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Contact CEH NORA team at
noraceh@ceh.ac.uk

1 **Coupled production and emission of short chain perfluoroalkyl acids**
2 **from a fast developing fluorochemical industry: evidence from yearly**
3 **and seasonal monitoring in Daling River Basin, China**

4 Pei Wang ^a, Yonglong Lu ^{a,*}, Tieyu Wang ^a, Zhaoyun Zhu ^{a,b}, Qifeng Li ^{a,b}, Jing Meng ^{a,b},
5 Hongqiao Su ^{a,b}, Andrew C. Johnson ^c, Andrew J. Sweetman ^{c,d}

6 ^a *State Key Lab of Urban and Regional Ecology, Research Center for Eco-Environmental*
7 *Sciences, Chinese Academy of Sciences, Beijing 100085, China*

8 ^b *University of Chinese Academy of Sciences, Beijing 100049, China*

9 ^c *Centre for Ecology & Hydrology, Maclean Building, Crowmarsh Gifford Wallingford,*
10 *Oxon, OX 10 8BB, UK*

11 ^d *Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK*

12

13

14 Corresponding author:

15 *Yonglong Lu

16 Tel: 86-10-62917903

17 Fax: 86-10-62918177

18 E-mail: yllu@rcees.ac.cn

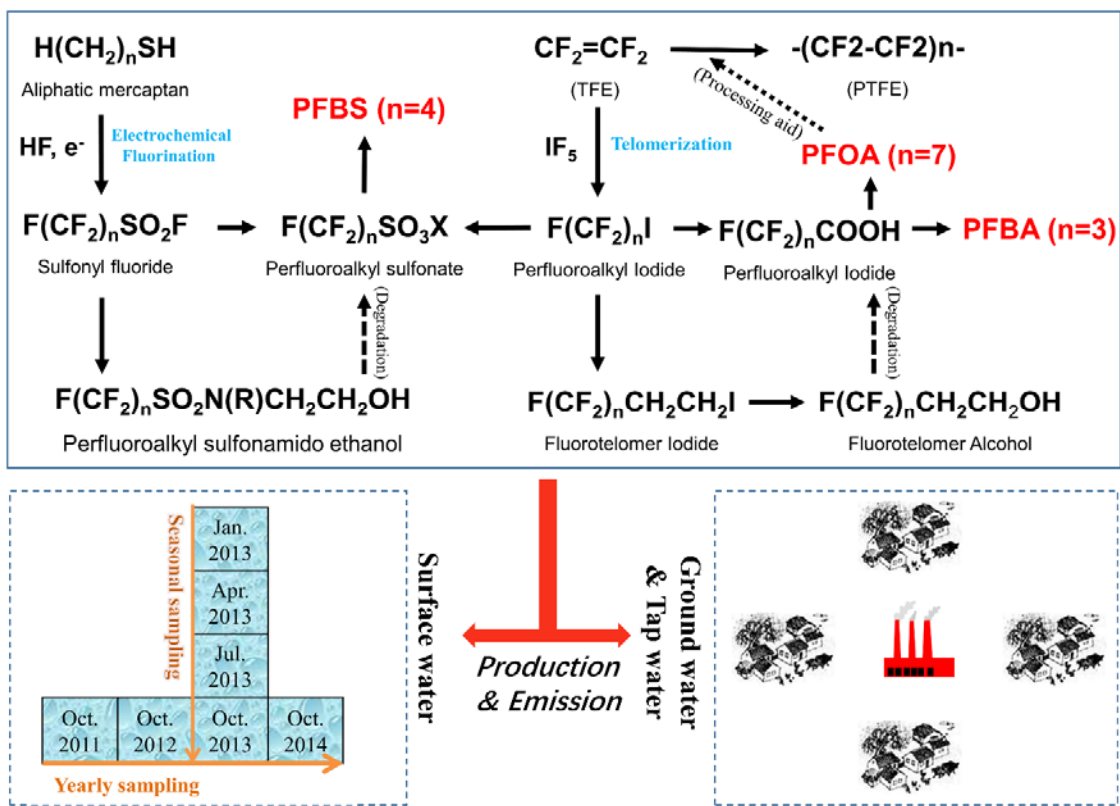
19

20 ABSTRACT: Short chain perfluoroalkyl acids (PFAAs) have been developed since 2002
21 by the major manufacturers to replace the conventional C8 and higher homologues, with
22 much of the world production shifted to China in recent years. In this study, we
23 conducted a continuous monitoring program over the period 2011-2014 with seasonal
24 monitoring in 2013 for PFAAs emitted from two rapidly developing fluorochemical
25 industry parks located in the Daling River Basin, Northern China. The trend of PFAA
26 contamination was identified, dominated by perfluorobutane sulfonic acid (PFBS),
27 perfluorobutanoic acid (PFBA) and perfluorooctanoic acid (PFOA), with the maximum
28 concentrations of 3.78 $\mu\text{g/L}$, 3.70 $\mu\text{g/L}$, and 1.95 $\mu\text{g/L}$, respectively. Seasonal monitoring
29 uncovered the occasional emission of perfluorooctane sulfonic acid (PFOS). Construction
30 trends of new facilities and associated manufacturing capacity of the main products were
31 also analyzed to assess correlations with PFAA emissions. An assessment of the data
32 over the period 2011 to 2014 found a positive correlation with fluorocarbon alcohol
33 (FCA) production and emission of PFAAs. Groundwater and tap water around the main
34 source indicated that the dominant PFAAs had different diffusion behaviors. PFBS levels
35 were higher in surface water, while PFBA was dominant in groundwater and tap water,
36 with PFOA levels being higher in downstream groundwater. Considering the continuous
37 expansion and development of fluorochemical industry in the Daling River Basin, this
38 study will provide abundant information on the effectiveness of risk assessment and
39 management.

40 Capsule: Increasing levels of PFBS, PFBA and PFOA in surface water were correlated
41 with certain fluorochemical products, and influenced local ground water and tap water.

42 KEYWORDS: Yearly trend; Seasonal trend; PFBS; PFBA; PFOA; PFAA production

43 Graphical Abstract:



44

45 **1. Introduction**

46 Perfluoroalkyl acids (PFAAs) have been widely used in both polymer applications, based
47 on their water- and grease- repellent properties, and in surfactant applications, due to
48 their unparalleled aqueous surface tension-lowering property since the 1950s (Buck et al.,
49 2011). Historically, PFAAs were mostly produced and used in the long-chain forms,
50 especially perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA)
51 (Paul et al., 2009). However, the persistent, bio-accumulative and toxic (PBT) properties
52 of long-chain PFAAs have led to their phase-out in production by the major
53 manufacturers since 2000 (3M, 2000), followed by more and stricter regulations on their
54 production, emission and use in multiple countries and regions including United States
55 (US), European Union (EU), Norway, Canada and Germany (Holt, 2011). In 2009, PFOS
56 and its related substances were listed in Annex B of the Stockholm Convention on
57 Persistent Organic Pollutants (UNEP, 2009), which put the restrictions on a global scale.
58 Apart from the major manufacturers, downstream users and individual customers are
59 moving away from long-chain PFAAs due to health concerns. As a result, the
60 perfluorinated chemical industry has been working on the development of alternatives
61 (Wang et al., 2015b).

62 In 2002, the major manufacturer 3M developed new fluorochemical surfactants based
63 on perfluorobutane sulfonic acid (PFBS). With four perfluorinated carbon atoms, PFBS
64 was considered as a sustainable alternative to PFOS, and was claimed not to be PBT by
65 3M at that time. PFBS-based surfactants were subsequently commercialized in the US
66 and other countries including China (3M, 2002). With four carbon atoms (three

67 perfluorinated ones), perfluorobutanoic acid (PFBA) had also been manufactured for
68 many years before 1998, particularly in making photographic film. 3M ceased the
69 production of PFBA in 1998 due to decreased demand (3M, 2008). However, when C8
70 PFOA production was partially controlled in 2000, it appears that C4 PFBA manufacture
71 recommenced. This was linked to very high levels of PFBA in the surrounding water
72 environment of 3M's production site, where PFBA levels were dozens or even a hundred
73 times greater than that for PFOA (Oliaei et al., 2013). Known fluorinated alternatives
74 including short chain PFAAs and perfluoroether carboxylic and sulfonic acids (PFECAs
75 and PFESAs) can adequately replace most C8 and higher homologue uses in many
76 fluoropolymer applications. Although they are less persistent in the biota than the long
77 chain PFASs, they are of concern because they do not break down in the environment and
78 may cause similar toxicological effects as the long chain PFASs (Wang et al., 2013;
79 Scheringer et al., 2014; Blum et al., 2015; Strynar et al., 2015). However, the
80 consequences of the increased production and emission of short chain PFAAs are still
81 largely unknown.

82 Currently, research on the sources of PFAAs has mostly focused on sewage treatment
83 plants, atmospheric deposition, aqueous firefighting foams used at military bases, airports,
84 and fire training facilities, as well as other non-fluorochemical sources in those countries
85 or regions with strict regulation on PFAAs production (Post et al., 2012; Ahrens and
86 Bundschuh, 2014). However, in China the most important source of PFAAs comes
87 directly from fluoro-polymer/-telomer manufacture due to the production shift in recent
88 years. With the implementation of the Stockholm Convention, the production and
89 emission of PFOS has been regulated in China, but other PFAAs remain outside of any

90 restriction (POPs Action in China, 2014). Our previous studies identified the source and
91 transportation routes of high levels of short chain PFAAs emitted from two
92 fluorochemical industry parks in the Daling River Basin of North China (Wang et al.,
93 2015a). However, the two parks have expanded very rapidly with frequent changes in
94 production capacity of various fluorochemicals, so it is very important to trace the
95 dynamic correlations between production and emission of dominant PFAAs.

96 A 4-year (2011-2014) and 4-season (2013) continuous monitoring of PFAAs in the
97 Daling River was carried out in this study, and when combined with previous studies
98 (Bao et al., 2010; Wang et al., 2011), a temporal trend of 7 years from 2008 to 2014 can
99 be established, reflecting the fast development period of short-chain PFAAs in China.
100 Furthermore, groundwater around Park 1 has also been analyzed to explore the different
101 transport behavior of dominant PFAAs compared with surface water. The overall aim of
102 the study was to establish the emission characteristics and temporal trends of PFAAs
103 from an emerging fluorochemical industry in China, which can be used to provide a basis
104 for effective surface water and groundwater management and risk assessment.

105

106 **2. Materials and Methods**

107 *2.1 Sampling campaign.*

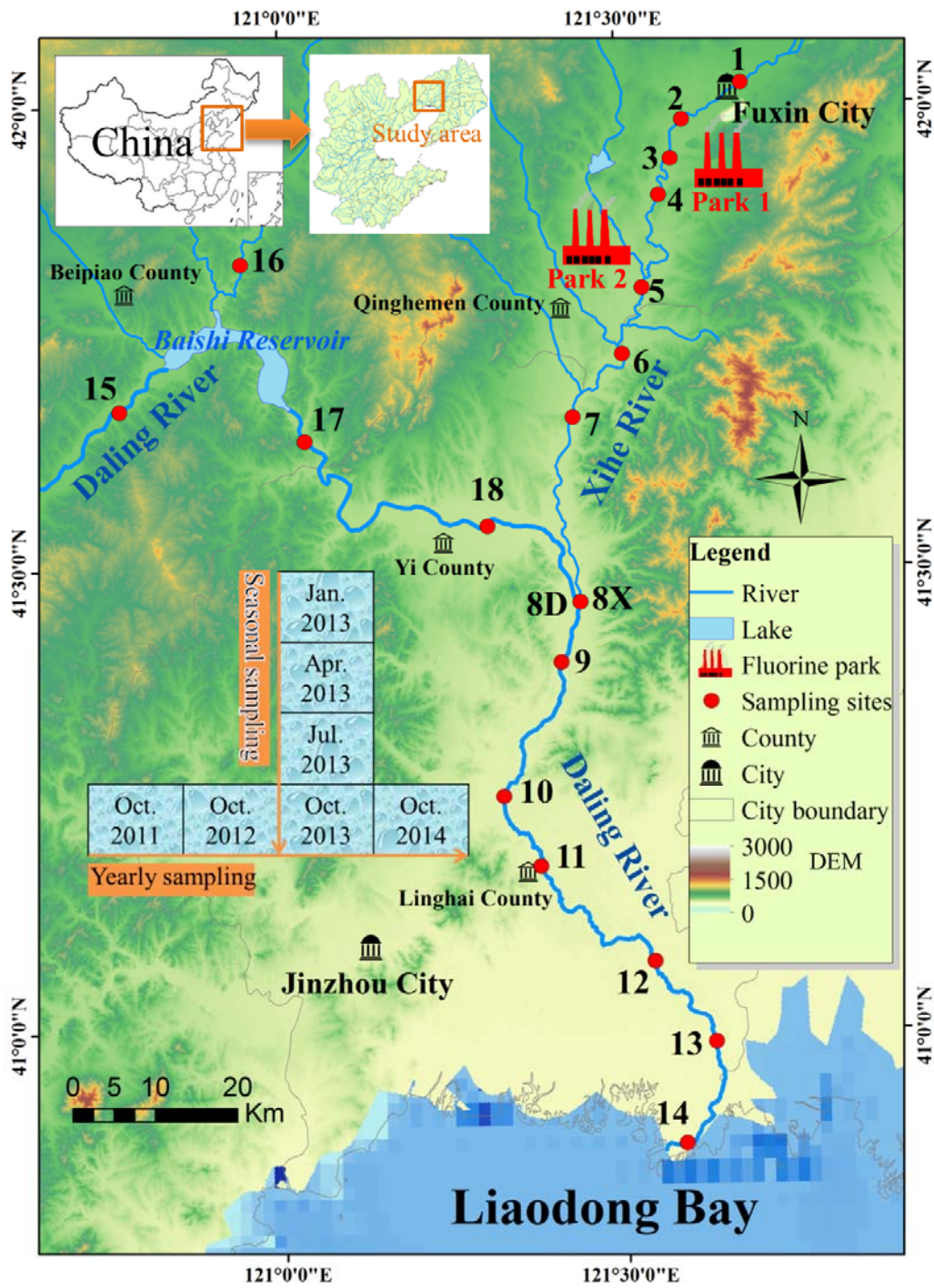
108 *2.1.1 Yearly and seasonal sampling of river water in Daling River Basin.*

109 As the two fluorochemical industry parks are located in the Xihe River, suitable
110 sampling sites were identified upstream and downstream of the parks on this river up to

111 the confluence point to the Daling River (site 1 to 8X) and then along the Daling River
112 down to the estuary (site 9 to 14) (Figure 1). The distance from site 1 to site 8 is 82 km,
113 and from site 8 to site 14 is 90 km. Sites on the Daling River further upstream of the
114 confluence point with the Xihe River (site 15 to 18 and site 8D) were selected as control
115 sites. According to our previous study in 2011, the two parks did not discharge sewage
116 into the small tributaries of the Xihe River (Wang et al., 2015a), so these tributaries were
117 not included in this study.

118 Yearly sampling campaigns were conducted in October of the years from 2011 to
119 2014, while seasonal samplings were conducted in January (winter), April (spring), July
120 (summer) and October (autumn) in the year 2013. For all field samplings, only surface
121 water (top 1-20cm) was collected using 1L pre-rinsed polypropylene (PP) bottles.
122 Parameters including water temperature, pH, dissolved oxygen, and conductivity were
123 measured *in situ* using a HQd Portable and Benchtop Meter Configurator (HACH
124 Company, USA) (Table S2-S3). Suspended substances in water samples were removed
125 by settling for 24 hours at room temperature and the supernatant was used for the
126 following analysis.

127



128

129

130

Figure 1. Sampling sites in the Daling River Basin

131 *2.1.2 Ground water and tap water sampling in villages around Park 1.*

132 The results of yearly (prior to 2014) and seasonal monitoring revealed that Park 1 had
133 always been a significant point source of PFBS, PFBA and PFOA. So in 2014, along with
134 the yearly sampling campaign in October, groundwater and tap water samples were also
135 taken. Four villages in four directions local to Park 1 were selected (Figure S1), batches
136 of samples including ground water (5-7m household wells) and tap water were sampled
137 at randomly selected homes in each village using 1L pre-rinsed PP bottles. The treatment
138 of these samples was the same as that for the river water samples.

139 *2.2 Extraction and analysis of target analytes.*

140 During the first sampling event in 2011, 17 PFAAs were analyzed and results indicated
141 that perfluoroalkyl carboxylic acids (PFCAs) C13 and higher, and perfluoroalkane
142 sulfonic acids (PFSAs) C10 were close to detection limits (Wang et al., 2015a). So in the
143 later analysis, only 12 linear PFAAs including C4 to C12 PFCAs and 3 PFSAs were
144 quantified (Table S4). A 400mL aliquot of water spiked with 10 ng mass-labelled
145 standards was extracted using OASIS WAX-SPE following published methods (Taniyasu
146 et al., 2005) with some modifications. Briefly, prior to loading samples, the Oasis WAX
147 cartridges (6 cc, 150 mg, 30 µm, Waters, Milford, MA) were preconditioned with 4 mL
148 of 0.1% NH₄OH in methanol, 4 mL of methanol, and 4 mL of Milli-Q water. After
149 loading the samples, cartridges were washed with 4 mL 25 mM ammonium acetate
150 (pH=4) and air-dried. Target analytes were then eluted with 4 mL of methanol and 4 mL
151 of 0.1% NH₄OH in methanol, respectively. The extracts were reduced to 1 mL under high
152 purity nitrogen (99.999%) and passed through a nylon filter (13 mm, 0.2 µm, Chromspec,

153 Ontario, Canada), then transferred into a 1.5 mL PP snap top brown glass vial with
154 polyethylene (PE) septa. Individual PFAA was separated and quantified via Agilent 1290
155 Infinity HPLC System coupled to an Agilent 6460 Triple Quadrupole LC/MS System
156 (Agilent Technologies, Palo Alto, CA) operated in the negative electrospray ionization
157 (ESI-) mode. Conditions under which the instrument was operated were listed in Table
158 S5.

159 2.3 QA/QC.

160 Since the manufacturers and local residents were not informed of the sampling campaign,
161 this study can be assumed to reflect routine production activities in the two parks. The
162 yearly/seasonal sampling was conducted at the same date of the year/season and the same
163 time of a day as much as possible. These were designed to provide parallel comparisons.
164 Use of polytetrafluoro-ethylene (PTFE) or other fluoro-polymer/-telomer materials was
165 avoided throughout the study. In order to avoid cross contamination during sampling, the
166 outside of the 1L PP bottles was immediately washed with pure water after the samples
167 were taken, wiped with clean towel paper and then kept in sealed PP bags. Field,
168 transport, procedure and solvent blanks were prepared with every sample batch to
169 monitor potential interferences. Quantification of the 12 PFAAs in water were carried out
170 using 10-point external standard curves with concentrations ranging from 0.01 to 1000
171 ng/mL. 10 ng/mL of mass-labelled standards as surrogates were also added to the
172 samples to monitor the matrix effect. The injection volume was 5 μ L. The regression
173 coefficients (R^2) for all the target analytes were over 0.99. The limit of detection (LOD)
174 and limit of quantification (LOQ) were defined as the peak of analyte that needed to yield
175 a signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively. LOD and LOQ in this study

176 were checked along every sampling event, and the final values were combined and
177 presented at the highest ones. LODs ranged from 0.01 to 0.15 ng/L, while LOQs ranged
178 from 0.06 to 0.71 ng/L. Recovery tests were also conducted along all sampling events,
179 and the values were combined together to give the means and standard deviations for
180 individual PFAA. Matrix spike recoveries ranged from 73 to 113%, while procedure
181 recovery ranged from 81 to 124%. For extracts containing concentrations of PFAAs
182 greater than 1000 ng/mL, the samples were reduced in volume and extracted again to
183 make sure the concentrations of PFAAs were within the calibration range. Detailed
184 QA/QC measurements of target PFAAs are given in the Supplementary Material.

185 *2.4 Statistical and spatial analysis.*

186 Statistical analysis was performed using SPSS Statistics V20.0 (SPSS Inc. Quarry Bay,
187 HK), Minitab 16 (Minitab Inc. PA, USA) and OriginPro 9.1 (Northampton, MA, USA).
188 Prior to the statistical analysis, tests of normality were carried out to ensure that data met
189 the assumptions used for further analysis. Trend analysis for dominant PFAAs was
190 processed using one-way ANOVA with post-hoc tukey test at the significance level of
191 0.05 and 95% Confidence. Spatial distributions of the sampling sites were illustrated
192 using the Arcmap module in ArcGIS V10.0 software (ESRI, Redland, CA). GIS data
193 used for sampling design was obtained from the National Geomatics Center of China
194 (Haidian District, BJ).

195 *2.5 Data representation.*

196 Due to the large variation in the orders of magnitude, and the fact that the accuracy of all
197 data was presented with three significant figures, value units for concentrations in water
198 were ng/L or $\mu\text{g/L}$.

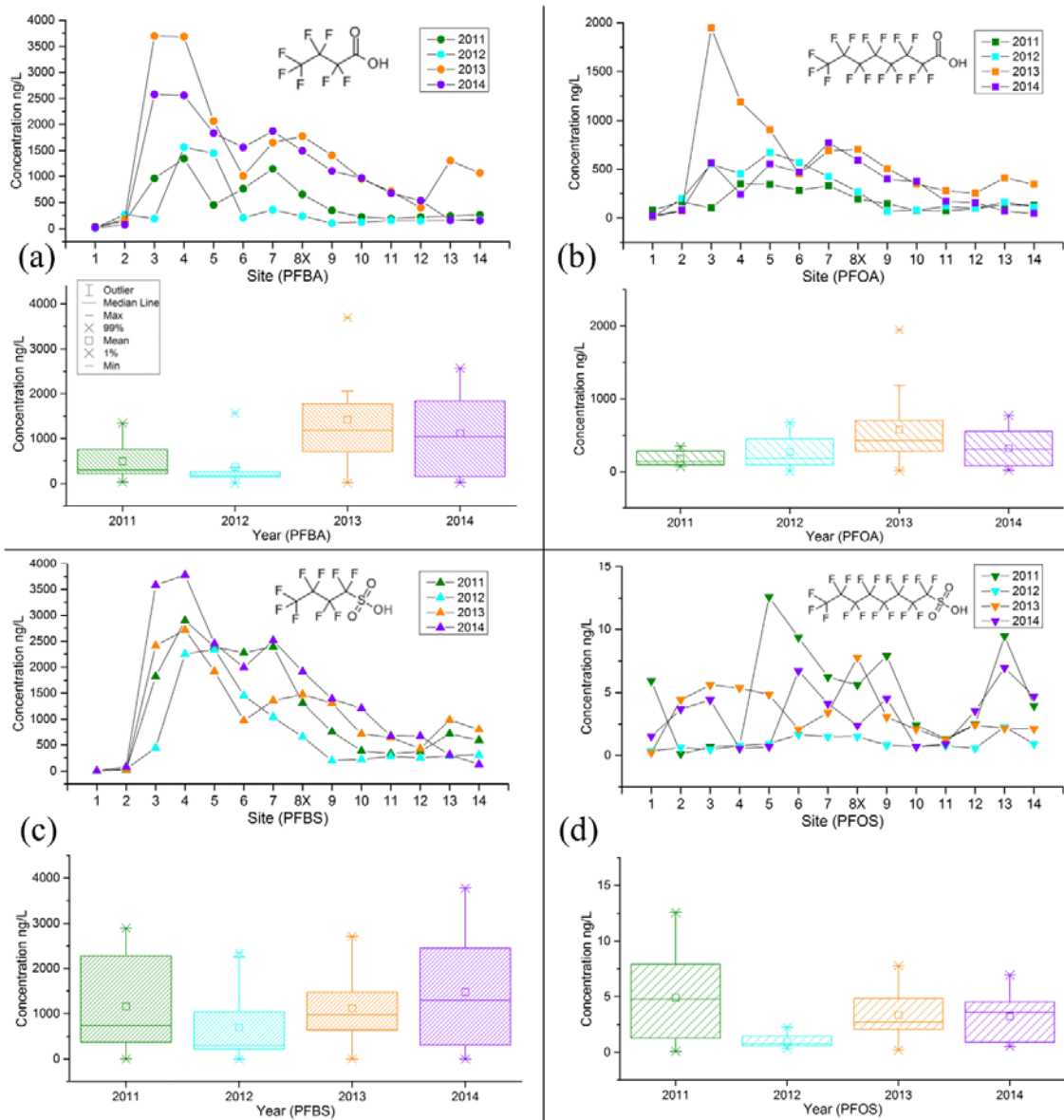
199 **3. Results and Discussion**

200 *3.1 Yearly trend of PFAAs emitted to the Daling River water.*

201 From 2011 to 2014, PFBS and PFBA have always been the dominant PFAAs, followed
202 by PFOA, and then C5-C7 PFCAs (Table 1, Table S6-S9, Figure 2). The C9-C12 PFCAs
203 and PFHxS were detected in both low ratios and low concentrations, indicating they were
204 seldom produced in the study area, thus these PFAAs will not be discussed in the
205 following sections. The highest concentrations of PFBS were 2.90 $\mu\text{g/L}$ in 2011, 2.34
206 $\mu\text{g/L}$ in 2012, 2.71 $\mu\text{g/L}$ in 2013 and 3.78 ng/L in 2014. For PFBA, the highest
207 concentrations were 1.35 $\mu\text{g/L}$ in 2011, 1.57 $\mu\text{g/L}$ in 2012, 3.70 $\mu\text{g/L}$ in 2013 and 2.58
208 $\mu\text{g/L}$ in 2014. For PFOA, the highest concentrations were 348 ng/L in 2011, 675 ng/L in
209 2012, 1.95 $\mu\text{g/L}$ in 2013 and 772 ng/L in 2014, respectively. One-way ANOVA analysis
210 for PFAA concentrations at sites downstream of the parks in the Xihe River (site 3 to site
211 8X) indicated that PFBA levels showed a significant increase from 2011 to 2014, PFBS
212 levels showed a significant increase from 2012 to 2014, and PFOA levels showed no
213 clear trend (Table S16). Concentrations of PFOS were far below those of the three
214 dominant PFAAs, with the overall highest concentration of 12.6 ng/L observed in 2011.
215 Among the C5-C7 PFCAs, C6 PFHxA was dominant with the highest concentration up to
216 795 ng/L in 2013. C6 PFAAs were also considered to be one of the potential alternatives
217 to long chain PFAAs (Wang et al., 2015b). However, even in the site with the highest

218 concentration, PFHxA level was a factor of 5 less than PFBA, indicating a lower
 219 importance than C4 PFBA as an alternative.

220



221

222 Figure 2. Temporal trends of main PFAAs in the Xihe and Daling River water from 2011

223

to 2014.

224 Table 1. Summary of PFAAs concentrations in Yearly monitoring (ng/L).

Time		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFOS
Yearly								
2011	Min.	0.31	0.04	0.03	0.04	0.09	0.04	0.05
	Max.	1350	82.2	59.2	15.9	348	2900	12.6
	Mean	374	20.4	18.3	4.24	132	856	3.97
	Median	223	15.9	14.3	3.34	102	386	2.50
2012	Min.	1.56	0.25	0.09	0.08	0.58	0.47	0.16
	Max.	1570	81.2	180	45.5	675	2340	2.27
	Mean	276	19.6	49.4	12.7	200	516	0.89
	Median	156	12.1	29.5	7.80	113	253	0.77
2013	Min.	1.62	0.05	0.08	0.10	0.61	0.74	0.06
	Max.	3700	198	795	103	3950	2710	11.4
	Mean	1050	41.8	100	22.3	533	830	3.59
	Median	945	34.0	56.4	20.1	344	712	2.43
2014	Min.	1.42	ND	0.11	0.10	2.17	ND	0.47
	Max.	2580	56.1	196	55.0	772	3780	6.95
	Mean	830	23.6	60.7	19.3	239	1090	2.60
	Median	536	21.1	42.2	15.5	155	668	1.52

225

226 As to the spatial distribution, the highest concentrations of PFBS and PFBA were
 227 associated with Park 1 (site 3 and 4) throughout the four years (Figure 2). For PFOA, the
 228 spike in concentration from site 3 was less obvious than those of PFBS and PFBA except
 229 in 2013. Further distribution from Park 2 maintained the elevated levels of the three
 230 dominant PFAAs from site 5 to site 8X, whilst the decreasing levels in site 6 might be
 231 caused by the dilution from the tributaries entering the Xihe River. Along the Daling
 232 River (from site 8X to site 12), concentrations were generally reduced by over 50% due

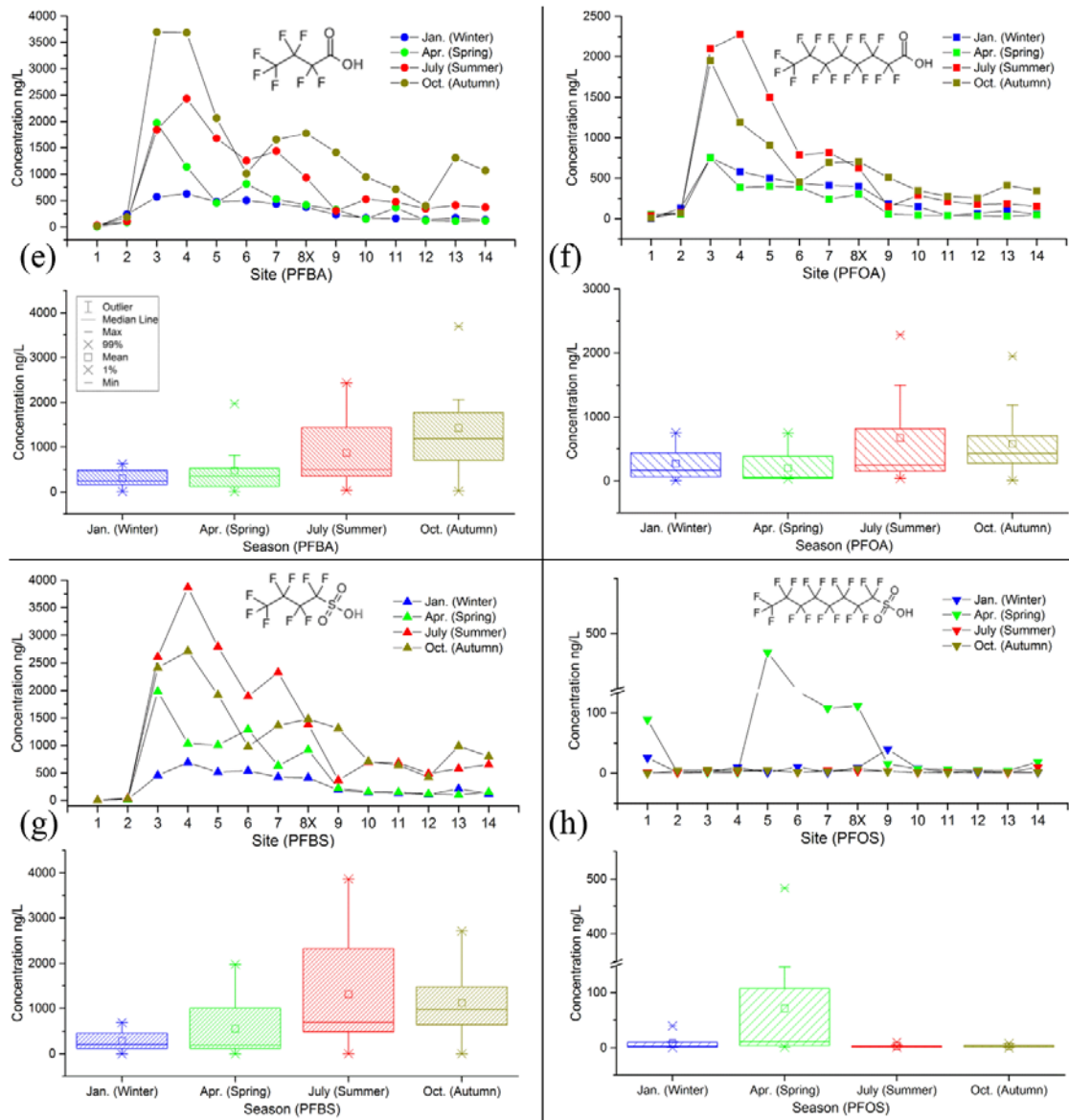
233 to dilution. The fluctuation of concentrations in site 13 and site 14 at the estuary could be
234 affected by factors including the frequent mixture of fresh and saline water, aquaculture
235 pools using the river water, construction activities, and so forth. Meanwhile,
236 concentrations of PFAAs at the reference sites from 15 to 17 indicated no other point
237 sources from the upstream parts of the Daling River over the study period. The relatively
238 notable PFAAs levels in site 18 and 8D could originate from domestic emissions in Yi
239 County.

240

241 *3.2 Seasonal trend of PFAAs emitted into the Daling River water.*

242 Seasonal monitoring in 2013 was conducted as a supplement for the yearly data, to
243 illustrate the general scientific findings in more detail. Differences in PFAA levels could
244 be observed over the different seasons of 2013 (Table 2, Table S10-S13, Figure 3). For
245 PFBS, the overall concentrations from site 1 to site 14 were highest in summer (max.
246 3.87 µg/L) and autumn (max. 2.71 µg/L) with lower levels in spring (max. 1.98 µg/L)
247 and winter (max. 690 ng/L), while the trend was autumn (3.70 µg/L) > summer (2.44
248 µg/L) > spring (1.97 µg/L) > winter (628 ng/L) for PFBA, and summer (2.28 µg/L) >
249 autumn (1.95 µg/L) > winter (753 ng/L) > spring (749 ng/L) for PFOA, respectively.
250 PFOS was found at low concentrations, but there was an apparent point-source emission
251 in site 5, downstream of Park 2, with a concentration of 483 ng/L. Relatively high levels
252 of C6 PFHxA have been emitted since the summer of 2013. This indicated that even
253 though PFBS, PFBA and PFOA were the dominant PFAAs emitted from the two parks,
254 other homologues including PFOS could still be produced and emitted in some occasions.

255 This was maybe due to the unstable status of construction and production in the parks,
 256 which will be discussed later.



257

258 Figure 3. Levels of main PFAAs in the Xihe and Daling River water in four seasons of
 259 the year 2013.

260

261 Table 2. Summary of PFAAs concentrations in seasonal monitoring (ng/L).

Time		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFOS
Seasonal								
Winter	Min.	0.64	0.06	0.33	0.12	0.27	0.04	0.87
	Max.	628	139	183	29.4	753	690	39.9
	Mean	231	38.7	45.0	8.20	202	209	7.94
	Median	171	12.9	17.0	5.69	102	130	4.08
Spring	Min.	1.36	0.05	0.02	0.08	0.47	0.04	0.59
	Max.	1970	79.6	168	36.8	749	1980	483
	Mean	351	15.7	32.8	8.53	150	409	54.0
	Median	125	5.06	9.65	2.84	47.9	149	6.54
Summer	Min.	5.78	0.21	0.15	0.38	2.51	0.26	1.02
	Max.	2440	273	603	119	2280	3870	21.2
	Mean	643	60.1	122	26.8	495	969	4.27
	Median	372	20.7	43.0	10.1	179	581	2.90
Autumn	Min.	1.62	0.05	0.08	0.10	0.61	0.52	0.06
	Max.	3700	198	795	103	3950	2710	11.4
	Mean	1050	41.8	100	22.3	533	830	3.49
	Median	945	34.0	56.4	20.1	344	712	2.43

262

263 For the important compounds of PFBA, PFBS and PFOA, the highest levels in river
 264 water were found in either summer or autumn. Given that rainfall and hence river flow
 265 (and dilution) tends to be highest in summer and autumn in China, this may appear as
 266 something of a surprise. Considering the occasional high emission of PFOS (483 ng/L)
 267 in spring, the seasonal pattern of PFAA emissions might depend on fluctuating request
 268 from market. Besides, the construction of existing and new facilities, and seasonal
 269 variations in river discharge would also have influences on the emission patterns. All the

270 factors could form general industrial cycles, which were also partially reflected in the
271 trend of yearly sampling. There were several studies on the seasonal variations of PFAAs
272 in water environment (Tsuda et al., 2010; Zhao et al., 2015), while the overall levels were
273 low without identification of potential sources. As far as we know, this is the first study
274 on yearly and seasonal monitoring of PFAAs emitted from fluorochemical industry.

275

276 *3.3 PFAA emission characteristics related to construction and production.*

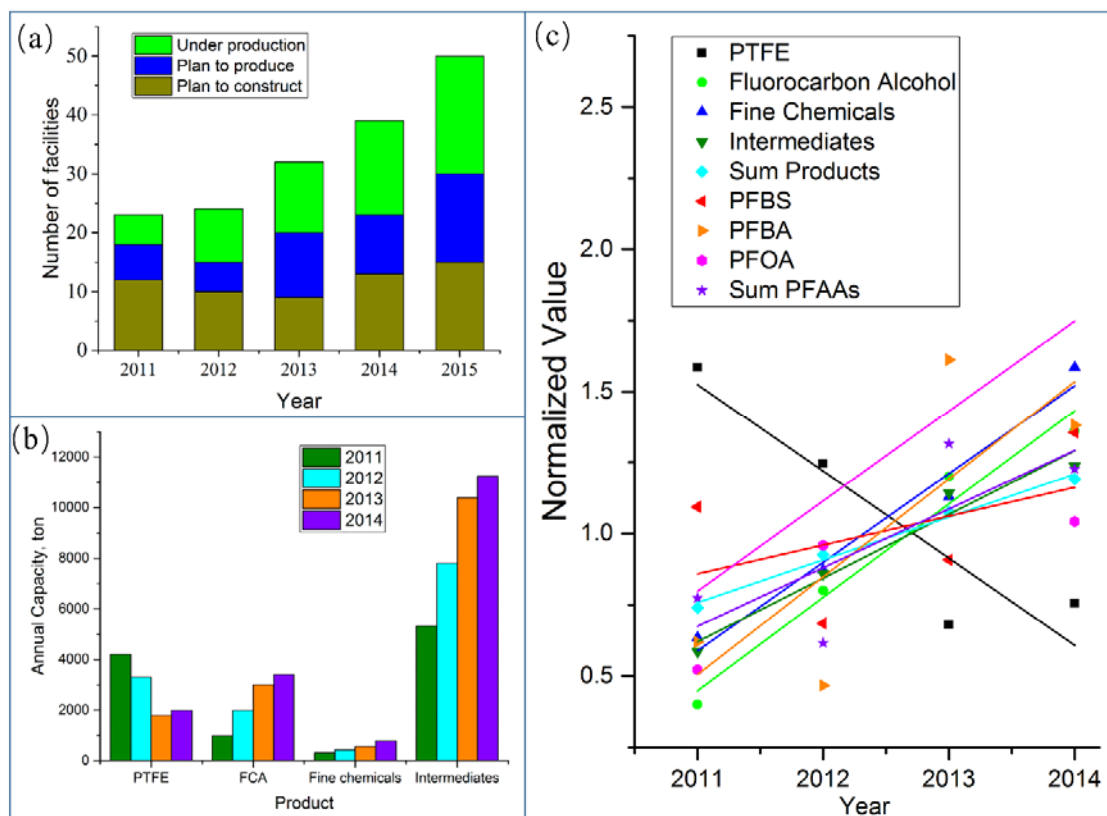
277 The dominant PFAAs levels showed different trends over the study period (Figure 4c),
278 which can be used to identify potential changes to emission sources and can also reflect
279 the dynamic of market need and production capacity. Concentration ratios can provide
280 comparisons on the temporal variations of the dominant PFAAs. It can be seen from
281 Table 3 that, the mean values of the PFBS/PFBA ratio from site 3 to site 8X were 2.7 and
282 3.0 in 2011 and 2012, respectively. But the ratios became 0.8 in 2013 and 1.4 in 2014.
283 For PFBA/PFOA ratios, the mean values also showed a general increasing trend from
284 2012-2014. These might imply that emission of PFBA increased more than that of PFBS
285 and PFOA over the most recent years, with PFBA more important in the fluorochemical
286 applications. Spatial variations of the concentration ratios indicated that the emission
287 intensity from the two parks for the dominant PFAAs had been changing. This was
288 consistent with the status that the planning and construction of fluoropolymer facilities in
289 the two parks had been changing all the time.

290

291 Table 3 Concentration ratios of PFBS/PFBA and PFBA/PFOA in the sites 3-8X.

Site	PFBS/PFBA				PFBA/PFOA			
	2011	2012	2013	2014	2011	2012	2013	2014
3	1.9	2.3	0.7	1.4	9.4	0.3	0.9	4.6
4	2.2	1.4	0.7	1.5	3.9	3.5	3.1	10.6
5	5.3	1.6	0.9	1.3	1.3	2.1	2.3	3.3
6	3.0	7.0	1.0	1.3	2.7	0.4	2.2	3.3
7	2.1	2.9	0.8	1.3	3.5	0.9	2.4	2.4
8X	2.0	2.7	0.8	1.3	3.4	0.9	2.5	2.5
<i>Mean</i>	2.7	3.0	0.8	1.4	4.0	1.3	2.2	4.5

292

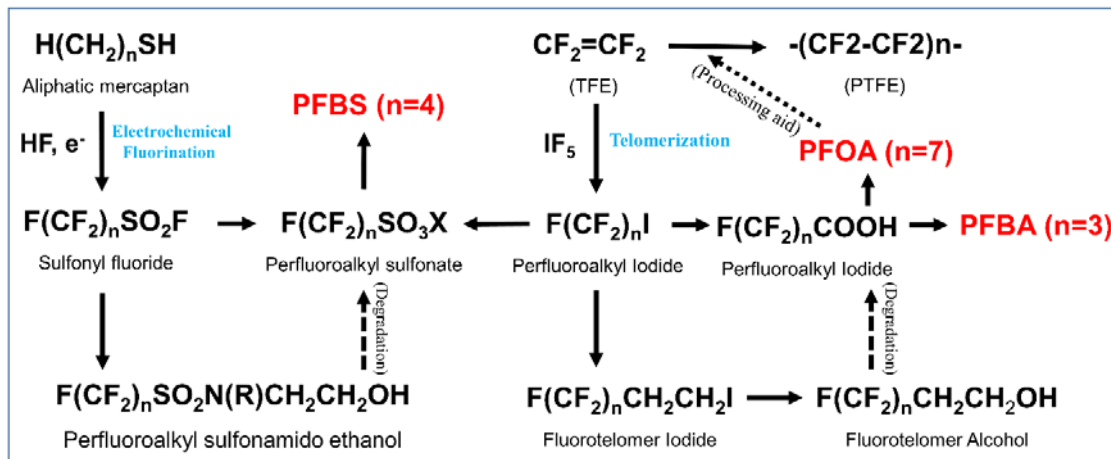


293

294 Figure 4. (a) Construction status of fluorochemical facilities, (b) the main organo-fluorine
 295 products in the two parks and (c) The temporal trends based on the normalization of
 296 related values divided by median.

297 In our previous study in 2011, there were limited fluoropolymer facilities in the study
298 area, and production processes could be identified (Wang et al., 2015a). However, due to
299 continuing site development, this task has become more complex. From 2011-2014, there
300 were dozens of facilities under development, planning to produce or planning to construct
301 (Figure 4a), especially the number (accumulated value) of facilities under production
302 showed a steadily increasing trend. This brought an increasing capacity of organo-
303 fluorine products that related to the emission of PFAAs (Figure 4b, Table S15).
304 Especially, the production of fluorocarbon alcohol (FCA) and PTFE would directly
305 generate or use PFAAs (Figure 5), but the trends were quite different (Figure 4c).
306 According to the manufacturers, FCA including perfluoroalkyl iodides (PFAIs),
307 fluorotelomer alcohols (FTOHs) and related products are all featured products in the
308 study area, so the production capacity showed an increasing trend. There are various
309 processes including electrochemical fluorination and telomerization that could generate
310 the emission of the dominant PFAAs (Figure 5). The production of PTFE would use
311 PFOA as a processing aid, and lead to the emission of PFOA (European Commission,
312 2010). However, PTFE and its related products have not been the main products for the
313 fluorochemical manufacturers in this study, which have a sum capacity of only thousands
314 of tons. So when other manufacturers with PTFE as one of their main products increased
315 the production capacity, such as one in the Xiaoqing River Basin in the same economic
316 circle, with a PTFE capacity of 49,000 tons (Wang et al., 2016), the manufacturers in this
317 study chose to reduce the PTFE capacity. Besides, there is a large and increasing capacity
318 for the production of various intermediates for pesticides and medicines using
319 organofluorine. Furthermore, the development of a central wastewater treatment plant

320 (WWTP) in the parks could also have effects on the emission of PFAAs to the river, as
 321 some processes were designed specifically for the removal of fluorine in wastewater from
 322 individual fluorochemical facilities in Park 2, which needs more detailed study.



324 Figure 5. Main production processes and products in the parks correlated with the
 325 emission of the dominant PFAAs

326

327 3.4 PFAAs in groundwater and tap water around Park 1.

328 The yearly and seasonal monitoring data indicated that Park 1 discharged high levels of
 329 PFBS and PFBA directly and continuously to the Xihe River. It is possible that these
 330 short-chain PFAAs might migrate to the groundwater through river leakage or other
 331 pathways (Liu et al., 2016), and then lead to the exposure of local residents via water
 332 abstraction using shallow wells (5-7 m). Unlike short-chain PFAAs that are usually
 333 produced at liquid form, long-chain PFAAs are present at solid or powder forms (Wang
 334 et al., 2015a), which make them more susceptible to atmospheric dispersion followed by

335 migration into groundwater via precipitation (Davis et al., 2007). In this study, very high
336 levels of PFAAs were detected in the groundwater taken from the wells in villages nearby
337 Park 1 (Table 4, Table S14, Figure 6). The site W1 is very close to site 3 in the Xihe
338 River (<100 m), comparisons on PFAAs levels showed that unlike in river water, PFOA
339 was the dominant compound here. In this case the PFOA was found at W1 with
340 concentration up to 4.15 $\mu\text{g/L}$ and an overall contribution of 37.5% of $\sum\text{PFAAs}$ (sum of
341 PFAAs), followed by PFBA (3.61 $\mu\text{g/L}$, 32.7%) > PFHxA (1.18 $\mu\text{g/L}$, 10.6%) > PFPeA
342 (951 ng/L, 8.6%) > PFBS (588 ng/L, 5.3%) > PFHpA (579 ng/L, 5.2%). For W2-W4,
343 which are located further away from Park 1, PFAAs levels decreased and contributions of
344 individual PFAA also changed. PFBA was more dominant at the W2 groundwater site
345 with concentration of 1.78 $\mu\text{g/L}$ and contribution of 41.4%, followed by PFOA (1.39
346 $\mu\text{g/L}$, 32.4%). PFBS accounted for a larger portion (865 ng/L, 20.2%). The concentrations
347 and profiles of PFAAs were quite comparable in W3 and W4 with $\sum\text{PFAAs}$ of 536 ng/L
348 and 463 ng/L, respectively. PFBA accounted for about 80%, contributions of PFOA
349 reduced to 12.0% and 17.6%, respectively, while PFBS and C5-C7 PFACs accounted for
350 even less. The spatial distribution of W1-W4 indicated that apart from the distance to
351 Park 1, local environmental conditions combined with PFAA properties may explain the
352 varied levels and profiles of PFAAs in groundwater. W1 is adjacent to the Aliphatic
353 fluoride zone of Park 1 (Figure 4), which is the zone of direct production and use of
354 PFOA. PFOA could be released as dust, solid waste or impurities in products, and
355 migrate with runoff into groundwater. The high mobility of PFBA led to its high presence
356 in W3 and W4, and dominance in W1 and W2 (Oliaei et al., 2013). PFBS was mainly

357 emitted to and found in river water. Σ PFAAs in tap water of W1-W3 were all below 10
 358 ng/L, only tap water in W4 presented Σ PFAAs level of 74.2 ng/L.

359 Table 4. Concentrations of the main PFAAs (ng/L) in the groundwater and tap water in
 360 this study, and available health drinking water criteria (ng/L) in the world.

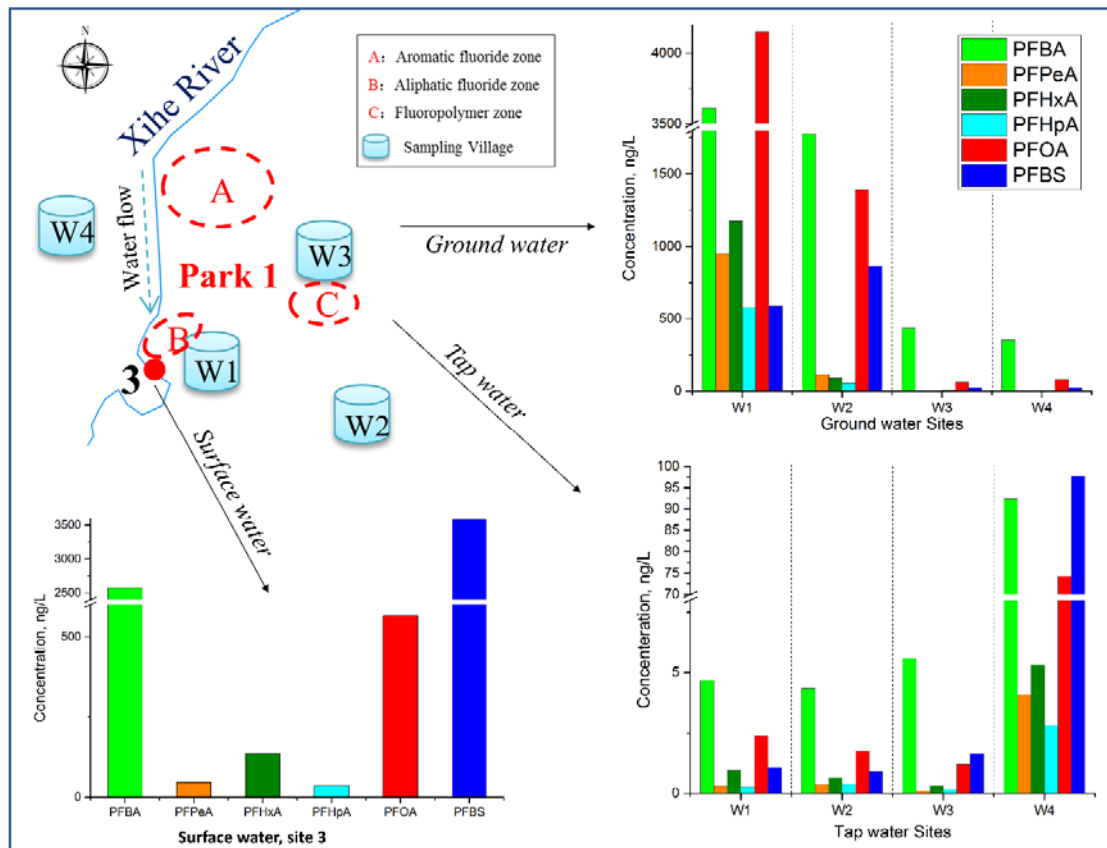
Region	Type	PFBA	PFOA	PFBS	PFOS	year
This study						
W1	Groundwater	3610	4150	588	1.05	2014
	Tap water	4.68	2.38	1.09	0.30	2014
W2	Groundwater	1780	1390	865	0.20	2014
	Tap water	4.34	1.74	0.93	0.35	2014
W3	Groundwater	434	64.5	22.7	0.20	2014
	Tap water	5.59	1.21	1.64	0.43	2014
W4	Groundwater	352	81.7	22.4	0.15	2014
	Tap water	92.3	74.2	97.8	0.13	2014
United States <i>Regulatory value</i>						
Vermont	Drinking Water Health Advisories	-	20 ^a	-	20 ^a	2016
New Jersey	Preliminary Health-Based Guidance	-	40	-	-	2007
USEPA	Lifetime Health Advisories	-	70 ^b	-	70 ^b	2016
North Carolina	Interim Maximum Allowable Concentration	-	1000	-	-	2010
Minnesota	Chronic Health Risk Limit	7000	300	7000	300	2011
Maine	Maximum Exposure Guideline	-	100	-	-	2014
United Kingdom	Further Provision	-	300	-	300	2009
	Potential Danger to Human Health	-	5000	-	1000	
	Notification of Events	-	45000	-	9000	
Germany	Health-Related Indication Value	7000	300	3000	300	2006/2010
Canada	Drinking Water Protection	-	700	-	300	2010
Italy	AA – EQS ^c (Freshwater)	7000	100	3000		2016

361 ^a: The value 20 is for the total of PFOA plus PFOS.

362 ^b: The value 70 is for the total of PFOA plus PFOS.

363 °: AA – EQS = Annual Average – Environmental Quality Standards.
 364 References: (NJDEP, 2007; DRINKING WATER INSPECTORATE, 2009; MDH, 2011;
 365 Paterson et al., 2012; Maine Center., 2014; HealthVermont, 2016; USEPA, 2016;
 366 Valsecchi et al., 2016)

367



368

369 Figure 6. Distribution of PFAAs levels among groundwater, tap water and river water
 370 nearby Park 1 in 2014.

371

372 Previous studies reported that in areas with relatively high PFOA levels in surface
 373 water, the tap water could also contain higher PFOA levels (Saito et al., 2004). In this
 374 study, PFOA levels in tap water of site W4 exceeded the Preliminary Health-Based

375 Guidance value (40 ng/L) in New Jersey, USA (NJDEP, 2007), and especially, the
376 newest Vermont Drinking Water Health Advisories (20 ng/L) and USEPA Lifetime
377 Health Advisories (20 ng/L), which were both derived in 2016 (HealthVermont, 2016;
378 USEPA, 2016). According to the general office of the local tap water company, the
379 source of tap water comes from several reservoirs nearby, which are protected well.
380 However, there are five waterworks, so it is not clear why the tap water nearby Park 1
381 presented notable PFAAs levels, which requires immediate investigation by the supplier.
382 As for the groundwater in domestic wells, the local residents have been aware of the
383 pollution from the fluorochemical facilities, and kept it away from drinking for a long
384 time. However, the groundwater is still used in daily life for irrigation of crops and
385 vegetables, watering domestic animals, washing clothes, cleaning etc. Therefore,
386 potential adverse effects may still exist if groundwater from W1 and W2 was used, as
387 PFOA levels in the wells of the two villages exceeded almost all criteria values (Table 4).
388 Besides, there is a trend for more stringent safety values for PFOA (MDH, 2007; 2011;
389 USEPA, 2014; 2016), and considering the long emission history of PFOA and the
390 accumulation of PFOA in groundwater, further studies are needed to ensure that the
391 development of the fluorochemical industry would do little harm to local residents.

392

393 *3.5 Conclusions and perspectives.*

394 The yearly monitoring indicated that the emissions of PFAAs from two fast developing
395 fluorochemical industry parks in North China were continuous with a general increasing
396 trend from 2008 to 2014. PFBS, PFBA and PFOA were identified as the most dominant

397 PFAAs, followed by C5-C7 PFCA. Seasonal monitoring identified summer and autumn
398 as the peak river contamination periods in this location, which also identified occasional
399 PFOS emission. Construction of new facilities and annual capacity of the main organo-
400 fluorine products had potential relationship with the dominant PFAAs emissions. The
401 capacities of FCA showed an increasing trend along with most processes that generate
402 the emissions of PFAAs. Analysis of groundwater and tap water samples taken from the
403 nearby villages of Park 1 showed different profiles of PFAAs in groundwater compared
404 to river water, with PFBA having the highest mobility, and being the dominant presence
405 in groundwater of all directions. PFBS were more dominant in river water than in
406 groundwater. PFOA was dominant in the groundwater only in the nearest and
407 downstream village of a specific production site. PFAAs levels in tap water were mostly
408 below the criteria values except in one site (W4), which should be noticed by the tap
409 water supplier and local government.

410 The fluorochemical industry is a complex source of PFAAs, as it generates numerous
411 organic fluorine substances through various raw materials and processes. This study
412 provided abundant information on the PFAA source identification, spatial and temporal
413 trends, and different environmental behaviors of dominant PFAAs between surface water
414 and groundwater. However, there are still some issues that need to be further studied in
415 the future:

416 1) The possible presence in the discharges (and thereby in the rivers and groundwater)
417 of PFAA precursors such as fluorotelomers (Figure 5), which can modify the PFAA
418 patterns in the different water bodies;

419 2) As a gathering of dozens of fluorochemical facilities, the removal efficiency of
420 PFASs in the central WWTP needs to be evaluated to explore more effective approach
421 for PFASs elimination;

422 3) With more facilities under development, higher PFAAs emission and potential
423 health risks can be anticipated. Thus, the health risks of nearby residents need to be
424 further investigated and managed.

425

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432

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