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3 **Per- and polyfluoroalkyl substances in Chinese and German river water –**

4 **Point source- and country-specific fingerprints including unknown precur-**

5 **sors**

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Abstract

This study aimed at comparing source-specific fingerprints of per- and polyfluoroalkyl substances (PFASs) in river water from China and Germany as countries with different histories of PFAS production. Samples were collected up- and downstream of seven suspected point sources in autumn 2018. 24 of the 29 analysed legacy and emerging PFASs were detected, with a sum ranging from 2.7 ng/L (Alz River) to 420,000 ng/L (Xiaoqing River). While mass flow estimates for the Xiaoqing River and Yangtze River (mean 20 and 43 t/yr) indicated ongoing high emissions of the legacy compound PFOA in China, its ether-based replacements HFPO-DA and DONA showed the highest contribution downstream of a German fluoropolymer manufacturing site (50% and 40% of ΣPFASs measured). In river water impacted by manufacturing sites for pharmaceutical and pesticide intermediates, the short-chain compound PFBS was the most prevalent substance in both countries. The German Ruhr River, receiving discharges from electroplating industry, was characterized by the PFOS replacement 6:2 FTSA. Isomer profiling revealed a higher proportion of branched isomers in the Chinese Xi River and Xiaoqing River than in other rivers. This points to different synthesis routes and underlines the importance to include branched isomers in risks assessments. Upon oxidative conversion in the total oxidizable precursor (TOP) assay, the increase of the short-chain compound PFBA was higher in German samples than in Chinese samples (88±30% versus 12±14%), suggesting the presence of a higher proportion of unknown precursors to PFBA in the German environment. Of the ether-based replacements, HFPO-DA showed an increase upon oxidation at particular sites, whereas DONA and 6:2 Cl-PFESA were fully or partially degraded to not targeted oxidation products. This indicates that the inclusion of ether-based PFASs and their oxidation products in the TOP assay can help to capture a larger amount of the unknown PFAS fraction.

51 **Capsule**

52 Conventionally analysed PFASs only represent a fraction of the PFASs present in German and

53 Chinese river water impacted by point sources, indicating that environmental and human exposure

54 may be underestimated.

55 **Keywords**

56 Emerging contaminants, PFASs, surface water, LC-MS/MS, isomer profiling, total oxidizable pre-

57 cursor assay

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a group of anthropogenic chemicals that have been used for over 60 years due to their high thermal and chemical stability along with their amphiphilic nature (Kissa, 2001). 6330 PFAS-related CAS numbers are currently included in the "PFAS Master List", which was compiled by the United States Environmental Protection Agency (US EPA) based on the "New Comprehensive Database of PFASs" (OECD, 2018) and other publicly available lists (US EPA, 2020). The chemicals are used in a wide range of industrial applications and consumer products, such as fluoropolymer manufacture, fire-fighting foams, metal plating and surface treatment agents (Buck et al., 2011). Among the large number of PFASs, research has focused on long-chain perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$, n≥7) and perfluoroalkyl sulfonic acids (PFSAs, $C_nF_{2n+1}SO_3H$, n≥6), leading to their recognition as global contaminants of high concern. Along with their gradual phase-out and regulations in North America, Europe and Japan, an industrial transition has taken place. Production of long-chain PFCAs and PFSAs has been shifted to countries with less stringent regulations, especially to China and other Asian countries (Wang Z. et al., 2014a), and production has moved towards replacement compounds (Wang Z. et al., 2013). The common practice to replace one phased-out compound by multiple others is one reason for an increasingly large and diverse number of PFASs (Wang Z. et al., 2017). Potential adverse properties, environmental occurrence and fate of replacements are often largely unknown when the compounds are introduced into the market. By means of conventional compound-specific analytical methods, only a small fraction of the PFASs on the global market can be determined, indicating that environmental and human exposure to PFASs may be underestimated. To address this concern, targeted analytical methods have been complemented with sum parameters (McDonough et al., 2019) and high-resolution mass spectrometry (HRMS)-based approaches (Liu et al., 2019) to characterize the unknown pool of PFASs. Sum parameters include the Total Oxidizable Precursor (TOP) assay, which gives an estimate of the total precursors in a sample that oxidize to (selected) targeted PFASs (Houtz and Sedlak, 2012). Application of the

84   TOP assay to river water samples from Japan (Ye et al., 2014) and France (Boiteux et al., 2017) has

85   revealed the presence of a significant proportion of unidentified precursors, albeit varying in

86   amount. The mentioned studies have not considered replacement compounds, such as PFECAs

87   and PFESAs, as terminal products or precursors in the TOP assay. A recent study highlighted that

88   this can result in missing a fraction of the total PFAS amount (Zhang et al., 2019).

89   Studies investigating the impact of industrial point sources on the environment typically focus on

90   one study site, one geographical region and one type of source (Jin et al., 2015; Shi et al., 2015;

91   Chen et al., 2018). Due to differing analytical scopes in target analysis, especially regarding emerging

92   PFASs, and non-standardized bulk and HRMS-based approaches, there is often a lack of compa-

93   rability across studies. Consequently, a comparison of various types of point sources from regions

94   with a different history of PFAS production using one set of analytical methods can give a more

95   comprehensive picture.

96   In this study, river water samples were collected at 58 locations, up- and downstream of suspected

97   point sources at three sites in China and four sites in Germany. The sources covered major areas

98   of PFAS production and application, including fluoropolymer production, manufacturing sites for

99   pharmaceutical and pesticide intermediates, and electroplating industry. The aim was to character-

100   ize the different study sites by PFAS "fingerprints", based on the hypothesis that the fingerprints

101   depend on the type of point source and on the history of PFAS production in the two countries.

102   More specifically, the objectives were i) to investigate occurrence and composition profiles of 29

103   legacy and emerging PFASs by using target analysis, ii) to further characterize source fingerprints

104   based on isomer profiling and principal component analysis (PCA), iii) to evaluate the significance

105   of unknown precursors relative to targeted PFASs by applying the TOP assay with an expanded

106   list of target analytes, including replacement compounds, and iv) to estimate riverine PFAS mass

107   flows. To complement these results, a PFAS suspect screening was performed. The results of this

108   HRMS-based approach will be presented in a second manuscript (Joerss et al., 2020, in prepara-

109   tion).

2. Materials and methods

2.1 Study sites

River water samples were collected at seven sites, which had been previously reported to be impacted by industrial point sources (Figures S1 to S3). Site XQ was located in the Chinese Xiaoqing River basin (Huantai, Shandong Province), receiving discharge of one of the largest Asian fluoropolymer production sites (Figure S3). The chemical park's annual polytetrafluoroethylene (PTFE) production capacity was rapidly expanded from 3 kt in 2002 to 30 kt in 2009 (Wang Z. et al., 2014). In 2015, its capacity was 44.3 kt of PTFE, 13 kt of vinylidene fluoride (VDF), 10 kt of hexafluoropropylene (HFP), 10 kt of fluoroelastomers (FKM) and 8.4 kt of polyvinylidene fluoride (PVDF) (Song et al., 2018). Site FX was situated at the Xi River (Fuxin, Liaoning Province, Daling River Basin), where two fluorochemical industrial parks have been built due to the local abundance of fluorite (Bao et al, 2011). Main products include short-chain PFAAs and other fluorine-containing pharmaceutical and pesticide intermediates, as well as fluorotelomers (Chen et al., 2018). Site YZ is located at the Yangtze River in Changshu, Jiangsu Province, and in close proximity to the "Advanced Materials Industrial Park (AMIP)" with more than 15 domestic and oversea fluorochemical companies (Jin et al., 2015). Various plants for different operations have been built since 1999, e.g. for production of PTFE, PVDF and fluoroelastomers.

In Germany, samples were collected from the Alz River (site AZ), up- and downstream of a chemical park for production of fluoropolymers and fluoromonomers (Figure S2). Here, salts of PFOA have been used as processing aid until 2008 before being replaced by the ether-based compound ammonium 2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]propionate (ADONA) (Fromme et al., 2017). The three additional German sites were located along the Rhine River and its tributaries. Site MA is situated at the Main River tributary, just before discharging into the Rhine River and close to Frankfurt Airport as well as a chemical park with more than 90 companies. Amongst others, pesticide formulations containing perfluoroalkyl phosphinic acids (PFPiAs) and perfluoroalkyl phosphonic acids (PFPAs) are produced by a large agricultural chemical company operating here (Wang et al., 2016). Approximately 200 km downstream of the Main

137 River mouth, the largest chemical park in Germany is situated at the Rhine River, mainly dedicated

138 to production of pharmaceuticals and pesticides (site RH). In addition, samples were collected from

139 the Ruhr River (site RU). Historically characterized by coal mining, iron and steel production since

140 the 19th century (Bode, 1998), the Ruhr Area is still a center of metal plating. As reference site (site

141 REF), the River Rhine tributary Lahn was selected because it had been previously described as river

142 with little industrial influence and background PFAS concentrations (Skutlarek et al., 2006; Möller

143 et al., 2010).

144 **2.2 Sample collection**

145 Sampling was performed from pontoons, bridges, moles or the riverside in September 2018 (Ger-

146 many) and November 2018 (China). Water was collected 0.5 m below the surface at six to ten

147 sampling locations per site, up- and downstream of the potential source (Figures S2 and S3). In

148 total, samples for target analysis were taken at 58 stations in 1 L polypropylene (PP) bottles. At 31

149 of the stations, two aliquots of each sample were filled into 125 mL high density polyethylene

150 (HDPE) bottles for application of the TOP assay. Samples were stored at 4 °C and processed in

151 the laboratory within four weeks after sampling. Water temperature, salinity and pH were measured

152 onsite using a portable measuring device. The sampling coordinates and the results for the physi-

153 cochemical parameters are given in Tables S1 and S2.

154 **2.3 Target analytes and chemicals**

155 The analytical method included 29 target analytes from eight structural classes: 11 PFCAs (C_4 to

156 C_{14}), five PFSAs ($C_4, C_6, C_7, C_8, C_{10}$), the cyclic PFAS PFECHS, four PFECAs and PFESAs (HFPO-

157 DA, DONA; 6:2 and 8:2 Cl-PFESA), two PFPiAs (6:6 PFPiA, 6:8 PFPiA), three fluorotelomer

158 sulfonic acids (4:2 FTSA, 6:2 FTSA, 8:2 FTSA) and three sulfonamide-containing precursors

159 (FOSA, EtFOSE, N-EtFOSAA). A total of 15 internal standards was used, which included seven

160 isotopically labelled PFCAs ($^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-

161 PFUnDA, $^{13}C_2$-PFDoDA), three PFSAs ($^{13}C_3$-PFBS, $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS), one PFECA ($^{13}C_3$-

162 HFPO-DA) and two FTSAs ($^{13}C_2$-4:2 FTSA, $^{13}C_2$-8:2 FTSA) and two sulfonamide-containing pre-

163 cursors ($^{13}C_8$-FOSA, d9-N-EtFOSE). $^{13}C_8$-PFOA was used as the injection standard. CAS numbers

164 of the target analytes as well as information on the analytical standards is provided in Tables S3

165 and S4. Additional chemicals used for sample analysis are listed in Table S5.

2.4 Sample pretreatment and extraction

167 Glass microfiber filters (Whatman, grade GF/F, pore size 0.7 μm, diameter 47 mm, GE

168 Healthcare, USA) were used for filtration of the samples after baking them at 450 °C in a Muffle

169 furnace over night. Based on concentrations reported in previous studies (low ng/L to high μg/L

170 range) (Heydebreck et al., 2015; Jin et al., 2015; Chen et al., 2018) and the linear range of the

171 instrument, samples from the different sites were categorized in four categories (Table S6). Ac-

172 cordingly, 1 L river water, 500 mL, 100 mL or 1 mL diluted in 250 mL ultrapure water were used

173 for target analysis. Solid phase extraction (SPE) was performed as described previously (Joerss et

174 al., 2019). Briefly, samples were spiked with internal standards (5 ng each) and loaded onto precon-

175 ditioned SPE cartridges (Oasis WAX, 6 cc, 500 mg sorbent, 60 μm particle size, Waters, USA).

176 After a washing step with 15 mL of an 80:20 (v/v) water/methanol solution, the cartridges were

177 dried under vacuum. Up to here, extraction of the German samples took place at Helmholtz-

178 Zentrum Geesthacht (HZG), whereas Chinese samples were processed at the Yantai Institute of

179 Coastal Zone Research (YIC). The dried cartridges were shipped from China to Germany and all

180 further steps of analysis were performed at HZG (Section S1). PFASs were analyzed by liquid

181 chromatography coupled to tandem mass spectrometry (LC-MS/MS), on which detailed infor-

182 mation is given in Tables S7 to S9. Quantification of PFASs, including linear (*n-*) and the sum of

183 branched (*br-*) isomers of particular target analytes, is explained in Section S2.

184 The TOP assay was performed according to Houtz and Sedlak (2012). One of the two 125 mL

185 sample aliquots was amended with 2 g potassium persulfate (60 mM) and 1.9 mL of 10 N sodium

186 hydroxide solution (150 mM). The samples were placed in a temperature-controlled water bath at

187 85 °C for 6 h. After cooling them down in an ice bath, the pH of the samples was adjusted to a

188 value between 6 and 8. The oxidized aliquot and a second untreated aliquot were spiked with in-

189 ternal standards (1.5 ng each) and processed using the target analysis method.

2.5 Quality assurance and quality control for target analysis

191 A 14-point calibration curve ranging from 0 pg/µL to 100 pg/µL was generated and measured

192 before and after each sample batch (Section S2). Due to prior categorization of the samples and

193 extraction of different sample volumes, measured concentrations were mostly within the linear

194 range of the instrument. If the linear range was exceeded, the extract was diluted with the sample

195 solvent and measured again. In a few cases, in which concentrations were still above the calibration

196 range, results have to be considered as semiquantitative (marked in Tables S17 and S18).

197 Matrix spike recovery tests for PFASs in Elbe river water at a spiking level of 3 ng/L resulted in

198 relative recoveries from 78±1% to 109±5%, except for 6:8 PFPiA with a recovery of 60±3% (Table

199 S10). Absolute recoveries of internal standards are provided in Table S11.

200 Results for target analytes that were detected in the procedural laboratory blank samples were cor-

201 rected by subtracting the average PFAS concentration in the blank samples from the concentra-

202 tions in the samples. Mean blank values plus 3 or 10 times the standard deviation were defined as

203 method detection limits (MDLs) and method quantification limits (MQLs) for compounds present

204 in the blank samples. For target analytes other than that, the calculation of the MDLs and MQLs

205 was based on a signal-to-noise ratio of 3 or 10, derived from low-level or spiked samples. As sam-

206 ples from German and Chinese rivers were processed in different laboratories, campaign-specific

207 MDLs and MQLs were calculated. MQLs ranged from 0.017 ng/L (L-FOSA) to 0.33 ng/L (PFBA)

208 in 1 L water samples. Lower sample volumes resulted in correspondingly higher MQLs (Table S12).

209 Relative standard deviations of quantifiable compounds in triplicate samples were below 20%.

2.6 Quality assurance and quality control for the TOP assay

211 To validate the TOP assay, oxidation tests with model substances were performed, including n:2

212 fluorotelomer precursors (4:2 FTSA and 6:2 FTSA), sulfonamide-containing precursors (N-Et-

213 FOSAA, N-EtFOSE) and ether-based replacement compounds (DONA; HFPO-DA and 6:2 Cl-

214 PFESA). The single compounds were added to ultrapure water at a spiking level of 15 ng/L (n=3)

215 and the TOP assay was performed as described in section 2.4. The results of the oxidation tests are

216 discussed in section 3.4.

217 Absolute recoveries of internal standards were lower in oxidized sample aliquots compared to un-

218 oxidized aliquots (Table S11). This difference has also been reported by Janda (2019). A possible

219 explanation are the sulfate anions in the oxidized aliquots, generated upon oxidation of persulfate,

220 which may compete with the anionic target analytes for ion-exchange sites of the SPE sorbent. In

221 addition, concentrations of particular target analytes (C_4-C_8 PFCAs, L-PFOS) were higher in oxi-

222 dized procedural blanks than in unoxidized procedural blanks. Consequently, MDLs and MQLs

223 were calculated separately for oxidized and unoxidized samples. For the German sampling cam-

224 paign, MQLs were in the range of 0.50 ng/L (PFUnDA) to 2.5 ng/L (L-PFOS) for unoxidized

225 samples and of 0.50 ng/L (PFUnDA) to 7.9 ng/L (PFOA) for oxidized samples (Table S14). Rel-

226 ative standard deviations of quantifiable compounds in both aliquots of triplicate samples were

227 below 20% for both aliquots.

228 **2.7 Data analysis**

229 PCA was performed with OriginPro 2018 (version 9.5) on the proportions of single PFAS con-

230 centrations to the sum of PFASs to compare the different source patterns. Eigenvalue decompo-

231 sition was performed on the correlation matrix of the dataset. Only PFASs with a detection fre-

232 quency >40% were included. Measured values between MDL and MQL were used unaltered for

233 the calculations and results <MDL were considered as $\sqrt{2}/2 \cdot$MDL.

234 PFAS mass flows in the respective rivers [t/year] were calculated by multiplying the measured

235 concentration [ng/L] with the mean annual water flow of the river [L/year] and 10^{-15} as conversion

236 factor from ng to t. Water flow data was compiled from public sources for the gauging stations

237 closest to the respective sampling sites (Table S15).

238 **3. Results and discussion**

239 **3.1 PFAS concentrations and composition patterns**

240 24 of the 29 target analytes were detected in the Chinese and/or German river water samples: three

241 ether-based compounds (DONA, HFPO-DA; 6:2 Cl-PFESA), the phosphinic acid 6:6 PFPiA, the

242   cyclic PFAS PFECHS, ten PFCAs (C_4 to C_{13} PFCAs, including *n-/br*-PFHpA and *n-/br*-PFOA),

243   four PFSAs (PFBS, *n-/br*-PFHxS, PFHpS and *n-/br*-PFOS) and five precursors (4:2, 6:2 and 8:2

244   FTSA, *n-/br*-FOSA and N-EtFOSAA). The sum of these compounds ranged from 2.7 ng/L in the

245   German Alz River upstream of the point source (sample AZ_002) to 420,000 ng/L in the Chinese

246   Xiaoqing River Basin downstream of the point source (sample XQ_007). Results for individual

247   samples are provided in Tables S16 to S19.

248   HFPO-DA, used to substitute PFOA in fluoropolymer manufacture (Wang Z et al., 2013), was

249   detected in 98% of all samples. This underlines the widespread use and ubiquitous presence of this

250   compound. In contrast, the 6:2 Cl-PFESA only occurred in China, having a detection frequency of

251   82%. Presumably, this is related to the production and use of F-53B, which contains the potassium

252   salt of 6:2 Cl-PFESA as a major compound and has been applied by Chinese manufacturers as

253   alternative to PFOS salts in metal plating since the 1970s (Wang S et al., 2013). The compounds

254   DONA, PFECHS and 6:6 PFPiA were predominantly detected in German samples. However,

255   lower detection frequencies in the Chinese samples can result from higher MDLs (Table S12). Of

256   the PFCAs, PFSAs and their precursors, detection frequencies of ≥90 % in samples from both

257   countries were observed for C_4-C_9 PFCAs, PFBS, L-PFHxS and L-PFOS.

258   The comparison of PFAS concentrations and patterns before and after the suspected point sources

259   clearly indicated an impact of the source at five of the seven sites, exemplified for sites XQ and

260   AZ in Figure 1. An exception were the sites at the Yangtze River (site YZ) and the Ruhr River (site

261   RU), where no significant changes in the PFAS concentration and pattern were observed. For site

262   YZ, a strong dilution due to the large river size (mean annual discharge 27,400 m^3/s) in combina-

263   tion with an already high PFAS load due to upstream sources (Pan et al., 2018) may be an explana-

264   tion. For site RU, the results indicate that major sources are further upstream than suspected.
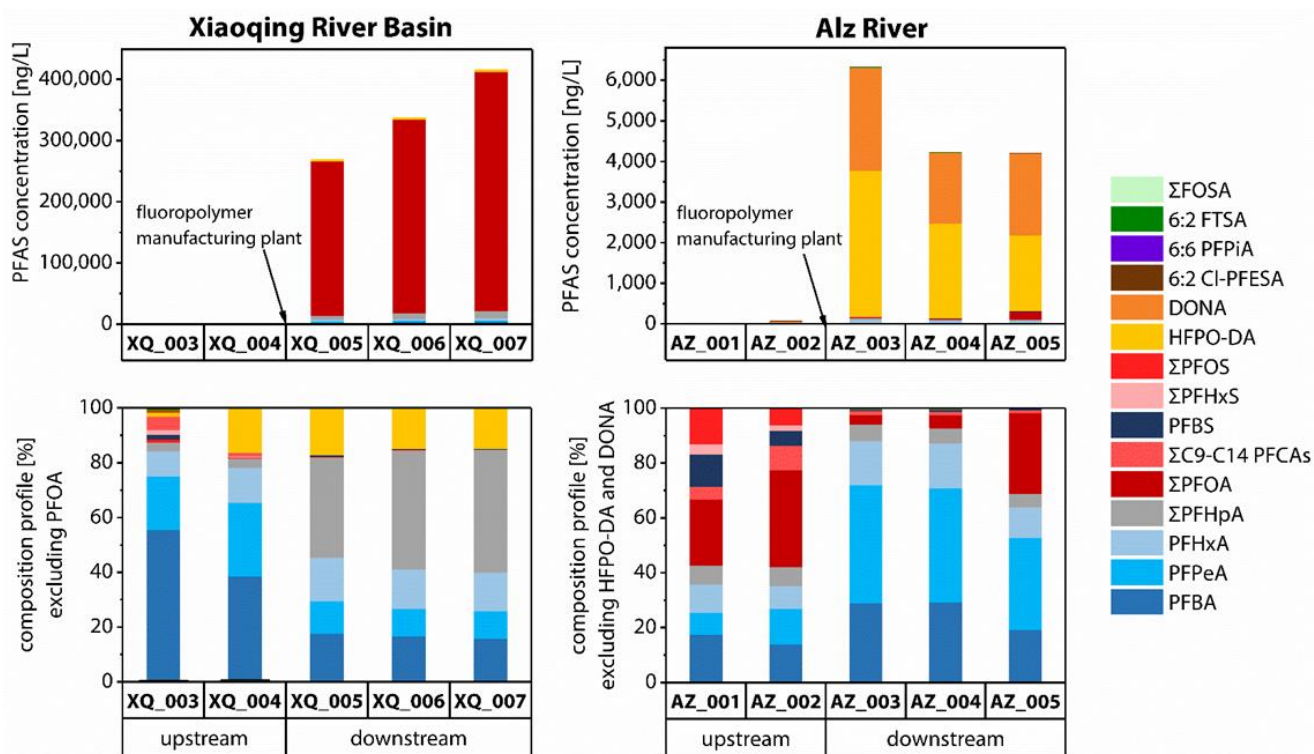
Figure 1: PFAS concentrations and composition profiles up- and downstream of the point sources at site XQ (Xiaoqing River Basin, Dong Zhulong tributary, Huantai, China) and at site AZ (Alz River, Burgkirchen, Germany). The composition profiles do not include the most dominant compounds (PFOA at site XQ and HFPO-DA and DONA at site AZ).

PFAS composition patterns of the different point sources are compared in Figure 2. The well-known legacy compound PFOA was the most prevalent substance at the Chinese fluoropolymer manufacturing site XQ, contributing approximately 90% to ΣPFASs. In contrast, its replacement compounds HFPO-DA and DONA were the predominant PFASs close to the German fluoro-polymer production facility at site AZ, contributing approximately 50% and 40% to ΣPFASs. This difference between Chinese and German fluoropolymer production sites reflects the geographical shift of production with a phase-out of long-chain PFCAs in Europe and a limited phase-out in Asian countries (Wang et al., 2014). The short-chain compound PFBS was the predominant substance downstream of the point sources at the Xi River in China (site FX) and the Rhine River in Germany (site RH), having a share of 70±6%, or respectively 66±8%. At these sites, pharmaceutical and pesticide intermediates are produced or applied, indicating the importance of short-chain PFASs or their precursors in this industrial branch. This is reinforced by a global market report,

282 according to which the second and third largest application of PFBS in 2015 was its use as inter-

283 mediate in the pharmaceutical industry (4.4 t) and as insecticide or for manufacture of insecticides

284 (1.4 t). 19 t of PFBS were used globally as surfactants or for their manufacture(Norwegian Envi-

285 ronment Agency, 2017). In comparison to the Lahn River as a River Rhine tributary with little

286 industrial influence (site REF), the Ruhr River was characterized by a higher proportion of 6:2

287 FTSA (1.1% of total PFASs vs. 14±3%). This can be related to the hard chrome plating shops

288 located in the highly industrialized Ruhr catchment, where salts of 6:2 FTSA are typically used to

289 replace PFOS salts as mist suppressants (Wang et al., 2013). The Main River (site MA) showed a

290 similar profile compared to site REF, albeit with a marginally higher proportion of PFHxS,

291 PFECHS, HFPO-DA and 6:6 PFPiA. This may be attributed to the close airport or the chemical

292 park located here. The Yangtze River (site YZ) was characterized by a large contribution of PFOA

293 (40±11%) and PFHxA (39±12%).
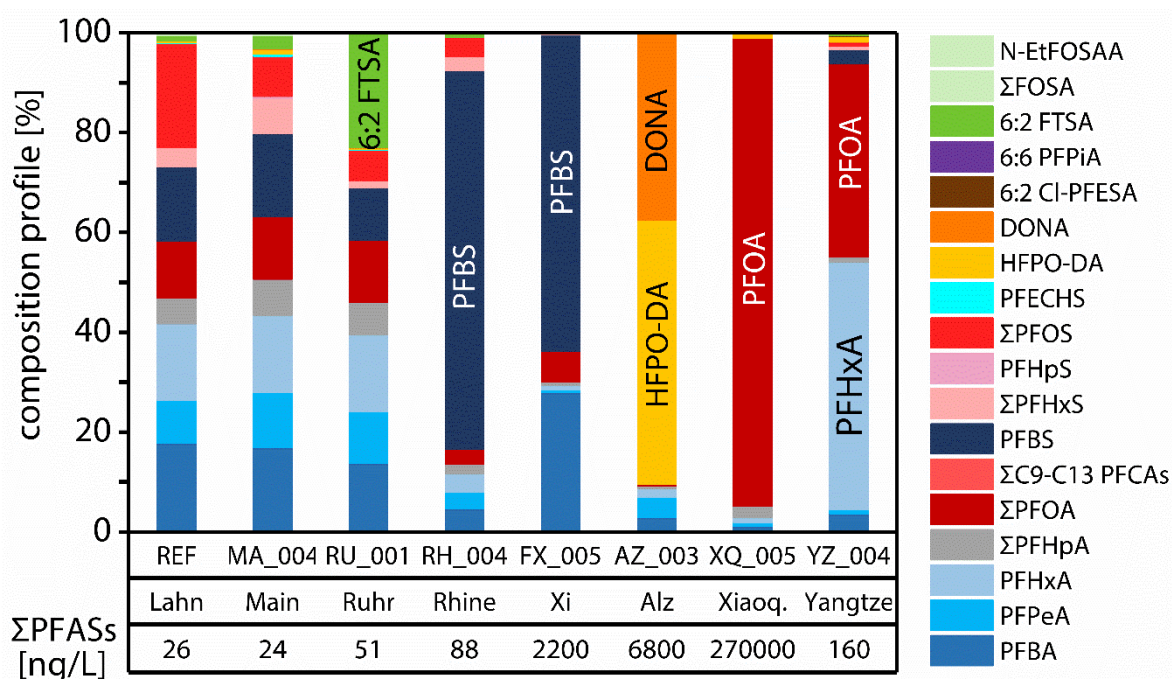
294

295 **Figure 2:** Contributions of individual PFASs to ΣPFASs in selected samples, downstream of the suspected
296 point sources in the investigated rivers.

297 **3.2 Source characterization by principal component analysis**

298 Principal component analysis revealed three distinct groupings of PFASs, explaining 72% of the

299 variability in river water concentrations (Figure 3). Detailed loadings are provided in Figure S5.

300 The first component explained 41% of the variability and included legacy long-chain PFASs other

301 than PFOA (PFNA, PFDA, ΣPFOS, ΣPFHxS and ΣFOSA), as well as the short-chain PFCAs

302 PFPeA and ΣPFHpA. This component separated the German sites at the Rhine River and its

303 tributaries from the Chinese sites and the German site at the Alz River. The second component

304 explained 16% of the variability and was dominated by the short-chain homologues PFBS and

305 PFBA (with loadings of -0.52 and -0.48) and the ether-based replacements HFPO-DA and DONA

306 (0.47 each). It had high negative scores at the site in the Xi River and high positive scores in the

307 Alz River samples. The third component explained 14% of the variability and had high negative

308 loadings of PFCAs (PFOA and PFHxA) and the PFOS alternative 6:2 Cl-PFESA. Based on this

309 component, the Xiaoqing River Basin and Yangtze River sites was distinguishable from the other

310 rivers.

311 The PCA plot shows a clear distinction between the samples taken before and after the respective

312 point source for sites AZ, XQ and RH. The closer the upstream samples were taken to the source,

313 the smaller was the variability in PFAS profiles in comparison to the samples taken after the source,

314 shown for site XQ and site AZ in Figure 3. Upstream samples taken close to the source might be

315 influenced by atmospheric inputs or other ways of PFAS discharge.
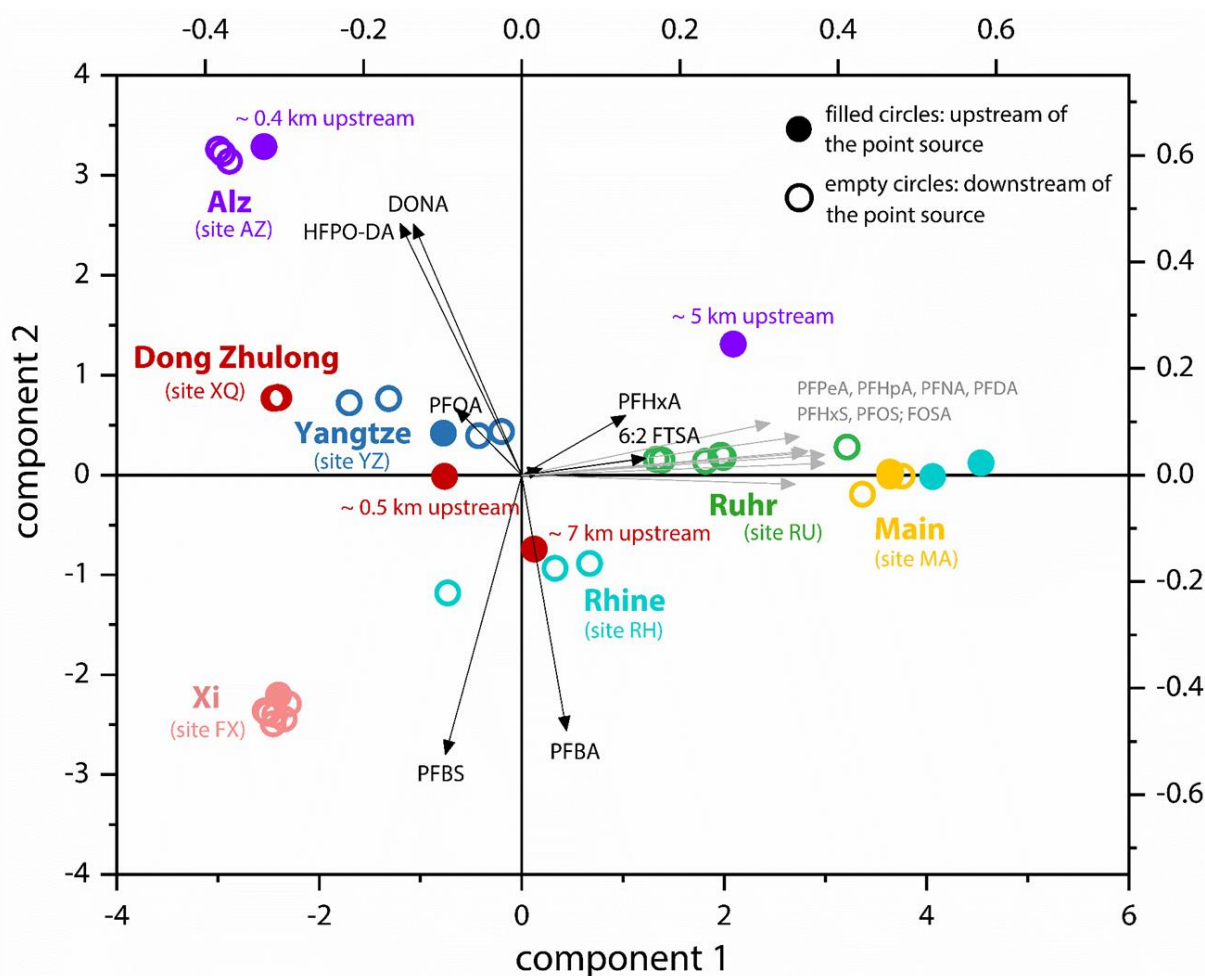
Figure 3: Results from principal component analysis (PCA) on PFASs measured up- and downstream of the suspected point sources. The figure depicts only samples taken from the rivers at which the point sources were located, not including tributaries. First and second components were plotted against each other and coloured by point source. Dominant compounds for each component are shown as vectors.

3.3 Source characterization by isomer profiling

The contribution of branched isomers to the sum of the respective compounds revealed differences between rivers and countries (Table S20). In the German samples, the percentage of the sum of branched PFOS isomers (*br*-PFOS) was 19±7 % (Figure 4A). This is in accordance with a previous study in Europe, reporting a contribution of 20% *br*-PFOS in Swedish surface waters (n=285) (Gobelius et al., 2018). The observed pattern indicates a major contribution from the historical electrochemical fluorination (ECF) manufacturing process by the 3M company, typically yielding 30% branched isomers (Benskin et al., 2010). ECF PFOS from major Chinese producers has been reported to contain a similar percentage of branched PFOS (28 to 34%) (Jiang et al., 2015). Consequently, a higher proportion of *br*-PFOS in the Chinese Yangtze River (44±12%) and Xi River

331 (77±8%) points to a higher contribution from a different synthesis route. A possible explanation

332 is a telomerization process using branched telogens as the starting material, which yields relatively

333 pure isopropyl (branched) isomers (Kissa et al., 2001; Benskin et al., 2010). For PFHxS, a similar

334 difference between German rivers and the Xi River was observed. However, the contribution of

335 21±5% *br*-PFHxS in the Yangtze River was more similar to the German samples (Figure 4A). This

336 indicates that PFHxS and PFOS in the Yangtze River result from different types of production.

337 For PFHpA and PFOA, the percentage of branched isomers was higher in the Xiaoqing River

338 Basin and in the Xi River Basin than in the German rivers and the Yangtze River (Figure 4B). The

339 percentage of branched isomers in commercial ECF PFOA products from Chinese manufacturers

340 (20-26%) has been reported to be similar to that of 3M ECF PFOA (22%) (Jiang et al., 2015; Shi

341 et al., 2015). *br*-PFOA in the Xiaoqing River Basin (19±3%) and Xi River Basin (20±2%) was

342 comparable to that of the commercial ECF products, indicating that ECF is the dominant source.

343 The lower percentage of *br*-PFOA in the other rivers (9-15%) can probably be attributed to pro-

344 duction of PFOA or fluorotelomer-based precursors by telomerization, yielding linear PFOA and

345 diluting the ECF signature. In addition, differential transport of linear and branched isomers may

346 be an explanation.

347 A higher proportion of branched isomers in the Chinese environment compared to earlier studies

348 focusing on Europe and North America (Benskin et al., 2010) has also been reported previously.

349 This includes PFOA close to fluoropolymer manufacturing plants in the Xiaoqing River Basin

350 (23% branched) (Shi et al., 2015) and in the upper Yangtze River (26±5 % branched) (Fang et al.,

351 2020) in contrast to the lower Yangtze River (12% branched) (Wang et al., 2016). These findings

352 underline that the consideration of both linear and branched isomers is important to assess envi-

353 ronmental and human health risks.
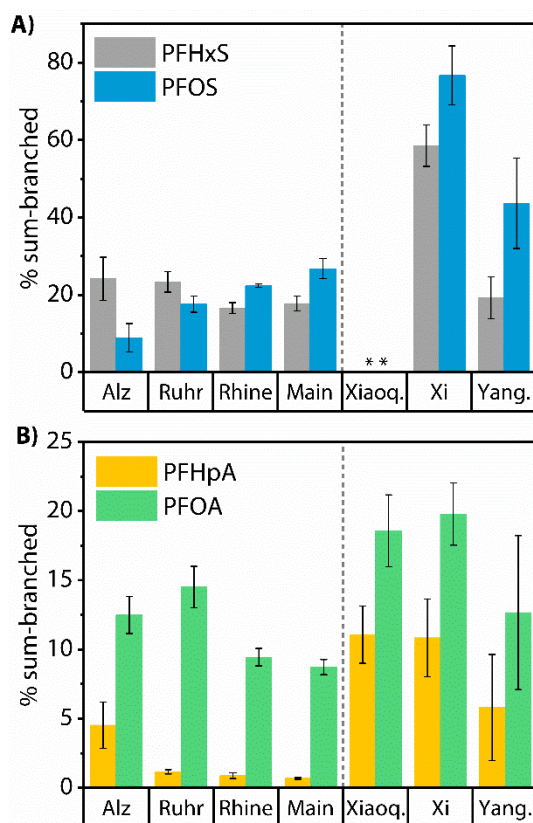
Figure 4: Percent contribution of the sum of branched isomers A) to total PFHxS and PFOS, and B) to total PFHpA and PFOA in investigated rivers (mean±standard deviation (SD)). **As results of both linear and branched isomers were below MDL in more than 50% of the samples, no mean values for the Xiaoqing River were calculated for the Xiaoqing River Basin (Xiaoq.) in A).

3.4 Contributions of unknown precursors

Molar conversion yields for oxidation tests with model precursors (section 2.6) were in good agreement with literature data (Houtz and Sedlak, 2012; Janda, 2019; Martin et al., 2019) (Table S13). Upon oxidation of n:2 fluorotelomer precursors, a mix of PFCAs resulted, whereas PFOA was the prevailing product upon oxidation of sulfonamide-containing precursors. In contrast to the results of Houtz and Sedlak (2012), the sulfonamide-containing precursors showed reproducible formation of 3-4% PFHpA in addition to the major product PFOA. This has also been reported by Martin and coauthors (2019). As its predecessor PFOA, the perfluorinated ether-based replacement compound HFPO-DA was stable under TOP assay conditions. This was also observed by Zhang et al. (2019) and indicates that the introduction of an ether bond does not improve degradability and the compound represents a new terminal end product, which should be monitored

370 when performing the TOP assay. In contrast, the polyfluorinated ether-based replacement com-

371 pounds DONA and 6:2 Cl-PFESA were partially degraded by 78±4% and 26±7% (Figure S4).

372 Based on the targeted PFASs, the oxidation products could not be identified. Zhang and coworkers

373 (2019) identified PFMOPrA as oxidation product of DONA, suggesting that the -O-CHF- moiety

374 is the site of hydroxyl radical attack. In contrast to our observations, 6:2 Cl-PFESA was reported

375 not degradable under TOP assay conditions by Zhang et al. (2019). Possible explanations for the

376 different observations are different spiking levels and concentrations of added persulfate. However,

377 in a mechanochemical destruction study by milling with KOH, 6:2 Cl-PFESA also showed better

378 degradability compared to the perfluorinated compound PFOS. Based on observations for addi-

379 tional compounds in their study, the authors concluded that the replacement of one fluorine atom

380 by chlorine rather than the introduction of the ether bond improves the degradability of the mol-

381 ecule (Zhang et al., 2016). The results underline that the TOP assay gives only a minimum estimate

382 of the sum of unknown precursors in a sample because it does not consider not targeted oxidation

383 products and not oxidizable not targeted PFASs.

384 Analysis of the river water samples resulted in an increase of ΣC_4-C_7 PFCAs by 18% to 82% in

385 German samples (mean±SD 59±19%) and up to 32% in Chinese samples (15±10%), varying be-

386 tween countries, sources and individual samples (Figure 5). In general, a higher increase of the

387 short-chain compound PFBA could be observed in German samples (88±30%) than in Chinese

388 samples (12±14%). In contrast, PFHpA showed a larger increase in Chinese samples (21±15%)

389 than in German samples (2±9%). This indicates the presence of a higher proportion of precursors

390 to short-chain PFCAs in German rivers and precursors to longer-chain PFCAs in Chinese rivers,

391 reflecting the geographical shift of production.

392 The increase of PFOA was <25% in Chinese samples, except for sample YZ_006 with a PFOA

393 increase of 460% (Table S22). This sample was not taken from flowing river water, but from stag-

394 nant, shallow water at the riverside. Possibly, the large difference between the oxidized and unox-

idized aliquot of this sample is related to a higher impact of stack emissions of the nearby fluoro-chemical industrial park, which may contain unmonitored precursors to long-chain PFCAs, such as fluorotelomer alcohols (FTOHs) or polyfluoroalkyl phosphate esters (PAPs). Due to the differences between MQLs of oxidized and unoxidized samples (see section 2.6 and Table S14), C_8 to C_{10} PFCAs were below MQL in at least one of the sample aliquots in more than 80% of the German samples. Consequently, this data was not considered for further evaluation. Results for individual samples are provided in Tables S21 and S22.

In addition to PFCAs, the replacement compound HFPO-DA showed an increase upon oxidation at particular sites. An increase of 23±9% was observed in the three Alz River samples after the point source, where HFPO-DA is a major compound and occurs in high concentrations. This indicates the presence of unknown ether-based precursors to this compound at one of its manufacturing sites and underlines the significance of HFPO-DA as terminal product.
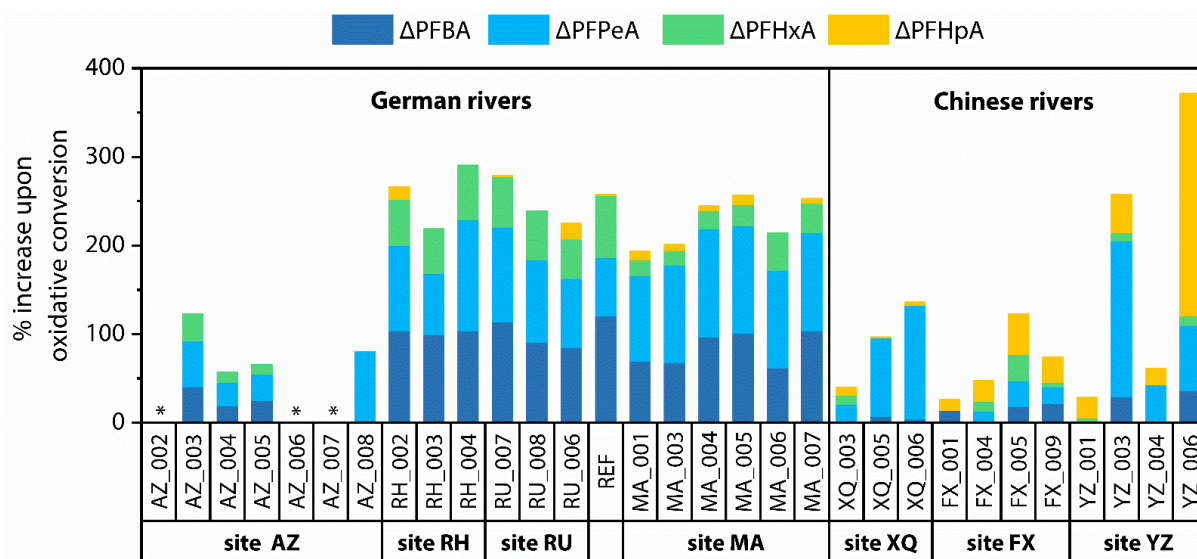
Figure 5: Percent increase of C_4 to C_7 PFCAs upon oxidative conversion by application of the TOP assay in A) German river water samples and B) Chinese river water samples. * Due to values <MDL, the % increase was not calculated for three samples from the Alz River.

Of the precursors, 6:2 FTSA was detected in 30 % of the unoxidized samples whereas it was not detectable after oxidation. Based on the molar conversion yields of 6:2 FTSA, determined during validation of the TOP assay, the percentage of the increase of C_4 to C_7 PFCAs that can be attributed to oxidation of 6:2 FTSA was calculated (Tables S23 and S24). In the 11 German samples, in which

415   6:2 FTSA was detected, 97-99% of the molar increase of C_4 to C_7 PFCAs remained unexplained

416   (Figure S6). In the two Yangtze River samples YZ_003 and YZ_004, a comparatively high propor-

417   tion of 83% and 29% of the molar increase of C_4 to C_7 PFCAs could be attributed to 6:2 FTSA,

418   pointing to direct emissions of this precursor at the manufacturing site.

419   As observed in the oxidation tests with model substances, 6:2 Cl-PFESA was degraded partially in

420   the samples (by 12±16 %). In contrast, DONA was nearly fully oxidized, e.g. the DONA concen-

421   tration in the Alz River samples decreased from 740±43 ng/L pre-TOP to 1.8±1.0 ng/L post-

422   TOP. As shown during method validation, the oxidation products of 6:2 Cl-PFESA and DONA

423   are not targeted. Consequently, the results of this study underline that the TOP assay gives a min-

424   imum estimate for oxidizable precursors and depends on targeted PFASs. The inclusion of oxida-

425   tion products other than PFCAs and of newly identified terminal products such as HFPO-DA can

426   help to capture a larger amount of total PFASs at a specific site.

427   **3.5 PFAS mass flow estimates**

428   The mean mass flow estimates for the sum of PFASs varied between 0.03 t/yr for the Lahn River

429   as a small River Rhine tributary and 100 t/yr for the Yangtze River (mean annual discharge 41 m^3/s

430   versus 27,400 m^3/s). Estimates for the individual PFASs in the investigated rivers are provided in

431   Table S25. It has to be noted that this calculation is based on a small number samples for each

432   river, taken close to point sources in different distance to the river mouths at one point in time

433   (Figure S1). Mass flows may vary due to discontinuous emissions of PFASs by the industrial plants,

434   variations in water discharge or seasonal trends. Consequently, the provided PFAS mass flows have

435   to be considered as rough estimates.

436   The sum of the mass flows was highest for PFOA, with major contributions from the Chinese

437   Xiaoqing River (mean 20 t/yr) and Yangtze River (43 t/yr). This is approximately a factor 250

438   higher than in the German Rhine River, a major contributor to PFOA discharges from the Euro-

439   pean continent (McLachlan et al, 2007; Lindim et al., 2016), underlining the significance of Chinese

440   point sources for global PFOA emissions. PFOA mass flows were in the same order of magnitude

441 as calculated in earlier studies for the Xiaoqing River (23-67 t/yr) (Shi et al., 2015) and for the

442 Yangtze River (6.7-26 t/yr) (Wang T. et al., 2016). However, the mass flow of PFHxA estimated

443 for the Yangtze River in this study (41 t/yr), based on samples from 2018, was considerably higher

444 than estimated total PFHxA discharges from 19 Chinese rivers in 2013, including the Yangtze River

445 (2.2-4.0 t/yr) (Wang T. et al., 2016). This finding suggests an increasing relevance of PFHxA in

446 China.

447 Compared to PFOA and PFHxA, the mass flows of the short-chain compound PFBS in the Ger-

448 man Rhine River had a higher contribution to the sum of transported PFASs. Although the mean

449 annual discharge of the Rhine River is only about 6% of that of the Yangtze River, the PFBS mass

450 flow in the Rhine River (2.3 t/yr) was approximately half of that in the Yangtze River (4.3 t/yr)

451 (Wang T. et al, 2016). Möller and coauthors (2010) estimated a PFBS mass flow of 5.1 t/yr for the

452 Rhine River based on samples taken at similar sampling locations in 2008. This indicates ongoing

453 emissions from the point source at site RH for more than ten years.

454 With respect to the ether-based PFASs, mass flows of HFPO-DA were in the same range in the

455 Yangtze River, Xiaoqing River and the small German Alz River (0.9, 0.3 and 0.4 t/yr), whereas the

456 Alz River was the dominant contributor for DONA (0.4 t/yr) and the Yangtze River for 6:2 Cl-

457 PFESA (0.2 t/yr).

458 The increase of C_4-C_7 PFCAs upon oxidative conversion in the TOP assay (Figure 5) indicates that

459 riverine discharge derived from conventional target analysis reveals only part of the PFASs present

460 in a sample which can ultimately be transformed to endpoint PFASs of concern, e.g. when trans-

461 ported from the rivers to the seas and further to remote areas.

462 **4. Conclusions**

463 The analysis of 29 legacy and emerging PFASs in German and Chinese river water impacted by

464 industrial point sources revealed source- and country-specific PFAS fingerprints. Estimation of

465 annual riverine mass flows underlined the ongoing high emissions of the legacy compound PFOA

466 in China from point sources in the Xiaoqing River Basin and along the Yangtze River. HFPO-DA

467 as one of its replacement compounds in fluoropolymer production could be detected in 98% of

468 the samples in this study, with highest concentration close to a German fluoropolymer manufac-

469 turing site. As PFOA has been recently added to the Stockholm Convention (BRS Secretariat,

470 2019), it can be expected that major producers in continental Asia will reduce emissions of PFOA

471 and its precursors in the foreseeable future (Wang Z. et al., 2017). Although HFPO-DA is not as

472 well-studied as PFOA, several studies indicate that it has similar properties and can be considered

473 as a "regrettable substitute" to PFOA (Gomis et al., 2015; Wang Z. et al., 2015; Gomis et al., 2018).

474 In order not to repeat the industrial transition from PFOA to HFPO-DA, which has been taking

475 place in the Western countries since the 2000s, in continental Asia, the evaluation and regulation

476 of HFPO-DA and other replacements on an international level is essential.

477 Both the higher percentage of branched isomers at Chinese sites compared to German rivers and

478 the increase of C_4 to C_7 PFCAs upon oxidative conversion in the TOP assay underline the limita-

479 tions of conventional target analysis. Dependent on the type of point source and the spectrum of

480 target analytes, human and environmental health risks may be considerably underestimated, when

481 analysing only a small proportion of the PFASs on the worldwide market. Although the TOP assay

482 is a more inclusive method, it still depends on targeted PFASs and only gives a minimum estimate

483 of the unknown oxidizable precursors present in an environmental sample. Consequently, un-

484 known PFASs in the samples can be missed by both target analysis and TOP assay. To close this

485 balance, the results from target analysis and TOP assay will be complemented by a follow-up study

486 (Joerss et al. 2020, in preparation) using a HRMS-based approach.

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