1 **Coupled production and emission of short chain perfluoroalkyl acids**

2 **from a fast developing fluorochemical industry in Daling River Basin,**

3 **China: evidence from yearly and seasonal monitoring**

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ABSTRACT: Short chain perfluoroalkyl acids (PFAAs) have been developed by the fluorochemical manufacturing industry to replace the conventional C8 and higher homologues since 2002. Much of this production has shifted to China over recent years. In this study, we conducted a continuous monitoring program over the period 2011-2014 with seasonal monitoring in 2013 for PFAAs emitted from two rapidly developing fluorochemical industry parks located in the Daling River Basin, Northern China. Over the study period from 2011 to 2014 an increasing trend of PFAAs concentrations was identified, with perfluorobutane sulfonic acid (PFBS), perfluorobutanoic acid (PFBA) and perfluorooctanoic acid (PFOA) being dominant, showing highest concentrations of 3780 ng/L, 3698 ng/L, and 1948 ng/L, respectively. Seasonal monitoring uncovered the occasional emission of perfluorooctane sulfonic acid (PFOS). Construction trends of new facilities and associated manufacturing capacity of the main products were also analyzed to assess correlations with PFAAs emissions. An assessment of the data over the period 2011 to 2014 found a positive correlation with fluorocarbon alcohol (FCA) production and emission of PFAAs. Groundwater and tap water around the main source indicated that the dominant PFAAs had different diffusion behaviors. PFBS levels was higher in surface water, while PFBA was dominant in groundwater and tap water, with PFOA levels being higher in downstream groundwater. With the continuous expansion and development of fluorochemical industry in the Daling River Basin, this study will provide abundant information on the effectiveness of any future risk management programs.

KEYWORDS: Yearly trend; Seasonal trend; PFBS; PFBA; PFOA; Production

1. Introduction

Perfluoroalkyl acids (PFAAs) have been widely used in both polymer applications based on their water- and grease- repellent property and surfactant applications based on the unparalleled aqueous surface tension-lowering property since the 1950s (Buck et al., 2011). Historically, PFAAs were mostly produced and used in the long-chain forms, especially perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (Paul et al., 2009). However, the persistent, bio-accumulative and toxic potentials (PBT) of long chain PFAAs have led to their phase-out in their production by the major manufacturers since 2000 (3M, 2000). This was followed by increasingly strict regulations on their production, emission and use in multiple countries and regions including United States (US), European Union (EU), Norway, Canada and Germany (Holt, 2011). In 2009, PFOS and its related substances were listed in Annex B of the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2009), which put the restrictions on global scale. Apart from the major manufacturers, downstream users and individual customers are moving away from long-chain PFAAs as a result over human health concerns. As a result, the perfluorinated manufacturing industries have been working on the development of alternatives (Holt, 2011).

In 2002, the major manufacturer 3M developed new fluorochemical surfactants based on perfluorobutane sulfonic acid (PFBS). With four perfluorinated carbon atoms, PFBS was considered as a sustainable alternative to PFOS, and was identified not to be a PBT. PFBS-based surfactants were subsequently commercialized in the US and other countries including China (3M, 2002). Perfluorobutanoic acid (PFBA) with four carbon atoms

64   (three perfluorinated ones) had also been manufactured for many years before 1998, with

65   primary application in the production of photographic film. 3M ceased the production of

66   PFBA in 1998 due to decreased demand (3M, 2008). However, when C8 PFOA

67   production was partially controlled in 2000, it appears that C4 PFBA production was

68   reintroduced. This led to very high levels of PFBA in the surrounding environment of

69   3M's production site including in groundwater, wastewater effluent and river water, with

70   PFBA levels up to a hundred time greater than PFOA (Oliaei et al., 2013). The

71   development of alternatives has demonstrated that non-fluorinated alternatives, like

72   hydrocarbons, surfactants or silicone products, do not work as well, especially in extreme

73   low surface tension applications. However, C4 PFAAs can adequately replace most C8

74   and higher homologue applications (Holt, 2010). However, the consequences of these

75   factors on the expansion of production and emission of short chain PFAAs are still

76   largely unknown.

77   Research on the sources of PFAAs has mostly focused on sewage treatment plants and

78   atmospheric deposition in those countries or regions with strict regulation on the

79   production of PFAAs (Ahrens and Bundschuh, 2014). In China the most important source

80   of PFAAs comes directly from fluoro-polymer/-telomer manufacture due to the

81   production shift in recent years. As a result of the implementation of the Stockholm

82   Convention the production and emission of PFOS has been controlled in China, but other

83   PFAAs remain outside of any restriction (POPs Action in China, 2014). Our previous

84   studies identified the source and transportation routes of high levels of short chain

85   PFAAs emitted from two fluorochemical industry parks in the Daling River Basin of

86   North China (Wang et al., 2015). However, the two parks have expanded very fast with

87 frequent changes on production capacity of various fluorochemicals, so it's very

88 important to trace the dynamic correlations between production and emission of

89 dominant PFAAs.

90   A 4-year study has been conducted between 2011 and 2014 with a 4-season (2013)

91 continuous monitoring of PFAAs in the Daling River, and when combined with previous

92 studies (Bao et al., 2010; Wang et al., 2011), a temporal trend of 7 years from 2008 to

93 2014 can be established, reflecting the fast development period of short-chain PFAAs in

94 China. Furthermore, groundwater samples around Park 1 have also been analyzed to

95 explore the different transportation behavior of dominant PFAAs compared with surface

96 water. The overall aim of the study was to establish the emission characteristics and

97 temporal trends of PFAAs from an emerged fluorochemical industry in China, which can

98 be used to provide a basis for effective surface water and groundwater management and

99 risk assessment.

100 ## 2. Materials and Methods

101 *2.1 Sampling campaign.*

102 *2.1.1 Yearly and seasonal sampling of river water in Daling River Basin.*

103 The two fluorochemical industry parks included in this study are located in the Xihe

104 River. The sampling sites were selected from the upstream of the parks to the confluence

105 point to the Daling River (site 1 to 8X) and then to the Daling River estuary (site 9 to 14).

106 The distance from site 1 to site 8 is 82 km, and from site 8 to site 14 is 90 km. Sites in the

107 upstream of the confluence point in the Daling River (site 15 to 18 and site 8D) were set

108   as reference locations. According to a previous study in 2011, the two parks didn't

109   discharge sewage to the tributaries of the Xihe River (Wang et al., 2015), so these

110   tributaries were not included in this study. Yearly sampling campaigns were conducted in

111　October　from　2011　to　2014,　while　seasonal　samplings　were
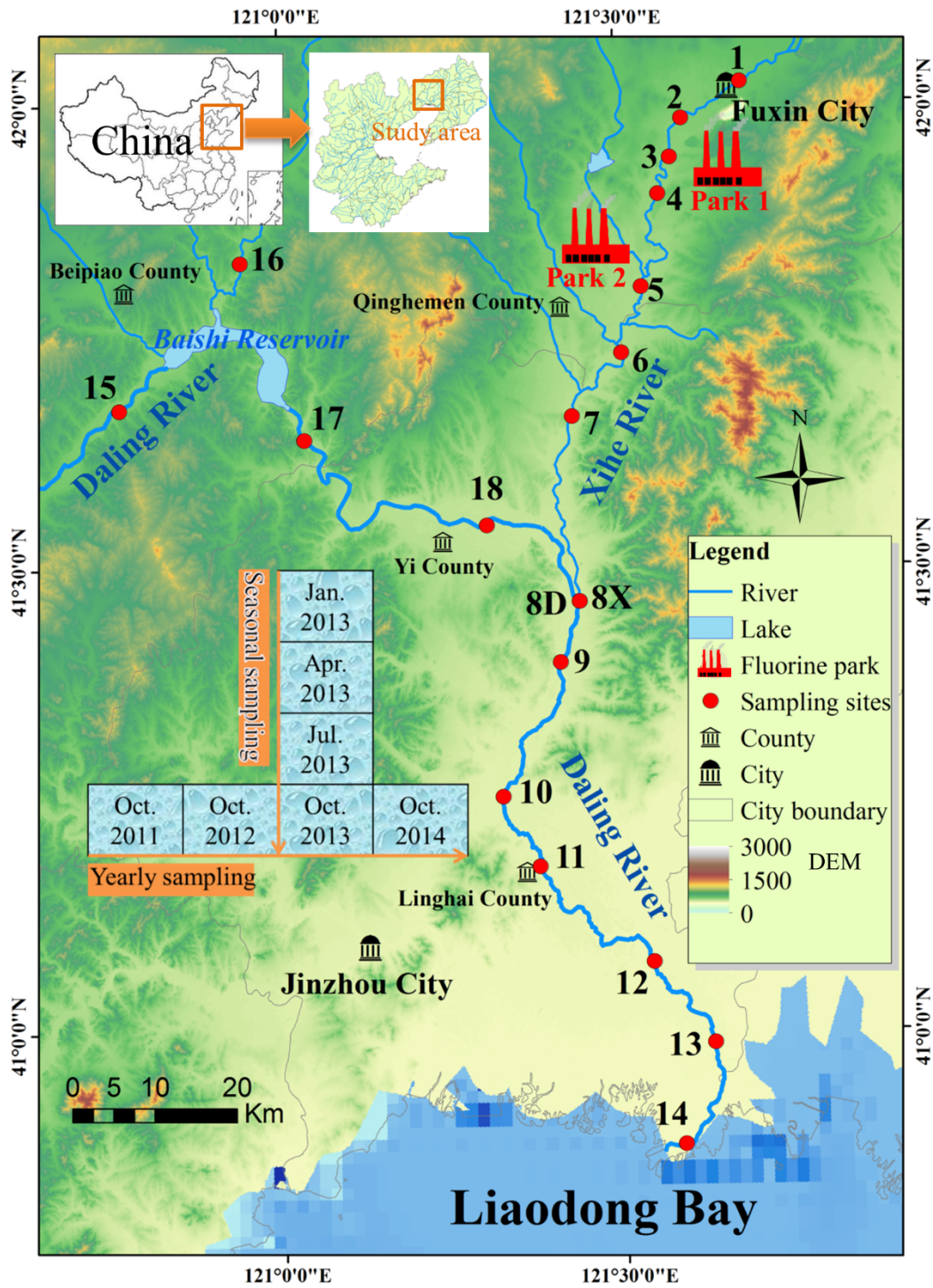

Figure 1. Sampling sites in the Daling River Basin

114   conducted in January (winter), April (spring), July (summer) and October (autumn) in

115   2013. Field samples consisted of surface water (top 1-20cm) collected using 1L pre-

116   rinsed polypropylene (PP) bottles. Parameters including water temperature, pH, dissolved

117   oxygen and conductivity were measured *in situ* using a HQd Portable and Benchtop

118   Meter Configurator (HACH Company, USA) (Table S1-S2). Suspended particles present

119   in the water samples were removed by settling for 24 hours with the supernatant being

120   used for the analysis.

121   *2.1.2 Ground water and tap water sampling in villages around Park 1.*

122   The results of yearly (prior to 2014) and seasonal monitoring showed that park 1 had

123   always been a significant point source of PFBS, PFBA and PFOA. So in 2014, along with

124   the yearly sampling campaign in October, groundwater and tap water samples were also

125   taken. Four villages at four locations around Park 1 were selected (Figure S1), and

126   ground water (5-7m household wells) and tap water were sampled at randomly selected

127   homes in each village using 1L pre-rinsed PP bottles. The treatment of these samples was

128   the same as that for the river water samples.

129   *2.2 Extraction and analysis of target analytes.*

130   During the first sampling event in 2011, 17 PFAAs were analyzed and results indicated

131   that long chain PFAAs were close to detection limits (Wang et al., 2015). As a result,

132   during the later sampling events, only 12 linear PFAAs including C4 to C12

133   perfluoroalkyl carboxylic acids (PFCAs) and 3 perfluoroalkane sulfonic acids (PFSAs)

134   were quantified (Table S3). A 400mL aliquot of water spiked with 10 ng mass-labelled

135   standards was extracted using OASIS WAX-SPE following published methods (Taniyasu

136 et al., 2005) with some modifications. Briefly, prior to loading samples, the Oasis WAX

137 cartridges (6 cc, 150 mg, 30 μm, Waters, Milford, MA) were preconditioned with 4 mL

138 of 0.1% NH_4OH in methanol, 4 mL of methanol, and 4 mL of Milli-Q water. After

139 loading the samples, cartridges were washed with 4 mL 25 mM ammonium acetate

140 (pH=4) and air-dried. Target analytes were then eluted with 4 mL of methanol and 4 mL

141 of 0.1% NH_4OH in methanol, respectively. The extracts were reduced to 1 mL under high

142 purity nitrogen (99.999%) and passed through a nylon filter (13 mm, 0.2 μm, Chromspec,

143 Ontario, Canada), then transferred into a 1.5 mL PP snap top brown glass vial with

144 polyethylene (PE) septa. Individual PFAA was separated and quantified via Agilent 1290

145 Infinity HPLC System coupled to an Agilent 6460 Triple Quadrupole LC/MS System

146 (Agilent Technologies, Palo Alto, CA) operated in the negative electrospray ionization

147 (ESI-) mode. Conditions under which the instrument was operated were listed in Table

148 S4.

149 *2.3 QA/QC.*

150 The manufacturing plants were not informed of the sampling campaign and so this study

151 can be assumed to reflect the routine production activities in the two parks. The

152 yearly/seasonal sampling was conducted at the same date of the year/season and the same

153 time of a day as much as possible. These were designed to provide parallel comparisons.

154 Use of polytetrafluoro- ethylene (PTFE) or other fluoro-polymer/-telomer materials was

155 avoided throughout the study. In order to avoid cross contamination during sampling, the

156 outside of the 1L PP bottles was immediately washed with Milli-Q water after the

157 samples were taken, wiped with clean towel paper and then kept in sealed PP bags. Field,

158 transport, procedure and solvent blanks were prepared with every sample batch to

159 monitor potential interferences. Quantification of the 12 PFAAs in water were carried out

160 using 10-point external standard curves with concentrations ranging from 0.01 to 1000

161 ng/mL. 10 ng/mL of mass-labelled standards as surrogates were also added to the

162 samples to monitor the matrix effect. The injection volume was 5 μL. The regression

163 coefficients (R^2) for all the target analytes were over 0.99. The limit of detection (LOD)

164 and limit of quantification (LOQ) were defined as the peak of analyte that needed to yield

165 a signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively. LOD and LOQ in this study

166 were checked along every sampling event, and the final values were combined and

167 presented at the highest ones. LODs ranged from 0.01 to 0.15 ng/L, while LOQs ranged

168 from 0.06 to 0.71 ng/L. Recovery tests were also conducted along all sampling events,

169 and the values were combined together to give the means and standard deviations for

170 individual PFAA. Matrix spike recoveries ranged from 73 to 113%, while procedure

171 recovery ranged from 81 to 124%. For extracts containing concentrations of PFAAs in

172 excess of 1000 ng/mL, the volume of the samples was reduced and the samples extracted

173 again to make sure the concentrations of PFAAs were within the calibration range.

174 Detailed QA/QC measurements of target PFAAs are given in Supplementary Material.

175 *2.4 Statistical and spatial analysis.*

176 Statistical analysis was performed using Microsoft Office 2010 and OriginPro 9.1

177 (Northampton, MA, USA). Spatial distributions of the sampling sites were illustrated

178 using the Arcmap module in ArcGIS V10.0 software (ESRI, Redland, CA). GIS data

179 used for sampling design was obtained from the National Geomatics Center of China

180 (Haidian District, BJ).

3. Results and Discussion

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

From 2011 to 2014, PFBS and PFBA have always been the dominant PFAAs, followed by PFOA, and then C5-C7 PFCAs (Table 1, Table S5-S8). C9-C12 PFCAs and PFOS were detected in both low ratios and low concentrations, indicating they were seldom produced in the study area. The highest concentrations of PFBS were 2896 ng/L in 2011, 2341 ng/L in 2012, 2714 ng/L in 2013 and 3780 ng/L in 2014. For PFBA, the highest concentrations were 1346 ng/L in 2011, 1566 ng/L in 2012, 3698 ng/L in 2013 and 2575 ng/L in 2014. For PFOA, the highest concentrations were 348 ng/L in 2011, 675 ng/L in 2012, 1948 ng/L in 2013 and 772 ng/ in 2014, respectively. Concentrations of PFOS were far below those of the three dominant PFAAs, with the overall highest concentration of 12.6 ng/L observed in 2011. Among the C5-C7 PFCAs, C6 PFHxA were dominant with an increasing trend from 2011-2013, with the highest concentration up to 795 ng/L in 2013. C6 PFAAs were also considered to be one of the potential alternatives to long chain PFAAs (Holt, 2010). However, even in the site with the highest concentration, PFHxA level was a factor of 5 less than PFBA, indicating a lower importance than C4 PFBA as an alternative. The spatial distribution data from the upstream of the two fluorochemical industry parks in the Xihe River to the estuary of the Daling River clearly demonstrated that emissions of PFBS and PFBA started from site 3 throughout the four year period (Figure 2), with site 3 or site 4 providing the highest concentrations. This indicated that Park 1 has been a major source of PFBS and PFBA since 2011. For PFOA, the general increasing trend from site 3 was less obvious than those of PFBS and PFBA

203   except in 2013, when a high concentration was observed. Contributions from Park 2

204   made the levels of the three dominant PFAAs consistent from site 5 to site 8X, with the

205   decreasing levels in site 6 potentially caused by dilution from the tributaries. From site

206   8X to site 12 general decreasing trends were observed for the three dominant PFAAs,

207   with the observed fluctuation of concentrations in site 13 and site 14 of the estuary being

208   affected by the frequent mixture of fresh and saline water. Meanwhile, concentrations of

209   PFAAs at the reference sites from 15 to 17 indicated no other point sources from the

210   upstream parts of the Daling River over the study period. The relatively notable PFAAs

211   levels in site 18 and 8D could have originated from domestic emissions in Yi County.

212   Currently, there are few data on the temporal trend of PFAAs, especially PFOS and

213   PFOA in the environment. Solid matrices like sediment and biological samples are often

214   used in such research (Murakami et al., 2011; Myers et al., 2012; Zennegg et al., 2013).

215   However, short-chain PFAAs have very low affinity to sediment (Ahrens and Bundschuh,

216   2014) and have much shorter elimination time in organisms (Oliaei et al., 2013). As a

217   result, direct sampling in rivers can be more suitable to trace the temporal trends of short

218   chain PFAAs emission, but related studies are very limited. As to the PFAAs levels, it

219   has been reported that 3M converted production to short-chain PFAAs after the phase-out

220   of PFOS (Oliaei et al., 2013). This led to increasing levels of PFBS observed in sediment

221   cores from Lake Michigan, which is located to the west of 3M facility (Codling et al.,

222   2014). PFBS or PFBA were also found dominant in Tangxun Lake, China (Zhou et al.,

223   2013), River Rhine (Eschauzier et al., 2010; Moller et al., 2010), Italian river basins

224   (Valsecchi et al., 2014) and German drinking water supplies (Wilhelm et al., 2010).

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226   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.	1 346	82.2	59.2	15.9	348	2 896	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.	1 566	81.2	180	45.5	675	2 341	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.	3 698	198	795	103	3 948	2 714	11.4
	Mean	1 051	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.	2 575	56.1	196	55.0	772	3 780	6.95
	Mean	830	23.6	60.7	19.3	239	1 090	2.60
	Median	536	21.1	42,2	15.5	155	668	1.52

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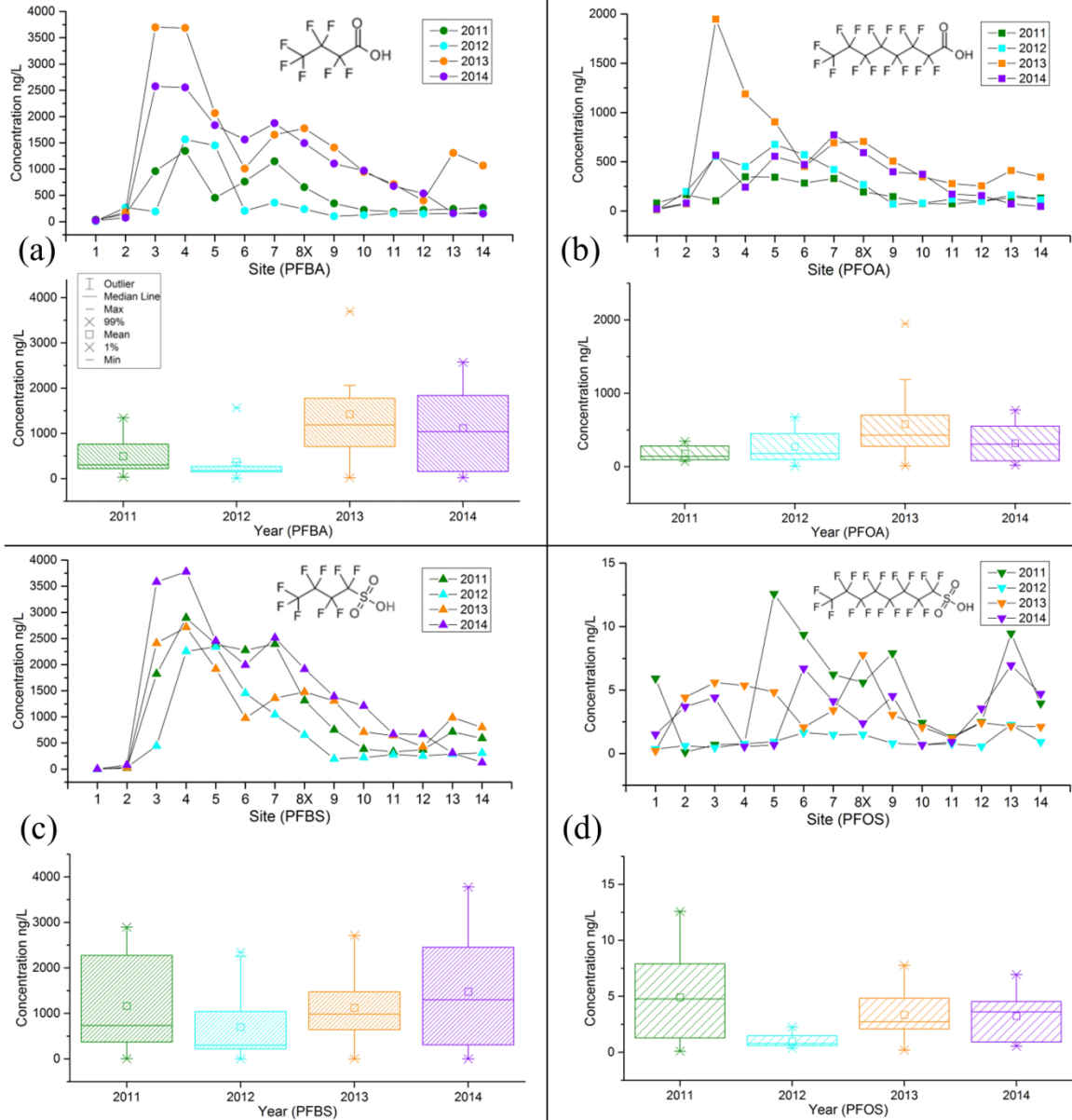
Figure 2. Temporal trends of main PFAAs in the Daling River water from 2011 to 2014.

3.2 Seasonal trends of PFAAs emitted into the Daling River water.

While yearly monitoring can provide a temporal trend of PFAAs levels, seasonal monitoring reveals the production and emission of dominant PFAAs from the manufacturers within a yearly cycle. Results from this study showed that the spatial

234   distribution of the three dominant PFAAs levels in all seasons were quite consistent with

235   those collected over the four year study. This indicated that the locations of PFAAs

236   emissions remained the same. However, PFAAs levels changed considerably over the

237   different seasons of 2013, and the seasonal trend of the three dominant PFAAs were also

238   different (Table 2, Table S9-S12, Figure 3). For PFBS, the overall concentrations from

239   site 1 to site 14 were presented in a decreasing trend of summer (max. 3870 ng/L) >

240   autumn (max. 2714 ng/L) > spring (max. 1980 ng/L) > winter (max. 690 ng/L), while the

241   trend was autumn (3698 ng/L) > summer (2435 ng/L) > spring (1973 ng/L) > winter (628

242   ng/L) for PFBA, and summer (2279 ng/L) > autumn (1948 ng/L) > winter (753 ng/L) >

243   spring (749 ng/L) for PFOA, respectively. Although PFOS was found with relatively low

244   concentrations and no point-source input in the yearly monitoring, the seasonal

245   monitoring did show an apparent point-source emission of PFOS at site 5 (located in the

246   downstream of Park 2) with concentration of 483 ng/L. The levels then decreased from

247   site 5 to site 8X because of dilution after the Xihe River confluence with the Daling River.

248   C5-C7 PFAAs showed quite consistent trends with the yearly monitoring data, except

249   that relatively high levels of C6 PFHxA were emitted since the summer of 2013. This

250   indicated that even though PFBS, PFBA and PFOA were the dominant PFAAs emitted

251   from the two parks, other homologues including PFOS could still be produced and

252   emitted in some occasions. This was largely due to the unstable status of construction and

253   production in the parks, which will be discussed later.

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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.	1 973	79.6	168	36.8	749	1 980	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.	2 435	273	603	119	2 279	3 870	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.	3 698	198	795	103	3 948	2 714	11.4
	Mean	1 051	41.8	100	22.3	533	830	3.49
	Median	945	34.0	56.4	20.1	344	712	2.43

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Tsuda et al. (2010) studied the seasonal changes of PFOS and PFOA in Lake Biwa

Japan in 2009, with highest levels of 5.3 ng/L for PFOS and 26 ng/L for PFOA,

respectively. No specific sources were discussed, for the levels were relatively low. Zhao

et al. (2014) performed a detailed study on the seasonal variations of PFAAs in the rivers

Elbe and lower Weser and the North Sea in 2011. PFBS, PFOA, PFHxA and PFBA were

dominant PFAAs, which was comparable with this study. However, the overall levels

265   were relatively low with no discussion of potential point sources included. The highest

266   reported concentration of PFBS was 240 ng/L, with the authors attributing it to

267   occasional discharge of wastewater from some unidentified industrial plants. As far as we

268   know, this is the first study on yearly and seasonal monitoring of PFAAs emitted from

269   fluorochemical industry.
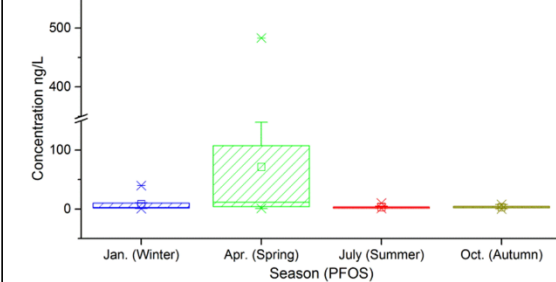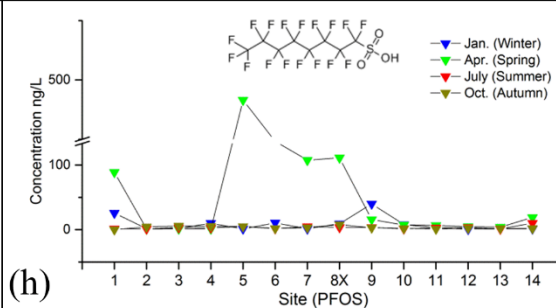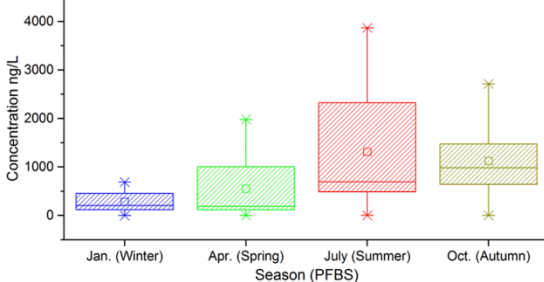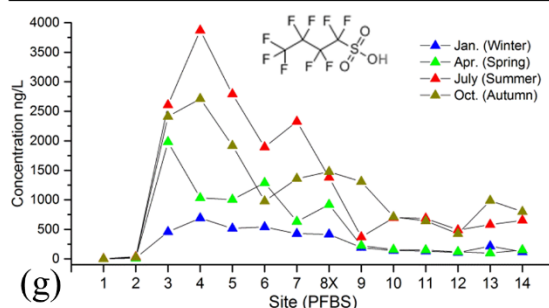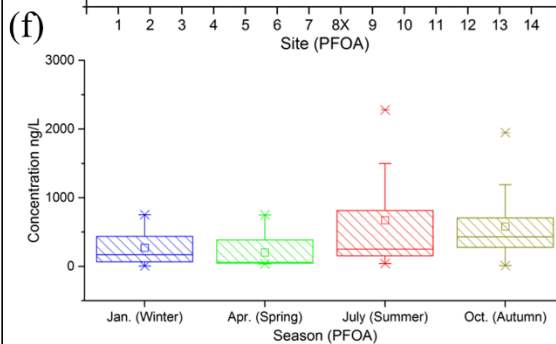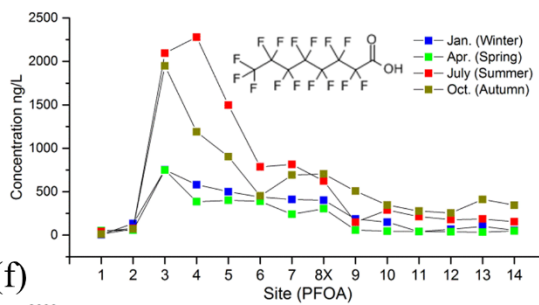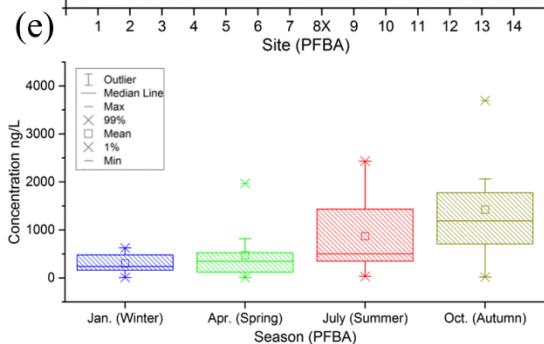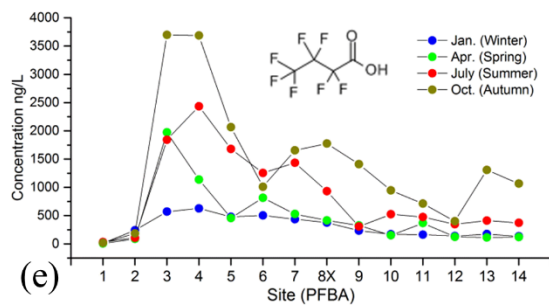
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271   Figure 3. Levels of main PFAAs in the Daling River water in four seasons of the year

272   2013.

3.3 PFAAs emission characteristics related to construction and production.

274   Although all dominant PFAAs levels showed general increasing trends over the study

275   period, the extent was different (Figure 4c), which can be used to identify potential

276   changes to emission sources and can also reflect the dynamic of market need, production

277   capacity and etc. Concentration ratios can provide comparisons on the temporal

278   variations of the dominant PFAAs. It can be seen from Table 3 that, the mean values of

279   the PFBS/PFBA ratio from site 3 to site 8X were 2.7 and 3.0 in 2011 and 2012,

280   respectively. But the ratios became 0.8 in 2013 and 1.4 in 2014. For PFBA/PFOA ratios,

281   the mean values also showed an increasing trend from 2012-2014. These might imply

282   that emission of PFBA increased more than that of PFBS and PFOA over the most recent

283   years, with PFBA becoming more important in fluorochemical applications. Spatial

284   variations of the concentration ratios indicated that the emission intensity from the two

285   parks for the dominant PFAAs had been changing. This was consistent with the status

286   that the planning and construction of fluoropolymer facilities in the two parks had been

287   regulated all the time.

288   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
Mean	2.7	3.0	0.8	1.4	4.0	1.3	2.2	4.5
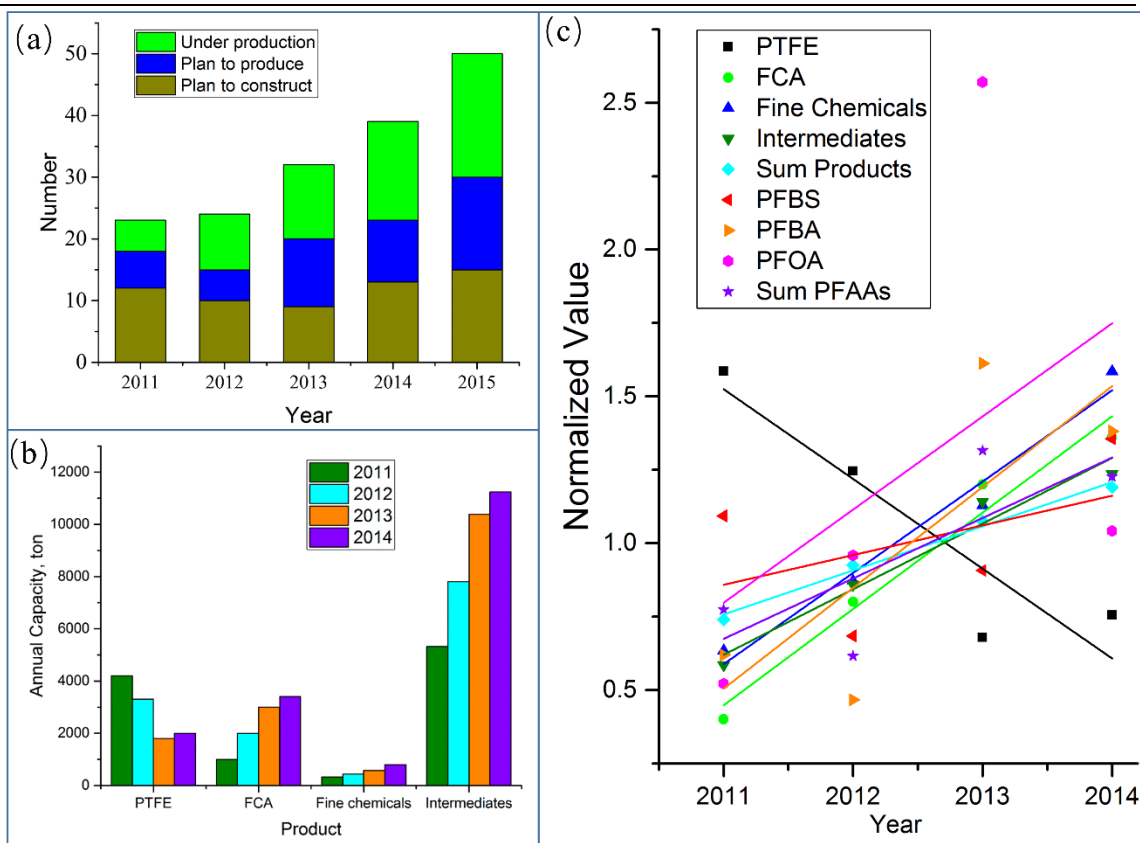
Figure 4. (a) Construction status of fluorochemical facilities, (b) the main organo-fluorine products in the two parks and (c) The temporal trends based on the normalization of related values divided by median.

In our previous study in 2011 there were limited fluoropolymer facilities in the study area (Wang et al., 2015). However, after years of construction of more facilities and wastewater treatment plants, it is more complicated to identify any correlations of production and emission for the dominant PFAAs. We investigated the construction and production status over the period 2011-2014 to explore the emission characteristics of the fluorochemical industry. From 2011-2014 there were dozens of facilities under

299   production, planning to produce or planning to construct (Figure 4a), especially the

300   number (accumulated value) of facilities under production showed a steady increasing

301   trend. This resulted in the increasing capacity of organo-fluorine production that relates

302   to the emission of PFAAs (Figure 4b). PTFE, Fluorocarbon alcohol (FCA) were directly

303   correlated with the emission of PFAAs, but the trends were quite different (Figure 4c).

304   PTFE capacity showed a decreasing trend, which might be influenced by other

305   manufacturers with a higher production capacity, such as in the Xiaoqing River Basin of

306   the same economic circle which had a PTFE capacity of 49000 tons (Wang et al., 2016).

307   FCA including perfluoroalkyl Iodides (PFAIs), Fluorotelomer Alcohols (FTOHs) and

308   related products such as surfactants are all featured products in the study area, with

309   various processes including electrochemical fluorination and telomerization that could

310   generate the emission of the dominant PFAAs (Figure 5). Besides these potential sources,

311   the production of various intermediates for pesticides and medicines is prevalent in the

312   area from which PFAAs could be used and emitted. Furthermore, the central wastewater

313   treatment plant (WWTP) in the parks could also have effects on the emission of PFAAs

314   to the river, which needs more detailed study.

315
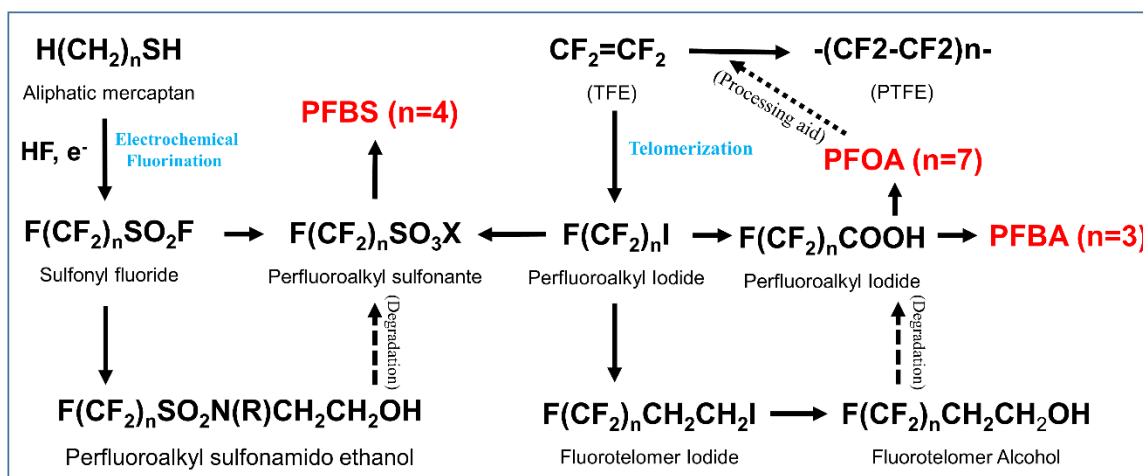
Figure 5. Main production processes and products in the parks correlated with the

emission of the dominant PFAAs

3.4 PFAAs in groundwater and tap water around Park 1.

The yearly and seasonal monitoring data indicated that Park 1 discharged high levels of PFBS and PFBA directly and continuously to the Xihe River. It is possible that these short-chain PFAAs might migrate to the groundwater through river leakage or other pathways (Liu et al., 2016), resulting in exposure to local residents via water abstraction using shallow wells (5-7 m). Unlike short-chain PFAAs that are usually present at liquid form, long-chain PFAAs are present at solid or powder forms (Wang et al., 2015), which make them more susceptible to atmospheric dispersion followed by migration into groundwater via precipitation (Davis et al., 2007). In this study, very high levels of PFAAs were detected in the groundwater taken from the wells in villages nearby Park 1 (Table 5, Table S13, Figure 6). W1 is very close to site 3 in the Xihe River (<100 m), comparisons on PFAAs levels showed that unlike that in river water, PFOA was dominant in groundwater of W1 with concentration up to 4151 ng/L contributing to 37.5% of ∑PFAAs (sum of PFAAs), followed by PFBA (3613 ng/L, 32.7%) > PFHxA (1175 ng/L, 10.6%) > PFPeA (951 ng/L, 8.6%) > PFBS (588 ng/L, 5.3%) > PFHpA (579 ng/L, 5.2%). For W2-W4, which are located farther from Park 1 than W1, PFAAs levels decreased and contributions of individual PFAA also changed. PFBA was more dominant in W2 with concentration of 1775 ng/L and contribution of 41.4%, followed by PFOA (1391 ng/L, 32.4%). PFBS accounted for a larger contribution to the total (865 ng/L, 20.2%), while the contributions of C5-C7 PFAAs were reduced. The concentrations and

338 profiles of PFAAs were comparable in W3 and W4 with ∑PFAAs of 536 ng/L and 463

339 ng/L, respectively. PFBA accounted for about 80%, contributions of PFOA reduced to

340 12.0% and 17.6%, respectively, while PFBS and C5-C7 PFACs accounted for even less.

341 The spatial distribution of W1-W4 indicated that apart from the distance to Park 1, local

342 environmental conditions combined with PFAAs properties could be important reasons

343 for the varied levels and profiles of PFAAs in groundwater. W1 is adjacent to the

344 Aliphatic fluoride zone of Park 1 (Figure 4), which is the zone of direct production and

345 use of PFOA. PFOA could be released as dust, solid waste or impurities in products, and

346 migrate with runoff into groundwater. The high mobility of PFBA led to its high

347 contributions to totals in W3 and W4, and dominance in W1 and W2 (Oliaei et al., 2013).

348 PFBS is less mobile than PFBA, so was mainly emitted to and found in river water.

349 ∑PFAAs in tap water of W1-W3 were all below 10 ng/L, only tap water in W4 presented

350 ∑PFAAs level of 74.2 ng/L, which might be due to different tap water suppliers.

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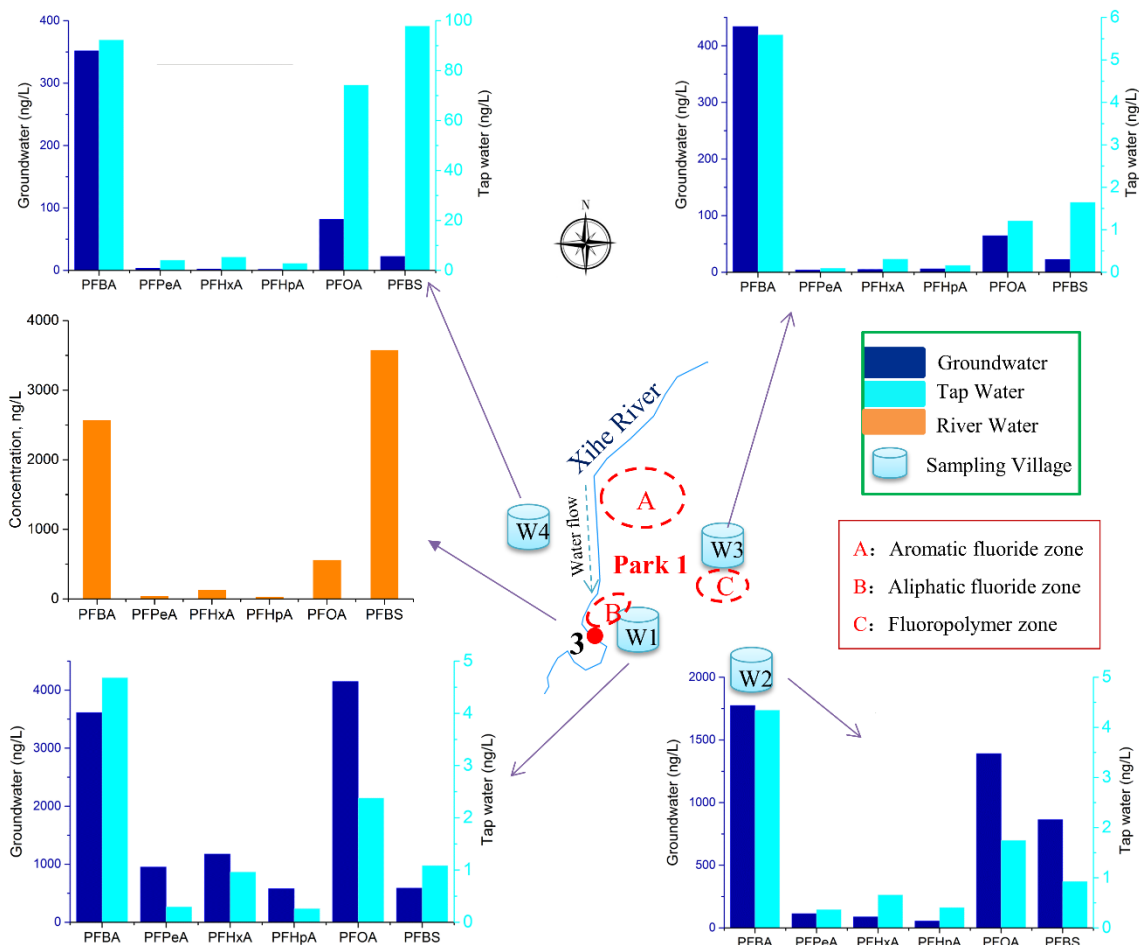
Figure 6. Distribution of PFAAs levels among groundwater, tap water and river water

nearby Park 1 in 2014.

Table 5. Concentrations of the main PFAAs (ng/L) in the groundwater and tap water in
this study, and available health drinking water criteria (ng/L) in the world.

Region	Type	PFBA	PFOA	PFBS	PFOS	year
This study						
W1	Groundwater	3 613	4 151	588	1.05	2014
	Tap water	4.68	2.38	1.09	0.30	2014
W2	Groundwater	1 775	1 391	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	*Value name*					
New Jersey	Preliminary Health-Based Guidance	-	40	-	-	2007
USEPA	Provisional Health Advisory	-	400	-	200	2009
North Carolina	Interim Maximum Allowable Concentration	-	1 000	-	-	2010
Minnesota	Chronic Health Risk Limit	7 000	300	7 000	300	2011
Maine	Maximum Exposure Guideline	-	100	-	-	2014
United Kingdom	Further Provision	-	300	-	300	2009
	Potential Danger to Human Health	-	5 000	-	1 000	
	Notification of Events	-	45 000	-	9 000	
Germany	Health-Related Indication Value	7 000	300	3 000	300	2006/2010
Canada	Drinking Water Protection	-	700	-	300	2010

356 References: (NJDEP, 2007; DRINKING WATER INSPECTORATE, 2009; Wilhelm et
357 al., 2010; MDH, 2011; Paterson et al., 2012; Maine Center., 2014; USEPA, 2014).

358

359   Previous studies reported that in areas with relatively high PFOA levels in surface

360   water, the tap water could also contain higher PFOA concentrations (Saito et al., 2004).

361   In this study, PFOA levels in tap water at location W4 exceeded the Preliminary Health-

362   Based Guidance value (40 ng/L) in New Jersey, USA (NJDEP, 2007), which required

363   immediate investigation on the supplier. Although groundwater accounted for a limited

364   contribution to drinking water consumption, it was still used for irrigation of crops,

365   providing water for domestic animals, washing clothes, cleaning etc. Therefore potential

366   adverse effects may still exists if groundwater from W1 and W2 was used, as PFOA

367   levels in the wells of the two villages exceeded almost all criteria values (Table 5). There

368   is a decreasing trend on the criteria values of PFOA (MDH, 2007; 2011), and when

369   considering the increasing trend of the emission of PFOA and the accumulation of PFOA

370   in groundwater, further studies are needed to ensure the development of fluorochemical

371   industry is not having an adverse effect on local residents.

372   *3.5 Conclusions.*

373   This study has provided a systematic yearly and seasonal study of PFAAs emitted to the

374   Daling River Basin from two fast developing fluorochemical industry parks in Northern

375   China. The yearly monitoring data indicated that emissions were continuous and

376   demonstrated a generally increasing trend from 2008 to 2014. PFBS, PFBA and PFOA

377   were identified as the most dominant PFAAs, followed by C5-C7 PFCAs. Seasonal

378   monitoring added additional information to the yearly increasing trend, which also

379   identified occasional PFOS emission in Spring. Construction of new facilities and

380   increasing annual manufacturing capacity of the main organo-fluorine products were also

381   investigated to explore their relationship with the dominant PFAAs emissions. The

382   number of facilities under construction showed an increasing trend, while the trends of

383   the products also varied considerably. The capacities of FCA showed an increasing trend

384   along with most processes that generate the emissions of PFAAs. In order to assess the

385   potential risk of PFAAs to human health, groundwater and tap water samples were taken

386   from the nearby villages. Results showed different profiles of PFAAs in groundwater

387   compared with river water, with PFBA showing the highest mobility being dominant in

388   groundwater at all locations. PFBS were more dominant in river water than in

389   groundwater. PFOA was dominant in the groundwater at the nearest downstream village.

390   PFAAs levels in tap water were mostly below criteria values except at location W4,

391   which should be investigated further. With an increasing number of facilities under

392   production in the future, more studies are required on the relationship between production

393   processes, wastewater treatment facilities and PFAAs emission, along with an assessment

394   of the potential human health risk of PFAAs through the use of groundwater and river

395   water.

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