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1 Distribution and sources of polyfluoroalkyl substances (PFAS) in the River
2 Rhine watershed

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25 **Abstract**

26 The concentration profile of 40 polyfluoroalkyl substances (PFAS) in surface water
27 along the River Rhine watershed from the Lake Constance to the North Sea was
28 investigated. The aim of the study was to investigate the influence of point as well as
29 diffuse sources, to estimate fluxes of PFAS into the North Sea and to identify
30 replacement compounds of perfluorooctane sulfonate (PFOS) and perfluorooctanoic
31 acid (PFOA). In addition, an interlaboratory comparison of the method performance
32 was conducted. The PFAS pattern was dominated by perfluorobutane sulfonate (PFBS)
33 and perfluorobutanoic acid (PFBA) with concentrations up to 181 ng/L and 335 ng/L,
34 respectively, which originated from industrial point sources. Fluxes of \sum PFAS were
35 estimated to be ~6 tonnes/year which is much higher than previous estimations. Both,
36 the River Rhine and the River Scheldt, seem to act as important sources of PFAS into
37 the North Sea.

38

39 *Capsule:* The short-chained polyfluoroalkyl substances PFBA and PFBS replace
40 PFOA and PFOA as dominating PFAS in surface waters in the River Rhine watershed.

41

42 *Keywords:* polyfluoroalkyl substances (PFAS); polyfluoroalkyl compounds (PFCs);
43 perfluorooctane sulfonate (PFOS); perfluorobutanoic acid (PFBA); Rhine

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49 **1. Introduction**

50 Polyfluoroalkyl substances (PFAS) are man-made chemicals which have been
51 produced for over 50 years. Due to their unique chemical and physical properties, they
52 are used in paper, leather and textile coatings, fire-fighting foams and in the polymer
53 industry (Kissa, 2001). However, they are highly persistent and are known to have
54 bioaccumulative and toxic potential (Schultz et al., 2003; Lau et al., 2007) leading
55 increasing concern for the environment. PFAS have been detected ubiquitously in
56 various environmental compartments including water (Ahrens et al., 2010; Yamashita et
57 al., 2005), air (Butt et al., 2010), sediment (Ahrens et al., 2009; Zushi et al., 2010) and
58 organisms (Houde et al., 2006). They have been found in all aquatic matrixes: rain (Kim
59 and Kannan, 2007), snow (Kim and Kannan, 2007), groundwater (Schultz et al., 2004),
60 tap water (Ericson et al., 2008), rivers (Hansen et al., 2002; McLachlan et al., 2007;
61 Ahrens et al., 2009b), lakes (Boulanger et al., 2004) and coastal and offshore seawaters
62 (Yamashita et al., 2004; Yamashita et al., 2005) with the C₈-based compounds –
63 perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) – usually being
64 the dominating compounds. Sources of PFAS in surface water reported in the literature
65 are fluorochemical manufacturing facilities (Hansen et al., 2002), discharge of fire-
66 fighting foam (Moody et al., 2002), release of treated wastewater (Becker et al., 2008),
67 surface runoff water (Murakami et al., 2009), landfill leachates (Busch et al., 2010) and
68 degradation of precursor compounds (Ellis et al., 2004).

69 Due to the phase-out of PFOS-based products by 3M, the major PFAS producing
70 company 3M in 2002 (USEPA, 2002) and the restriction of PFOS in industrial and
71 consumer products by the EU directive 2006/122/EC in 2008 (EPC, 2006),
72 perfluorobutane sulfonate (PFBS), a short-chained perfluoroalkyl sulfonate (PFSA), has

73 been introduced as a substitute compound. In 2006 and 2007, Skutlarek et al. (2006) and
74 Lange et al. (2007) reported PFBS to be the predominating compound along the River
75 Rhine with local hot-spots. In River Rhine water infiltrated in dunes for drinking water
76 production PFBS was also found to be the most abundant PFAS (Eschauzier et al.,
77 2010). In addition to PFBS, perfluorobutanoic acid (PFBA), a short-chained
78 perfluoroalkyl carboxylic acid (PFCA), has already been detected in seawater from the
79 North Sea (Ahrens et al., 2009a). However, the sources of PFBS and PFBA in the
80 aquatic environment remain unknown.

81 In the present study, 75 water samples were taken along the entire course of the
82 River Rhine from the Lake Constance to the North Sea, including several major
83 tributaries like the Rivers Neckar, Main and Ruhr and waters from the Rhine-Meuse
84 delta like the Rivers Meuse and Scheldt. For 19 samples, the method performance and
85 results were compared between the GKSS Research Centre Geesthacht GmbH,
86 Germany (GKSS) and the Institute for Biodiversity and Ecosystem Dynamics,
87 University of Amsterdam, The Netherlands (IBED). This paper presents the
88 concentration profile of 40 PFAS along the entire course of the River Rhine. The
89 objectives of this study were the verification of replacement compounds of PFOS and
90 PFOA and the identification of possible (diffuse and point) sources of PFAS, especially
91 of the short-chained compounds PFBS and PFBA, in the watershed. The C₄-based
92 compounds, PFBS and PFBA, were found to be the predominating PFAS with a
93 percentage contribution of up to 94%. Therefore, this study shows that recent
94 estimations of total PFAS fluxes in rivers, e.g., published by McLachlan et al. (2007),
95 and into the North Sea have to be corrected upwards.

96

97 **2. Material and methods**

98 *2.1. Water sampling*

99 Raw freshwater and seawater samples were collected at 75 stations in September
100 and October 2008 (see Fig. 1). 36 samples were taken along the River Rhine (stations
101 1–36), 12 samples were taken from major tributaries of the River Rhine (e.g., Rivers
102 Neckar, Main, Ruhr, samples 37–48) and 20 samples were taken from waters in the
103 Rhine-Meuse delta (stations 49–68). Seven seawater samples from the North Sea along
104 the Dutch coastline were taken by the Rijkswaterstaat Waterdienst – Ministerie van
105 Verkeer en Waterstaat, The Netherlands (RWS) from the research vessel *R/V Zirfaea*
106 via a ship intake system (stations 69–75). Samples at the stations 36, 49, 51, 52, 54–57,
107 59, 61, 62 and 67 were taken by RWS via a ship intake system or from the shore. The
108 samples taken by RWS were analysed both by GKSS and IBED. The remaining
109 samples were taken by GKSS via a stainless steel bucket from bridges, pontoons or
110 from the shore and analysed only by GKSS. All samples were taken at a water depth
111 ≤ 1 m. The following secondary parameters were investigated additionally: temperature,
112 pH-value, particulate organic carbon (POC), dissolved organic carbon (DOC), total
113 organic carbon (TOC), suspended particular matter (SPM) and salinity (see Table S1
114 and S2 in the SI).

115

116 *2.2. Analysis by GKSS*

117 40 PFAS were analysed including 16 PFCAs, 7 PFSAAs, 6:2 fluorotelomer sulfonate
118 (6:2 FTS), 3 perfluoroalkyl sulfinates (PFSiAs), 4 perfluoroalkyl sulfonamides
119 (FASAs), 3 perfluoroalkyl sulfonamidoethanols (FASEs), 3 fluorotelomercarboxylic
120 acids (FTCAs) and 3 unsaturated fluorotelomercarboxylic acids (FTUCAs). Chemical

121 standards, suppliers and purity are listed in Table S3 in the Supporting Information (SI).
122 Methanol (SupraSolv), acetonitrile (LiChrosolv), ammonium hydroxide (25% for
123 analysis) and ammonium acetate were purchased from Merck (Darmstadt, Germany).
124 Millipore water was supplied by a Milli-Q Plus 185 system (Millipore).

125 The surface water samples were filtered prior to the extraction using glass fibre
126 filters (GC/C, Whatman, \varnothing 47 mm, 1.2 μ m). The water samples were extracted in a
127 clean lab (class 10 000) based on the method described by Ahrens et al. (2009a).
128 Briefly, 400 mL water samples (1 litre for the seawater samples) were spiked with 10 ng
129 of a mass labelled internal standard (IS) mix including 20 internal standards (see Table
130 S3 in the SI for internal standards) and extracted by solid-phase extraction (SPE) using
131 Oasis WAX cartridges (Waters, 150 mg, 6 cc).

132 The extracts were analysed by a high performance liquid chromatography-negative
133 electrospray ionisation-tandem mass spectrometry (HPLC-(–)ESI-MS/MS) system
134 using a HP 1100 HPLC system (Agilent Technologies) coupled to an API 3000 triple-
135 quadrupole (Applied Biosystems/MDS SCIEX) with an electrospray interface in
136 negative ionisation mode (see Ahrens et al. (2009a) for more details). One transition
137 was recorded for each compound. An instrumental blank using methanol was injected
138 with every batch.

139 Compounds without available analytical standards (perfluoropentane sulfonate
140 (PFPS), perfluorononane sulfonate (PFNS), perfluoropentadecanoic acid (PFPeDA) and
141 perfluoroheptadecanoic acid (PFHpDA)), were quantified using calibration parameters
142 of the one carbon atom longer and shorter compounds.

143

144 2.3. Analysis by IBED

145 16 native standards of PFCAs (C₅–C₁₄), perfluorooctane sulfonamide (PFOSA) and
146 PFSAAs (C₄, C₆–C₈, C₁₀) plus 7 labelled ¹³C standards of PFCAs (C₆, C₈, C₉–C₁₂), and
147 [¹³C₄]-PFOS were included in the method (Wellington Laboratories). PFBA was also
148 included in the analysis, but no results could be calculated because of poor
149 chromatographic peak shapes. All solvents used were analytical grade obtained from
150 local suppliers. Polypropylene vessels were used where possible to avoid contamination
151 or loss of analytes due to wall sorption. The determination of PFAS followed a protocol
152 described in de Voogt et al. (2006). Briefly, after the filtration the IS were added to
153 100 mL of the filtrated water. The filtrate was extracted by SPE using Sep-PAK Vac
154 3cc C18 columns. Two blank samples composed of distilled deionized water were run
155 to control for possible contamination of the analytical procedure.

156 Analysis was performed by HPLC-(–)ESI-MS/MS using a 4000QTrap (Applied
157 Biosystems/MDS SCIEX) triple quadrupole mass analyser connected to a Shimadzu
158 HPLC system. The MS/MS was tuned to record 51 transitions (in principle two for each
159 analyte, one of which was used for quantitative purposes and the other for identity
160 confirmation). Analytes were considered quantifiable if recoveries of the ¹³C standards
161 were >40%.

162

163 2.4. *Quality control*

164 The analytical methods and quality of both laboratories were approved in an
165 interlaboratory comparison study (van Leeuwen et al., 2009).

166 Due to the widespread use of PFAS in various industrial products, care was taken to
167 avoid using materials made from fluorinated polymers, such as polytetrafluoroethylene
168 (PTFE), in any step of the analytical procedure. PFOA was found in all method blanks

169 above the limit of detection (LOD) in the pg/L range. Perfluorononanoic acid (PFNA),
170 perfluoroundecanoic acid (PFUnDA), perfluorohexadecanoic acid (PFHxDA) and
171 perfluorooctadecanoic acid (PFOcDA) were found occasionally slightly above the LOD.
172 All sample concentrations were corrected by the blank concentrations. The instrumental
173 blanks showed no contamination (GKSS). The blanks of IBED showed PFOA in the
174 low ng/L range. PFBS, perfluoroheptanoic acid (PFHpA) and PFOSA were found in the
175 pg/L range while blank correction was applied for all compounds where blank levels
176 were above the limit of quantification (LOQ).

177 The mean recoveries of the internal standards in the seawater samples ranged from
178 $6 \pm 1\%$ ($[^{13}\text{C}_4]$ -PFBA) to $69 \pm 12\%$ ($[^{13}\text{C}_2]$ -PFDA) with mean recoveries of PFCAs and
179 PFSAs of $38 \pm 24\%$ and $44 \pm 22\%$, respectively (GKSS). Mean recoveries of IBED
180 ranged from $2 \pm 2\%$ ($[^{13}\text{C}_2]$ -PFDoA) to $125 \pm 12\%$ ($[^{13}\text{C}_2]$ -PFHxA) with mean
181 recoveries of C₆–C₉ PFCAs, C₁₀–C₁₂ PFCAs and PFSAs of $119 \pm 29\%$, $21 \pm 21\%$ and
182 $63 \pm 63\%$ respectively. The recoveries in the river water samples were higher ranging
183 from $22 \pm 6\%$ ($[^{13}\text{C}_4]$ -PFBA) to $105 \pm 25\%$ ($[^{13}\text{C}_4]$ -PFOSi) with mean recoveries for
184 PFCAs and PFSAs of $55 \pm 27\%$ (GKSS) while the recoveries of IBED ranged from
185 $22 \pm 22\%$ ($[^{13}\text{C}_2]$ -PFDoDA) to $155 \pm 37\%$ ($[^{13}\text{C}_5]$ -PFNA) with mean recoveries of
186 C₆–C₉ PFCAs, C₁₀–C₁₂ PFCAs and PFSAs of $153 \pm 32\%$, $56 \pm 56\%$ and $110 \pm 28\%$,
187 respectively. The problem of a low recovery of short-chained PFCAs and PFSAs
188 (GKSS) was described by Skutlarek et al. (2006) and Moody et al. (2001) while the low
189 recoveries of the long-chained PFCAs (IBED) are probably partly due to the use of C18
190 SPE extraction. The relative recoveries of the analytes, which were corrected by the
191 recoveries of the internal standards, ranged from 58% (PFBS) to 182% (6:2 FTS) with a
192 mean recovery of PFCAs and PFSAs of $95 \pm 28\%$ and $74 \pm 10\%$, respectively (GKSS).

193 The LODs were determined at a signal to noise (S/N) ratio of three ranging from
194 0.004 ng/L (PFOSi) to 1.15 ng/L (PFBA) for the seawater samples and from 0.014 ng/L
195 (3,7m₂-PFOA) to 1.60 ng/L (PFBA) for the freshwater samples (GKSS). LODs of IBED
196 ranged from 0.008 ng/L for perfluorohexane sulfonate (PFHxS) to 0.09 ng/L for PFBS
197 and PFOSA.

198 The mean repeatability based on duplicate measurement of the same extract was
199 13.5% (1–28%) and the mean reproducibility based on triplicate extraction of the same
200 sample was 23% (9–46%) (IBED).

201

202 **3. Results and discussion**

203 *3.1. Interlaboratory comparison*

204 Both GKSS and IBED used SPE for extraction and a HPLC(–)ESI-MS/MS system
205 for analysis while the SPE-cartridges and the extracted sample volumes were different.
206 Interestingly, the recoveries of the internal standards of long-chained PFCAs (>C₁₀) in
207 the analysis by GKSS were found to be higher than by IBED while the recoveries of
208 short-chained PFCAs and PFSAAs were lower. This might be caused by the usage of
209 different sample volumes and SPE materials (weak anion exchanger vs. C18) and
210 therewith different sorption, breakthrough and elution behaviour. In general, the results
211 of GKSS and IBED are in very good comparison, especially for concentrations above
212 10 ng/L with similar spatial trends and PFAS contributions (see Figure 2 for the
213 comparison of the major compounds and Table S4 in the SI). Even at levels between 1
214 and 10 ng/L, the concentrations are well comparable while higher differences were
215 observed at levels close to the LODs. Very good agreement was observed for PFDA,
216 PFOA, PFBS, PFHxS and PFUnDA where the concentrations differed by mean factors

217 of 1.5 ± 0.3 (median 1.6), 1.8 ± 1.9 (median 1.2), 1.9 ± 2.6 (median 1.2), 1.9 ± 0.6
218 (median 1.8) and 1.9 ± 0.7 (median 2.0), respectively. The highest disagreements were
219 observed for PFPeA and PFHpA with mean factors of 3.7 ± 2.7 (median 3.4) and
220 3.7 ± 1.1 (median 3.6), respectively. PFOS differed by a mean factor of 2.3 ± 1.2
221 (median 2.1) which is compared to other PFAS and more important to the recent
222 interlaboratory comparison study of van Leeuwen et al. (2009) still in very good
223 agreement. The highest disagreement was observed for PFBS at station 73 with a factor
224 of 11.5. Van Leeuwen et al. (2009) reported relative standard deviations for the PFAS
225 analysis in water within an interlaboratory comparison study of 16–69% ($n = 21$
226 laboratories), while the minimum and maximum determined concentrations differed up
227 to a factor of 11 for PFHpA and even a factor of 60 for PFBS. Therewith, the results of
228 this interlaboratory comparison show in general much better agreements than reported
229 for the analysis of PFAS in water by van Leeuwen et al. (2009). Nevertheless, there
230 seem to be systematic differences caused by different extraction methods showing
231 future need for method comparison and development in the analysis of PFAS in water.

232

233 3.2. Concentration levels and sources along the River Rhine

234 In the water samples investigated, 30 out of 40 PFAS determined were quantified
235 including 6 PFSAs (C_4 - C_9 PFSAs), 6:2 FTS, 16 PFCAs (C_4 - C_{18} PFCAs and 3,7m₂-
236 PFOA), perfluorohexane sulfinate (PFHxSi), PFOSi, PFOSA, N-methylperfluorobutane
237 sulfonamide (MeFBSA), N-methylperfluorooctane sulfonamidoethanol (N-MeFOSE),
238 N-ethylperfluorooctane sulfonamidoethanol (N-EtFOSE) and N-methylperfluorobutane
239 sulfonamidoethanol (MeFBSE). Table 1 includes the concentration ranges of the major
240 PFAS quantified by GKSS and IBED in this study. The following discussions are based

241 on the results of GKSS. The Σ PFAS concentration ranged from 0.35 ng/L in the North
242 Sea to 621 ng/L in the River Scheldt while PFOS, PFOA, PFBS and PFBA usually were
243 the major compounds (see Table S5 for individual concentrations of PFBS, PFOS,
244 PFBA and PFOA).

245 The concentration profile of the major PFAS quantified along the River Rhine is
246 shown in Figure 3. PFHxS increased significantly (Mann-Whitney-U-test [$p < 0.01$])
247 from station 4 to 5 along the River Rhine by a factor of ~ 10 with a maximum
248 concentration of 14.5 ng/L at station 7. The source could not be verified; since PFHxS is
249 used in aqueous film-forming foams and for carpet treatments (Kärman et al., 2006),
250 the increase was likely caused by direct industrial emissions or indirectly via wastewater
251 treatment plant (WWTP) effluents.

252 In addition, the concentrations of PFBS and PFBA increased significantly (Mann-
253 Whitney-U-test [$p < 0.01$]) between station 27 and 28 by a factor of 10 (from 3.80 to
254 36.66 ng/L) and 33 (from 2.25 to 75.1 ng/L), respectively. Downstream of station 28,
255 the mean concentrations were relatively constant with 117 ± 40 ng/L for PFBA and
256 45.4 ± 30.2 ng/L for PFBS. The increase was found to be originating from the effluent
257 of a WWTP treating industrial wastewaters located near the city of Leverkusen
258 upstream of station 27 (State Office of Nature, Environment and Consumer Protection
259 North Rhine-Westphalia [LANUV NRW], personal communication, 06.04.2009). In
260 2006, Lange et al. (2007) had also observed that PFBS was the dominating PFAS in the
261 River Rhine and they found a regional increase of PFBS in the same region as in the
262 present study. By the end of 2008, the operating company of the WWTP took actions to
263 reduce the discharge of PFBS and PFBA. In January 2009, the PFBS and PFBA

264 concentrations in the River Rhine downstream of the wastewater discharge had
265 decreased to ~10 ng/L (LANUV NRW, personal communication, 06.04.2009).

266 Interestingly, at station 5 and 28 long carbon chained PFCAs from C₁₁–C₁₈ and
267 3,7m₂-PFOA were detected in the range from 0.04 ng/L for 3,7m₂-PFOA to 1.76 ng/L
268 for PFOcDA. To the knowledge of the authors, this is the first time that the PFCAs up
269 to a carbon chain length of C₁₈ have been reported in European surface waters. Since
270 both stations 5 and 28 were found to be influenced by point sources (WWTP discharge
271 for station 28 as mentioned above and a suspected unknown source for station 5), the
272 occurrence of long carbon chained PFCAs might be an indicator for the discharge of
273 industrial wastewaters. However, this suggestion needs to be verified by the analysis
274 these compounds in wastewater streams.

275 PFOA and PFOS correlated significantly along the River Rhine (Pearson correlation
276 [$p < 0.01$], see Table S6 in the SI). Both PFOA and PFOS were additionally correlated
277 with PFHxA and PFDA ($p < 0.01$). It is noteworthy that especially the even carbon
278 numbered PFCAs showed strong correlations between each other and with PFOS.
279 Conversely, no significant correlations were observed between the PFSAs (C₄–C₈). In
280 addition, PFOS, PFHxA, PFOA, PFDA ($p < 0.01$) and PFHpA ($p < 0.05$) were found to
281 be correlated with DOC. This suggests that these compounds have the same common
282 sources like runoff water (Murakami et al., 2009) and/or WWTP effluents (Becker et
283 al., 2008), whereas C₄–C₇ PFSAs might have individual sources. So et al. (So et al.,
284 2007) found correlations between C₆–C₁₀ PFCAs which were suggested to be resulted
285 from degradation of FTOHs to PFCAs, what might also explain the observed
286 correlations along the River Rhine. Skutlarek et al. (2006) and de Voogt et al. (2006)
287 reported approximately five times higher PFOS and PFOA concentrations in the River

288 Rhine compared to the present study with concentrations up to 30 and 24 ng/L,
289 respectively. The PFOS and PFOA concentrations along the River Rhine observed in
290 this study are comparable to the concentrations in the River Elbe reported by Ahrens et
291 al. (2009b). Huset et al. (2008) observed PFBS concentrations in the River Glatt
292 comparable the River Rhine downstream of station 27. In general, PFOA and PFOS
293 concentrations in riverine water samples in this study are lower, while PFBS and PFBA
294 concentrations are higher compared to riverine concentrations reported in recent studies
295 which might be a result of the decreasing usage of PFOA and PFOS and concurrent
296 reduction of their emissions into the aqueous environment, and the replacement of these
297 compounds by the C₄-based compounds PFBS and PFBA.

298 The River Moehne, a tributary of the River Ruhr, showed the highest concentrations
299 of PFAS among the investigated tributaries, dominated by the PFCAs PFBA, PFPeA,
300 PFHxA and PFOA. The source of the contamination of the River Moehne still seems to
301 be the accidental spill of PFAS, which were contaminants in soil improvers applied on
302 agricultural areas in the Moehne catchment in 2006 as presented by Skutlarek et al.
303 (2006). The presently observed contamination of the River Moehne was dominated by
304 the same compounds as in 2006. Again, this shows the high persistence of PFAS,
305 including the C₄ compounds, once emitted into the aqueous environment.

306

307 *3.3. Transport through the delta and discharge into the North Sea*

308 The observed concentration levels and PFAS profiles in the Rhine-Meuse delta are
309 comparable to the River Rhine upstream of station 27 with the dominating compounds
310 PFBS and PFBA which originated from the discharge of wastewater upstream of station
311 27 (see Table 1). The ΣPFAS concentration decreased towards stations influenced by

312 seawater like the New Waterway (station 52, salinity 3.1 psu) and the North Sea Canal
313 (station 62, salinity 5.6 psu) whereas the PFOA concentration in the River New Meuse
314 (station 51) and the New Waterway was higher compared to previous stations along the
315 River Rhine flow. Industrial sites and WWTPs in the heavily industrialized
316 metropolitan area of Rotterdam upstream of station 52 could explain the higher PFOA
317 concentrations at these stations. Since PFOS was found to be higher in the North Sea
318 Canal (station 62) than in the Lake IJsselmeer (station 61) and the River IJssel and River
319 Waal (station 49 and 60), there seem to be sources for this compound in the area of
320 Amsterdam. The industrial use of PFOS in photographic coatings or as mist suppressant
321 in chromium plating, which are excluded from the restrictions by the European Union
322 (EPC, 2006), could be possible applications by means of which PFOS is still discharged
323 into the environment.

324 The Σ PFAS concentration in the River Scheldt increased by a factor of ~ 2.5
325 downstream of Antwerp centre from 233 ng/L (station 63) to a maximum concentration
326 of 621 ng/L at station 67. Similar to the River Rhine, PFBS and PFBA were the
327 dominating pollutants with concentrations up to 335 and 153 ng/L, respectively. PFOSA
328 and MeFBSA, which are precursors of short-chained PFCAs and PFSA (D'Eon et al.,
329 2006; Martin et al., 2006), were observed in concentration ranges of 2.58–4.57 ng/L and
330 1.01–3.37 ng/L, respectively, pointing to the influence of industrial discharges.
331 Additionally, MeFBSE was detected at 0.66 ng/L in the River New Meuse. MeFBSA
332 and MeFBSE were detected for the first time in riverine surface waters. Ahrens et al.
333 (2009a) reported MeFBSA and MeFBSE concentrations below 0.75 ng/L in seawater
334 from the German Bight. Since the Rivers Rhine and Scheldt showed well comparable
335 PFAS composition profiles, similar or related production processes and products might

336 cause the contaminations of the River Rhine and the River Scheldt. Industrial plants
337 located in the harbour area of Antwerp, including a fluorochemical manufacturing
338 facility, are likely sources of the contamination of the River Scheldt.

339 Annual riverine PFAS mass flows were calculated using yearly mean water
340 discharges (2200 m³/s for the River Rhine close to the Dutch-German border, 800 m³/s
341 for the River New Meuse, 250 m³/s for the River Meuse, 100 m³/s for the River Scheldt)
342 and the observed PFAS concentrations. It should be noted that the calculation of the
343 riverine mass flows is based on only one spot sample. Huset et al. (2008) used 24-hour
344 flow-proportional samples of seven consecutive days for the calculation of mass flows
345 in the River Glatt, another tributary river of the River Rhine. The mass flows might vary
346 due to seasonal trends, variations in water discharges and discontinuous immissions of
347 PFAS by industrial plants or WWTPs. Hence, the mass flows calculated in this study
348 should be seen as rough estimations. Based on the mean concentrations at the stations
349 34–36 close to the Dutch-German border, a yearly mass flow of ~17 tonnes PFAS from
350 the River Rhine into the delta and further into the North Sea can be estimated. PFBA
351 and PFBS have the highest contribution with 10.5 and 5.1 tonnes, respectively, followed
352 by PFOS, PFPeA, PFHxA and PFOA with 0.4, 0.3, 0.2 and 0.2 tonnes, respectively.
353 But, it should be noted that the discharge of PFBS and PFBA by the WWTP into the
354 River Rhine decreased markedly in the end of 2008 as mentioned above. Assuming a
355 decrease of PFBA and PFBS to 10 ng/L, this leads to an annual flow of only 0.7 tonnes
356 of both PFBA and PFBS into the delta. For the River New Meuse, an additional yearly
357 discharge of 0.8 tonnes of PFOA by the supposed sources located upstream of station 52
358 can be estimated, leading to a total discharge of ~1 tonne of PFOA from the River
359 Rhine into the North Sea per year.

360 For the River Meuse a Σ PFAS mass flow of 0.4 tonnes/year could be calculated
361 whereby PFBS, PFPeA, PFOA, PFBA, PFHxA and PFOS dominated with 0.09, 0.08,
362 0.07, 0.05, 0.03 and 0.03 tonnes/year, respectively.

363 As described earlier, the River Scheldt seems to have an important influence on the
364 contamination of the North Sea. Based on a mean discharge of 100 m³/s and in
365 consideration of the influence of seawater due to the tides, a mass flow of ~2.5 tonnes
366 PFAS per year was calculated. PFBA, PFBS, PFPeA, PFOA and PFOS constitute the
367 largest contributions to this total, with 1.4, 0.5, 0.3, 0.2 and 0.07 tonnes, respectively.

368 The total flux including the delta, the Rivers Rhine, Meuse and Scheldt can be
369 estimated to be from ~6 tonnes/year considering the decrease in the end of 2008 to up to
370 20 tonnes/year. For the River Elbe, a total PFAS mass flow of 802 kg/year in the
371 dissolved phase was estimated with individual mass flows for PFBS and PFBA of 18
372 and 35 kg/year, respectively (Ahrens et al., 2009b). The total loadings to the marine
373 environment calculated for the Rhine-Meuse delta in this study is more than 7–20 times
374 higher than for the River Elbe, while the flows for PFBS and PFBA are even more than
375 20–100 times higher. This shows that the River Rhine is a major source of PFAS to the
376 North Sea and that its impact on the contamination of the North Sea by PFAS is much
377 higher than that of the River Elbe. McLachlan et al. (2007) estimated the annual riverine
378 flux of the PFCAs (C₆–C₉) from the major European rivers to be 18.2 tonnes with
379 individual fluxes of 2.8, 0.86, 14.3 and 0.26 tonnes/year, respectively. The calculated
380 annual fluxes of C₆–C₉ PFCAs in the River Rhine from the present study of 0.3, 0.04,
381 0.2 and 0.01 tonnes, respectively, are lower than reported for the River Rhine by
382 McLachlan et al. (2007) indicating again the decreasing usage and emissions of medium
383 and long-chained PFCAs. The results of the present study show that the short-chained

384 PFBA and PFBS should be considered in future mass balances and previous
385 calculations might be underestimated, since the C4-compounds were found to be the
386 predominating compounds with the highest fluxes in the watershed. Furthermore, rivers
387 passing through highly industrialised regions like the River Scheldt need to be included
388 as they might be regional hot-spots with high fluxes despite their comparably low water
389 discharges.

390 In seawater from the Dutch coastline, a strong decrease of the concentrations of
391 Σ PFAS with increasing distance offshore was observed from station 71 (10 kilometres
392 offshore) to 74 (175 kilometres offshore) (11.6–0.35 ng/L). PFBS and PFBA were the
393 dominating PFAS at the stations near the coastline with maximum concentrations of
394 4.76 and 4.16 ng/L, respectively (station 71). The PFBS and PFBA concentrations along
395 the Dutch Coast found in this study are well in agreement with the concentrations in the
396 German Bight reported by Ahrens et al. (2009a)

397

398 3.4. *Composition profile of PFAS*

399 The relative composition profile of PFAS in surface water from the Lake Constance
400 to the North Sea was very different depending on the sampling location (see Figure 4).
401 The stations 5–7 in the River Rhine showed PFHxS as the dominating compound with a
402 relative contribution of $34 \pm 3\%$ to the total sum of PFAS, indicating the influence of a
403 different source compared to all other stations. The composition profile of station 18
404 represents the section of the River Rhine from station 8–28. In this section, the
405 influence of diffuse sources can be assumed to be higher than of point sources. PFBS
406 and PFBA were the dominating compounds downstream of station 27 with a combined

407 contribution of $84 \pm 9\%$ in the River Rhine, Rhine-Meuse delta and River Scheldt (see
408 Figure 4, stations 28, 60 and 66).

409 The stations in the North Sea close to the coastline were also dominated by PFBS
410 with 30–41% and PFBA with 34–38% which is in good agreement with the percentage
411 contributions in the Rhine-Meuse delta. The concentrations of PFBS and PFBA
412 decreased rapidly with increasing offshore distance, e.g. from 4.76 ng/L at in 10 km
413 distance (station 71) to 0.13 ng/L at 50 km distance (station 72). Therefore, coastal
414 stations are River Rhine controlled and PFAS, especially PFBA and PFBS originating
415 from the Rivers Rhine and Scheldt, are transported along the coastline with the
416 prevailing ocean currents. Ahrens et al. (2009a) observed significantly higher PFBS and
417 PFBA concentrations in the German Bight than in estuary of the River Elbe. It was
418 supposed that the PFBS and PFBA contamination originates from the River Rhine and
419 PFAS are transported into the German Bight with the easterly current. As the River
420 Rhine is the most important afflux of fresh water to the Southern Bight and the North
421 Sea, and judging from the excessive occurrence of PFBS and PFBA, the River Rhine
422 acts as a major source of these contaminants in the North Sea.

423

424 **4. Conclusions**

425 In the current study, the contamination of surface waters in the watershed of the
426 River Rhine by PFAS was found to be dominated by PFBS and PFBA with relative
427 combined contributions to total PFAS up to 94% originating predominantly from
428 industrial discharges. For the River Rhine, an industrial WWTP was identified as point
429 source for these compounds and also the River Scheldt was found to be influenced by
430 industrial PFAS discharges. Both the River Rhine and the River Scheldt seem to be

431 major sources of PFAS into the North Sea. More detailed studies along the Dutch
432 coastline and south-westwards of the Rhine-Meuse-delta estuaries are needed to
433 investigate the influence of the Rivers Rhine Scheldt and Meuse on the PFAS
434 contamination of the North Sea. Furthermore, rivers discharging from the United
435 Kingdom and in addition the River Seine, discharging into the English Channel, should
436 be considered to estimate the total riverine PFAS flux into the North Sea and the
437 relative contribution of the individual rivers on the total flux.

438 For the first time long carbon chained PFCAs (up to C₁₈) and the short-chained
439 precursors MeFBSA and MeFBSE were detected in industrial regions, pointing to the
440 wide range of PFAS used in industrial applications. Therefore, future studies should
441 include various classes of PFAS to identify possible “new PFAS” and replacement
442 compounds for PFOS and PFOA.

443 The predominance of PFBS and PFBA in riverine surface waters shows the
444 replacement of the lead compounds PFOS and PFOA by the short-chained compounds
445 PFBS and PFBA which might be a result of the strict regulation of PFOS and the
446 decreasing usage and emissions of PFOA. These observations should be examined in
447 other important rivers in further studies to verify whether PFBS and PFBA are the new
448 lead compounds for (monitoring of) PFAS in water.

449

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455 PFAS in the Lower Rhine and the WWTP effluent.

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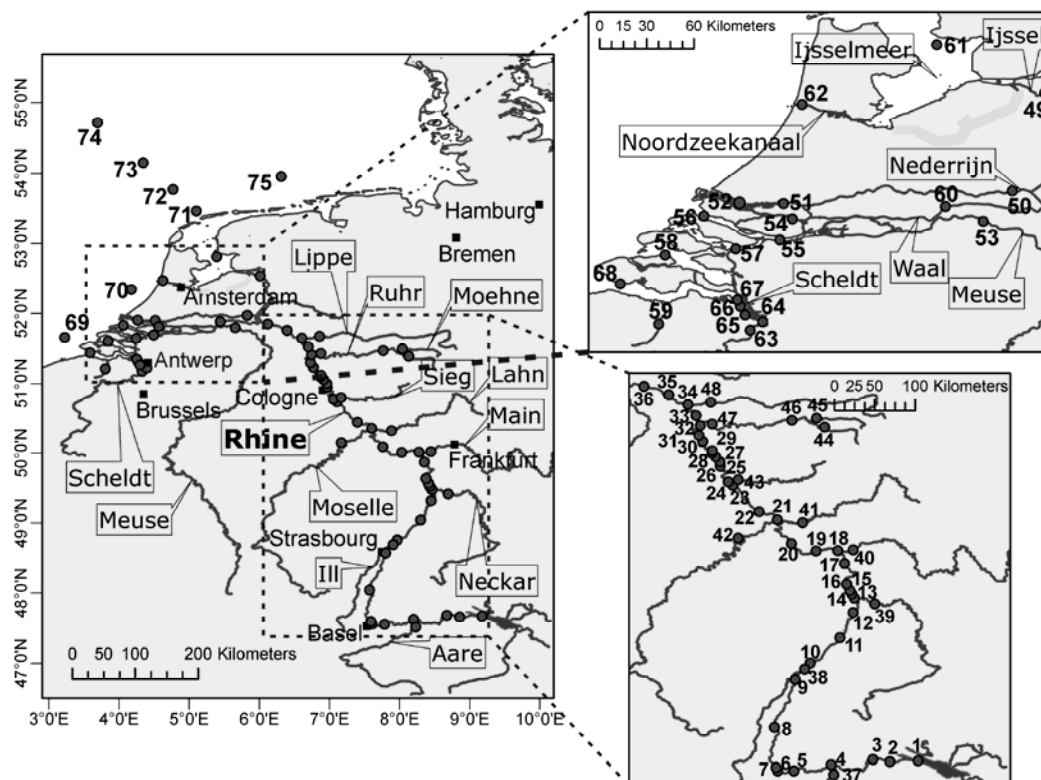
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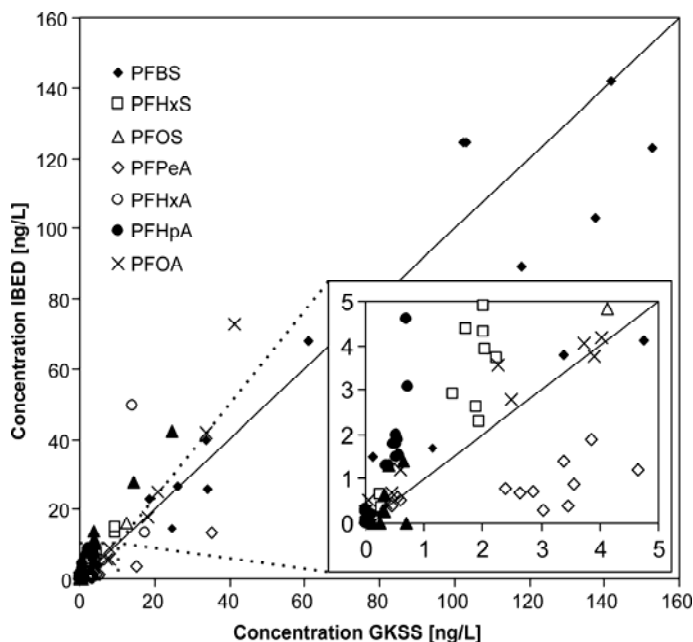
Table 1
Concentrations of individual PFAS and ΣPFAS in ng/L (mean values in brackets) in marine and freshwater samples analysed by GKSS (normal type) and IBED (*italic type*)^a.

Watersystem (stations)	PFBS	PFHxS	PFOS	PFBA ^b	PFPeA	PFHxA	PFHpA	PFOA	ΣPFAS
Rhine upstream Leverkusen (1–27)	0.59–6.58 (3.19)	<0.51–14.5 (3.04)	1.41–6.38 (3.70)	<1.60–2.48 (1.44)	<0.66–9.99 (3.65)	0.62–3.47 (2.00)	<0.12–0.97 (0.43)	0.61–3.44 (2.13)	4.08–38.5 (21.0)
Rhine downstream Leverkusen (28–36)	15.0–118 (45.40) 89.35	1.66–2.44 (1.93) 3.72	3.03–7.34 (4.13) 7.74	75.5–188 (117)	1.94–7.79 (4.28) 0.73	2.25–4.48 (2.86) <i>n.d.</i>	0.16–0.74 (0.49) 1.3	2.26–4.07 (3.11) 3.57	119–268 (181) 109
River Ruhr (44,46,47)	2.87–11.4 (7.08)	<0.51–0.53 (0.18)	0.89–10.1 (4.21)	10.8–27.5 (16.6)	15.5–27.6 (21.35)	5.66–13.8 (8.74)	0.73–1.23 (0.99)	8.93–17.9 (14.3)	64.8–96.9 (76.4)
River Moehne (45)	31.1	1.03	3.11	115	59.3	49.9	5.78	42.1	309
Other tributaries (37–43, 48)	0.22–6.82 (2.84)	<0.51–2.93 (1.41)	1.11–7.07 (3.62)	<1.60–8.38 (2.50)	<0.66–12.1 (4.61)	<0.25–9.86 (2.70)	<0.12–1.31 (0.52)	0.87–11.7 (3.47)	6.32–57.2 (22.9)
Nederrijn, Waal, IJssel (49,50,60)	138–181 (163) <i>103</i>	1.50–2.04 (1.80) 2.9	3.32–7.11 (4.88) 10.5	74.1–85.2 (79.4)	1.85–2.38 (2.16) 0.8	2.35–2.56 (2.47) <i>n.d.</i>	0.30–0.58 (0.41) 1.30	2.48–3.37 (3.05) 2.78	228–287 (260) 125
Hollands Diep (55)	142 <i>142</i>	1.71 4.39	3.95 10.0	106	3.45 0.41	2.85 <i>n.d.</i>	0.54 1.90	3.91 3.76	265 164
Volkerak-Zoom (57)	18.4 <i>23.0</i>	1.90 2.63	3.51 7.60	43.4	4.65 1.21	3.83 <i>n.d.</i>	0.72 3.08	7.96 5.75	86.1 47.3
Meuse (53)	10.8	1.16	3.74	5.84	9.57	4.16	2.12	9.09	49.3
New Meuse (51)	103 <i>125</i>	2.10 6.76	3.94 8.33	114	2.65 0.69	2.70 <i>n.d.</i>	0.51 2.00	33.9 41.62	265 187
Old Meuse (54)	102 <i>125</i>	2.02 4.31	3.92 13.7	115	3.56 0.89	2.92 <i>n.d.</i>	0.52 1.5	7.03 5.79	238 155
New Waterway (52)	61.0 <i>67.9</i>	2.02 4.92	1.34 8.05	105	3.38 1.39	2.99 <i>n.d.</i>	0.51 1.80	18.1 17.8	195 104
IJsselmeer (61)	34.0 <i>25.7</i>	1.95 2.30	4.12 4.84	36.0	5.42 1.07	3.70 <i>n.d.</i>	0.48 1.80	4.02 4.17	91.1 42.7
North Sea Canal (62)	24.8 <i>14.3</i>	4.42 7.05	12.4 16.1	32.4	3.85 1.91	3.70 <i>n.d.</i>	0.69 4.60	8.06 9.00	92.9 56.0
Haringvliet (56)	26.3 <i>26.4</i>	2.05 3.93	4.33 10.9	76.0	3.04 0.28	3.14 <i>n.d.</i>	0.57 1.53	3.74 4.07	121 50.5
Scheldt (63–67)	71.2–153 (108) <i>123</i>	7.70–9.75 (8.51) 13.2	12.9–18.6 (15.4) 27.8	87.9–335 (261)	14.1–69.5 (41.9) 13.5	9.99–17.4 (15.1) 13.5	2.38–4.73 (3.31) 8.79	16.7–41.4 (34.1) 72.9	233–621 (498) 279
Western Scheldt (68)	17.9	1.53	3.32	53.5	7.89	2.69	0.65	6.86	95.3
Eastern Scheldt (58)	7.33	<0.51	1.07	8.00	1.62	0.86	<0.12	1.92	20.8
Ghent-Terneuzen Canal (59)	33.8 <i>40.0</i>	9.52 14.8	24.8 42.1	49.8	15.3 3.79	14.1 49.6	3.31 7.93	20.9 24.8	197 210
North Sea (69–75)	<0.08–4.76 (1.72) <i>1.50–4.13</i> (2.78)	n.d.–0.28 (0.11) <i>0.08–0.66</i> (0.36)	0.25–0.70 (0.42) <i>0.26–1.40</i> (0.78)	<1.15–4.16 (1.59)	<0.15–0.59 (0.33) <i>0.08–0.58</i> (0.31)	<0.03–0.37 (0.18) <i>n.d.</i>	n.d.–<0.016 (0.21) <i>0.004–0.34</i> (0.20)	n.d.–0.59 (0.21) <i>0.11–1.20</i> (0.48)	0.35–11.6 (4.43) <i>1.02–9.80</i> (4.36)

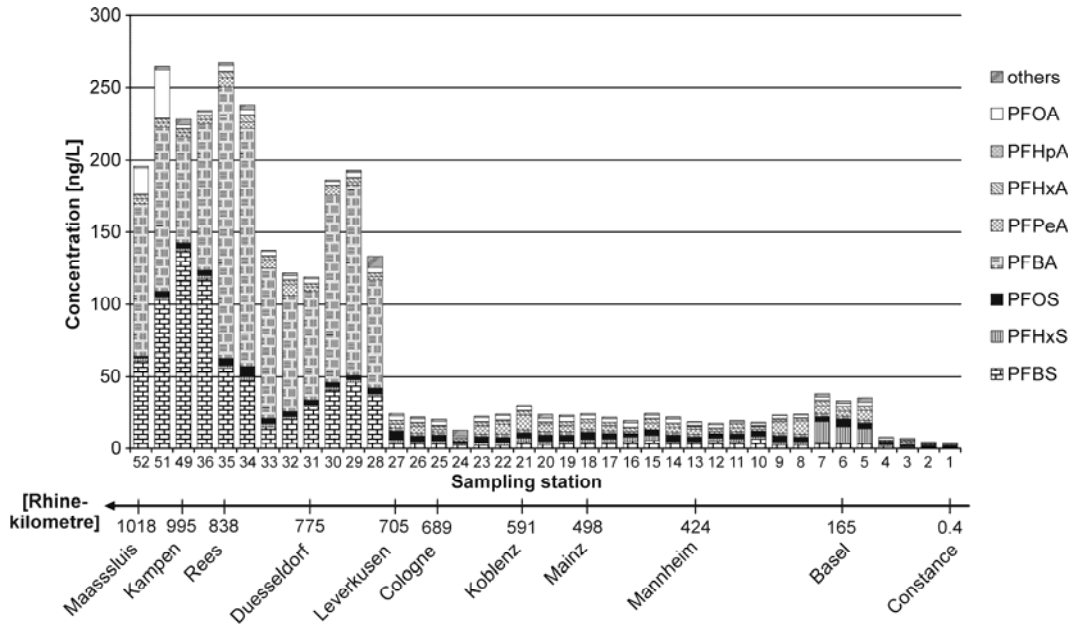
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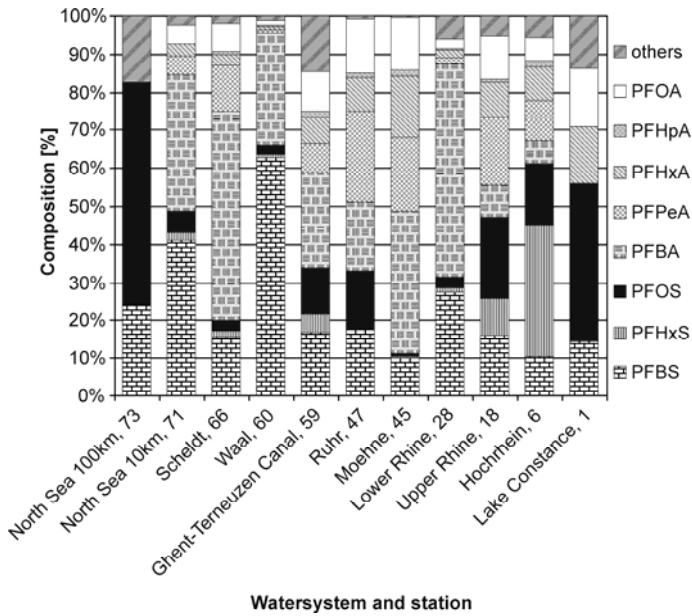
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 617 **Fig. 1.** Maps showing the sampling stations along the River Rhine, in the tributary
 618 rivers, in the Rhine- Meuse delta and in the North Sea. (Geographic data source: CCM
 619 River and Catchment Database, version 2.0 © European Commission–JRC, 2007 (Vogt
 620 et al., 2007)).
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623
 624 **Fig. 2.** Comparison of individual PFAS concentrations at sampling stations investigated
 625 by GKSS and IBED (only stations where GKSS and IBED determined concentrations
 626 above the LOD where included in the comparison).
 627



628
629 **Fig. 3.** PFAS concentration profile in surface water along the River Rhine.
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631



632
633 **Fig. 4.** Relative composition profile of individual PFAS in characteristic waters
634 investigated in this study.
635