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1 **Seasonal variations and spatial distributions of perfluoroalkyl**
2 **substances in the rivers Elbe and lower Weser and the North Sea**

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16
17 **Abstract**

18 The spatial distributions and seasonal variations of perfluoroalkyl substances (PFASs) in
19 surface waters were investigated for the German rivers Elbe and lower Weser, and the North
20 Sea. Σ PFAS concentrations ranged from 4.1 to 250 ng/L in the River Elbe, from 3.8 to 16
21 ng/L in the lower Weser, and from 0.13 to 10 ng/L in the North Sea. The most abundant
22 compound was perfluorobutanesulfonate (PFBS) with a proportion of 24% in river water and
23 31% in seawater samples. The concentrations of perfluorohexanoic acid (PFHxA) and
24 perfluorooctanoic acid (PFOA) in Elbe River water showed significant seasonal variation in
25 2011. The seasonal variations might be related to the variations of water discharge. The

26 highest concentrations of PFOA and PFHxA were detected in August. Pearson correlations
27 showed that perfluorobutanoic acid (PFBA) and PFBS had different sources from other
28 PFASs, and the current manufacturing and use of C₄-based products could explain the
29 distinction. The estimated fluxes of individual substances and \sum PFASs in the River Elbe
30 showed no significant seasonal variation. The annual fluxes of PFASs to the North Sea were
31 estimated to be 335 ± 100 kg/year from the River Elbe and 102 ± 22 kg/year from the River
32 Weser.

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

34

35 **1. Introduction**

36 Perfluoroalkyl substances (PFASs) have been produced for more than 50 years and are
37 globally ubiquitous in air (Dreyer and Ebinghaus, 2009), water (Yamashita et al., 2005),
38 sediment (Bao et al., 2010), and organisms (Kannan et al., 2006). Perfluorooctane sulfonic
39 acid (PFOS) and related substances were restricted by EU Directive 2006/122/EC in 2008 and
40 listed in the Stockholm Convention in 2009 (EPC, 2006; Secretariat, 2009). Subsequently, a
41 decreasing trend is predicted both for production and emission to the environment (Paul et al.,
42 2009). As for another C₈-PFAS perfluorooctanoic acid (PFOA), national programs in the
43 United States and Canada are aiming to eliminate this substance, its salts, and its precursors
44 (Vierke et al., 2012). In Norway, PFOA is to be phased out in consumer products from 2013,
45 but no regulatory activities are implemented in other European countries. Short-chained
46 PFASs (e.g., perfluorobutane sulfonic acid (PFBS) and perfluorobutanoic acid (PFBA)) were
47 introduced as substitute compounds for C₈- PFASs (3M, 2011), and relatively high
48 concentrations of PFBS and PFBA were reported in German environment i.e. the River Rhine
49 water (Möller et al., 2010), drinking water sources (Eschauzier et al., 2012), and precipitation
50 (Dreyer et al., 2010). PFASs concentrations in the River Elbe and North Sea were previously
51 investigated in 2003 and 2006 (Ahrens et al., 2009b; Ahrens et al., 2009c), and this study

52 presents the latest data for PFASs within a similar area.

53 Riverine levels of PFASs could reflect the emission of PFASs from a watershed, and the
54 estimation of the discharge flux is useful to investigate the transport of PFASs (McLachlan et
55 al., 2007; Pistocchi and Loos, 2009). The primary sources of riverine PFASs were waste
56 water treatment plants (WWTPs), local runoff, and dry and wet deposition, and PFAS
57 concentrations were found to vary with water flow. To our best knowledge, few studies were
58 related to the seasonal variations of PFASs in river water as well as its adjacent coastal water.

59 The River Elbe has a length of 1165 km with a drainage area of 144 000 km². The Hamburg
60 port at the downstream is the largest port in Germany. Hamburg City is the second largest city
61 in Germany with prosperous industry and economy. The River Weser is the second longest
62 river in Germany, with a length of 733 km and a drainage area of 46 300 km². Both of the
63 rivers discharge water into the North Sea, where the current transports North Atlantic water to
64 the German coast. Studies about the River Elbe, Weser and the North Sea could reflect the
65 contamination of PFASs in northwest Germany and the influence of rivers to the North Sea.

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

74 **2. Material and methods**

75 **2.1. Chemicals and standards**

76 Sixteen PFASs were analyzed, comprising 5 PFASs and 10 PFCAs (Table S1). Nine mass-
77 labeled PFASs were used as Internal Standards (IS) (Table S2). Methanol (Suprasolv) and

78 ammonium hydroxide (25%, Suprapur) were purchased from Merck (Darmstadt, Germany).
79 Millipore water was produced by a Milli-Q Plus 185 system by Millipore (Zug, Germany).
80 The methanol was distilled in a glass apparatus before use, and the Millipore water was pre-
81 cleaned by passing through Oasis Wax cartridges (Waters, 150 mg, 6 cc, 30 μm) to remove
82 PFASs.

83 **2.2. Sample collection and preparation**

84 Four sampling campaigns were performed by the Research Vessel *Ludwig Prandtl* in
85 February, April, August, and October 2011, to represent the four seasons (winter, spring,
86 summer, and autumn, respectively). The locations of the sampling sites are shown in Fig. 1,
87 and detailed information is listed in Table S3. During each campaign, 1 L surface water
88 samples were collected by glass bottles at 22 locations in the rivers Elbe and lower Weser and
89 the North Sea (Table S3). Samples were filtrated on-board by stainless steel devices through
90 glass fibre filters (GFC, $\text{\O}47$ mm, 1.2 μm). The dissolved phase was stored in a
91 polypropylene (PP) bottles at 4 $^{\circ}\text{C}$ until extraction, and the particle phase was stored at -20
92 $^{\circ}\text{C}$. Because the suspended particles had very small amount and some filters were broken
93 during the sampling, the particle phase was not analyzed in this study. Another three sampling
94 campaigns in April, June, and September 2011 were performed by the Research Vessel
95 *Heincke* at 14 locations in the North Sea (Fig. 1C and Table S4). Surface water was collected
96 in glass bottles and stored at 4 $^{\circ}\text{C}$ in PP bottles until filtration and extraction in a clean lab
97 (Class: 10 000). A total of 127 surface water samples were collected and analyzed in this
98 study. Sample preparation and extraction has been described in Zhao et al. (2012). The
99 volume of the extract was reduced to 150 μL under a gentle stream of ultra- high purity
100 nitrogen (99.999%). Before HPLC analysis, the samples were spiked with 1 ng 8:2 FTUCA as
101 an injection standard.

102 **2.4. Instrument analysis**

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

106 **2.5. Quality Assurance and Quality Control**

107 The instrument detection limit (IDL) was determined using a noise-to-signal ratio of 3:1.
108 IDLs for individual substances are listed in Table S1. For every experimental batch
109 (according to the sampling campaigns), three to six procedural blank samples were included.
110 Five compounds were detected in blanks samples, i.e., PFOS (mean 0.03 ng/L), PFBA (mean
111 0.06 ng/L), PFPeA (mean 0.02 ng/L), PFHxA (mean 0.05 ng/L), and PFOA (mean 0.04 ng/L).
112 The method detection limit (MDL) was determined by a noise-to-signal ratio of 10:1 for
113 substances that were not detected in blank samples. For PFOS, PFBA, PFPeA, PFHxA, and
114 PFOA, the MDLs were extrapolated under 98% confidence intervals with concentrations in
115 the blank samples and their standard deviations. MDLs ranged from 0.02 ng/L (PFDA and
116 PFUnDA) to 0.14 ng/L (PFBA) (Table S1). Overall recoveries varied from 51% ($\pm 21\%$) for
117 [$^{13}\text{C}_4$] - PFOS to 75% ($\pm 20\%$) for [$^{13}\text{C}_2$] - PFHxA (Table S2). The concentrations were
118 corrected by recoveries.

119 **3. Results and discussion**

120 **3.1. Detection frequency, concentrations and compositions of PFASs**

121 All the target substances were detectable in this study. Eleven substances were quantified in
122 more than 40% of the samples, i.e., PFBA, PFPeA, PFHxA, PFOA, PFNA, PFDA, PFUnDA,
123 PFBS, PFHxS, PFOS and FOSA. PFOA was detected in all samples, followed by PFBS (98%
124 of samples) and PFHxA (93% of samples). The latest data on the production of PFOA in
125 Germany are unavailable. According to a 3M report, their German plants ceased production of
126 PFOA and associated products at the end of 2008, but products containing PFOA remained on
127 the market until the end of 2010 (3M, 2010). This could result in the release of PFOA to the
128 environment for a long period. PFBS and PFHxA were introduced as replacements for C_8

129 homologous products, and were claimed to possess less environmental threat or human health
130 risks than PFOS and PFOA (Das et al., 2008; Olsen et al., 2009; Dupont, 2011). Significantly
131 higher concentrations of PFBS and PFHxA than PFOS and PFOA were found in water
132 samples from the River Rhine in 2008 (Möller et al., 2010). PFOS were detected in 84% of
133 the samples, following PFHxS (89%). It was reported that Germany stopped production of
134 PFOS in 2007, but that PFOS and its associated substances were still used in some
135 applications, e.g., metal plating, and photographic and semiconductors applications (Carloni,
136 2009). PFHxS was a by-product in the production of perfluorohexanesulfonyl fluoride
137 (PHFS), which was used in fire-fighting foams (Weiss et al., 2012). The manufacture of fire-
138 fighting foams and their usage in fire training might be the source. PFBA was detected in
139 46% samples. PFBA is another replacement substance for C₈-PFASs, and the production and
140 usage quantities in Germany and other countries are unknown. Nevertheless, it was reported
141 to be the dominant PFAS in the River Rhine (Möller et al., 2010; Eschauzier et al., 2011).
142 PFBA and PFBS cannot be removed by conventional water treatment, and therefore their
143 abundance in drinking water is expected to become problematic (Eschauzier et al., 2011).

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

148 In the rivers Elbe and lower Weser, the primary compounds were PFBS, PFOA, and
149 PFHxA, with mean composition percentages of 24%, 23%, and 20% of \sum PFAS, respectively.
150 The highest concentration of PFBS was 240 ng/L (site E619), which was three orders of
151 magnitude greater than the lowest concentration (0.24 ng/L at site E699) and thirty-six times
152 greater than the mean concentration (6.3 ng/L). The concentrations of PFOA and PFHxA
153 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),
154 respectively.

155 In the North Sea, the most abundant compounds were PFBS, PFOA, and PFBA, accounting
156 for 31%, 26%, and 20% of Σ PFASs, respectively. PFBS and PFOA concentrations ranged
157 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,
158 which were lower than those observed in the river samples. PFBA concentrations (<0.14 to
159 2.2 ng/L, mean 0.92 ng/L) were relatively similar to its concentrations in river samples (0.47
160 to 2.5 ng/L).

161 **3.2. Seasonal variations and spatial distributions of PFASs**

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

169 **3.2.1. The rivers Elbe and lower Weser**

170 PFBS did not present significant seasonal variations throughout the entire sampling year. The
171 highest concentration (240 ng/L) was detected at station E619, near Hamburg City, in
172 February. The high level of PFBS might be due to the occasional discharge of waste water
173 from nearby industrial plants. At the next three sites (E624–E639), located 20 km downstream,
174 the concentrations of PFBS were diluted by river water, and concentrations at E639 (4.8 ng/L)
175 were below the average level (6.3 ng/L). In the lower Weser, the concentrations varied from
176 0.80 to 1.9 ng/L (mean 1.4 ng/L), which were comparable with those in the North Sea (0.80–
177 2.8 ng/L).

178 The concentrations of PFOS in rivers Elbe and lower Weser, and the North Sea, were
179 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
180 ng/L, mean 0.50 ng/L), April (from 0.40 to 1.9 ng/L, mean 0.90 ng/L), and October (from

181 0.20 to 1.1 ng/L, mean 0.50 ng/L) (Fig. S1). In August, its concentration decreased from 2.2
182 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,
183 where the river runs through Hamburg City. At the Weser estuary, a concentration of 2.4 ng/L
184 was detected at W2, which was slightly higher than in the Elbe estuary (0.90 ng/L at E724).
185 Several WWTPs are located along the River Elbe, from E619 to E724, and these were
186 suggested as potential sources of PFASs in a previous study (Ahrens 2009a). Ahrens et al.
187 (2009a) found that the contributions of WWTPs to total PFAS fluxes in the River Elbe were
188 less than 24%. With the development of sewage treatment technologies, it is expected that
189 WWTPs contributions would decline in the future (Thompson et al.; Ochoa-Herrera and
190 Sierra-Alvarez, 2008; Li et al., 2011; Chen et al., 2012).

191 The spatial and seasonal distributions of PFOA and PFHxA in 2011 were similar in the
192 River Elbe and lower Weser (Fig. 2). Average seasonal concentrations of PFOA and PFHxA
193 in the River Elbe showed the following declining trend: August (4.2 ng/L PFHxA, 4.1 ng/L
194 PFOA) > October (2.0 ng/L PFHxA, 2.5 ng/L PFOA) > April (1.1 ng/L PFHxA, 1.4 ng/L
195 PFOA) > February (0.9 ng/L PFHxA, 1.4 ng/L PFOA). In the lower Weser, concentrations
196 declined as follows: August (3.5 ng/L PFHxA, 2.7 ng/L PFOA) > October (1.4 ng/L PFHxA,
197 1.7 ng/L PFOA) > April (1.3 ng/L PFHxA, 1.6 ng/L PFOA) > February (0.8 ng/L PFHxA, 1.0
198 ng/L PFOA) (Table S6a). The seasonal variations might relate to the variations of
199 precipitation at hot spots and the river runoff. Large river discharge resulted from heavy
200 precipitation at hot spots could lead to high concentrations of PFASs (Dreyer et al., 2010). For
201 example, in Hamburg City, average precipitation in August (70 mm) is heavier than other
202 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
203 concentrations of PFASs been detected in August. However, large amount discharge could
204 dilute the pollutants. In the River Elbe, the average stream declined in the following order:
205 February (1528 m³/s) > August (729 m³/s) > April (636 m³/s) > October (601 m³/s) in 2011.
206

207 Water from less contaminated areas diluted the concentration of PFASs which could explain
208 the relatively low concentrations of PFHxA and PFOA in February. Owing to the dilution
209 effect of the coastal water, the concentrations of PFHxA and PFOA decreased from the
210 estuaries to offshore area, i.e., from E719 to N5, and from W3 to N6, where brackish water
211 intrudes (Fig. 2). In August, PFBA was frequently detected in river samples, and in February
212 and April, it was frequently detected in estuaries and coastal samples. Average concentrations
213 of PFBA throughout the year were greater at sites E619 to E669 (1.4 ng/L) than that at sites
214 E679 to E724 (0.8 ng/L) (Fig. S1), and the discharge from Hamburg City might elevate the
215 concentrations in river water from sampling points E619 to E699. Different from other
216 PFCAs, the concentrations of PFBA did not significantly decrease in the North Sea where
217 dilution effects are strong, suggesting PFBA had other sources including the delivery from
218 River Elbe, Weser and Rhine (Ahrens et al., 2009c). PFBA could be detected in air and
219 precipitation samples from Northern Germany, which suggested air deposition as the potential
220 source of PFBA to the aquatic environment (Dreyer et al., 2010; Weinberg et al., 2011).

221 The distributions of PFHxS, PFPeA, PFNA, and PFDA are presented in Fig. S1. The
222 highest concentrations of PFHxS in different seasons varied at different sites of the River
223 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,
224 and 0.60 ng/L at E699 in October. The concentrations of PFPeA, PFNA, and PFDA all
225 decreased from the estuaries to the nearshore areas, due to the effects of dilution by the North
226 Sea water.

227 **3.2.2. The North Sea**

228 PFASs concentrations in the North Sea did not show consistent seasonal variation in 2011.
229 For PFOA, concentrations (sites 1 to 14) in June (0.13 to 1.8 ng/L) and September (0.10 to 1.5
230 ng/L) were slightly higher than those in April (0.13 to 0.79 ng/L) and relatively higher
231 concentrations were detected along the coast than in open areas (Fig. 3). Significantly higher
232 concentrations of PFOS were detected near the estuaries of the River Elbe (sites N1 and N2,

233 1.6 to 2.7 ng/L) and lower Weser (sites N6, 1.5 ng/L) in August than in other sampling
234 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
235 substances, i.e., PFBS, PFHxS, PFBA, PFPeA, PFHxA, PFNA, PFDA, and FOSA, no
236 significant seasonal trends were found in the North Sea (Figs. 4 and S2).

237 **3.3. Identification of sources**

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

258 **3.4. Comparison of PFAS concentrations in surface water**

259 At the same sites in the River Elbe (E619 to E724), PFASs concentrations were investigated
260 in August 2006 and June, 2007 (Ahrens et al., 2009b; Ahrens et al., 2009c). In 2006, PFOA
261 and PFOS were the predominant compounds and in 2007, PFOA and PFBS were the
262 predominant PFCAs and PFSAs. Together with the data collected in 2011 in this study, trends
263 of PFBS, PFOS, and PFOA concentrations are shown in Fig. 4a–c. All the samples were
264 collected and analyzed by the same research group in the same lab, and thus provide a good
265 opportunity to examine the short-term (2006–2011) trends for PFASs. A slightly decreasing
266 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
267 E639 (Fig. 4a). From E649 to E724, the concentrations of PFBS ranged from 1.7 to 3.0 ng/L
268 in August 2011. These were slightly higher than the concentrations in August 2006 (1.05–
269 2.00 ng/L) at the same sites. For PFOS, a significant decreasing trend from site E619 to E669
270 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
271 cessation of PFOS production and the declining release of PFOS from the upper streams. For
272 PFOA, a significant decreasing trend was found in 2006 (8.11 to 12.45 ng/L), 2007 (5.6 to 8.2
273 ng/L), and 2011 (3.8 to 5.1 ng/L) between site E619 and E679, which might be attributed to
274 the voluntarily phase-out of PFOA manufacturing. In the Elbe estuary (E719 to E724), the
275 concentrations of PFOS and PFOA were comparable from 2006 to 2011 (Fig. 4), which could
276 be explained by the dilution effect as well as the foreign PFOS and PFOA transported from
277 the River Rhine.

278 Previous studies investigated the concentrations of PFOS and PFOA in the North Sea in
279 2003, 2004, and 2007 (Table. 1). A significant decreasing trend of PFOA concentration was
280 found from 2003 (3 to 13 ng/L) (Caliebe et al., 2005) to 2011 (0.1 to 2.4 ng/L), implying that
281 the production and use of PFOA and its related products had decreased. Concentrations of
282 PFOS decreased from 2003 (0.25 to 7.0 ng/L) (Caliebe et al., 2005) to 2004 (0.28 to 3.1 ng/L)
283 (Theobald et al., 2007), which might be attributed to voluntarily phase-out by manufacturers
284 since 2003. Concentrations were stable in 2004 and 2011 (<0.07 to 2.7 ng/L), indicating that

285 there was no intensive production and use of C₈-based products after 2003, and the level
286 might remain stable until the pollutants degrade and the North Sea water be refreshed by river
287 and North Atlantic water. PFOS and PFOA concentrations in surface waters from rivers and
288 coastal areas around the world are summarized in Table S8.

289 **3.5. Riverine fluxes of PFASs into North Sea**

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

294 Fig. S3 presents the fluxes of Σ PFASs and individual homologues in the River Elbe. The
295 mass flows of Σ PFASs ranged from 4.5 mg/s to 23 mg/s, with an average value of 11 mg/s
296 (the samples of E619, E624, and E629 in February were excluded). Relatively high Σ PFAS
297 fluxes were found at sites E639 and E724 in February, due to the large amounts of PFBS. In
298 April, maximum Σ PFASs flux occurred at E659, due to the contributions of PFBS and
299 PFPeA. There might be point sources of PFBS and PFPeA, such as WWTPs, located near
300 sites E639, E659, and E724 (Ahrens et al., 2009b). The minimum Σ PFAS fluxes in February
301 occurred at site E699, because of smaller amounts of PFBA, PFPeA, PFHxA, PFOA, and
302 PFNA than at other sites. In August and October, PFAS fluxes were relatively stable from
303 E619 to E699. The mass flows increased slightly from E699 to E724 throughout the year
304 possibly due to the intruding of North Sea water. PFHxA and PFOA showed similar seasonal
305 variations, and both showed significantly higher fluxes in August and October than in
306 February. In August, the fluxes of PFOA and PFHxA dramatically decreased from site E709
307 to E724 with the converse salinity variation trend (4.2 to 21.2 PSU). The change in ionic
308 strength could enhance the adsorption of PFHxA and PFOA onto particles and sediment
309 which might result in the decreasing fluxes at the Elbe estuary (Xiao et al., 2011). For other
310 substances, no significant seasonal or spatial variations were observed.

311 The salinities were less than 1 PSU from E619 to E689 and the fresh water was presumed
312 to not be diluted by marine water. In this study, average PFAS concentrations from E619 to
313 E689 were introduced to estimate the annual discharges of PFASs from the River Elbe to the
314 North Sea. The results are shown in Fig. 5. \sum PFAS annual discharge was estimated as $335 \pm$
315 100 kg/year. This value was slightly less than that in 2007 (480 kg/year to 540 kg/year), while
316 the result obtained in 2007 included more substances than obtained in the present study, i.e.,
317 perfluoroheptanoic acid (PFHpA) (Ahrens et al., 2009b). The annual discharges of PFBS (69
318 ± 46 kg/year), PFHxA (71 ± 37 kg/year), and PFOA (83 ± 36 kg/year) were comparable, and
319 were greater than those of PFOS (35 ± 14 kg/year) and PFBA (29 ± 35 kg/year). For the River
320 Weser, no freshwater sample was collected, and the mass flux of \sum PFASs from the estuary
321 (W2) to the open North Sea was estimated to be 102 ± 22 kg/year. Pistocchi and Loos (2009)
322 estimated discharges of PFOA and PFOS from European rivers in 2007. The discharge of
323 PFOS (70 kg/year) in the River Elbe was higher than that in 2011 (35 ± 14 kg/year), and
324 discharges of PFOA were comparable in 2007 (80 kg/L) and 2011 (83 ± 36 kg/year). In the
325 River Weser, the discharge of PFOS in 2007 was estimated to be 120 kg/year, which was
326 significantly greater than that in 2011 (10 ± 7 kg/year), while PFOA discharge also decreased
327 from 90 kg/year in 2007 to 23 kg/year in 2011.

328 **4. Conclusion**

329 PFBS is the predominant compound in both surface water bodies, accounting for 24% and
330 31% of \sum PFASs concentrations in river and marine water, respectively. From 2006 to 2011,
331 PFOA and PFOS concentrations showed decreasing trends in the River Elbe at locations
332 where marine water did not intrude due to regulation of C₈-based products. WWTPs may not
333 be comparable to other sources of PFOS in the River Elbe from Hamburg City to the estuary,
334 considering the moderate contribution and the development of more effective treatment
335 methods. PFOA and PFHxA showed significant seasonal variation in 2011, which might
336 relate to variations in water discharge in the River Elbe. The entire year monitoring work in

337 the future were suggested to identify the occasional events, the point and non-point sources.
338 The concentrations of PFBA in river and marine waters were comparable and Pearson
339 correlations suggest unique sources. Air deposition was suggested to be a source, and further
340 monitoring studies should be conducted in this field. The production and use of PFBS should
341 be monitored, since it was the predominant compound in the rivers Elbe and Weser and North
342 Sea. The fluxes from the River Elbe to the North Sea did not show clear seasonal variation in
343 this study. The annual discharge of PFASs from the River Elbe was estimated to be 335 ± 100
344 kg/year, which was comparable with previous studies, and further monitoring work in this
345 area is still needed to get better understanding about the contribution of the River Elbe.

346

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350 **Appendix A. Supplementary data**

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458 **Figure caption**

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

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

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

468 Fig. 4. Comparison of PFBS, PFOS, and PFOA concentrations (ng/L) in the River Elbe in
469 2006, 2007 and 2011.

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