

Final Draft
of the original manuscript:

Zhang, Y.; Lai, S.; Zhao, Z.; Liu, F.; Chen, H.; Zou, S.; Xie, Z.; Ebinghaus, R.:

**Spatial distribution of perfluoroalkyl acids in the Pearl River of
Southern China**

In: Chemosphere (2013) Elsevier

DOI: [10.1016/j.chemosphere.2013.07.060](https://doi.org/10.1016/j.chemosphere.2013.07.060)

1 **Spatial Distribution of Perfluoroalkyl Acids in the Pearl**
2 **River of Southern China**

3 Yingyi Zhang¹, Senchao Lai^{1,*}, Zhen Zhao^{2,3}, Fobang Liu⁴, Hongwei Chen⁵, Shichun
4 Zou⁴, Zhiyong Xie^{2*}, and Ralf Ebinghaus²

5 *1. College of Environment and Energy, South China University of Technology,*
6 *Guangzhou, China*

7 *2. Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research,*
8 *Institute of Coastal Research, Geesthacht, Germany*

9 *3. Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of*
10 *Coastal Zone Research, CAS, Yantai, China*

11 *4. School of Marine Sciences, Sun Yat-sen University, Guangzhou, China*

12 *5. School of Chemistry & Environmental Engineering, Dongguan University of*
13 *Technology, Dongguan, China*

14

15 *Corresponding author. Tel.:+49-4152-872330; Fax: +49-4152-872332.

16 E-mail: zhiyong.xie@hzg.de

17 *Corresponding author. Tel.:+86-13570974216

18 Email: lai.senchao@gmail.com

19

20

21

22 **Abstract:**

23 An intensive campaign was conducted in September 2012 to collect surface water
24 samples along the tributaries of the Pearl River in southern China. Thirteen
25 perfluoroalkyl acids (PFAAs), including perfluorocarboxylates (PFCAs, C4-C11) and
26 perfluorosulfonates (PFSAs, C4, C6-C8, and C10), were determined using
27 high-performance liquid chromatography/negative electrospray ionization-tandem
28 mass spectrometry (HPLC/(-)ESI-MS/MS). The concentrations of total PFAAs
29 (Σ PFAAs) ranged from 3.0 to 52 ng/L, with an average of 19 ± 12 ng/L. The highest
30 concentrations of Σ PFAAs were detected in the surface water of the Dong Jiang
31 tributary (17-52 ng/L), followed by the main stream (13-25 ng/L) and the Sha Wan
32 Stream (3.0-4.5 ng/L). Perfluorooctanoate (PFOA), perfluorobutane sulfonate (PFBS),
33 and perfluorooctane sulfonate (PFOS) were the three most abundant PFAAs and on
34 average accounted for 20%, 24%, and 19% of Σ PFAAs, respectively. PFBS was the
35 most abundant PFAA in the Dong Jiang tributary, and PFOA was the highest PFAA
36 in the samples from the main stream of the Pearl River. A correlation was found
37 between PFBS and PFOA, which suggests that both of these PFAAs originate from
38 common source(s) in the region. Nevertheless, the slope of PFBS/PFOA was different
39 in the different tributaries sampled, which indicates a spatial difference in the source
40 profiles of the PFAAs.

41

42 **Keyword:** PFAAs, surface water, Pearl River, spatial variation

43 **1. Introduction**

44 Perfluorinated alkyl substances (PFASs) have been widely produced during
45 anthropogenic processes over the last 60 years (OECD, 2002; Ahrens, 2011) and are
46 used as fluoropolymer additives and surface coatings for textiles, furniture, and paper
47 products (Paul et al., 2009). Currently, PFASs are ubiquitous organic compounds in
48 various environments, i.e., atmosphere, aquatic bodies, soil, and organisms (Houde et
49 al., 2006; Busch et al., 2010b; Goosey and Harrad, 2012; Zhao et al., 2012). In the
50 past decades, the occurrence, transport, and fate of PFASs in the environment have
51 been studied due to their environmental persistency, bioaccumulation, and potential
52 adverse effects on the health of humans and wildlife (Houde et al., 2005; Pan and
53 You, 2010; Bao et al., 2011; Müller et al., 2012; Zhao et al., 2012).

54 Perfluoroalkyl acids (PFAAs), including perfluorocarboxylates (PFCAs) and
55 perfluorosulfonates (PFSAs), are the most important forms of PFASs in the
56 environment. Previous studies have reported that PFAAs can be detected in water
57 samples, including tap water (Jin et al., 2009; Llorca et al., 2012), lake water
58 (Delinsky et al., 2010; Zhou et al., 2012), river water (So et al., 2007; Wang et al.,
59 2012), and sea water (Yamashita et al., 2005; Ahrens et al., 2010). The direct source
60 of PFAAs in an aquatic environment includes air deposition, precipitation, discharge
61 from water treatment processes (Ahrens et al., 2009a), release during a PFAA-related
62 manufacturing process (Paul et al., 2009), leaching of landfills (Busch et al., 2010a),
63 and contaminated runoff (Cai et al., 2012). Public concerns that have focused on the

64 pollution of PFAAs have led to the phase-out of some PFAA species, such as
65 perfluorooctane sulfonate (PFOS). The European Union started to phase out PFOS in
66 2008, and this compound was later included in the list of Persistent Organic Pollutants
67 (POPs) of the Stockholm Convention in 2009.

68 China plays an important role in global production. On an annual basis, a large
69 amount of PFAAs are manufactured (e.g., 200 t PFOSF in 2006; Ministry of
70 Environmental Protection of China, 2008), and the contamination of PFAAs in
71 aquatic systems has been observed (So et al., 2007; Jin et al., 2009; Bao et al., 2012;
72 Sun et al., 2012). The Pearl River is the third longest river in China, and its tributaries
73 run through four provinces of southern China. The Pearl River Delta (PRD) region is
74 located in Guangdong Province and is one of the fastest developing regions of China.
75 In the past decades, industries related to the manufacture, application, and disposal of
76 PFASs have been emerging in this region, which has resulted in the aquatic system
77 being highly contaminated (So et al., 2007; Bao et al., 2010; Zhang et al., 2011).

78 The objectives of this study were (1) to investigate the concentrations and distribution
79 of PFAAs in the surface water of the Pearl River, (2) to compare the results with
80 previous studies, and (3) to understand the contamination and the sources of PFAAs
81 in the tributaries of the Pearl River.

82 **2. Materials and methods**

83 **2.1 Sampling**

84 The sampling of surface water was conducted along the tributaries of the Pearl River
85 in September 2012. Nineteen samples were collected in the main stream (MS, 10
86 samples denoted W7-W16), the Dong Jiang tributary (DJ, means East River, 6
87 samples denoted W1-W6), and the Sha Wan stream (SW, 3 samples denoted
88 W17-W19; see Figure 1). The six DJ samples were collected from three
89 sub-tributaries: the North sub-tributary (W1 and W2), the Dan Shui stream (W3 and
90 W4), and the South sub-tributary (W5 and W6). Five hundred milliliters of surface
91 water were collected in glass bottles, which were precleaned by rinsing with Milli-Q
92 water (18 M Ω , Millipore) and methanol in the laboratory. The glass bottles were
93 prebaked in the oven before sampling to remove any organic contamination. The
94 water samples were stored at 4°C in the dark. The samples were filtrated using glass
95 fiber filters (\varnothing 47 mm, 0.45 μ m, Whatman, UK) before extraction.

96 **2.2 Chemicals and standards**

97 Thirteen PFAAs, including PFCAs (C4-C11) and PFSAAs (C4, C6-C8 and C10), were
98 analyzed (see Table 1). Nine mass-labeled PFSAs were used as the internal standard
99 (IS) mixture, i.e., ¹³C-labeled ionic PFSAs and ¹⁸O-labeled perfluorohexane sulfonate
100 (PFHxS). 2H-perfluoro-[1,2-¹³C₂]-2-decenoic acid (8:2 FTUCA) was used as the
101 injection standard (InjS; Table 1). Methanol (SupraSolv) and ammonium hydroxide
102 (25%, Suprapur) were purchased from Merck (Darmstadt, Germany). The methanol
103 was distilled in a glass apparatus before use, and the Milli-Q water was precleaned
104 through cartridges (see Section 2.3) to remove any residual PFAAs in the water.

105 **2.3 Extraction and analysis**

106 The filtrates were solid-phase extracted (SPE) using glass funnels and SPE cartridges.
107 Oasis WAX cartridges (150 mg, 6 cm³, 30 mm, Waters) were used for SPE. The
108 pretreatment of the cartridges is described elsewhere (Zhao et al., 2012). After being
109 spiked with 1 ng IS (50 pg/μL, 20 μL), the filtrate was loaded onto the cartridge at a
110 rate of 2 drops per second. The cartridge was then washed with 10 mL of Milli-Q
111 water to remove the salt and dried by a vacuum pump to achieve a better recovery.
112 The dried cartridges were eluted using 10 mL of methanol with 0.1% ammonium
113 hydroxide. The elutes were reduced to 150 μL under a gentle stream of nitrogen
114 (>99.999%). Before being injected into the instrument, 1 ng (50 μL, 20 pg/μL) of
115 mass-labeled 8:2 FTUCA as the InjS was spiked into the vials.

116 The instrumental analysis was performed using a high-performance liquid
117 chromatography-negative electrospray ionization-tandem mass spectrometry system
118 (HPLC-(-)ESI-MS/MS) with an HP1100 HPLC system (Agilent, Germany) coupled
119 to an API 3000 triple-quadrupole mass spectrometer (Applied Biosystems/MDS
120 SCIEX). The instrumental setup is described elsewhere (Ahrens et al., 2009b).

121 **2.4 Quality assurance and quality control**

122 The method detection limit (MDL), recovery of each spiked sample, matrix spike
123 recoveries, field blank, and duplicate samples were measured. The results are shown
124 in Table 1. The MDLs were calculated at a signal-to-noise ratio (S/N) of 10, which
125 ranged from 0.02 ng/L (for both PFDA and PFUnDA) to 0.14 ng/L for PFBA. The

126 overall recoveries varied from $51\pm 21\%$ for $[^{13}\text{C}_4]$ -PFOS to $78\pm 20\%$ for
127 $[^{18}\text{O}_2]$ -PFHxS. The concentrations were corrected by the recoveries of IS in every
128 sample.

129

130 **3. Results and discussion**

131 Thirteen PFAAs were measured in the 19 surface water samples of Pearl River (Table
132 2). PFBA, PFPA, PFHxA, PFHpA, PFOA, PFBS, and PFOS were detected in all of
133 the samples. PFNA, PFDA, PFHxS, and PFDS were detectable in 18 of the 19
134 samples, whereas PFHpS and PFUnDA were measured in 16 and 11 samples,
135 respectively. The concentration of the total PFAA concentration (Σ PFAAs) was
136 ranged from 3.0 to 52 ng/L, with an average of 19 ± 12 ng/L. PFBS, PFOA, and PFOS
137 were the most abundant PFAAs in the samples and accounted for 24%, 20%, and 19%
138 of the Σ PFAAs.

139 **3.1 Spatial distribution**

140 The spatial distribution of the PFAA concentrations is shown in Table 3. The highest
141 concentrations of Σ PFAAs were measured in the DJ samples, which exhibited an
142 average of 29 ± 16 ng/L, followed by the MS samples (18 ± 4.2 ng/L) and the SW
143 samples (3.9 ± 0.83 ng/L). DJ has three sub-tributaries running through the city of
144 Dongguan, which is one of the most industrialized cities in the PRD region. A large
145 number of industries have been built in the past three decades, and many of these,
146 e.g., clothing, electronics, furniture, paper, and paper package making, are possible

147 sources of PFAAs (Yearbook Dongguan 2011). In 2010, the industrial production in
148 Dongguan increased by 20%, and more than 60% of this increase was due to
149 electronics, clothing, furniture manufacturing, production of packaging materials, and
150 chemical production (Yearbook Dongguan 2011). The industries in Dongguan are
151 considered the major sources of PFAA in the DJ samples. The highest and the second
152 highest concentrations of Σ PFAAs were detected in W6 (52 ng/L) and W5 (46 ng/L),
153 respectively. These two samples were collected from the south sub-tributary of DJ,
154 where the electronic and clothing industries were located. In 2010, the production
155 value of both of these industries exhibited increases of 29.50% and 17.14%,
156 respectively, in the town closest to this sub-tributary (Yearbook Dongguan 2011). The
157 concentrations of Σ PFAAs in these two samples were more than twofold higher than
158 those measured in the other DJ samples, which exhibited an average of 19 ng/L. The
159 highest concentrations of PFHpA (1.5 ng/L), PFNA (1.4 ng/L), and PFHpS (15 ng/L)
160 were measured in W5, and the three most abundant PFAAs in this sample were PFBS
161 (35%), PFHpS (32%), and PFOA (12%). The highest concentrations of PFBA (3.3
162 ng/L), PFPA (2.1 ng/L), PFHxA (2.6 ng/L), PFDA (0.64 ng/L), PFBS (23 ng/L),
163 PFHxS (1.0 ng/L), and PFOS (11 ng/L) were detected in W6. With the exception of
164 W5, PFBS (28-44%) and PFOS (18-24%) were the two most abundant PFAA species
165 in the DJ samples. Based on previous results in the same region (So et al., 2007), the
166 concentration of PFBS has increased in the past years, whereas the concentrations of
167 PFOS has markedly decreased (See Table 4). A recent study also showed a higher

168 PFBS concentration in the river sediment of the Pearl River compared with the
169 Yangtze River (Bao et al., 2011). This difference could be due to the global phase-out
170 of PFOS and the use of PFBS as a substitute for PFOS-based products. PFBS is also
171 related to the increasing production of n-methyl perfluorobutanesulfonamidoethanol
172 (MeFBSE) and its related products with four perfluorinated carbons (D'Eon et al.,
173 2006).

174 The MS samples were collected along more than 100 km of the course of the Pearl
175 River, and the concentration of Σ PFAAs in these samples ranged from 13 ng/L to 26
176 ng/L. Higher Σ PFAAs concentrations were detected in the river course in Guangzhou
177 city (i.e., samples W10 through W13, range of 19 to 26 ng/L) compared with the
178 upstream MS (15-18 ng/L) and downstream MS samples (13-16 ng/L). The highest
179 concentrations of Σ PFAAs were measured in W13 and W12 (26 and 24 ng/L,
180 respectively). The locations of these samples are close to downtown Guangzhou, and
181 two municipal waste water treatment plants (WWTPs) are located nearby. Since 2008,
182 most of the industries have moved out of Guangzhou (Yearbook Guangzhou 2011).
183 The waste water discharge in this urban area could be the major source for PFAAs in
184 the MS of the Pearl River. Guangzhou is a growing megacity in China with a
185 population of more than 15 million. Each day, 4.65×10^6 t of domestic waste water is
186 treated in Guangzhou, and more than 90% is treated in municipal WWTPs (Yearbook
187 Guangzhou 2011). WWTPs could be major point sources of PFAAs because the
188 treatment processes cannot efficiently remove PFAAs (Ahrens et al., 2009a; Bao et

189 al., 2010; Chen et al., 2012). Moreover, wet deposition in the region could also be
190 another possible source due to the frequent precipitation in the region during the
191 summer months (Liu et al., 2009). PFOA, PFBS, and PFOS were the three most
192 abundant PFAAs in the MS samples. In the urban MS samples, PFOA was the most
193 abundant PFAA (25-40%) with a concentration range of 4.9-8.7 ng/L, which is higher
194 than that obtained in the upstream (3.0-4.8 ng/L) and downstream MS samples
195 (2.4-3.2 ng/L). The downstream MS samples (W7-W9) were collected after the
196 confluence of MS and the sub-tributaries of DJ, and the concentration of Σ PFAAs was
197 in the range of 14-16 ng/L, which is lower than that obtained in the urban MS and DJ
198 samples. PFBS was the most abundant PFAA (26-31%) in the downstream MS
199 samples, which may imply the strong influence of DJ after confluence.

200 The lowest concentrations were measured in the SW samples. The concentration of
201 Σ PFAAs in these samples ranged from 3.0 to 4.5 ng/L, which is much lower than that
202 obtained in the MS and DJ samples. These results were consistent with those obtained
203 in a previous study, which showed that this tributary was less polluted by PFAAs (So
204 et al., 2007). This tributary runs through a less-developed area with a lower industry
205 and population density. PFOS and PFOA were the major PFAAs in the SW samples
206 and accounted for 17-35% and 19-24% of the total PFAA concentrations,
207 respectively.

208 **3.2 Source identification**

209 The sources of PFAAs in a river can be many. Point sources include the waste water
210 discharge of industries and WWTPs, whereas landfill leachate, dry or wet
211 atmospheric deposition, and soil/street surface runoff are suggested as non-point
212 sources (Ahrens, 2011).

213 A Spearman rank correlation analysis was conducted between the PFAAs analyzed in
214 this study. Significant positive correlations were observed between the C4-C10
215 PFCAs. With the exception of PFHpS, the other PFSAs also exhibited significant
216 correlations with each other. PFHpS was also positively correlated with PFHxA,
217 PFHpA, PFNA, PFBS, and PFHxS, which suggests that PFHpS may have other
218 potential sources. Of the three most abundant PFAAs (i.e., PFOA, PFBS, and PFOS),
219 PFOA has weak correlation with PFBS ($r = 0.376$) and PFOS ($r = 0.410$), and PFBS
220 has strong correlation with PFOS ($r = 0.722$), which suggests that PFBS and PFOS
221 may have common sources.

222 The relationship between the concentrations of PFBS and PFOA was further
223 analyzed. Linear correlations were found when the data were separated into two
224 groups (See Fig. 4). Group 1 includes the DJ and the downstream MS samples
225 (W7-W9), which indicates the influence of the DJ tributary. Group 2 includes the rest
226 of the samples, i.e., the upstream MS, urban MS, and SW samples. The strong
227 correlations found in our data showed that PFOA and PFBS might originate from
228 common sources. However, the different slope of PFBS/PFOA suggests a different
229 source profile of PFAAs in the tributaries of the Pearl River. The higher slope of

230 PFBS/PFOA observed in Group 1 may be attributed to industry-related sources, as
231 discussed above. The manufacture and usage of PFOA and its related chemicals have
232 been effectively limited after the voluntary stewardship program launched by the US
233 Environmental Protection Agency in 2006 (US Environmental Protection Agency,
234 2006). The use of short-chain PFSAAs (e.g., PFBS) as substitutes after the phase-out of
235 PFOS might explain the increase in the PFBS concentration. Similar results have been
236 observed in other rivers, such as the Rheine River in Germany (Möller et al., 2010).
237 Some previous studies have focused on the profiles of PFAAs in point sources, such
238 as WWTPs and specific industries (Ahrens et al., 2009a; Lin et al., 2009; Chen et al.,
239 2012). However, this type of work is still scarce and needs to be conducted in the
240 PRD region. Thus, further research should be conducted to understand the difference
241 in the slope of PFBS/PFOA in the different tributaries of the Pearl River and to
242 investigate the source profiles of PFAAs from specific point sources.

243

244 **3.3 Comparison with other studies**

245 The comparison of the concentrations of Σ PFAAs, PFOS, PFBS, and PFOA in the
246 rivers is shown in Table 4. The mean concentrations of Σ PFAAs were lower than
247 those found in a previous study conducted in the Pearl River in November 2004 (34
248 ng/L), whereas the range of the PFOA concentration was comparable. The PFOS
249 concentration exhibited a large decrease in the industrial area in 2012, whereas the
250 PFOS level in the less-developed region (i.e., SW) was similar. The concentration of

251 PFBS, especially that found in the DJ samples, was higher than that obtained in
252 previous study. Higher PFBS concentrations have been found in sediment samples
253 from the Pearl River compared with the Yangtze River (Bao et al., 2010). This finding
254 indicates the change in the source profiles of PFAAs after the phase-out of
255 PFOS-related products and the production of their substitutes.

256 Compared with the results in the Rhine River, the concentrations of PFAAs in this
257 study were lower than those obtained in the downstream samples (120-270 ng/L) but
258 comparable to those obtained in the upstream samples (4.1-39 ng/L). PFBS was
259 reported to be the predominant PFSA in the River Rhine, and industries were
260 suggested to be the main sources (Möller et al., 2010). Higher concentrations of
261 Σ PFAAs were found in the River Ruhr, where the most abundant PFAA was PFOA,
262 whereas the levels of PFBS and PFOS were similar (Möller et al., 2010). Markedly
263 higher concentrations of PFBS and PFOA were observed in this study compared to
264 those detected in Spanish rivers, although the range of the PFOA concentration was
265 comparable (Sanchez-Avila et al., 2010).

266 **4. Conclusions**

267 PFAAs, including PFCAs and PFSAs, were investigated in the tributaries of the Pearl
268 River in southern China. The concentration of Σ PFAAs was in the range of 3.0 to 52
269 ng/L, which is comparable to that obtained in a previous study in the Pearl River that
270 was conducted in November 2004. A decrease in the PFOS concentration and an
271 increase in the PFBS concentration were observed. These differences were due to the

272 global phase-out of PFOS and the rise in the manufacturing and consumption of
273 PFOS substitutes, such as PFBS. The highest concentration range of PFAAs was
274 observed in DJ, which is one of the tributaries of the Pearl River. The industries in the
275 city of Dongguan are likely the major sources of the relatively high levels of PFAAs
276 and the predominance of PFBS. In the MS samples, the contributions of urban point
277 sources (WWTPs) and non-point sources (precipitation) were suggested. The surface
278 water in the SW stream was found to be less contaminated by PFAAs. Linear
279 correlations between PFBS and PFOA were found in the tributaries of the Pearl River,
280 but these exhibited different PFBS/PFOA slopes, which indicate the different source
281 profiles of PFAAs in the tributaries of the Pearl River.

282

283 **Acknowledgments**

284 The authors would like to thank Prof. Feng Zeng at Sun Yat-sen University and Mr.
285 Jianzhen Tang at South China University of Technology for their help with the
286 laboratory preparation and sampling.

287

288 **References**

289 (OECD), O.f.E.C.-o.a.D., 2002. Hazard assessment of perfluorooctane sulfonate
290 (PFOS) and its salts.

291 Ahrens, L., 2011. Polyfluoroalkyl compounds in the aquatic environment: a review of
292 their occurrence and fate. *Journal of Environmental Monitoring* 13, 20-31.

293 Ahrens, L., Felizeter, S., Sturm, R., Xie, Z.Y., Ebinghaus, R., 2009a. Polyfluorinated
294 compounds in waste water treatment plant effluents and surface waters along the
295 River Elbe, Germany. *Marine Pollution Bulletin* 58, 1326-1333.

296 Ahrens, L., Gerwinski, W., Theobald, N., Ebinghaus, R., 2010. Sources of
297 polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea:
298 Evidence from their spatial distribution in surface water. *Marine Pollution Bulletin*
299 60, 255-260.

300 Ahrens, L., Plassmann, M., Xie, Z.Y., Ebinghaus, R., 2009b. Determination of
301 polyfluoroalkyl compounds in water and suspended particulate matter in the river
302 Elbe and North Sea, Germany. *Frontiers of Environmental Science & Engineering in*
303 *China* 3, 152-170.

304 Bao, J., Liu, W., Liu, L., Jin, Y., Ran, X., Zhang, Z., 2010. Perfluorinated compounds
305 in urban river sediments from Guangzhou and Shanghai of China. *Chemosphere* 80,
306 123-130.

307 Bao, J., Liu, W., Liu, L., Jin, Y.H., Dai, J.Y., Ran, X.R., Zhang, Z.X., Tsuda, S.,
308 2011. Perfluorinated Compounds in the Environment and the Blood of Residents
309 Living near Fluorochemical Plants in Fuxin, China. *Environmental Science &*
310 *Technology* 45, 8075-8080.

311 Bao, L.J., Maruya, K.A., Snyder, S.A., Zeng, E.Y., 2012. China's water pollution by
312 persistent organic pollutants. *Environ. Pollut.* 163, 100-108.

313 Busch, J., Ahrens, L., Sturm, R., Ebinghaus, R., 2010a. Polyfluoroalkyl compounds in
314 landfill leachates. *Environ. Pollut.* 158, 1467-1471.

315 Busch, J., Ahrens, L., Xie, Z.Y., Sturm, R., Ebinghaus, R., 2010b. Polyfluoroalkyl
316 compounds in the East Greenland Arctic Ocean. *Journal of Environmental Monitoring*
317 12, 1242-1246.

318 Cai, M.H., Yang, H.Z., Xie, Z.Y., Zhao, Z., Wang, F., Lu, Z.B., Sturm, R., Ebinghaus,
319 R., 2012. Per- and polyfluoroalkyl substances in snow, lake, surface runoff water and
320 coastal seawater in Fildes Peninsula, King George Island, Antarctica. *Journal of*
321 *Hazardous Materials* 209, 335-342.

322 Chen, H., Zhang, C., Han, J.B., Yu, Y.X., Zhang, P., 2012. PFOS and PFOA in
323 influents, effluents, and biosolids of Chinese wastewater treatment plants and
324 effluent-receiving marine environments. *Environ. Pollut.* 170, 26-31.

325 D'Eon, J.C., Hurley, M.D., Wallington, T.J., Mabury, S.A., 2006. Atmospheric
326 chemistry of N-methyl perfluorobutane sulfonamidoethanol,
327 $C_4F_9SO_2N(CH_3)CH_2CH_2OH$: Kinetics and mechanism of reaction with OH.
328 *Environmental Science & Technology* 40, 1862-1868.

329 Delinsky, A.D., Strynar, M.J., McCann, P.J., Varns, J.L., McMillan, L., Nakayama,
330 S.F., Lindstrom, A.B., 2010. Geographical Distribution of Perfluorinated Compounds
331 in Fish from Minnesota Lakes and Rivers. *Environmental Science & Technology* 44,
332 2549-2554.

333 Goosey, E., Harrad, S., 2012. Perfluoroalkyl substances in UK indoor and outdoor air:
334 Spatial and seasonal variation, and implications for human exposure. *Environment*
335 *International* 45, 86-90.

336 Houde, M., Martin, J.W., Letcher, R.J., Solomon, K.R., Muir, D.C.G., 2006.
337 Biological monitoring of polyfluoroalkyl substances: A review. *Environmental*
338 *Science & Technology* 40, 3463-3473.

339 Houde, M., Wells, R.S., Fair, P.A., Bossart, G.D., Hohn, A.A., Rowles, T.K.,
340 Sweeney, J.C., Solomon, K.R., Muir, D.C.G., 2005. Polyfluoroalkyl compounds in
341 free-ranging bottlenose dolphins (*Tursiops truncatus*) from the Gulf of Mexico and
342 the Atlantic Ocean. *Environmental Science & Technology* 39, 6591-6598.

343 Jin, Y.H., Liu, W., Sato, I., Nakayama, S.F., Sasaki, K., Saito, N., Tsuda, S., 2009.
344 PFOS and PFOA in environmental and tap water in China. *Chemosphere* 77, 605-611.

345 Li, F., Sun, H., Hao, Z., He, N., Zhao, L., Zhang, T., Sun, T., 2011. Perfluorinated
346 compounds in Haihe River and Dagu Drainage Canal in Tianjin, China. *Chemosphere*
347 84, 265-271.

348 Lin, A.Y.C., Panchangam, S.C., Lo, C.C., 2009. The impact of semiconductor,
349 electronics and optoelectronic industries on downstream perfluorinated chemical
350 contamination in Taiwanese rivers. *Environ. Pollut.* 157, 1365-1372.

351 Liu, W., Jin, Y., Quan, X., Sasaki, K., Saito, N., Nakayama, S.F., Sato, I., Tsuda, S.,
352 2009. Perfluorosulfonates and perfluorocarboxylates in snow and rain in Dalian,
353 China. *Environment International* 35, 737-742.

354 Llorca, M., Farre, M., Pico, Y., Muller, J., Knepper, T.P., Barcelo, D., 2012. Analysis
355 of perfluoroalkyl substances in waters from Germany and Spain. *Science of the Total*
356 *Environment* 431, 139-150.

357 Möller, A., Ahrens, L., Surm, R., Westerveld, J., van der Wielen, F., Ebinghaus, R.,
358 de Voogt, P., 2010. Distribution and sources of polyfluoroalkyl substances (PFAS) in
359 the River Rhine watershed. *Environ. Pollut.* 158, 3243-3250.

360 Müller, C.E., Gerecke, A.C., Bogdal, C., Wang, Z.Y., Scheringer, M., Hungerbühler,
361 K., 2012. Atmospheric fate of poly- and perfluorinated alkyl substances (PFASs): I.
362 Day-night patterns of air concentrations in summer in Zurich, Switzerland. *Environ.*
363 *Pollut.* 169, 196-203.

364 Ministry of Environmental Protection of China, 2008. Preliminary Information on
365 Risk Management Evaluation of PFOS's in China
366 (http://chm.pops.int/Portals/0/Repository/comments_draftRME2008/UNEP-POPS-PO
367 [PRC-DRME-08-CHI-SCCP.English.PDF](http://chm.pops.int/Portals/0/Repository/comments_draftRME2008/UNEP-POPS-PO)).

368 Pan, G., You, C., 2010. Sediment-water distribution of perfluorooctane sulfonate
369 (PFOS) in Yangtze River Estuary. *Environ. Pollut.* 158, 1363-1367.

370 Paul, A.G., Jones, K.C., Sweetman, A.J., 2009. A First Global Production, Emission,
371 And Environmental Inventory For Perfluorooctane Sulfonate. *Environmental Science*
372 *& Technology* 43, 386-392.

373 Sanchez-Avila, J., Meyer, J., Lacorte, S., 2010. Spatial distribution and sources of
374 perfluorochemicals in the NW Mediterranean coastal waters (Catalonia, Spain).
375 Environ. Pollut. 158, 2833-2840.

376 So, M.K., Miyake, Y., Yeung, W.Y., Ho, Y.M., Taniyasu, S., Rostkowski, P.,
377 Yamashita, N., Zhou, B.S., Shi, X.J., Wang, J.X., Giesy, J.P., Yu, H., Lam, P.K.S.,
378 2007. Perfluorinated compounds in the Pearl River and Yangtze River of China.
379 Chemosphere 68, 2085-2095.

380 Sun, H.W., Zhang, X.Z., Wang, L., Zhang, T., Li, F.S., He, N., Alder, A., 2012.
381 Perfluoroalkyl compounds in municipal WWTPs in Tianjin, China-concentrations,
382 distribution and mass flow. Environmental Science and Pollution Research 19,
383 1405-1415.

384 US Environmental Protection Agency, 2006. PFOA Stewardship Program. Docket
385 EPA-HQ-OPPT-2006-0621.

386 Wang, T.Y., Khim, J.S., Chen, C.L., Naile, J.E., Lu, Y.L., Kannan, K., Park, J., Luo,
387 W., Jiao, W.T., Hu, W.Y., Giesy, J.P., 2012. Perfluorinated compounds in surface
388 waters from Northern China: Comparison to level of industrialization. Environment
389 International 42, 37-46.

390 Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G., Gamo, T., 2005. A
391 global survey of perfluorinated acids in oceans. Marine Pollution Bulletin 51,
392 658-668.

393 Zhang, K., Zhang, B.Z., Li, S.M., Zeng, E.Y., 2011. Regional dynamics of persistent
394 organic pollutants (POPs) in the Pearl River Delta, China: Implications and
395 perspectives. *Environ. Pollut.* 159, 2301-2309.

396 Zhao, Z., Xie, Z.Y., Moller, A., Sturm, R., Tang, J.H., Zhang, G., Ebinghaus, R.,
397 2012. Distribution and long-range transport of polyfluoroalkyl substances in the
398 Arctic, Atlantic Ocean and Antarctic coast. *Environ. Pollut.* 170, 71-77.

399 Zhou, Z., Shi, Y.L., Li, W.H., Xu, L., Cai, Y.Q., 2012. Perfluorinated Compounds in
400 Surface Water and Organisms from Baiyangdian Lake in North China: Source
401 Profiles, Bioaccumulation and Potential Risk. *Bulletin of Environmental
402 Contamination and Toxicology* 89, 519-524.

403

404

405

406

List of Figure Captions

407 **Figure 1.** Map of the sampling locations in the tributaries of the Pearl River.

408 **Figure 2.** Concentration of PFAAs measured in the surface water samples of the Pearl
409 River.

410 **Figure 3.** Composition profiles of PFAAs in the surface water samples of the Pearl
411 River.

412 **Figure 4.** Linear correlation between PFOA and PFBS in the surface water samples of
413 the Pearl River.

414

415

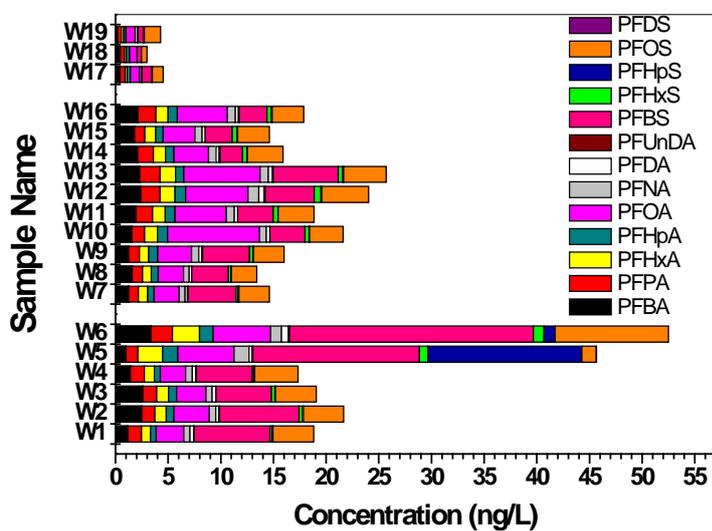
416

417



418

419 **Figure 1.**

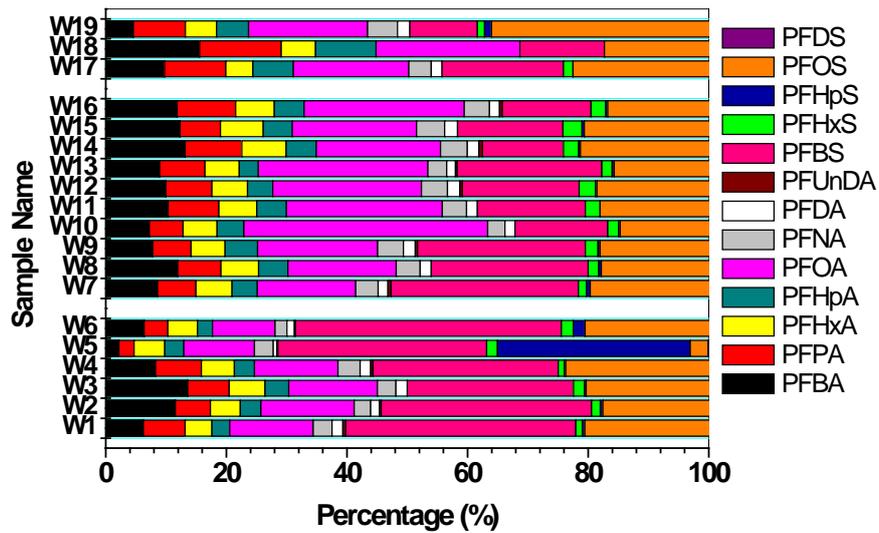


420

421 **Figure 2.**

422

423



424

425 **Figure 3.**

426

427

428

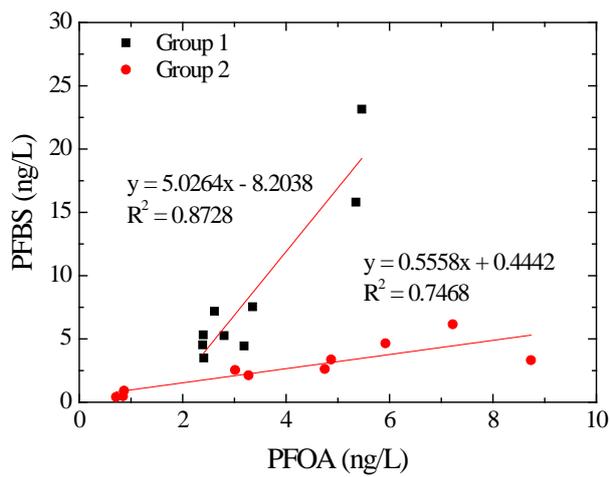
429

430

431

432

433



434 **Figure 4.**

1 **Table 1.** Analytes, acronym, precursor, and product ion for HPLC-MS/MS detection, method detection limit (MDL), and recoveries of internal standard in the
 2 water samples.

Analyte	Acronym	Precursor/ product ion [m/z]	MDL (ng/L)	Internal standard	Acronym	Precursor/ product ion [m/z]	Recovery (%)
Perfluorobutane sulfonate	PFBS	298.877/ 79.8	0.03	Perfluoro-n-(1,2,3,4- ¹³ C4)butanoic acid	[¹³ C4]-PFBA	216.823/171.8	61±22%
Perfluorohexane sulfonate	PFHxS	398.894/ 79.8	0.03	Perfluoro-1-hexane[¹⁸ O2]sulfonate	[¹⁸ O2]-PFHxS	402.981/ 83.9	78±25%
Perfluoroheptane sulfonate	PFHpS	449.034/ 79.3	0.07	Perfluoro-1-[1,2,3,4- ¹³ C4]octanesulfonate	[¹³ C4]-PFOS	502.899/ 79.5	51±21%
Perfluorooctane sulfonate	PFOS	498.971/ 79.7	0.07	Perfluoro-n-(1,2- ¹³ C2)hexanoic acid	[¹³ C2]-PFHxA	314.891/ 269.9	75±20%
Perfluorodecane sulfonate	PFDS	598.896/ 79.5	0.05	Perfluoro-n-[1,2,3,4- ¹³ C4]octanoic acid	[¹³ C4]-PFOA	416.978/ 371.8	73±20%
Perfluorobutanoic acid	PFBA	112.900/ 168.7	0.14	Perfluoro-n-[1,2,3,4,5- ¹³ C5]nonanoic acid	[¹³ C5]-PFNA	467.907/ 423.0	64±25%
Perfluoropentanoic acid	PFPA	262.825/ 218.9	0.05	Perfluoro-n-[1,2- ¹³ C2]decanoic acid	[¹³ C2]-PFDA	514.944/ 469.8	60±23%
Perfluorohexanoic acid	PFHxA	312.934/ 268.8	0.09	Perfluoro-n-[1,2- ¹³ C2]undecanoic acid	[¹³ C2]-PFUnDA	564.959/ 519.8	76±20%
Perfluoroheptanoic acid	PFHpA	862.980/818.9		Perfluoro-n-[1,2- ¹³ C2]dodecanoic acid	[¹³ C2]-PFDoDA	614.913/ 569.9	65±22%
Perfluorooctanoic acid	PFOA	412.987/ 368.9	0.07	2H-perfluoro-[1,2- ¹³ C2]-2-decenoic acid	8:2 FTUCA*	589.015/ 418.7	60±20%
Perfluorononanoic acid	PFNA	462.908/ 418.9	0.03				
Perfluorodecanoic acid	PFDA	512.876/ 469.0	0.02				
Perfluoroundecanoic acid	PFUnDA	562.865/ 519.0	0.02				
Perfluorododecanoic acid	PFDoDA	612.991/ 568.9	0.05				
Perfluorotridecanoic acid	PFTriDA	663.094/ 618.9	0.04				
Perfluorotetradecanoic acid	PFTeDA	713.036/ 669.0	0.04				

1 **Table 2.** Concentration of PFAAs (ng/L) in the surface water samples of the Pearl River Delta.

Sample	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFBS	PFHxS	PFHpS	PFOS	PFDS	ΣPFAAs
W1	1.2	1.3	0.84	0.55	2.6	0.58	0.35	0.09	7.2	0.20	0.08	3.9	<MDL	18
W2	2.50	1.25	1.08	0.74	3.4	0.59	0.31	0.07	7.5	0.32	0.09	3.8	<MDL	22
W3	2.60	1.31	1.13	0.75	2.8	0.59	0.36	<MDL	5.3	0.35	0.05	3.9	<MDL	19
W4	1.43	1.31	0.95	0.58	2.4	0.63	0.30	0.07	5.3	0.17	0.05	4.1	<MDL	17
W5	1.00	1.14	2.33	1.45	5.4	1.4	0.29	0.08	16	0.81	14	1.4	0.03	46
W6	3.34	2.06	2.58	1.30	5.5	1.0	0.64	0.10	23	1.0	1.0	11	<MDL	52
W7	1.26	0.93	0.87	0.61	2.4	0.54	0.24	0.07	4.5	0.20	0.09	2.9	<MDL	15
W8	1.60	0.96	0.83	0.66	2.4	0.53	0.25	<MDL	3.5	0.23	0.06	2.4	<MDL	13
W9	1.24	1.02	0.90	0.86	3.2	0.69	0.31	0.07	4.5	0.33	0.05	2.9	<MDL	16
W10	1.56	1.21	1.22	0.96	8.7	0.62	0.36	<MDL	3.3	0.39	0.06	3.2	<MDL	22
W11	1.95	1.58	1.18	0.93	4.9	0.76	0.34	<MDL	3.4	0.47	<MDL	3.4	<MDL	19
W12	2.39	1.84	1.41	1.01	5.9	1.0	0.50	0.10	4.7	0.65	0.06	4.5	<MDL	24
W13	2.29	1.93	1.47	0.81	7.2	0.81	0.37	0.08	6.2	0.44	0.09	4.0	<MDL	26
W14	2.09	1.49	1.17	0.80	3.3	0.70	0.31	0.09	2.1	0.40	0.05	3.4	<MDL	16
W15	1.80	0.98	1.03	0.71	3.0	0.68	0.31	<MDL	2.6	0.47	0.06	3.0	<MDL	15
W16	2.12	1.73	1.15	0.89	4.8	0.75	0.30	0.09	2.6	0.43	0.06	3.0	<MDL	18
W17	0.44	0.46	0.20	0.30	0.87	0.17	0.08	<MDL	0.91	0.07	<MDL	1.0	<MDL	4.5
W18	0.46	0.40	0.17	0.30	0.71	<MDL	<MDL	<MDL	0.42	<MDL	<MDL	0.52	<MDL	3.0
W19	0.20	0.37	0.22	0.23	0.85	0.21	0.09	<MDL	0.48	0.05	0.05	1.6	<MDL	4.3

2
3
4
5

1 **Table 3.** Range and mean concentration of Σ PFAAs and dominant PFAA in the tributaries of the Pearl River.

Location	Sub-tributary	Sample	Mean of Σ PFAAs (ng/L)	Range (ng/L)	Predominant PFAA (ng/L)
Dong Jiang (DJ)	North	2	20±2.0	19-22	PFBS(7.4)
	Dan Shui	2	18±1.2	17-19	PFBS(5.3)
	South	2	49±4.8	46-52	PFBS(19)
Main stream (MS)	Upstream	3	16±1.6	15-18	PFOA(3.7)
	Urban Guangzhou	4	23±3.0	19-26	PFOA(6.7)
	Downstream	3	15±1.3	13-16.	PFBS(4.2)
Sha Wan stream (SW)		3	4.0±0.83	3.0-4.5	PFOS(1.0)

2
3
4
5
6
7
8

1 **Table 4.** Comparison of PFAA concentrations (ng/L; mean value in parentheses) in surface water samples from rivers all over the world.

Location	Sampling year	Number of PFAAs	PFAAs	PFOS	PFBS	PFOA	Reference
Pearl River, China	2012	13	3.0-52 (19)	0.52-11 (3.3)	0.42-23 (5.4)	0.71-8.7 (3.7)	This study
Pearl River, China	2004	9	2.24-99.34 (20)	0.90-99 (23)	<0.03-3.4 (0.57)	0.85-13 (4.3)	(So et al., 2007)
Yangtze River, China	2004	10	30-290 (41)	0.62-14 (1.7)	0.96-2.1 (0.77)	22-260 (35)	(So et al., 2007)
Haihe River, China	2010	9	12-74	2.0-7.6 (3.7)	--	4.4-42 (15)	(Li et al., 2011)
Rhine River (upstream), Germany	2008	8	4.1-39 (21)	1.4-6.4 (3.7)	0.59-6.6 (3.2)	0.61-3.4 (2.1)	(Möller et al., 2010)
Rhine River (downstream), Germany	2008	8	120-270 (181)	3.0-7.3 (4.1)	15-120 (45)	2.3-4.1 (3.1)	(Möller et al., 2010)
River Ruhr, Germany	2008	8	65-97 (76)	0.89-10 (4.2)	2.9-11 (7.1)	8.9-18 (14.3)	(Möller et al., 2010)
Spanish Rivers	2009	5	2.2-22 (12)	<0.03-0.64 (5.1)	<0.07-0.88 (0.50)	0.79-9.6 (5.1)	(Sanchez-Avila et al., 2010)

2

3