Germany. The analytical method include 32 ionic PFCs (PFCAs, PFSAs, perfluorinated sulfinates (PFSiAs), fluorotelomercarboxylic acids (FTCAs) and unsaturated fluorotelomercarboxylic acids (FTUCAs)) as well as 7 neutral 'precursor' PFCs (perfluoroalkyl sulfonamides, perfluoroalkyl sulfonamidoethanols). This study provides information on the discharge of PFCs from WWTP effluents and their impact on the PFC load of the River Elbe. Furthermore, potential sources of PFCs along the River Elbe were investigated from its estuary mouth until approximately 120 km upstream. In addition, the impact of the EU directive and/or the phasing out of the POSF production by 3M on the PFC concentration level was investigated by the comparison of our results with two earlier studies from 2003 and 2006 in the River Elbe (Caliebe et al., 2004; Ahrens et al., 2009).

2. Methods

2.1 Sample collection

Effluent samples from 9 WWTPs along of the River Elbe from Lauenburg to Cuxhaven, Germany, were taken from May 29th to 31st 2007 (A to I in Fig. 1). The major WWTP (D) is treating waste water of about 2.2 million population equivalents (PEs), while the smallest one

covers about 14,000 PEs (detailed information see Table 1). One litre water samples in duplicate were taken in glass bottles, filtered over 1.2 μm glass fibre filters (GFF) and stored at 4°C.

In June 2007 one litre water samples were taken midstream at 15 locations of the River Elbe (1 to 15 in Fig. 1) on board of the research vessel "Ludwig Prandtl" using the water intake system of the ship (~1 m depth). Water samples were filtered subsequently (1.2 μm, GFF) on board and stored in glass bottles at 4°C until analysis (detailed information see Table S-1 in the Supporting Information (SI)).

2.2 Sample preparation and analysis

The standards used in this study are listed in Table S-2 in the SI. Methanol (SupraSolv), acetonitrile (LiChrosolv), ammonium hydroxide (25 % for analysis), formic acid (98 – 100 % suprapure) and ammonium acetate were purchased from Merck (Darmstadt, Germany).

For the determination of PFCs in all water samples solid phase extraction (SPE) described by Taniyasu et al. (2005) with some modifications was used (Ahrens et al., 2009). Prior to the extraction, the samples were spiked with 100 μL of a 0.1 μg mL^{-1} solution mix containing 19 mass-labelled internal standards (IS) (see Table S-2 in the SI). SPE was conducted with Oasis WAX cartridges (150 mg adsorbent, 6 cc, 30 μm, Waters) and a Teflon-free SPE-manifold supplied by Baker. Valves and tubes were made of polypropylene. The cartridges were preconditioned with 5 mL methanol and equilibrated with 5 mL Millipore water and then loaded with the water samples with a flow rate of approximately 3 drops per second. After loading the cartridges were washed with 5 mL Millipore water containing 0.1 % formic acid and dried using vacuum. Afterwards the cartridges were eluted by 14 mL acetonitrile followed by 5 mL methanol containing 0.1 % ammonium hydroxide. The combined extracts were concentrated using a rotary evaporator under a gentle stream of nitrogen to 150 μL.

Finally, the injection standard (InjS) N-deuterioethylperfluoro-1-octanesulfonamidoacetic acid (d$_5$-EtFOSAA) was added (50 µL of a 0.4 µg mL^{-1} solution).

A HP 1100 high performance liquid chromatography system (HPLC) by Agilent Technologies was used for separation. A Phenomenex Synergi Hydro RP 80A column was applied with a suitable guard column (Phenomenex Synergi 2 µ Hydro RP Mercury, 20 x 2 mm, 2 micron). Millipore water and methanol, each with 10 mM ammonium acetate as an ionisation aid, were used as mobile phases. The acquisition time was 40 minutes with a prior 7 minutes equilibration step. The gradient started with 30 % methanol, then increased to 70 % over 3 min, continuously increased to 90 % over 26 min and then to 100 % over 2 min. The gradient of 100 % methanol was held over 7 min and then decreased during the last 2 min to 30 %. The flow rate was set to 200 µL min^{-1} and 10 µL of the sample was injected. Prior to injection, the needle was rinsed with methanol. The temperature of the column oven was kept constant at 30 °C. Modifications of the HPLC system were made as described elsewhere (Yamashita et al., 2004) to eliminate instrumental blank contamination.

Detection and quantification of the PFCs were carried out by an API 3000 triple-quadrupole mass spectrometer by Applied Biosystems/MDS SCIEX with an electrospray ionisation source using negative ion mode. The mass spectrometer operated in a multiple reaction monitoring mode (MRM) with a dwell time of 15 msec. The ion spray voltage was set to -4,500 V and the temperature of the source block to 300°C. Nebuliser, curtain and collision gas were regulated to 14, 8 and 6 L min^{-1}, respectively. Details of the precursor and product ions for the mass spectrometer parameters are shown in Table S-3 in the SI. Quantification was performed by the internal standard method with an external calibration. A ten-point calibration curve (1, 5, 10, 25, 50, 100, 500, 1000, 2000 and 3000 pg injected) was used for calculation. For the compounds PFPS, PFNS, PFPeDA and PFHpDA no standards were available, thus these PFCs were calculated from the calibrations of corresponding substances with plus and minus one carbon atom in the carbon chain. For peak integration

only the main peak of a compound was used. The isomers were not included in the peak integration, because of the lack of standards.

2.3 Blanks, instrument detection limits, method quantification limits and recoveries

No instrumental blank contaminations were detected. All method blanks for the river and WWTP samples were below the method quantification limits (MQL). The instrument detection limits (IDLs) and method quantification limits (MQL) were calculated with the signal to noise ratio (S/N) of 3 and 10, respectively. The IDL ranged from 0.11 pg (PFDSi) to 4.50 pg absolute (FDEA) and the MQLs ranged from 0.004 (PFUnDA) to 0.5 ng L^{-1} (PFBS) (see detailed information in Table S-4 in the SI).

For the correction of sample preparation losses 19 mass-labelled IS were used. There was no appropriate IS for PFOSA, thus PFOSA remained uncorrected. d_5-EtFOSAA was applied as InjS to correct volume differences and to verify the instrumental performance. The mean recovery of the IS ranged from 66 % ($^{13}C_2$-PFHxA) to 117 % ($^{13}C_2$-FDUEA) for the WWTPs and from 40 % (d_3-MeFOSA) to 91 % ($^{13}C_4$-PFOSi) for the surface water samples of the River Elbe. Detailed information about the allocation of the IS to the target analytes and the IS recoveries in the samples is given in Tables S-4 to S-6 in the SI.

3. Results and Discussion

3.1 PFC concentrations and compositions in effluents of WWTPs

Overall, 21 substances of 39 analysed compounds were detected in WWTP effluents. The $\sum$PFC discharge of each WWTP and their composition profiles are shown in Fig. 2, whereas individual PFC concentrations are listed in Table 2. The $\sum$PFC concentrations in WWTP effluents ranged from 30 ng L^{-1} (WWTP I) to 266 ng L^{-1} (WWTP B). The composition profile in the WWTP B to D and F to I were relatively similar, whereas PFCAs were the major group with approximately 70 % of the $\sum$PFC amount. WWTP A and E had a different composition,

where 6:2 FTS and PFOS dominated, respectively. In 6 of the 9 WWTPs the concentrations of the PFSAs were 2-7 times lower than the concentrations of the PFCAs, in WWTP B they were even lower by a factor of 25 whereas in WWTP A and E the amounts of PFSAs were about two times higher than the amounts of PFCAs.

PFBS and PFHxS were detected in all WWTP effluents. Concentrations of PFBS varied between 1.7 ng L^{-1} (WWTP B) and 25.9 ng L^{-1} (WWTP A). PFOS was not found in WWTP G and H, but the PFOS concentration in WWTP E was the highest concentration of all compounds measured in this survey (82.2 ng L^{-1}). In the remaining WWTPs (A to F and I) PFOS concentrations ranged from 0.4 to 5.8 ng L^{-1}. 6:2 FTS had high concentrations at WWTP A and D (37.9 and 32.8 ng L^{-1}, respectively), while it was not detected in WWTP B, C, G and I and only low concentrated in WWTP E, F and H (below MQL to 1.6 ng L^{-1}). Other PFSAs were found at low concentration levels with a maximum concentration for PFPS (2.9 ng L^{-1}; WWTP A), PFHxS (6.3 ng L^{-1}; WWTP G) and PFHpS (0.4 ng L^{-1}; WWTP I). PFHxSi and PFOSi were detected at all WWTPs in concentrations ranging from 0.1 to 0.9 ng L^{-1} (PFHxSi) and from 0.07 to 1.1 ng L^{-1} (PFOSi). PFOSi was proposed to degrade to PFOS in activated sludge (Rhoads et al., 2008).

C_5 to C_{10} PFCAs were found in all WWTP effluents. PFOA was the predominant substance with concentrations ranging from 12.3 ng L^{-1} to 77.6 ng L^{-1}. The highest ∑PFC concentration was found at WWTP B. Additionally PFUnDA, PFDoDA and PFTriDA were detected sporadically, but only PFUnDA was detected with a noteworthy concentration at WWTP B (8.7 ng L^{-1}). The three potential precursors, PFOSA, MeFBSA and MeFBSE, were found in all WWTPs, whereas PFOSA can degrade to PFOS (Rhoads et al., 2008) and the C_4 compounds MeFBSA and MeFBSE could possibly degrade to the C_4 homologues of PFCAs and PFSAs (D'eon et al., 2006; Martin et al., 2006).

The origin of the WWTP influent (domestic or industrial) was estimated by the operating WWTP company. WWTP C, F, G, H and I were not influenced by industrial sewage water,

on the other hand WWTP A, B, D and E have rather high industrial influences with about 20 % to 40 % industrial/commercial waste water. In average, ∑PFC concentrations of these four WWTP effluents were more than 4 times higher (171 ng L^{-1}) than the effluents of WWTPs without industrial waste water parts (36 ng L^{-1}). Thus it is presumed that industrial or commercial waste water had an influence on the PFC contamination level and profile, according to a previous study (Sinclair and Kannan, 2006). The waste water of a big textile-service company, located close to WWTP A, might be responsible for the high concentrations of 6:2 FTS and MeFBSA in the effluent. Whereas a carpet factory located close to WWTP B might be responsible for the increased PFCA concentrations, because PFCs are used as coatings on textiles and carpets (Kissa, 2001). The mean ∑PFC concentration in WWTP effluents (~99 ng L^{-1}) were about 5 times higher, compared to the mean concentrations of river water samples (~19 ng L^{-1}). Therefore, WWTPs are potential sources of PFCs to the marine environment.

In comparison to this study, Schultz et al. (2006a) found similar amounts in the effluents of ten WWTPs in North America depending on the composition of the waste water (PFOA: 2.5-97 ng L^{-1}, PFOS: 1.1-130 ng L^{-1}). Another study reported higher concentrations in six WWTPs (USA), especially of PFOA (maximum values 850-1050 ng L^{-1}), probably influenced by industrial wastewater (Sinclair and Kannan, 2006). Boulanger et al. (2005) investigated a WWTP in Iowa City, USA, for PFOA and PFOS. The specified effluent concentrations were 22 ng L^{-1} for PFOA and 26 ng L^{-1} for PFOS. The concentrations found by Bossi et al. (2008) in ten Danish WWTPs were generally in the same range as the concentrations in this study, except for one industrial WWTP which showed very high PFOS concentrations of 336-1115 ng L^{-1}.

PFCs discharges from the WWTPs into the River Elbe were roughly estimated from the PFC concentration and mean water discharge per day of the effluent and river flow, respectively (PFCs discharge = PFC concentration * water discharge) (see Fig. 2). Although

the effluent of WWTP B had the highest PFC concentrations per litre its contribution to the environment was rather low (1.6 g day^{-1}) due to its low effluent volume. WWTP D and E had the main portion of PFC contamination of the River Elbe with 55.6 and 11.6 g day^{-1}, respectively. The remaining 6 WWTPs had a combined discharge of 3.8 g day^{-1} into the River Elbe (see Fig. 2). The total discharges per year were estimated assuming that the concentrations were stable throughout the whole year. The samples were taken in a dry period with almost no precipitation, so the samples were not influenced by rain water. The total discharge of ∑PFCs from all nine WWTPs was approximately 26 kg per year based on a rough estimation, PFOA having the highest percentage (~47 %), followed by 6:2 FTS (~20 %), PFOS (~12 %) and PFBS (~5.5 %). WWTP D and E were responsible for approximately 95 % of the total discharge.

3.2 PFC concentrations and compositions in surface water of the River Elbe

The water samples of the River Elbe showed ∑PFC concentrations ranging from 7.6 ng L^{-1} at the estuary mouth (location 15) to 26.4 ng L^{-1} at Hamburg City (location 4). At all 15 sampling locations 17 PFCs were found, ten of them at each location (i.e. PFBS, PFHxS and PFOS of the PFSAs, C$_5$ to C$_{10}$ of the PFCAs and PFOSA) (see Table 3). The PFCAs were the major group with approximately 70 % of the ∑PFC amount. In all samples PFOA was the predominant substance with concentrations ranging from 2.8 ng L^{-1} (location 15) to 9.6 ng L^{-1} (location 6). PFHxA concentrations were the second highest after PFOA and ranged from 1.58 to 4.96 ng L^{-1}. PFOS concentrations varied between 0.5 ng L^{-1} (location 9) and 2.9 ng L^{-1} (location 6) and were mostly lower than PFBS concentrations (<MQL to 3.4 ng L^{-1}).

McLachlan et al. (2007) found similar concentrations of PFHpA, PFOA and PFNA in the River Elbe, whereas the concentration of PFHxA was three times higher. The highest PFOA concentration from other European rivers was detected in the River Po, Italy, with 200 ng L^{-1}

followed by the River Thames, England, with 23 ng L^{-1}. In 2006, in another study of the rivers Rhine, Ruhr and Moehne in Germany were found much higher ∑PFC concentrations of up to 100 ng L^{-1} (i.e. C$_4$ to C$_{12}$ PFCAs and PFBS, PFHxS and PFOS), except for some parts in which concentrations up to 43.3 µg L^{-1} were detected (Skutlarek et al., 2006). In addition, the concentration in the river Elbe is ~10 times lower than in the drinking water in the Ruhr area. These high concentrations were attributed to contaminated sewage sludge applied to neighbouring agricultural fields (Kröfges et al., 2007). In the year 2000, Hansen et al. (2002) analysed water samples of the Tennessee River near a fluorochemical manufacturing facility discharge and found PFOA and PFOS concentrations, which were up to 50 times higher than the concentrations in the River Elbe in this study. A recent study of So et al. (2007) showed comparable concentrations of PFCs in Chinese rivers, except for locations near Shanghai, where PFCs concentrations were significantly higher. In general, the PFC concentrations in surface water of the River Elbe were in the same range or lower than PFC concentrations of river water mentioned in the literature.

In Fig. 3 the mass flows of individual PFCs in the River Elbe are shown. For this estimation the single spot measurements of the water samples were used, which is a rough estimation assuming a constant mass flow over the day. While the mass flow of the ∑PFC at location 2 (approximately 120 km upstream) was 950 g day^{-1}, it decreased towards the estuary mouth to 312 g day^{-1}. The mass flow between location 1 and location 11 was relatively constant, whereas towards the estuary mouth (location 12 to 15) the decreasing mass flow of ∑PFC was accompanied by an increase of the conductivity (see Table S-1 in the SI), caused by mixing of the river water with North Sea water. The decrease in the mass flow of ∑PFC at location 10 could be due to dilution by the tributary 'Stör', which is the biggest tributary (21.7 m³ s^{-1} stream flow) in the investigated area. The higher values at locations 4, 6 and 11 can be explained by influences of different kinds of sources. Therefore, the locations 4 and 6 could be influenced by the discharge of the WWTPs D and E, respectively, which had the highest

discharges of all examined WWTPs (Fig. 2). Near the city of Brunsbüttel (between location 10 and 11) a large industrial park is located, consisting of a variety of chemical factories (i.e. petroleum, textile-colouring and polymer industries), which are equipped with own WWTPs. Hence the higher mass flow at location 11 might be caused by these factories, even though WWTP H (close to location 11) had only a low contribution with a discharge of 0.05 g day^{-1}.

In 2003, Caliebe et al. (2004) found PFOS and PFOA concentrations of about 20 ng L^{-1} in the River Elbe. In addition, they noticed a decrease of PFOS concentrations by approximately a factor of 10 from May to July. In 2006, a sampling campaign along the River Elbe resulted in two times higher PFC concentrations than during this sampling campaign in 2007 (Ahrens et al., 2009). In 2006, especially PFOS and PFOSA were detected in significantly higher concentrations (1.3 to 8.3 ng L^{-1} and 0.9 to 8.9 ng L^{-1}, respectively) than in 2007 (0.5 to 2.9 and 0.1 to 1.0 ng L^{-1}, respectively). The sampling campaign in the present study was done during a dry weather period. The River Elbe estuary stream flow in 2007 (474 m³ s^{-1}) was only the half of the mean flow in 2006. One possible explanation for the higher concentration levels in 2006 could be a runoff of PFCs from contaminated soil, as shown for the River Möhne and the River Ruhr, where PFCs were washed out by precipitation from contaminated soils applied to agricultural areas (Skutlarek et al., 2006). However, no contaminated soil has been observed along the River Elbe up to now. A second explanation could be that PFC contaminated rain water led directly to an increase of PFC concentration in the River Elbe. Scott et al. (2006) found total PFCA fluxes between 540 and 12 471 ng m^{-2} in precipitation. This could explain the higher concentrations of PFCAs in 2006 because the samples were taken during a wet weather period with an estuary stream flow of 916 m³ s^{-1}. The lower concentration levels of PFOS and PFOSA cannot be explained by the higher amount of rain water, because PFCAs were the dominating PFCs in precipitation (Taniyasu et al., 2008). The most likely and straightforward explanation for the low PFOS and PFOSA concentrations in 2007 could be the impact of the new EU directive, which regulates the general use of PFOS

and their derivates like PFOSA. Even though the use was not prohibited before July 2008, it might be possible that companies stopped using PFOS or switched to substitute compounds like the shorter chained PFBS or their precursors already before the directive came into effect (D'eon et al., 2006; Skutlarek et al., 2006). The reasons for using shorter chained substitutes are their lower toxicity and their lower bioaccumulation potential compared to longer chained PFCs (Lau et al., 2007).

Assuming that the concentrations found in this study were constant throughout the whole year and assuming that the concentrations measured at the surface were representative over the whole profile of the river, a rough estimation of the PFC mass flow reaching the German Bight through the River Elbe could be done. The long term mean water discharges of the River Elbe at the locations 1 and 11 were 752 and 812 $m^3 s^{-1}$, respectively (personal communication "ARGE Elbe"). Using these data the calculation of the annual $\sum$PFC discharge results in 480 kg per year (location 1) to 540 kg per year (location 11). McLachlan et al. (2007) estimated the annual discharge of C_6 to C_9 PFCAs with ~585 kg per year in the River Elbe, which is approximately two times higher than in this study (~294 kg per year for C_6 to C_9 PFCAs).

3.3 Conclusion

No significant relationship between $\sum$PFC concentrations and dissolved organic carbon (DOC) in WWTPs ($r^2 < 0.01$, see Fig. S-1 in the SI) and in surface water ($r^2 = 0.29$, see Fig. S-2 in the SI) was found, respectively. A positive relationship between sorption to sediment and TOC amount was found from Higgins and Luthy (2006), whereas the DOC may have a less influence on the distribution and concentration level of PFCs in the aquatic environment.

The mass flow of $\sum$PFC from the effluents of the WWTPs and the surface water along the River Elbe is shown in Fig. 4. Upstream Hamburg City (location 1) the $\sum$PFC mass flow was 729 g day^{-1}, whereas the mass flow increased to 964 g day^{-1} (location 4). This increase could

be caused by WWTPs C and D with a combined discharge of 56.3 g day^{-1}, which is about 24 % of the total increase (235 g day^{-1}). The lacking 76 % could originate from other point sources like industrial waste water effluents or diffuse sources from surface runoff, which were not covered in this study. An increasing $\sum$PFC mass flow was also observed between locations 5 and 6, whereas ~10 % could stem from WWTP E with a discharge of 11.6 g day^{-1}. The other WWTPs showed no influence on the mass flow along the River Elbe. However, the PFC composition profile in surface water in the River Elbe is relatively similar to the compositions of WWTP B to D and F to I. These results suggest that the PFC contamination in these WWTPs and the River Elbe were caused by similar sources, whereas WWTP A and E were influenced by other sources. However, the contamination in the river Elbe is relatively low in comparison to other European rivers (Skutlarek et al., 2006; McLachlan et al., 2007).

In further studies chemical substitutes of PFOS and PFOA should be investigated to see any production shifts to shorter chained or less fluorinated PFCs. Furthermore, it is recommended to use flow-proportional composite samples over a longer period (e.g., 24 h for 7 day, as described elsewhere (Huset et al., 2008)) to get a better estimation of the mass flow. In addition, to WWTPs, further sources are likely to exist which have not been identified yet. How to reduce the riverine discharge of PFCs into the marine ecosystem will be an important challenge for the future.

References

Ahrens, L., Plassmann, M., Xie, Z., Ebinghaus, R., 2009. Determination of polyfluoroalkyl compounds in water and suspended particulate matter in the River Elbe and North Sea, Germany. Front. Environ. Sci. Engin. China. 3, 151-170.

Austin, M.E., Kasturi, B.S., Barber, M., Kannan, K., Mohan Kumar, P.S., Mohan Kumar, S.M.J., 2003. Neuroendocrine effects of perfluorooctane sulfonate in rats. Environ. Health Perspect. 111, 1485-1489.

Bossi, R., Strand, J., Sortkjaer, O., Larson, M.M., 2008. Perfluorinated compounds in Danish wastewater treatment plants and aquatic environments. Environ. Intern. 34, 443-450.

Boulanger, B., Vargo , J., Schnoor, J.L., Hornbuckle, K., 2005. Evaluation of perfluorooctane surfactants in a wastewater treatment system and in a commercial surface protection product. Environ. Sci. Technol. 39, 5524-5530.

Caliebe, C., Gerwinski, W., Hühnerfuss, H., Theobald, N., 2004. Occurrence of perfluorinates organic acids in the water of the North Sea. Organohalogen Comp. 66, 4074-4078.

D'eon, J.C., Hurley, M.D., Wallington, T.J., Mabury, S.A., 2006. Atmospheric chemistry of n-methyl perfluorobutane sulfonamidoethanol, C4F9SO2N(CH3)CH2CH2OH: kinetics and mechanism of reaction with OH. Environ. Sci. Technol. 40, 1862-1868.

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

European Parliament and Council, **2006**. Directive 2006/122/ECOF.

Goecke-Flora, C.M., Reo, N.V., 1996. Influence of carbon chain length on the hepatic effects of perfluorinated fatty acids. A ^{19}F- and ^{31}P-NMR investigation. Chem. Res. Toxicol. 9, 689-695.

Hansen, K.J., Johnson, H.O., Eldridge, J.S., Butenhoff, J.L., Dick, L.A., 2002. Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River. Environ. Sci. Technol. 36, 1681-1685.

Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediment. 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 Perspect. 116, 651-657.

Huset, C.A., Chiaia, A.C., Barfosky, D.F., Jonkers, N., Kohler, H.-P.E., Ort, C., Giger, W., Field, J.A., 2008. Occurrence and mass flows of fluorochemicals in the Glatt Valley watershed, Switzerland. Environ. Sci. Technol. 42, 6369–6377.

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

Joensen, U.N., Bossi, R., Leffers, H., Jensen, A.A., Skakkebæk, N.E., Jørgensen, N., 2009. Do perfluoroalkyl compounds impair human semen quality? Environ. Health Perspec. in press, doi: 10.1289/ehp.0800517.

Kissa, E., 2001. Fluorinated surfactants and repellents. Marcel Dekker 97.

Kröfges, P., Skutlarek, D., Färber, H., Baitinger, C., Gödeke, I., Weber, R., 2007. PFOS/PFOA contaminated megasites in Germany polluting the drinking water supply of millions of people. Organohalogen Comp. 69, 877-880.

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

Martin, J.W., Ellis, D.A., Mabury, S.A., Hurley, M.D., Wallington, T.J., 2006. Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of n-ethyl perfluorobutanesulfonamide. Environ. Sci. Technol. 40, 864-872.

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

McLachlan, M.S., Holmstrom, K.E., Reth, M., Berger, U., 2007. Riverine discharge of perfluorinated carboxylates from the European continent. Environ. Sci. Technol. 41, 7260-7265.

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

Renner, R., 2001. Growing concern over perfluorinated chemicals. Environ. Sci. Technol., A-Pages 35, 154A-160A.

Rhoads, K.R., Janssen, E.M.-L., Luthy, R.G., Criddle, C.S., 2008. Aerobic biotransformation and fate of n-ethyl perfluorooctane sulfonamidoethanol (n-EtFOSE) in activated sludge. Environ. Sci. Technol. 42, 2873-2878.

Schultz, M.M., Barofsky, D.F., Field, J.A., 2006a. Quantitative determination of fluorinated alkyl substances by large-volume-injection liquid chromatography tandem mass spectrometry-characterization of municipal wastewaters. Environ. Sci. Technol. 40, 289-295.

Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F., Field, J.A., 2006b. Fluorochemical mass flows in a municipal wastewater treatment facility. Environ. Sci. Technol. 40, 7350-7357.

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

Skutlarek, D., Exner, M., Färber, H., 2006. Perfluorinated surfactants in surface and drinking waters. Environ. Sci. Pollut. Res. 13, 299-307.

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

Taniyasu, S., Kannan, K., So, M.K., Gulkowska, A., Sinclair, E., Okazawa, T., Yamashita, N., 2005. Analysis of fluorotelomer alchols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. J. Chromatogr. A 1093, 89-97.

Taniyasu, S., Kannan, K., Yeung, L.W.Y., Kwok, K.Y., Lam, P.K.S., Yamashita, N., 2008. Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2–C4) in precipitation by liquid chromatography–tandem mass spectrometry: comparison to patterns of long-chain perfluorinated acids (C5–C18). Anal. Chim. Acta. 619, 221-230.

Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Okazawa, T., Petrick, G., Gamo, T., 2004. Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-tandem mass spectrometry. Environ. Sci. Technol. 38, 5522-5528.

Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G., Gamo, T., 2005. A global survey of perfluorinated acids in oceans. Marine Poll. Bull. 51, 658-668.

Yamashita, N., Taniyasu, S., Petrick, G., Wei, S., Gamo, T., Lam, P.K.S., Kannan, K., 2008. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere 70, 1247-1255.
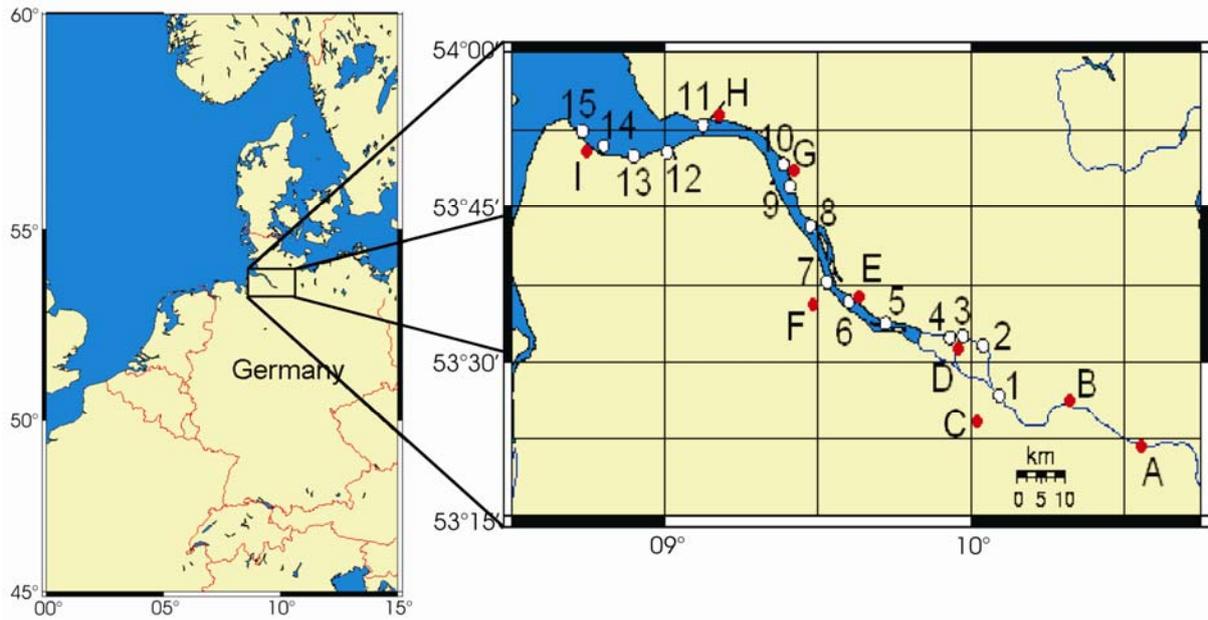
Fig. 1. Sampling locations for surface water samples (white dots with numbers) and at the effluents of waste water treatment plants (red dots with letters) along the River Elbe, Germany.
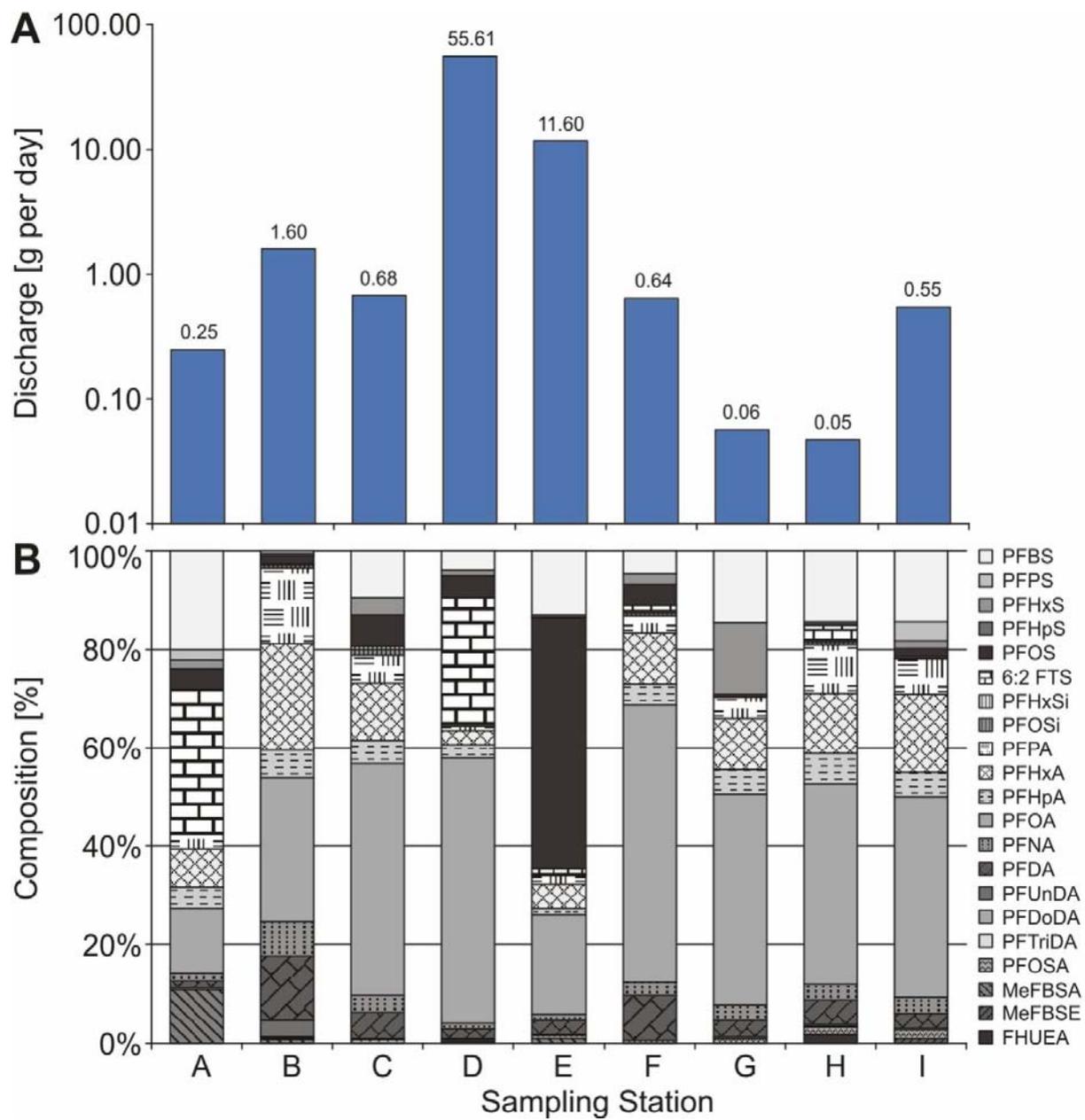
Fig. 2. A: Discharge of ∑PFCs in g per day by the effluents of waste water treatment plants (note: Logarithmic scale). B: Percentage composition of individual PFCs in effluents of waste water treatment plants.
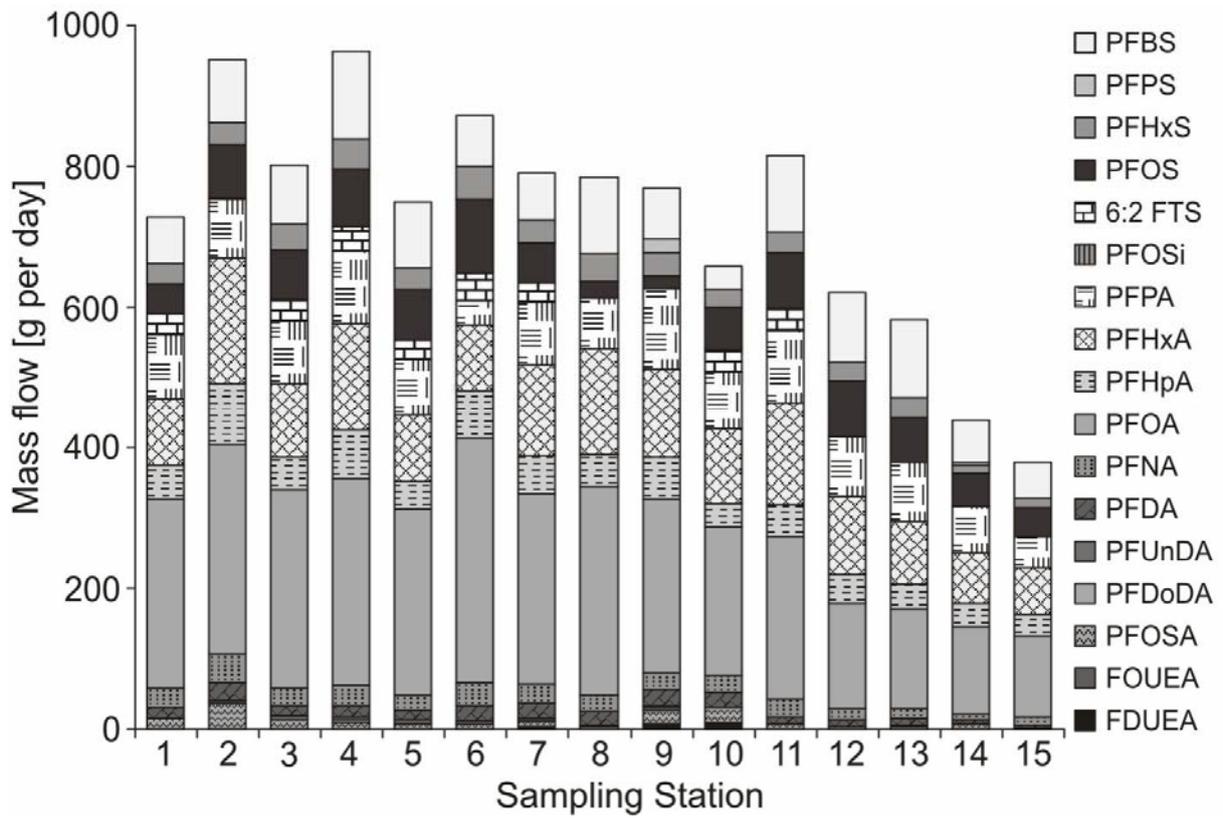
Fig. 3. Mass flow of individual PFCs in g per day in surface water along the River Elbe.
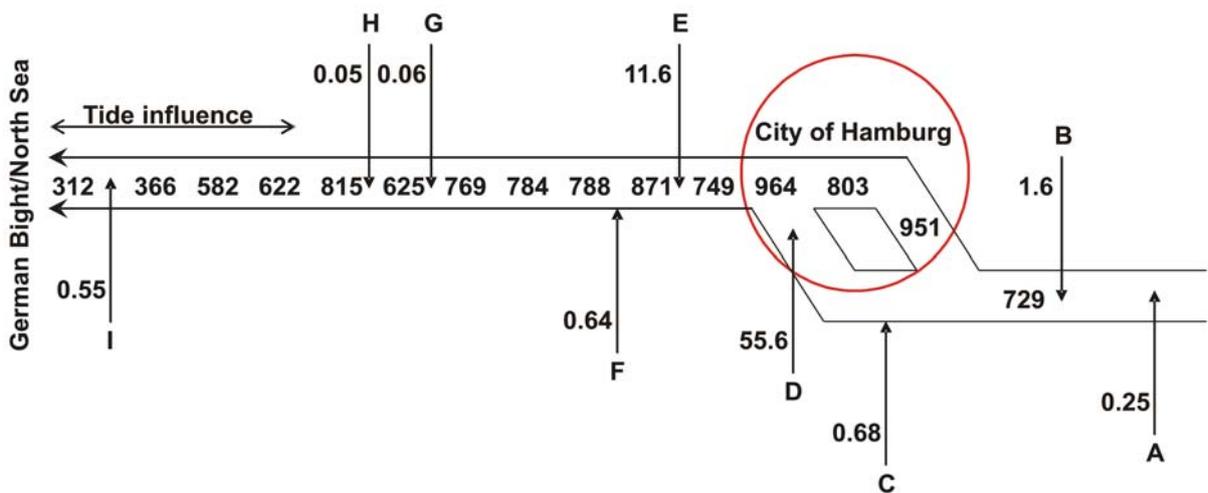
Fig. 4. Estimated mass flow of ∑PFCs in g per day of surface water and effluents of waste water treatment plants along the River Elbe, Germany.

Table 1

Sampling parameters of the waste water treatment plants

|	A	B	C	D	E	F	G	H	I
Population equivalents	25 000	45 000	90 000	2 200 000	650 000	150 000	14 000	20 000	400 000
Effluent volume [m³ day⁻¹]	1 900	6 000	17 000	432 000	72 000	13 200	1 285	1 000	18 000
Domestic waste water [%]	~60-70%	~60-70%	~100%	~80%	~65-70%	~100%	~100%	~100%	~100%
Industrial/commercial waste water [%]	~30-40%	~30-40%	~0%	~20%	~30-35%	~0%	~0%	~0%	~0%
Dissolved organic carbon [mg L⁻¹]	10.9	7.1	8.1	13.7	14.1	17.3	14.5	14.4	14.8
Particulate organic carbon [mg L⁻¹]	0.3	1.0	4.2	1.6	1.3	2.5	1.1	n.a.	0.6
Particulate matter [mg L⁻¹]	1.74	2.37	8.57	3.81	4.47	6.24	1.40	0.95	1.29
pH	7.0	7.3	6.9	7.4	7.0	7.4	8.0	7.1	7.7
Temperature [°C]	20.6	19.3	19.0	n.a.	18.9	20.1	15.8	16.6	24.7
Sampling date	20/06/07	29/05/07	31/05/07	31/05/07	29/05/07	07/06/07	29/05/07	29/05/07	07/06/07
Sampling time	09:45	09:45	10:30	08:00	11:35	11:00	13:30	14:15	13:30

n.a. = not available.

Table 2

Concentrations of PFCs in waste water treatment plant effluents in ng per litre [a]

Analyte	A	B	C	D	E	F	G	H	I
PFBS	25.9 ± 1.7	1.8 ± 0.2	3.8 ± 0.04	5.1 ± 0.4	20.9 ± 2.3	2.3 ± 0.4	6.3 ± 0.7	6.7 ± 0.6	4.4 ± 0.2
PFPS [b]	2.9 ± 0.003	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFHxS	2.1 ± 0.1	0.6 ± 0.04	1.4 ± 0.003	1.4 ± 0.2	0.8 ± 0.2	1.0 ± 0.2	6.3 ± 1.3	(0.3) ± 0.1	1.2 ± 0.1
PFHpS	(0.2) ± 0.04	<0.08	<0.08	<0.08	0.3 ± 0.01	<0.08	<0.08	<0.08	0.5 ± 0.1
PFOS	5.5 ± 0.6	4.7 ± 0.8	2.5 ± 0.7	5.8 ± 0.5	82.2 ± 6.5	2.1 ± 0.4	<0.06	<0.06	0.5 ± 0.1
PFHxSi	0.2 ± 0.03	0.9 ± 0.04	0.3 ± 0.02	0.1 ± 0.01	0.2 ± 0.01	0.1 ± 0.03	0.2 ± 0.01	0.2 ± 0.03	0.1 ± 0.04
PFOSi	0.3 ± 0.04	1.2 ± 0.04	0.5 ± 0.04	0.4 ± 0.002	0.3 ± 0.001	0.4 ± 0.002	0.1 ± 0.03	0.3 ± 0.01	0.1 ± 0.01
6:2 FTS	37.9 ± 2.5	<0.2	<0.2	32.8 ± 7.4	1.6 ± 0.8	(0.6) ± 0.2	<0.2	1.3 ± 0.2	<0.2
PFPA	3.6 ± 0.5	40.9 ± 4.5	2.2 ± 0.04	1.5 ± 0.01	2.8 ± 0.3	1.7 ± 0.1	1.9 ± 0.4	4.6 ± 0.2	2.2 ± 0.3
PFHxA	10.0 ± 0.1	57.4 ± 4.5	4.7 ± 0.1	3.7 ± 0.6	7.8 ± 0.2	5.0 ± 0.2	4.6 ± 0.1	5.8 ± 0.03	4.8 ± 0.5
PFHpA	5.7 ± 0.2	15.7 ± 1.1	2.0 ± 0.2	3.5 ± 0.2	2.3 ± 0.4	2.1 ± 0.1	2.2 ± 0.9	2.8 ± 0.03	1.6 ± 0.6
PFOA	16.9 ± 0.6	77.6 ± 0.3	18.7 ± 0.03	69.3 ± 6.2	32.5 ± 0.2	27.5 ± 2.0	18.6 ± 0.2	19.0 ± 0.7	12.3 ± 1.7
PFNA	2.0 ± 0.2	18.6 ± 0.7	1.4 ± 0.1	1.4 ± 0.1	2.1 ± 0.03	1.3 ± 0.1	1.4 ± 0.1	1.5 ± 0.2	1.0 ± 0.01
PFDA	1.9 ± 0.03	34.5 ± 2.8	2.1 ± 0.2	2.4 ± 0.3	4.4 ± 0.3	4.4 ± 0.1	1.4 ± 0.1	2.3 ± 0.1	0.9 ± 0.1
PFUnDA	<0.004	8.8 ± 2.0	0.1 ± 0.04	0.3 ± 0.04	0.3 ± 0.01	<0.004	0.2 ± 0.01	0.2 ± 0.004	0.1 ± 0.01
PFDoDA	(0.02) ± 0.01	0.5 ± 0.02	<0.01	0.1 ± 0.01	<0.01	<0.01	<0.01	0.1 ± 0.01	<0.01
PFTriDA	<0.02	0.4 ± 0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PFOSA	0.6 ± 0.1	0.6 ± 0.02	0.3 ± 0.02	0.5 ± 0.1	1.1 ± 0.1	0.3 ± 0.01	0.5 ± 0.03	0.7 ± 0.003	0.5 ± 0.002
MeFBSA	14.0 ± 0.4	2.1 ± 0.1	<0.2	<0.2	1.4 ± 0.1	<0.2	<0.2	<0.2	<0.2
MeFBSE	<0.1	<0.1	<0.1	0.5 ± 0.01	(0.1) ± 0.01	<0.1	<0.1	<0.1	0.3 ± 0.1
FHUEA	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	0.9 ± 0.2	<0.07
∑PFCs	**129.4 ± 7.0**	**266.3 ± 17.2**	**39.9 ± 1.5**	**128.7 ± 15.9**	**161.0 ± 11.3**	**48.1 ± 3.6**	**43.6 ± 3.7**	**46.2 ± 2.3**	**30.5 ± 3.7**

[a] values in brackets are between MDL and MQL and are not included in the sum concentrations. <x, below the respective MDL. [b] not available as standard.

Table 3

Concentrations of PFCs in surface water of the River Elbe in ng per litre

Analyte	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
PFBS	1.8 ± 0.2	2.4 ± 0.2	2.3 ± 0.2	3.4 ± 0.3	2.5 ± 0.2	2.0 ± 0.4	1.8 ± 0.2	2.9 ± 0.4	2.0 ± 0.4	(0.9) ± 1.2	2.8 ± 0.7	2.5 ± 0.8	2.8 ± 0.8	(1.5) ± 0.1	(1.2) ± 0.6
PFPS [b]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.5 ± 0.03	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFHxS	0.85 ± 0.2	0.9 ± 0.1	1.0 ± 0.2	1.2 ± 0.1	0.8 ± 0.002	1.3 ± 0.03	0.9 ± 0.03	1.1 ± 0.04	0.9 ± 0.1	0.7 ± 0.1	0.7 ± 0.03	0.7 ± 0.02	0.8 ± 0.2	(0.3) ± 0.01	(0.3) ± 0.1
PFOS	1.16 ± 0.2	2.1 ± 0.03	1.9 ± 0.04	2.2 ± 0.1	2.0 ± 0.1	2.9 ± 0.3	1.5 ± 0.7	0.6 ± 0.1	0.5 ± 0.3	1.6 ± 1.1	2.1 ± 0.2	2.0 ± 0.1	1.6 ± 0.0003	1.2 ± 0.03	1.0 ± 0.2
PFOSi	<0.01	0.1 ± 0.004	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
6:2 FTS	0.83 ± 0.2	<0.2	0.9 ± 0.03	0.96 ± 0.2	0.8 ± 0.1	1.1 ± 0.4	0.8 ± 0.1	<0.2	<0.2	0.8 ± 0.03	0.8 ± 0.3	<0.2	<0.2	<0.2	<0.2
PFPA	2.54 ± 0.4	2.3 ± 0.3	2.5 ± 0.3	2.8 ± 0.04	2.2 ± 0.1	0.9 ± 0.2	2.4 ± 0.1	2.0 ± 0.2	3.1 ± 0.1	2.2 ± 0.04	2.7 ± 0.4	2.2 ± 0.1	2.1 ± 0.03	1.6 ± 0.03	1.1 ± 0.04
PFHxA	2.63 ± 0.2	5.0 ± 0.01	2.9 ± 0.4	4.1 ± 0.3	2.6 ± 0.1	2.6 ± 0.3	3.6 ± 0.3	4.1 ± 0.1	3.5 ± 0.02	2.8 ± 0.1	3.7 ± 0.4	2.8 ± 0.5	2.2 ± 0.1	1.8 ± 0.01	1.6 ± 0.04
PFHpA	1.38 ± 0.2	2.4 ± 0.03	1.3 ± 0.1	1.9 ± 0.02	1.1 ± 0.1	1.8 ± 0.01	1.5 ± 0.1	1.3 ± 0.1	1.6 ± 0.2	0.9 ± 0.1	1.2 ± 0.03	1.0 ± 0.003	0.9 ± 0.04	0.9 ± 0.1	0.8 ± 0.04
PFOA	7.44 ± 0.5	8.2 ± 0.4	7.8 ± 0.7	8.1 ± 0.04	7.2 ± 0.1	9.6 ± 0.1	7.4 ± 0.2	8.1 ± 0.3	6.8 ± 0.2	5.6 ± 0.4	5.9 ± 0.04	3.8 ± 0.3	3.6 ± 0.4	3.1 ± 0.1	2.8 ± 0.2
PFNA	0.73 ± 0.03	1.1 ± 0.1	0.7 ± 0.1	0.8 ± 0.03	0.6 ± 0.1	0.9 ± 0.04	0.7 ± 0.1	0.6 ± 0.02	0.7 ± 0.04	0.6 ± 0.04	0.7 ± 0.1	0.4 ± 0.04	0.3 ± 0.02	0.2 ± 0.02	0.3 ± 0.01
PFDA	0.43 ± 0.006	0.7 ± 0.02	0.4 ± 0.03	0.5 ± 0.02	0.4 ± 0.01	0.6 ± 0.02	0.6 ± 0.001	0.5 ± 0.1	0.6 ± 0.1	0.6 ± 0.03	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.01	0.2 ± 0.02	(0.2) ± 0.01
PFUnDA	<0.004	0.1 ± 0.02	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.02 ± 0.002	0.1 ± 0.02	0.03 ± 0.01	0.1 ± 0.004	<0.004	<0.004	<0.004	0.03 ± 0.01	<0.004	<0.004
PFDoDA	<0.01	<0.01	<0.01	0.1 ± 0.01	<0.01	0.1 ± 0.004	<0.01	<0.01	0.1 ± 0.0001	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PFOSA	0.46 ± 0.1	1.0 ± 0.2	0.4 ± 0.03	0.3 ± 0.1	0.2 ± 0.02	0.2 ± 0.1	0.3 ± 0.01	0.1 ± 0.03	0.5 ± 0.002	0.6 ± 0.1	0.2 ± 0.03	0.1 ± 0.01	0.1 ± 0.03	0.2 ± 0.04	(0.2) ± 0.01
FOUEA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.1 ± 0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
FDUEA	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	(0.1) ± 0.02	<0.03	0.2 ± 0.01	0.3 ± 0.1	<0.03	<0.03	<0.03	<0.03	<0.03
∑PFCs	20.3 ± 2.1	26.3 ± 1.3	22.2 ± 2.1	26.4 ± 1.2	20.5 ± 0.8	23.8 ± 1.8	21.6 ± 1.6	21.4 ± 1.4	21.1 ± 1.4	16.6 ± 2.1	21.1 ± 2.2	15.8 ± 1.8	14.7 ± 1.5	9.1 ± 0.27	7.6 ± 0.5

[a] values in brackets are between MDL and MQL and are not included in the sum concentrations. <x, below the respective MDL. [b] not available as standard.