Final Draft of the original manuscript:


DOI: 10.1016/j.chemosphere.2014.03.050
Seasonal variations and spatial distributions of perfluoroalkyl substances in the rivers Elbe and lower Weser and the North Sea

Zhen Zhao 1,2,3, Zhiyong Xie1, *, Jianhui Tang2,*, Renate Sturm1, Yingjun Chen2, Gan Zhang3, Ralf Ebinghaus1

1Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Institute of Coastal Research, Geesthacht, Germany

2Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, CAS, Chunhui Road 17, Yantai 264003, China

3State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, CAS, Guangzhou 510631, China

*Corresponding author: Tel: +49-4152-87-2353, Fax: +49-4152-87-2332, Email: zhiyong.xie@hzg.de (Dr. Xie); Tel:+86 535 2109151, Fax: +86 535 2109000, Email: jhtang@yic.ac.cn (Dr. Tang)

Abstract

The spatial distributions and seasonal variations of perfluoroalkyl substances (PFASs) in surface waters were investigated for the German rivers Elbe and lower Weser, and the North Sea. ΣPFAS concentrations ranged from 4.1 to 250 ng/L in the River Elbe, from 3.8 to 16 ng/L in the lower Weser, and from 0.13 to 10 ng/L in the North Sea. The most abundant compound was perfluorobutanesulfonate (PFBS) with a proportion of 24% in river water and 31% in seawater samples. The concentrations of perfluorohexanoic acid (PFHxA) and perfluorooctanoic acid (PFOA) in Elbe River water showed significant seasonal variation in 2011. The seasonal variations might be related to the variations of water discharge. The
highest concentrations of PFOA and PFHxA were detected in August. Pearson correlations showed that perfluorobutanoic acid (PFBA) and PFBS had different sources from other PFASs, and the current manufacturing and use of C₄-based products could explain the distinction. The estimated fluxes of individual substances and ΣPFASs in the River Elbe showed no significant seasonal variation. The annual fluxes of PFASs to the North Sea were estimated to be 335 ± 100 kg/year from the River Elbe and 102 ± 22 kg/year from the River Weser.

**Keyword:** PFAS, Seasonal variation, the River Elbe, Riverine flux, the North Sea

1. **Introduction**

Perfluoroalkyl substances (PFASs) have been produced for more than 50 years and are globally ubiquitous in air (Dreyer and Ebinghaus, 2009), water (Yamashita et al., 2005), sediment (Bao et al., 2010), and organisms (Kannan et al., 2006). Perfluorooctane sulfonic acid (PFOS) and related substances were restricted by EU Directive 2006/122/EC in 2008 and listed in the Stockholm Convention in 2009 (EPC, 2006; Secretariat, 2009). Subsequently, a decreasing trend is predicted both for production and emission to the environment (Paul et al., 2009). As for another C₈-PFAS perfluorooctanoic acid (PFOA), national programs in the United States and Canada are aiming to eliminate this substance, its salts, and its precursors (Vierke et al., 2012). In Norway, PFOA is to be phased out in consumer products from 2013, but no regulatory activities are implemented in other European countries. Short-chained PFASs (e.g., perfluorobutane sulfonic acid (PFBS) and perfluorobutanoic acid (PFBA)) were introduced as substitute compounds for C₈- PFASs (3M, 2011), and relatively high concentrations of PFBS and PFBA were reported in German environment i.e. the River Rhine water (Möller et al., 2010), drinking water sources (Eschauzier et al., 2012), and precipitation (Dreyer et al., 2010). PFASs concentrations in the River Elbe and North Sea were previously investigated in 2003 and 2006 (Ahrens et al., 2009b; Ahrens et al., 2009c), and this study
presents the latest data for PFASs within a similar area. Riverine levels of PFASs could reflect the emission of PFASs from a watershed, and the estimation of the discharge flux is useful to investigate the transport of PFASs (McLachlan et al., 2007; Pistocchi and Loos, 2009). The primary sources of riverine PFASs were waste water treatment plants (WWTPs), local runoff, and dry and wet deposition, and PFAS concentrations were found to vary with water flow. To our best knowledge, few studies were related to the seasonal variations of PFASs in river water as well as its adjacent coastal water.

The River Elbe has a length of 1165 km with a drainage area of 144 000 km$^2$. The Hamburg port at the downstream is the largest port in Germany. Hamburg City is the second largest city in Germany with prosperous industry and economy. The River Weser is the second longest river in Germany, with a length of 733 km and a drainage area of 46 300 km$^2$. Both of the rivers discharge water into the North Sea, where the current transports North Atlantic water to the German coast. Studies about the River Elbe, Weser and the North Sea could reflect the contamination of PFASs in northwest Germany and the influence of rivers to the North Sea.

In this study, the concentrations of PFASs were detected in surface water samples from the rivers Elbe and lower Weser and from the North Sea. The spatial and temporal trends of PFASs were investigated with reference to the previous studies conducted in the same area (Ahrens et al., 2009b; Ahrens et al., 2009c). Sources of individual compounds were discussed. Sampling campaigns were conducted at the same stations in different seasons. Seasonal variations were investigated in river and marine surface waters for the first time. The fluxes of PFASs from the River Elbe to the North Sea were estimated in different seasons and the annual discharge was calculated.

2. Material and methods

2.1. Chemicals and standards

Sixteen PFASs were analyzed, comprising 5 PFSAs and 10 PFCAs (Table S1). Nine mass-labeled PFASs were used as Internal Standards (IS) (Table S2). Methanol (Suprasolv) and
ammonium hydroxide (25%, Suprapur) were purchased from Merck (Darmstadt, Germany). Millipore water was produced by a Milli-Q Plus 185 system by Millipore (Zug, Germany). The methanol was distilled in a glass apparatus before use, and the Millipore water was pre-cleaned by passing through Oasis Wax cartridges (Waters, 150 mg, 6 cc, 30 μm) to remove PFASs.

2.2. Sample collection and preparation

Four sampling campaigns were performed by the Research Vessel *Ludwig Prandtl* in February, April, August, and October 2011, to represent the four seasons (winter, spring, summer, and autumn, respectively). The locations of the sampling sites are shown in Fig. 1, and detailed information is listed in Table S3. During each campaign, 1 L surface water samples were collected by glass bottles at 22 locations in the rivers Elbe and lower Weser and the North Sea (Table S3). Samples were filtrated on-board by stainless steel devices through glass fibre filters (GFC, Ø47 mm, 1.2 μm). The dissolved phase was stored in a polypropylene (PP) bottles at 4 °C until extraction, and the particle phase was stored at -20 °C. Because the suspended particles had very small amount and some filters were broken during the sampling, the particle phase was not analyzed in this study. Another three sampling campaigns in April, June, and September 2011 were performed by the Research Vessel *Heincke* at 14 locations in the North Sea (Fig. 1C and Table S4). Surface water was collected in glass bottles and stored at 4 °C in PP bottles until filtration and extraction in a clean lab (Class: 10 000). A total of 127 surface water samples were collected and analyzed in this study. Sample preparation and extraction has been described in Zhao et al. (2012). The volume of the extract was reduced to 150 μL under a gentle stream of ultra-high purity nitrogen (99.999%). Before HPLC analysis, the samples were spiked with 1 ng 8:2 FTUCA as an injection standard.

2.4. Instrument analysis
The instrumental analysis was performed with a high-performance liquid chromatography-
negative electrospray ionization-tandem mass spectrometry (HPLC-ESI-MS/MS) system.  
Further details can be found in the reference (Ahrens et al., 2009a).

2.5. **Quality Assurance and Quality Control**

The instrument detection limit (IDL) was determined using a noise-to-signal ratio of 3:1.  
IDLs for individual substances are listed in Table S1. For every experimental batch  
(according to the sampling campaigns), three to six procedural blank samples were included.  

Five compounds were detected in blanks samples, i.e., PFOS (mean 0.03 ng/L), PFBA (mean  
0.06 ng/L), PFPeA (mean 0.02 ng/L), PFHxA (mean 0.05 ng/L), and PFOA (mean 0.04 ng/L).  
The method detection limit (MDL) was determined by a noise-to-signal ratio of 10:1 for  
substances that were not detected in blank samples. For PFOS, PFBA, PFPeA, PFHxA, and  
PFOA, the MDLs were extrapolated under 98% confidence intervals with concentrations in  
the blank samples and their standard deviations. MDLs ranged from 0.02 ng/L (PFDA and  
PFUnDA) to 0.14 ng/L (PFBA) (Table S1). Overall recoveries varied from 51% (± 21%) for  
[\textsuperscript{13}C\textsubscript{4}] - PFOS to 75% (± 20%) for [\textsuperscript{13}C\textsubscript{2}] - PFHxA (Table S2). The concentrations were  
corrected by recoveries.

3. **Results and discussion**

3.1. **Detection frequency, concentrations and compositions of PFASs**

All the target substances were detectable in this study. Eleven substances were quantified in  
more than 40% of the samples, i.e., PFBA, PFPeA, PFHxA, PFOA, PFNA, PFDA, PFUnDA,  
PFBS, PFHxS, PFOS and FOSA. PFOA was detected in all samples, followed by PFBS (98%  
of samples) and PFHxA (93% of samples). The latest data on the production of PFOA in  
Germany are unavailable. According to a 3M report, their German plants ceased production of  
PFOA and associated products at the end of 2008, but products containing PFOA remained on  
the market until the end of 2010 (3M, 2010). This could result in the release of PFOA to the  
environment for a long period. PFBS and PFHxA were introduced as replacements for C\textsubscript{8}
homologous products, and were claimed to possess less environmental threat or human health risks than PFOS and PFOA (Das et al., 2008; Olsen et al., 2009; Dupont, 2011). Significantly higher concentrations of PFBS and PFHxA than PFOS and PFOA were found in water samples from the River Rhine in 2008 (Möller et al., 2010). PFOS were detected in 84% of the samples, following PFHxS (89%). It was reported that Germany stopped production of PFOS in 2007, but that PFOS and its associated substances were still used in some applications, e.g., metal plating, and photographic and semiconductors applications (Carloni, 2009). PFHxS was a by-product in the production of perfluorohexanesulfonyl fluoride (PHFS), which was used in fire-fighting foams (Weiss et al., 2012). The manufacture of fire-fighting foams and their usage in fire training might be the source. PFBA was detected in 46% samples. PFBA is another replacement substance for C₈-PFASs, and the production and usage quantities in Germany and other countries are unknown. Nevertheless, it was reported to be the dominant PFAS in the River Rhine (Möller et al., 2010; Eschauzier et al., 2011). PFBA and PFBS cannot be removed by conventional water treatment, and therefore their abundance in drinking water is expected to become problematic (Eschauzier et al., 2011).

$\sum$PFASs represents the total concentrations of 11 frequently detected ($\geq 40\%$ detection frequency) substances (Table S5a–b). Overall, the concentrations of $\sum$PFASs ranged from 4.1 to 250 ng/L (mean 15 ng/L) in the River Elbe (Table S6a–b), from 3.8 to 16 ng/L (mean 8.0 ng/L) in the lower Weser, and from 0.13 to 10 ng/L (mean 3.8 ng/L) in the North Sea.

In the rivers Elbe and lower Weser, the primary compounds were PFBS, PFOA, and PFHxA, with mean composition percentages of 24%, 23%, and 20% of $\sum$PFAS, respectively.

The highest concentration of PFBS was 240 ng/L (site E619), which was three orders of magnitude greater than the lowest concentration (0.24 ng/L at site E699) and thirty-six times greater than the mean concentration (6.3 ng/L). The concentrations of PFOA and PFHxA ranged from 0.78 to 5.1 ng/L (mean 2.3 ng/L), and from 0.50 to 5.3 ng/L (mean 2.0 ng/L), respectively.
In the North Sea, the most abundant compounds were PFBS, PFOA, and PFBA, accounting for 31%, 26%, and 20% of $\sum$PFASs, respectively. PFBS and PFOA concentrations ranged from <0.03 to 2.9 ng/L (mean 1.2 ng/L) and 0.10 to 2.4 ng/L (mean 0.84 ng/L), respectively, which were lower than those observed in the river samples. PFBA concentrations (<0.14 to 2.2 ng/L, mean 0.92 ng/L) were relatively similar to its concentrations in river samples (0.47 to 2.5 ng/L).

3.2. Seasonal variations and spatial distributions of PFASs

The seasonal variations and spatial distributions of PFASs were investigated in the River Elbe (E619 to E724), the lower Weser (W1 to W3), and the nearshore area of the North Sea (N1 to N6) (Fig. 1) using samples collected during four Prandtl campaigns. The distribution characteristics are presented in Figs. 2 and S1. The samples collected in three Heincke sampling campaigns, and those collected at sites N1 to N6 during four Prandtl campaigns revealed the seasonal variations and spatial distributions of PFASs in the North Sea. The concentration and distribution details are shown in Figs. 4 and S2.

3.2.1. The rivers Elbe and lower Weser

PFBS did not present significant seasonal variations throughout the entire sampling year. The highest concentration (240 ng/L) was detected at station E619, near Hamburg City, in February. The high level of PFBS might be due to the occasional discharge of waste water from nearby industrial plants. At the next three sites (E624–E639), located 20 km downstream, the concentrations of PFBS were diluted by river water, and concentrations at E639 (4.8 ng/L) were below the average level (6.3 ng/L). In the lower Weser, the concentrations varied from 0.80 to 1.9 ng/L (mean 1.4 ng/L), which were comparable with those in the North Sea (0.80–2.8 ng/L).

The concentrations of PFOS in rivers Elbe and lower Weser, and the North Sea, were higher in August (from 0.50 to 3.0 ng/L, mean 1.7 ng/L) than in February (from 0.10 to 1.0 ng/L, mean 0.50 ng/L), April (from 0.40 to 1.9 ng/L, mean 0.90 ng/L), and October (from
0.20 to 1.1 ng/L, mean 0.50 ng/L) (Fig. S1). In August, its concentration decreased from 2.2 ng/L (at E619) to 1.2 ng/L (at E639), and then increased to 3.0 ng/L at E679 in the River Elbe, where the river runs through Hamburg City. At the Weser estuary, a concentration of 2.4 ng/L was detected at W2, which was slightly higher than in the Elbe estuary (0.90 ng/L at E724).

Several WWTPs are located along the River Elbe, from E619 to E724, and these were suggested as potential sources of PFASs in a previous study (Ahrens 2009a). Ahrens et al. (2009a) found that the contributions of WWTPs to total PFAS fluxes in the River Elbe were less than 24%. With the development of sewage treatment technologies, it is expected that WWTPs contributions would decline in the future (Thompson et al.; Ochoa-Herrera and Sierra-Alvarez, 2008; Li et al., 2011; Chen et al., 2012).

The spatial and seasonal distributions of PFOA and PFHxA in 2011 were similar in the River Elbe and lower Weser (Fig. 2). Average seasonal concentrations of PFOA and PFHxA in the River Elbe showed the following declining trend: August (4.2 ng/L PFHxA, 4.1 ng/L PFOA) > October (2.0 ng/L PFHxA, 2.5 ng/L PFOA) > April (1.1 ng/LPFHxA, 1.4 ng/L PFOA) > February (0.9ng/L PFHxA, 1.4ng/L PFOA). In the lower Weser, concentrations declined as follows: August (3.5 ng/L PFHxA, 2.7 ng/L PFOA) > October (1.4 ng/L PFHxA, 1.7 ng/L PFOA) > April (1.3 ng/L PFHxA, 1.6 ng/L PFOA) > February (0.8 ng/L PFHxA, 1.0 ng/L PFOA) (Table S6a). The seasonal variations might relate to the variations of precipitation at hot spots and the river runoff. Large river discharge resulted from heavy precipitation at hot spots could lead to high concentrations of PFASs (Dreyer et al., 2010). For example, in Hamburg City, average precipitation in August (70 mm) is heavier than other sampling months (40-60 mm) (http://www.weather-and-climate.com/average-monthly-precipitation-Rainfall,Hamburg,Germany), which could be the reason that relatively high concentrations of PFASs been detected in August. However, large amount discharge could dilute the pollutants.In the River Elbe, the average stream declined in the following order: February (1528 m³/s) > August (729 m³/s) > April (636 m³/s) > October (601m³/s) in 2011.
Water from less contaminated areas diluted the concentration of PFASs which could explain the relatively low concentrations of PFHxA and PFOA in February. Owing to the dilution effect of the coastal water, the concentrations of PFHxA and PFOA decreased from the estuaries to offshore area, i.e., from E719 to N5, and from W3 to N6, where brackish water intrudes (Fig. 2). In August, PFBA was frequently detected in river samples, and in February and April, it was frequently detected in estuaries and coastal samples. Average concentrations of PFBA throughout the year were greater at sites E619 to E669 (1.4 ng/L) than at sites E679 to E724 (0.8 ng/L) (Fig. S1), and the discharge from Hamburg City might elevate the concentrations in river water from sampling points E619 to E699. Different from other PFCAs, the concentrations of PFBA did not significantly decrease in the North Sea where dilution effects are strong, suggesting PFBA had other sources including the delivery from River Elbe, Weser and Rhine (Ahrens et al., 2009c). PFBA could be detected in air and precipitation samples from Northern Germany, which suggested air deposition as the potential source of PFBA to the aquatic environment (Dreyer et al., 2010; Weinberg et al., 2011).

The distributions of PFHxS, PFPeA, PFNA, and PFDA are presented in Fig. S1. The highest concentrations of PFHxS in different seasons varied at different sites of the River Elbe, i.e., 1.0 ng/L at E624 in February, 0.8 ng/L at E639 in April, 1.0 ng/L at E679 in August, and 0.60 ng/L at E699 in October. The concentrations of PFPeA, PFNA, and PFDA all decreased from the estuaries to the nearshore areas, due to the effects of dilution by the North Sea water.

3.2.2. The North Sea

PFASs concentrations in the North Sea did not show consistent seasonal variation in 2011. For PFOA, concentrations (sites 1 to 14) in June (0.13 to 1.8 ng/L) and September (0.10 to 1.5 ng/L) were slightly higher than those in April (0.13 to 0.79 ng/L) and relatively higher concentrations were detected along the coast than in open areas (Fig. 3). Significantly higher concentrations of PFOS were detected near the estuaries of the River Elbe (sites N1 and N2,
1.6 to 2.7 ng/L) and lower Weser (site N6, 1.5 ng/L) in August than in other sampling months (0.15 to 0.69 ng/L at N1 and N2, <0.07 to 0.55 ng/L at N6) (Fig. S2). For other substances, i.e., PFBS, PFHxS, PFBA, PFPeA, PFHxA, PFNA, PFDA, and FOSA, no significant seasonal trends were found in the North Sea (Figs. 4 and S2).

3.3. Identification of sources

Pearson rank correlations for concentrations of individual substances during different seasons of the Prandtl campaigns are presented in Table S7a–d. Significant correlations were found among the C6–C10 PFCA concentrations and between PFOS and FOSA concentrations, which were consistent with previous studies (So et al., 2007; Ahrens et al., 2009c). Discharges from WWTPs, surface runoff, and wet deposition were suggested as sources of C6–C10 PFCAs, and degradation from FOSA to PFOS could explain the relationship between these two compounds. Concentrations of C6–C10 PFCAs were also significantly correlated within different seasons, indicating that the sources were consistent throughout the year. PFBS (concentrations at E619, E624, and E629 in February were excluded) was not significantly correlated with PFHxS and PFOS implying distinct sources of PFBS. As a substitute of C8-PFASs, PFBS had been introduced and used in industrial activities. Relatively high concentrations of PFBS (up to 181 ng/L) in the River Rhine watershed were reported previously (Möller et al., 2010). Via the North Sea current, PFBS could be transported to the River Elbe estuary (Howarth, 2001; Ahrens et al., 2009c). PFBS in water phase had a possible source from the air deposition, because it is a possible degradation product of N-methyl perfluorobutane sulfonamidoethanol (NMeFBSE) (D'Eon et al., 2006). PFHxS was another substitute of C8-PFASs. The PFHxS-contained products had being sold in Europe since 2005 (Zhang et al., 2012) which might release PFHxS into the environment. In February, PFBA was significantly correlated with the other 9 PFASs except PFOS, while in other sampling months it was not significantly related to most of the other substances.

3.4. Comparison of PFAS concentrations in surface water
At the same sites in the River Elbe (E619 to E724), PFASs concentrations were investigated in August 2006 and June, 2007 (Ahrens et al., 2009b; Ahrens et al., 2009c). In 2006, PFOA and PFOS were the predominant compounds and in 2007, PFOA and PFBS were the predominant PFCAs and PFSAs. Together with the data collected in 2011 in this study, trends of PFBS, PFOS, and PFOA concentrations are shown in Fig. 4a–c. All the samples were collected and analyzed by the same research group in the same lab, and thus provide a good opportunity to examine the short-term (2006–2011) trends for PFASs. A slightly decreasing trend of PFBS is observed from 2007 (2.3–3.4 ng/L to 2011 (1.5 –1.9 ng/L) from site E619 to E639 (Fig. 4a). From E649 to E724, the concentrations of PFBS ranged from 1.7 to 3.0 ng/L in August 2011. These were slightly higher than the concentrations in August 2006 (1.05–2.00 ng/L) at the same sites. For PFOS, a significant decreasing trend from site E619 to E669 was found from 2006 (5.47 to 7.47 ng/L) to 2011 (1.2 to 2.7 ng/L). This may be due to the cessation of PFOS production and the declining release of PFOS from the upper streams. For PFOA, a significant decreasing trend was found in 2006 (8.11 to 12.45 ng/L), 2007 (5.6 to 8.2 ng/L), and 2011 (3.8 to 5.1 ng/L) between site E619 and E679, which might be attributed to the voluntarily phase-out of PFOA manufacturing. In the Elbe estuary (E719 to E724), the concentrations of PFOS and PFOA were comparable from 2006 to 2011 (Fig. 4), which could be explained by the dilution effect as well as the foreign PFOS and PFOA transported from the River Rhine.

Previous studies investigated the concentrations of PFOS and PFOA in the North Sea in 2003, 2004, and 2007 (Table. 1). A significant decreasing trend of PFOA concentration was found from 2003 (3 to 13 ng/L) (Caliebe et al., 2005) to 2011 (0.1 to 2.4 ng/L), implying that the production and use of PFOA and its related products had decreased. Concentrations of PFOS decreased from 2003 (0.25 to 7.0 ng/L) (Caliebe et al., 2005) to 2004 (0.28 to 3.1 ng/L) (Theobald et al., 2007), which might be attributed to voluntarily phase-out by manufacturers since 2003. Concentrations were stable in 2004 and 2011 (<0.07 to 2.7 ng/L), indicating that
there was no intensive production and use of C₈-based products after 2003, and the level might remain stable until the pollutants degrade and the North Sea water be refreshed by river and North Atlantic water. PFOS and PFOA concentrations in surface waters from rivers and coastal areas around the world are summarized in Table S8.

3.5. Riverine fluxes of PFASs into North Sea

The mass flows of individual PFASs and ∑PFASs in the River Elbe and lower Weser were calculated based on the concentrations from this study, and on water discharge data from the River Basin Community of Elbe and Weser. The equation and the uncertainty of this method were described elsewhere (Ahrens et al., 2009b).

Fig. S3 presents the fluxes of ∑PFASs and individual homologues in the River Elbe. The mass flows of ∑PFASs ranged from 4.5 mg/s to 23 mg/s, with an average value of 11 mg/s (the samples of E619, E624, and E629 in February were excluded). Relatively high ∑PFAS fluxes were found at sites E639 and E724 in February, due to the large amounts of PFBS. In April, maximum ∑PFASs flux occurred at E659, due to the contributions of PFBS and PFPeA. There might be point sources of PFBS and PFPeA, such as WWTPs, located near sites E639, E659, and E724 (Ahrens et al., 2009b). The minimum ∑PFAS fluxes in February occurred at site E699, because of smaller amounts of PFBA, PFPeA, PFHxA, PFOA, and PFNA than at other sites. In August and October, PFAS fluxes were relatively stable from E619 to E699. The mass flows increased slightly from E699 to E724 throughout the year possibly due to the intruding of North Sea water. PFHxA and PFOA showed similar seasonal variations, and both showed significantly higher fluxes in August and October than in February. In August, the fluxes of PFOA and PFHxA dramatically decreased from site E709 to E724 with the converse salinity variation trend (4.2 to 21.2 PSU). The change in ionic strength could enhance the adsorption of PFHxA and PFOA onto particles and sediment which might result in the decreasing fluxes at the Elbe estuary (Xiao et al., 2011). For other substances, no significant seasonal or spatial variations were observed.
The salinities were less than 1 PSU from E619 to E689 and the fresh water was presumed to not be diluted by marine water. In this study, average PFAS concentrations from E619 to E689 were introduced to estimate the annual discharges of PFASs from the River Elbe to the North Sea. The results are shown in Fig. 5. $\Sigma$PFAS annual discharge was estimated as 335 ± 100 kg/year. This value was slightly less than that in 2007 (480 kg/year to 540 kg/year), while the result obtained in 2007 included more substances than obtained in the present study, i.e., perfluorohexanoic acid (PFHxA) (Ahrens et al., 2009b). The annual discharges of PFBS (69 ± 46 kg/year), PFHxA (71 ± 37 kg/year), and PFOA (83 ± 36 kg/year) were comparable, and were greater than those of PFOS (35±14 kg/year) and PFBA (29 ± 35 kg/year). For the River Weser, no freshwater sample was collected, and the mass flux of $\Sigma$PFASs from the estuary (W2) to the open North Sea was estimated to be 102 ± 22 kg/year. Pistocchi and Loos (2009) estimated discharges of PFOA and PFOS from European rivers in 2007. The discharge of PFOS (70 kg/year) in the River Elbe was higher than that in 2011 (35 ± 14 kg/year), and discharges of PFOA were comparable in 2007 (80 kg/L) and 2011 (83 ± 36 kg/year). In the River Weser, the discharge of PFOS in 2007 was estimated to be 120 kg/year, which was significantly greater than that in 2011 (10 ± 7 kg/year), while PFOA discharge also decreased from 90 kg/year in 2007 to 23 kg/year in 2011.

4. Conclusion

PFBS is the predominant compound in both surface water bodies, accounting for 24% and 31% of $\Sigma$PFASs concentrations in river and marine water, respectively. From 2006 to 2011, PFOA and PFOS concentrations showed decreasing trends in the River Elbe at locations where marine water did not intrude due to regulation of C₈-based products. WWTPs may not be comparable to other sources of PFOS in the River Elbe from Hamburg City to the estuary, considering the moderate contribution and the development of more effective treatment methods. PFOA and PFHxA showed significant seasonal variation in 2011, which might relate to variations in water discharge in the River Elbe. The entire year monitoring work in
the future were suggested to identify the occasional events, the point and non-point sources. The concentrations of PFBA in river and marine waters were comparable and Pearson correlations suggest unique sources. Air deposition was suggested to be a source, and further monitoring studies should be conducted in this field. The production and use of PFBS should be monitored, since it was the predominant compound in the rivers Elbe and Weser and North Sea. The fluxes from the River Elbe to the North Sea did not show clear seasonal variation in this study. The annual discharge of PFASs from the River Elbe was estimated to be 335 ± 100 kg/year, which was comparable with previous studies, and further monitoring work in this area is still needed to get better understanding about the contribution of the River Elbe.

Acknowledgments

This research was partially supported by the grant from the Chinese Academy of Sciences (No. KZCX2-EW-QN210 and KZZD-EW-14-02).

Appendix A. Supplementary data
References:


Huanjing Kexue 33, 1795-1800.


Dupont, 2011. DuPont™ CAPSTONE® Repellents and Surfactants - An Overview


Thompson, J., Eaglesham, G., Reungoat, J., Poussade, Y., Bartkow, M., Lawrence, M.,


Weinberg, I., Dreyer, A., Ebinghaus, R., 2011. Landfills as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air.

Atmospheric Environment 45, 935-941.


Figure caption

Fig. 1. A. Sampling locations during the Prandtl and Heinke campaigns; B. Sampling sites in the North Sea during the Heincke campaigns; C. Sampling sites in the River Elbe and lower Weser and the North Sea during the Prandtl campaigns.

Fig. 2. Concentrations, seasonal variations and spatial distributions of PFBS, PFHxA, PFOA, and ∑PFASs in the River Elbe (E619-E724), lower Weser (W1-W3) and the North Sea (N1-N6) (Prandtl campaigns).

Fig. 3. Concentrations, seasonal variations and spatial distributions of PFBS, PFBA, PFOA and ∑PFASs in the North Sea (Legend 1102, 1104, 1106, 1108, 1109 and 1110 means water sampling was carried out in Feb. Apr. Jun. Aug., Sep. Oct. 2011).

Fig. 4. Comparison of PFBS, PFOS, and PFOA concentrations (ng/L) in the River Elbe in 2006, 2007 and 2011.

Fig. 5. Annual discharges of individual PFASs and ∑PFASs from the River Elbe.