

## Article (refereed) - postprint

---

Wang, Pei; Lu, Yonglong; Wang, Tiejyu; Zhu, Zhaoyun; Li, Qifeng; Meng, Jing; Su, Hongqiao; Johnson, Andrew C.; Sweetman, Andrew J.. 2016. **Coupled production and emission of short chain perfluoroalkyl acids from a fast developing fluorochemical industry: evidence from yearly and seasonal monitoring in Daling river basin, China.** *Environmental Pollution*, 218. 1234-1244. [10.1016/j.envpol.2016.08.079](https://doi.org/10.1016/j.envpol.2016.08.079)

© 2016 Elsevier Ltd

This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>



This version available <http://nora.nerc.ac.uk/516163/>

NERC has developed NORA to enable users to access research outputs wholly or partially funded by NERC. Copyright and other rights for material on this site are retained by the rights owners. Users should read the terms and conditions of use of this material at <http://nora.nerc.ac.uk/policies.html#access>

NOTICE: this is the author's version of a work that was accepted for publication in *Environmental Pollution*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Environmental Pollution*, 218. 1234-1244. [10.1016/j.envpol.2016.08.079](https://doi.org/10.1016/j.envpol.2016.08.079)

[www.elsevier.com/](http://www.elsevier.com/)

Contact CEH NORA team at  
[noraceh@ceh.ac.uk](mailto: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 <sup>a</sup>, Yonglong Lu <sup>a,\*</sup>, Tieyu Wang <sup>a</sup>, Zhaoyun Zhu <sup>a,b</sup>, Qifeng Li <sup>a,b</sup>, Jing Meng <sup>a,b</sup>,  
5 Hongqiao Su <sup>a,b</sup>, Andrew C. Johnson <sup>c</sup>, Andrew J. Sweetman <sup>c,d</sup>

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

8 <sup>b</sup> *University of Chinese Academy of Sciences, Beijing 100049, China*

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

11 <sup>d</sup> *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](mailto: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 µg/L, 3.70 µg/L, and 1.95 µg/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



## 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.*

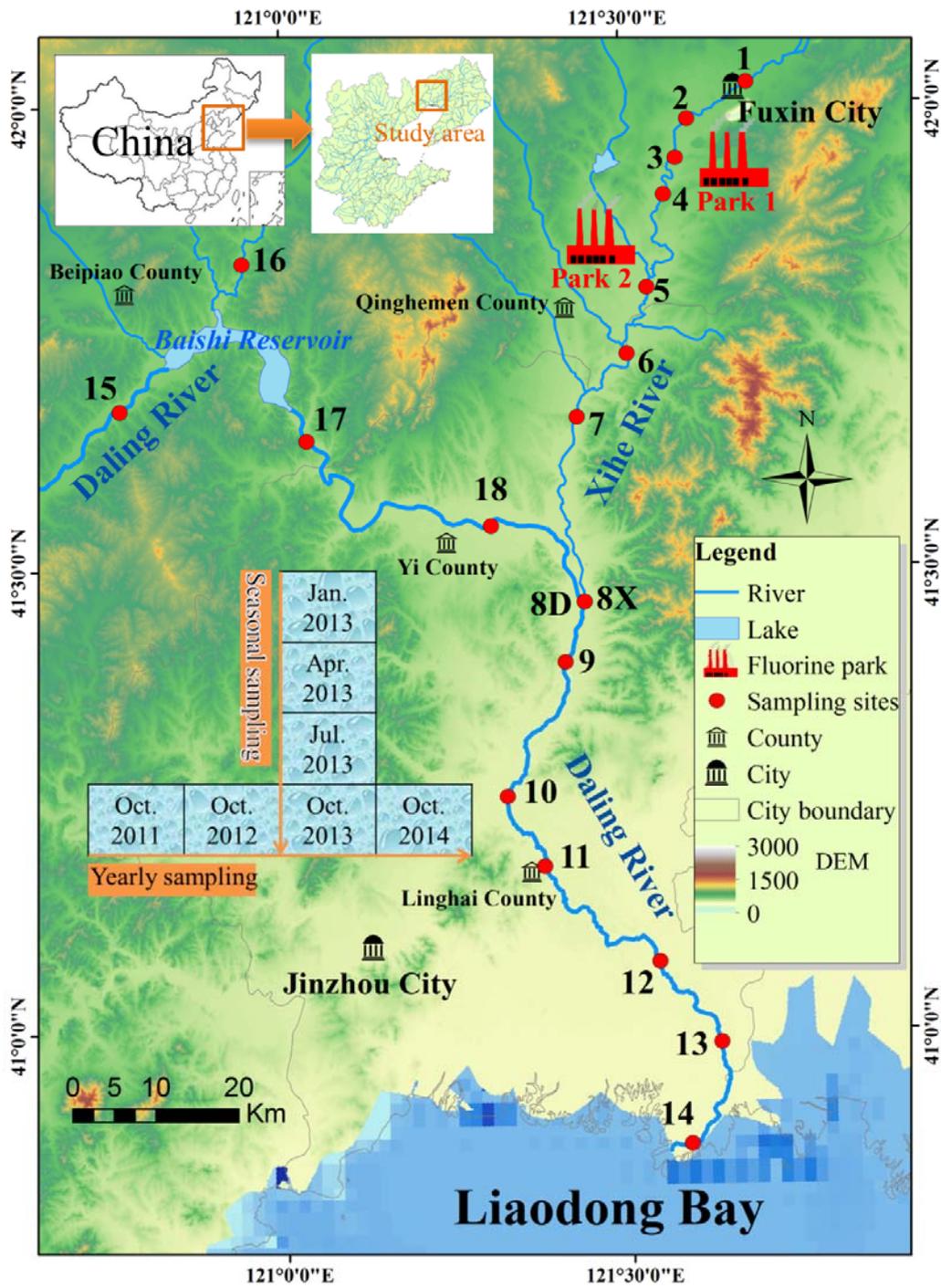
#### 108 *2.1.1 Yearly and seasonal sampling of river water in Daling River Basin.*

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  $\mu$ m, Waters, Milford, MA) were preconditioned with 4 mL  
148 of 0.1% NH<sub>4</sub>OH 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% NH<sub>4</sub>OH 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  $\mu$ m, 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  $\mu$ 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  $\mu\text{g/L}$ .

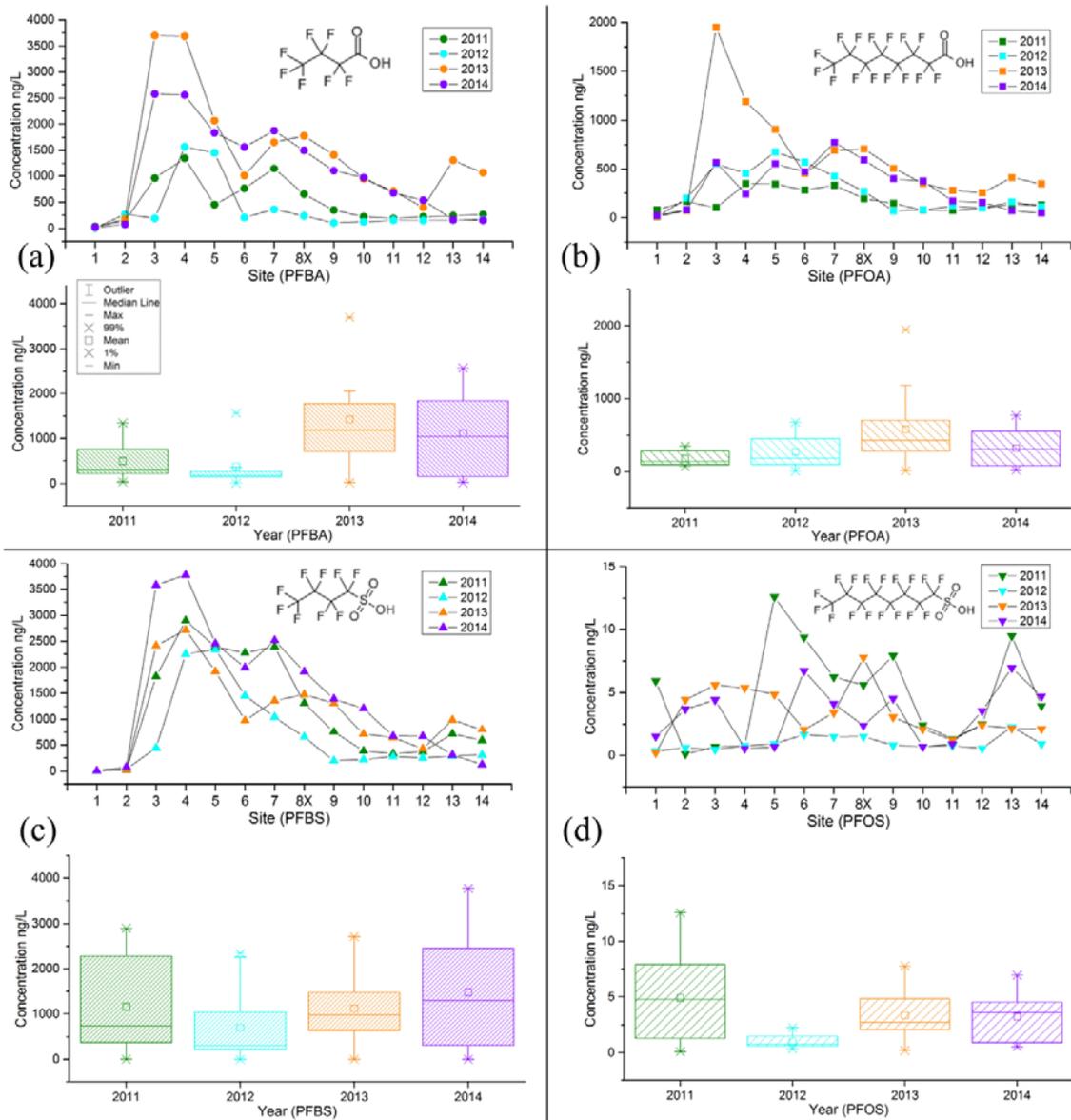
### 199 **3. Results and Discussion**

#### 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
<b>Yearly</b>								
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

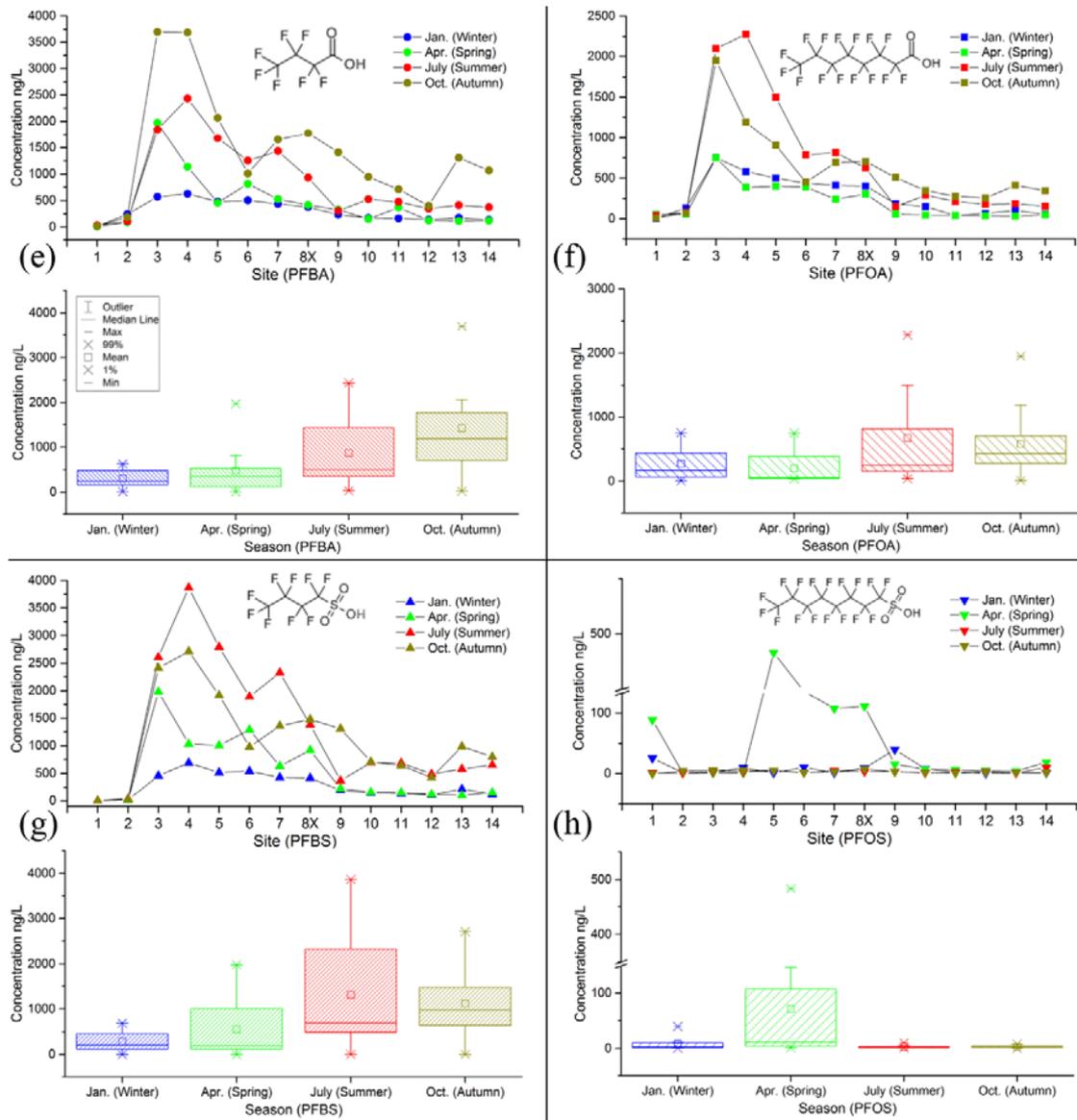
233 to dilution. The fluctuation of concentrations in site 13 and site 14 at the estuary could be  
234 affected by factors including the frequent mixture of fresh and saline water, aquaculture  
235 pools using the river water, construction activities, and so forth. Meanwhile,  
236 concentrations of 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  $\mu\text{g/L}$ ) and autumn (max. 2.71  $\mu\text{g/L}$ ) with lower levels in spring (max. 1.98  $\mu\text{g/L}$ )  
247 and winter (max. 690  $\text{ng/L}$ ), while the trend was autumn (3.70  $\mu\text{g/L}$ ) > summer (2.44  
248  $\mu\text{g/L}$ ) > spring (1.97  $\mu\text{g/L}$ ) > winter (628  $\text{ng/L}$ ) for PFBA, and summer (2.28  $\mu\text{g/L}$ ) >  
249 autumn (1.95  $\mu\text{g/L}$ ) > winter (753  $\text{ng/L}$ ) > spring (749  $\text{ng/L}$ ) 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  $\text{ng/L}$ . 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
<b>Seasonal</b>								
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.*

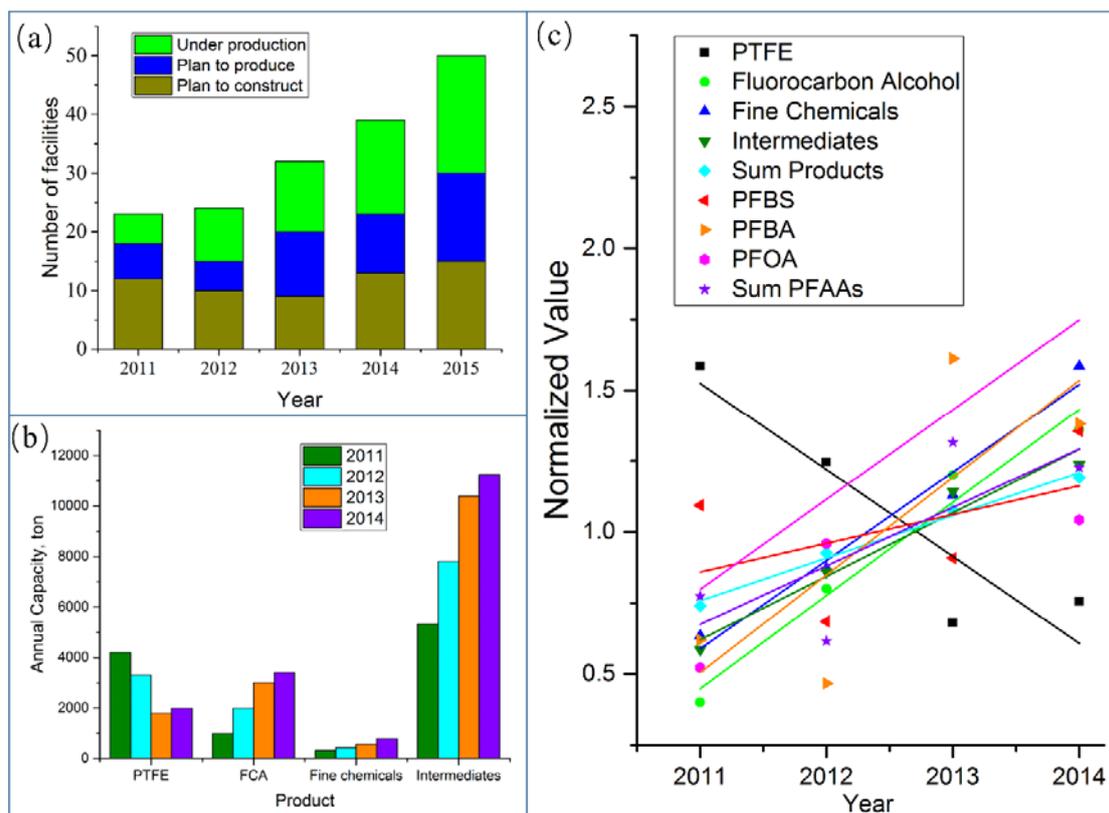
277 The dominant PFAAs levels showed different trends over the study period (Figure 4c),  
278 which can be used to identify potential changes to emission sources and can also reflect  
279 the dynamic of market need and production capacity. Concentration ratios can provide  
280 comparisons on the temporal 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



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.  $\Sigma$ PFAAs in tap water of W1-W3 were all below 10  
 358 ng/L, only tap water in W4 presented  $\Sigma$ 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.

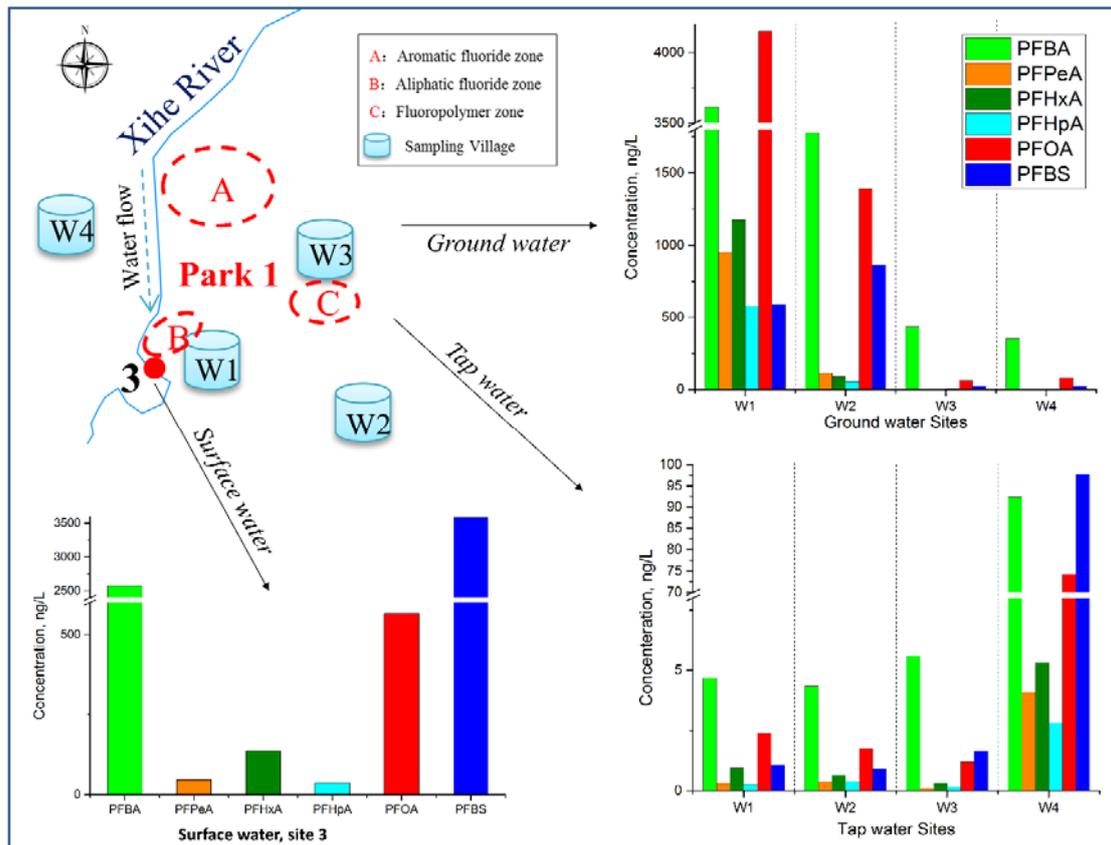
Region	Type	PFBA	PFOA	PFBS	PFOS	year
This study						
W1	Groundwater	3610	4150	588	1.05	2014
	Tap water	4.68	2.38	1.09	0.30	2014
W2	Groundwater	1780	1390	865	0.20	2014
	Tap water	4.34	1.74	0.93	0.35	2014
W3	Groundwater	434	64.5	22.7	0.20	2014
	Tap water	5.59	1.21	1.64	0.43	2014
W4	Groundwater	352	81.7	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 <sup>a</sup>	-	20 <sup>a</sup>	2016
New Jersey	Preliminary Health-Based Guidance	-	40	-	-	2007
USEPA	Lifetime Health Advisories	-	70 <sup>b</sup>	-	70 <sup>b</sup>	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 <sup>c</sup> (Freshwater)	7000	100	3000		2016

361 <sup>a</sup>: The value 20 is for the total of PFOA plus PFOS.

362 <sup>b</sup>: 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

#### 426 **Acknowledgement**

427 This study was supported by the National Natural Science Foundation of China under  
428 Grant No. 414201040045 and No. 41371488, the International Scientific Cooperation  
429 Program with Grant No. 2012DFA91150, and the Key Project of the Chinese Academy  
430 of Sciences under Grant No.KZZD-EW-TZ-12. We would like to thank the editors and  
431 reviewers for their valuable comments and suggestions.

432

433

434 **References**

- 435 3M. 2000. Phase-out Plan for PFOS-based Products. USEPA Docket, U.S. Environmental  
436 Protection Agency.
- 437 3M, 2002. Environmental, Health, Safety, and Regulatory (EHSR). Profile of Perfluorobutane  
438 Sulfonate (PFBS).  
439 [http://solutions.3m.com/3MContentRetrievalAPI/BlobServlet?locale=en\\_US&lmd=1120](http://solutions.3m.com/3MContentRetrievalAPI/BlobServlet?locale=en_US&lmd=1120194514000&assetId=1114270648708&assetType=MMM_Image&blobAttribute=ImageFile)  
440 [194514000&assetId=1114270648708&assetType=MMM\\_Image&blobAttribute=ImageF](http://solutions.3m.com/3MContentRetrievalAPI/BlobServlet?locale=en_US&lmd=1120194514000&assetId=1114270648708&assetType=MMM_Image&blobAttribute=ImageFile)  
441 [ile](http://solutions.3m.com/3MContentRetrievalAPI/BlobServlet?locale=en_US&lmd=1120194514000&assetId=1114270648708&assetType=MMM_Image&blobAttribute=ImageFile). (July 22, 2016)
- 442 3M, 2008. Frequently asked questions about PFBA.  
443 [http://multimedia.3m.com/mws/media/437903O/frequently-asked-questions-about-](http://multimedia.3m.com/mws/media/437903O/frequently-asked-questions-about-pfba.pdf)  
444 [pfba.pdf](http://multimedia.3m.com/mws/media/437903O/frequently-asked-questions-about-pfba.pdf). (July 22, 2016)
- 445 Ahrens, L., Bundschuh, M. 2014. Fate and Effects of Poly- and Perfluoroalkyl Substances in the  
446 Aquatic Environment: A Review. *Environmental Toxicology and Chemistry*. 33(9):  
447 1921-1929.
- 448 Bao, J., Liu, W., Liu, L., Jin, Y., Dai, J., Ran, X., Zhang, Z., Tsuda, S. 2010. Perfluorinated  
449 Compounds in the Environment and the Blood of Residents Living near Fluorochemical  
450 Plants in Fuxin, China. *Environmental Science & Technology*. 45(19): 8075-8080.
- 451 Blum, A., Balan, S. A., Scheringer, M., Trier, X., Goldenman, G., Cousins, I. T., Diamond, M.,  
452 Fletcher, T., Higgins, C., Lindeman, A. E. 2015. The Madrid statement on poly-and  
453 perfluoroalkyl substances (PFASs). *Environmental health perspectives*. 123(5): A107-  
454 A111.
- 455 Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., de Voogt, P., Jensen, A. A.,  
456 Kannan, K., Mabury, S. A., van Leeuwen, S. P. J. 2011. Perfluoroalkyl and  
457 polyfluoroalkyl substances in the environment: Terminology, classification, and origins.  
458 *Integrated Environmental Assessment and Management*. 7(4): 513-541.
- 459 Davis, K. L., Aucoin, M. D., Larsen, B. S., Kaiser, M. A., Hartten, A. S. 2007. Transport of  
460 ammonium perfluorooctanoate in environmental media near a fluoropolymer  
461 manufacturing facility. *Chemosphere*. 67(10): 2011-2019.
- 462 DRINKING WATER INSPECTORATE, 2009. Guidance on the Water Supply (Water Quality)  
463 Regulations specific to PFOS (perfluorooctane sulphonate) and PFOA (perfluorooctanoic  
464 acid) concentrations in drinking water [http://dwi.defra.gov.uk/stakeholders/information-](http://dwi.defra.gov.uk/stakeholders/information-letters/2009/10_2009annex.pdf)  
465 [letters/2009/10\\_2009annex.pdf](http://dwi.defra.gov.uk/stakeholders/information-letters/2009/10_2009annex.pdf). (July 22, 2016)
- 466 European Commission, 2010. Analysis of the risks arising from the industrial use of  
467 Perfluorooctanoic acid (PFOA) and Ammonium Perfluorooctanoate (APFO) and from  
468 their use in consumer articles. Evaluation of the risk reduction measures for potential  
469 restrictions on the manufacture, placing on the market and use of PFOA and APFO.  
470 [http://ec.europa.eu/enterprise/sectors/chemicals/files/docs\\_studies/final\\_report\\_pfoa\\_pfos](http://ec.europa.eu/enterprise/sectors/chemicals/files/docs_studies/final_report_pfoa_pfos_en.pdf)  
471 [\\_en.pdf](http://ec.europa.eu/enterprise/sectors/chemicals/files/docs_studies/final_report_pfoa_pfos_en.pdf). (July 22, 2016))
- 472 HealthVermont, 2016. Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS)  
473 Vermont Drinking Water Health Advisory.  
474 [https://anrweb.vt.gov/PubDocs/DEC/PFOA/PFOA - PFOS Health](https://anrweb.vt.gov/PubDocs/DEC/PFOA/PFOA - PFOS Health Advisories/Vermont/PFOA PFOS HealthAdvisory June 22 2016.pdf)  
475 [Advisories/Vermont/PFOA PFOS HealthAdvisory June 22 2016.pdf](https://anrweb.vt.gov/PubDocs/DEC/PFOA/PFOA - PFOS Health Advisories/Vermont/PFOA PFOS HealthAdvisory June 22 2016.pdf). (July 22, 2016)
- 476 Holt, R., 2011. The influence of global regulatory changes and customer preferences on the  
477 development of alternatives to long chain fluorinated chemicals.  
478 [www.oecd.org/ehs/pfc/46233887.ppt](http://www.oecd.org/ehs/pfc/46233887.ppt). (July 22, 2016)
- 479 Liu, Z., Lu, Y., Wang, T., Wang, P., Li, Q., Johnson, A. C., Sarvajayakesavalu, S., Sweetman, A.  
480 J. 2016. Risk assessment and source identification of perfluoroalkyl acids in surface and  
481 ground water: Spatial distribution around a mega-fluorochemical industrial park, China.  
482 *Environment International*. 91: 69-77.

483 Maine Center., 2014. Maximum Exposure Guideline for Perfluorooctanoic Acid in Drinking  
484 Water. [http://www.maine.gov/dhhs/mecdc/environmental-](http://www.maine.gov/dhhs/mecdc/environmental-health/eohp/wells/documents/pfoameg.pdf)  
485 [health/eohp/wells/documents/pfoameg.pdf](http://www.maine.gov/dhhs/mecdc/environmental-health/eohp/wells/documents/pfoameg.pdf). (July 22, 2016)  
486 MDH, 2007. Health Based Values for Perfluorooctanoic (PFOA).  
487 <http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/pfoamemo0307.pdf>. (July 22,  
488 2016)  
489 MDH, 2011. Health-Based Guidance for Water.  
490 <http://www.health.state.mn.us/divs/eh/risk/guidance/gw/table.html>. (July 22, 2016)  
491 NJDEP, 2007. Guidance for PFOA in Drinking Water at Pennsgrove Water Supply Company.  
492 [http://www.nj.gov/dep/watersupply/pdf/pfoa\\_dwguidance.pdf](http://www.nj.gov/dep/watersupply/pdf/pfoa_dwguidance.pdf). (July 22, 2016)  
493 Oliaei, F., Kriens, D., Weber, R., Watson, A. 2013. PFOS and PFC releases and associated  
494 pollution from a PFC production plant in Minnesota (USA). Environ Sci Pollut R. 20(4):  
495 1977-1992.  
496 Paterson, L., Mitchell, I., Chatwell, I., Birk, R., 2012. Evaluation of Groundwater Transport of  
497 Perfluorinated Chemicals at a Former Fire-Fighting Training Area. [http://www.rpic-](http://www.rpic-ibic.ca/documents/2012_fcs_presentations/Paterson_E.pdf)  
498 [ibic.ca/documents/2012\\_fcs\\_presentations/Paterson\\_E.pdf](http://www.rpic-ibic.ca/documents/2012_fcs_presentations/Paterson_E.pdf). (July 22, 2016)  
499 Paul, A. G., Jones, K. C., Sweetman, A. J. 2009. A First Global Production, Emission, And  
500 Environmental Inventory For Perfluorooctane Sulfonate. Environmental Science &  
501 Technology. 43(2): 386-392.  
502 POPs Action in China, 2014. <http://www.china-pops.org>. (March 19, 2015)  
503 Post, G. B., Cohn, P. D., Cooper, K. R. 2012. Perfluorooctanoic acid (PFOA), an emerging  
504 drinking water contaminant: a critical review of recent literature. Environmental  
505 Research. 116: 93-117.  
506 Saito, N., Harada, K., Inoue, K., Sasaki, K., Yoshinaga, T., Koizumi, A. 2004. Perfluorooctanoate  
507 and perfluorooctane sulfonate concentrations in surface water in Japan. Journal of  
508 Occupational Health. 46(1): 49-59.  
509 Scheringer, M., Trier, X., Cousins, I. T., de Voogt, P., Fletcher, T., Wang, Z., Webster, T. F. 2014.  
510 Helsingør Statement on poly- and perfluorinated alkyl substances (PFASs). Chemosphere.  
511 114: 337-339.  
512 Strynar, M., Dagnino, S., McMahan, R., Liang, S., Lindstrom, A., Andersen, E., McMillan, L.,  
513 Thurman, M., Ferrer, I., Ball, C. 2015. Identification of Novel Perfluoroalkyl Ether  
514 Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using  
515 Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS). Environmental Science &  
516 Technology. 49(19): 11622-11630.  
517 Taniyasu, S., Kannan, K., So, M. K., Gulkowska, A., Sinclair, E., Okazawa, T., Yamashita, N.  
518 2005. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain  
519 perfluorinated acids in water and biota. Journal of Chromatography A. 1093(1-2): 89-97.  
520 Tsuda, T., Inoue, A., Igawa, T., Tanaka, K. 2010. Seasonal Changes of PFOS and PFOA  
521 Concentrations in Lake Biwa Water. B Environ Contam Tox. 85(6): 593-597.  
522 UNEP, 2009. The conference of the parties 4 of the Stockholm Convention (COP-4) in Geneva  
523 placed perfluorooctane sulfonate and perfluorooctane sulfonyl fluoride (PFOS and  
524 PFOSF) in Annex B.  
525 [http://chm.pops.int/Convention/Pressrelease/COP4Geneva9May2009/tabid/542/language/](http://chm.pops.int/Convention/Pressrelease/COP4Geneva9May2009/tabid/542/language/en-US/Default.aspx)  
526 [en-US/Default.aspx](http://chm.pops.int/Convention/Pressrelease/COP4Geneva9May2009/tabid/542/language/en-US/Default.aspx). (July 22, 2016)  
527 USEPA, 2014. Emerging Contaminants-Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic  
528 Acid (PFOA). [http://www2.epa.gov/sites/production/files/2014-](http://www2.epa.gov/sites/production/files/2014-04/documents/factsheet_contaminant_pfos_pfoa_march2014.pdf)  
529 [04/documents/factsheet\\_contaminant\\_pfos\\_pfoa\\_march2014.pdf](http://www2.epa.gov/sites/production/files/2014-04/documents/factsheet_contaminant_pfos_pfoa_march2014.pdf). (July 22, 2016)  
530 USEPA, 2016. PFOA & PFOS Drinking Water Health Advisories. [https://www.epa.gov/ground-](https://www.epa.gov/ground-water-and-drinking-water/supporting-documents-drinking-water-health-advisories-pfoa-and-pfos)  
531 [water-and-drinking-water/supporting-documents-drinking-water-health-advisories-pfoa-](https://www.epa.gov/ground-water-and-drinking-water/supporting-documents-drinking-water-health-advisories-pfoa-and-pfos)  
532 [and-pfos](https://www.epa.gov/ground-water-and-drinking-water/supporting-documents-drinking-water-health-advisories-pfoa-and-pfos). (July 22, 2016)

- 533 Valsecchi, S., Conti, D., Crebelli, R., Polesello, S., Rusconi, M., Mazzoni, M., Preziosi, E.,  
534 Carere, M., Lucentini, L., Ferretti, E., Balzamo, S., Simeone, M. G., Aste, F. 2016.  
535 Deriving environmental quality standards for perfluorooctanoic acid (PFOA) and related  
536 short chain perfluorinated alkyl acids. *Journal of hazardous materials* (In press). DOI:  
537 10.1016/j.jhazmat.2016.04.055
- 538 Wang, P., Lu, Y., Wang, T., Meng, J., Li, Q., Zhu, Z., Sun, Y., Wang, R., Giesy, J. P. 2016.  
539 Shifts in production of perfluoroalkyl acids affect emissions and concentrations in the  
540 environment of the Xiaoqing River Basin, China. *Journal of hazardous materials*. 307:  
541 55-63.
- 542 Wang, P., Lu, Y., Wang, T., Zhu, Z., Li, Q., Zhang, Y., Fu, Y., Xiao, Y., Giesy, J. P. 2015a.  
543 Transport of short-chain perfluoroalkyl acids from concentrated fluoropolymer facilities  
544 to the Daling River estuary, China. *Environmental science and pollution research*  
545 *international*. 22(13): 9626-9636.
- 546 Wang, S., Huang, J., Yang, Y., Hui, Y., Ge, Y., Larssen, T., Yu, G., Deng, S., Wang, B., Harman,  
547 C. 2013. First Report of a Chinese PFOS Alternative Overlooked for 30 Years: Its  
548 Toxicity, Persistence, and Presence in the Environment. *Environmental Science &*  
549 *Technology*. 47(18): 10163-10170.
- 550 Wang, T. Y., Lu, Y. L., Chen, C. L., Naile, J. E., Khim, J. S., Park, J., Luo, W., Jiao, W. T., Hu,  
551 W. Y., Giesy, J. P. 2011. Perfluorinated compounds in estuarine and coastal areas of  
552 north Bohai Sea, China. *Mar Pollut Bull*. 62(8): 1905-1914.
- 553 Wang, Z., Cousins, I. T., Scheringer, M., Hungerbuehler, K. 2015b. Hazard assessment of  
554 fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors:  
555 status quo, ongoing challenges and possible solutions. *Environ Int*. 75: 172-179.
- 556 Zhao, Z., Xie, Z., Tang, J., Sturm, R., Chen, Y., Zhang, G., Ebinghaus, R. 2015. Seasonal  
557 variations and spatial distributions of perfluoroalkyl substances in the rivers Elbe and  
558 lower Weser and the North Sea. *Chemosphere*. 129: 118-125.

559