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Perfluoroalkyl acids (PFAAs) in indoor and outdoor dusts around a mega fluorochemical industrial park in China: implications for human exposure

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Highlights

- ◆ 12 PFAAs were detected in dusts around a mega fluorochemical industrial park.

- ◆ PFOA was the predominant PFAAs followed by C4-C7 PFCAs.

- ◆ PFAAs congener patterns in outdoor dusts were similar to those in indoor dusts.

- ◆ PFAAs concentrations were higher in indoor dusts than in corresponding outdoor dusts at every site.

- ◆ High EDI of PFOA, though below the tolerable levels, is posing human health risk.

Abstract

44   The manufacture of fluorochemicals can lead to high levels of perfluoroalkyl acids

45   (PFAAs) contaminating the surrounding environment and consequently elevated

46   exposure to the local residents. In this study, measurements of PFAAs associated with

47   indoor and outdoor dusts around a mega fluorochemical industrial park (FIP) were

48   made. Perfluorooctanoic acid (PFOA) and short-chain perfluoroalkyl carboxylic acids

49   (C4-C7 PFCAs) were the predominant forms in all samples. The signature of the

50   PFAAs in dusts in the local area matched that found within the FIP complex. The

51   contamination plume in the local area could be linked to the prevailing wind direction

52   starting from the FIP. The dust concentrations decreased exponentially with distance

53   from the FIP (noticeably in the first 5 km). PFAAs contamination could be detected at

54   the furthest location, 20 km away from the FIP. The concentrations of PFAAs were

55   higher in indoor dust (73-13,500 ng/g, median: 979 ng/g) than those in outdoor dust (5-

56   9,495 ng/g, median: 62 ng/g) at every location. The highest estimated daily intake of

57   PFOA via dust ingestion (26.0 ng/kg.bw/day) was for toddlers (2-5 yrs) living 2 km

58   away from the FIP, which is posing human health risk, though exposure remains within

59   the provisional tolerable daily intake values.

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65   **1. Introduction**

66   Perfluoroalkyl acids (PFAAs), including perfluorocarboxylates (PFCAs) and

67   perfluorosulfonates (PFSAs), are synthesized chemicals which have high surface

68   activity, thermal and acid resistance, and repellency of water and oil (Giesy and Kannan,

69   2002). These properties have led to their use in various commercial products and

70   industrial processes, such as textile, food containers, upholstery, fire-fighting foams,

71   metal plating and fluoropolymer manufacturing (OECD, 2002; Buck et al., 2011; Wang

72   et al., 2014b). Their presence in so many products and non-biodegradability has led to

73   their wide distribution in the environment. With a potential for bioaccumulation and

74   potential adverse effects in biota and humans, they have attracted increasing scientific

75   attention and enhanced awareness among regulators (Lindstrom et al., 2011). In 2009,

76   perfluorooctane sulfonic acid (PFOS), its salts, and perfluorooctane sulfonyl fluoride

77   (POSF) were listed as persistent organic pollutants (POPs) by the Stockholm

78   Convention (UNEP, 2009). Perfluorooctanoic acid (PFOA), another highly investigated

79   PFAA, is due to be phased out in the USA following agreements with industry in that

80   country by 2015 (USEPA, 2006). There has been a trend for the manufacture of PFAAs

81   and fluoro-polymers/-telomers to shift from North America and Europe to emerging

82   economies, especially China (Wang et al., 2014a; Wang et al., 2016).

83   In humans, statistical associations between PFOS or PFOA levels and reduced birth

84   weight (Stein et al., 2009), cholesterol (Nelson et al., 2010), uric acid (Steenland et al.,

85   2010), sperm quality (Joensen et al., 2009), kidney and testicular cancer (Barry et al.,

86   2013), and ulcerative colitis (Steenland et al., 2013) have been reported. The main

87   routes for human exposure to PFAAs include ingestion of dust, food and drinking water

88   consumption, and inhalation of PFAAs-contaminated air (Fromme et al., 2009;

89   D'Hollander et al., 2010). A number of studies have reported that household dust

90   contains PFAAs (Björklund et al., 2009; Goosey and Harrad, 2011; Fraser et al., 2013).

91   Indoor dust is mixture of settled particles, human skin and fabric micro fibres, whereas

92   outdoor dust is mostly made of microorgansisms, spores, traffic-related emissions and

93   soil-derived particles. Humans can mitigate their exposure to contaminants in food or

94   beverages by choosing different products, but this choice does not exist when the

95   contaminant is present in their physical environment where they work, live and play.

96   Given the association of PFAAs with dust, it is likely that young children who are often

97   in close contact with floors and dusty surfaces and have a greater propensity to put their

98   hands and objects in their mouths will be particularly exposed.

99   Our previous studies have found an important point source of PFAAs, a mega

100   fluorochemical industrial park (FIP), in the Xiaoqing River basin in northern China

101   (Wang et al., 2014a). PFAAs levels up to 1.06 mg/L, with a mass load of 174 kg/d, were

102   identified at downstream of the FIP (Wang et al., 2016). The FIP is one of the largest

103   production facilities of the fluorochemical industry in Asia. It was founded in 1987 and

104   began to produce polytetrafluoroethylene (PTFE) in 2001, with a production capacity

105   of 49,000 tons in 2013. This FIP also produces other fluoropolymers (FP) that involve

106   PFOA as a processing aid (Wang et al., 2014a; Wang et al., 2016). Whilst PFOA is

107   largely released via the production and use of Ammonium Perfluorooctanoate (APFO)

108   (Wang et al., 2014b), the C4-C7 PFCAs mainly come from impurities of PFCAs in

109   FP/fluoroelastomer (FE) products or degradation of FP precursors (Shi et al., 2015).

110　　This study provides a detailed and systematic investigation on the concentration and

111　distribution of PFAAs in indoor and outdoor dust samples from households around the

112　FIP. The objective was to determine the influence of PFAAs emitted from the FIP and

113　estimate the daily intake of dominant PFAAs present in dust. Such information is

114　necessary for effective management of PFAAs production from the FIP and for human

115　health risk assessment.

116　## 2.　Materials and methods

117　### 2.1 Sampling design and collection

118　The sampling sites are shown in Fig. 1a. With the FIP in Huantai as the center, samples

119　were taken with the radius of 2, 5, 10 and 20 km in four directions (East, E; South, S;

120　West, W; North, N). 16 pairs of indoor and corresponding outdoor dusts samples were

121　collected from randomly selected homes at each sampling site in October of 2014. An

122　outdoor dust sample was also collected from a road in the FIP at the same time. At each

123　site, dust samples were swept with a pre-cleaned brush from the inside and outside of

124　the house, respectively. Individual samples were wrapped in aluminum foil and further

125　sealed in polyethylene zip bags, and then they were transported to the laboratory and

126　stored at -20 ℃ until analysis. Before chemical analysis, large debris and particles

127　(visible hairs, fibers or grits etc.) were removed from the samples by using a methanol

128　rinsed pair of tweezers.

129　### 2.2 Standards and reagents

130　A total of 12 native PFAAs, including perfluorobutanoic acid (PFBA),

131　perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA),

132 perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA),

133 perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA),

134 perfluorododecanoic acid (PFDoA), perfluorobutane sulfonate (PFBS),

135 perfluorohexane sulfonate (PFHxS), PFOS and 9 mass-labeled PFAAs, including

136 $^{13}C_4PFBA$, $^{13}C_4PFHxA$, $^{13}C_4PFOA$, $^{13}C_4PFNA$, $^{13}C_4PFDA$, $^{13}C_4PFUnDA$, $^{13}C_2PFDoA$,

137 $^{18}O_2PFHxS$ and $^{13}C_4PFOS$ were purchased from Wellington Laboratories with purities

138 of >98% (Guelph, Ontario, Canada). Detailed information about standards and reagents

139 is given in the Supplementary Information.

140 **2.3 Sample extraction and instrumental analysis**

141 Samples were extracted according to published methods (Wang et al., 2015) with some

142 modifications. A sub-sample of 2 g dust was spiked with 5 ng mass-labeled internal

143 standards, digested with 2 mL 100 mM NaOH in acetonitrile and ultrasonicated for 30

144 min. A 20 mL volume of acetonitrile was added into the mixture and then the samples

145 were shaken at 250 rpm for 30 min. Subsequently, 0.1 mL 2 M HCl was added, followed

146 by centrifugation at 3000 rpm for 15 min. The process of extraction of acetonitrile was

147 repeated twice. The supernatants were combined together and concentrated under a

148 gentle flow of high-purity nitrogen to 1 mL.

149 Clean-up was performed with solid phase extraction (SPE) using ENVI-Carb

150 cartridges and Oasis-WAX cartridges. Supelco ENVI-Carb cartridges (250 mg, 3 mL,

151 Sigma-Aldrich, St. Louis, USA) were conditioned with 1 mL methanol for three times,

152 and then the extracts were loaded and collected. The cartridges were further washed

153 with 1 mL methanol for three times and collected together with the extracts. All the

154 extracts were diluted in 100 mL Milli-Q water and subjected to Oasis WAX-SPE

155 cleanup. The Oasis WAX cartridges (6 cc, 150 mg, 30 μm, Waters, Milford, MA) were

156 conditioned with 4 mL of 0.1% ammonium hydroxide in methanol, 4 mL methanol and

157 4 mL Milli-Q water successively. After loading the extracts, the cartridges were washed

158 with 4 mL 25 mM ammonium acetate (pH 4) and air-dried. The analytes were eluted

159 with 4 mL methanol, followed by 4 mL 0.1% ammonium hydroxide in methanol. The

160 eluate was then evaporated under gentle flow of high-purity nitrogen to 1 mL, filtered

161 through a 0.2 μm nylon filter, and transferred into a 1.5 mL PP snap top brown glass

162 vial with polyethylene (PE) septa for HPLC analysis.

163   All PFAAs were analyzed via an Agilent 1290 Infinity HPLC System coupled to an

164 Agilent 6460 Triple Quadrupole LC/MS System (Agilent Technologies, Palo Alto, CA).

165 The instrument conditions are listed in Table S1, S2.

166 **2.4 Quality control and quality assurance**

167 To avoid contamination, PTFE and other fluoropolymer materials were not used in

168 sample preparation. Field blanks and procedural blanks were prepared using anhydrous

169 sodium sulfate as an alternative of dust to monitor contamination during sample

170 collection and extraction. Solvent blanks using methanol were run for every 10 samples

171 to check background interferences of the instrument. Matrix spike recovery was

172 performed with 50 ng native PFAAs standards added into 2 g outdoor dust samples at

173 site E4, S4, W4 and N4, respectively.

174   A 10-point internal quantification curves ranging from 0.01 to 1000 ng/mL were

175 prepared for the quantification of individual PFAAs with coefficients of determination

176 (r^2) for all the target analytes higher than 0.99. Where samples had concentrations of

177 PFAAs higher than 1000 ng/mL, we reduced the amount and extracted again to make

178 sure the PFAAs concentrations in the extracts fell within the range of the calibration

179 series. Concentrations of all target PFAAs in any of field and procedural blanks were

180 less than the limit of detection (LOD), which was defined as 3 times of signal-to-noise

181 ratio (S/N). The limit of quantification (LOQ) was set as 10 times of S/N. Matrix spike

182 recoveries of PFAAs ranged from 73 to 118%. Detailed QA/QC measurements of

183 PFAAs in dust are shown in Table S3.

184 **2.5 Statistical analysis**

185 Data analysis was performed with SPSS Statistics V20.0 (SPSS Inc, USA) and Origin

186 Pro 9.0 (Northampton, USA). For the purposes of this analysis, where a detection was

187 less than the LOD they were given a value by dividing the LOD by the square root of

188 two, and those less than LOQ were set to half of the LOQ (Wang et al., 2014a). Spatial

189 distributions of PFAAs were analyzed using ArcGIS V10.0 (ESRI)

190 **3. Results and discussion**

191 **3.1 PFAAs in indoor dusts**

192 Concentrations of total PFAAs (ΣPFAAs) measured in indoor dust samples ranged from

193 73 to 13,500 ng/g, with a median of 979 ng/g (Table S4). The frequency of detection

194 for C4 to C10 PFCAs and PFBS, PFHxS and PFOS were 100%, and those of C11 and

195 C12 PFCAs were 82% and 94%, respectively.

196   The mean concentrations of ΣPFAAs at 2, 5, 10 and 20 km sampling circles were

197 6402, 1568, 812 and 243 ng/g, respectively. The concentrations of ΣPFAAs decreased

198 exponentially with the increase of distance from the source ($R^2 \geq 0.990$) (Fig. 2). The

199 mean ΣPFAAs levels in indoor dusts from the 2, 5 and 10 km circles were at least one

200 order of magnitude greater than the median levels in house dusts from more

201 contaminated areas such as UK (350 ng/g), Germany (517 ng/g) and the US (619 ng/g),

202 and they were also up to 2-3 orders of magnitude higher than those from slightly

203 polluted areas like Egypt (1.7 ng/g) and Belgium (1.2 ng/g) (Shoeib et al., 2016).

204   For all indoor dust samples, PFOA (56-8,873 ng/g) was found to be the dominant

205 PFAA, contributing 80.4% of ΣPFAAs, followed by short chain PFCAs, including

206 PFPeA (2.90-3,362 ng/g, 6.3%), PFBA (5.82-220 ng/g, 5.0%), PFHpA (1.34-662 ng/g,

207 3.9%), PFHxA (4.75-424 ng/g, 3.8%) (Fig. 1c). For the other long chain PFCAs and all

208 PFSAs (2.16-18.5 ng/g), the contribution to the total was less than 1%. The congener

209 pattern of PFAAs in dusts was consistent with that in surface water and sediment in this

210 area, in which PFOA and short chain PFCAs dominated as well (Wang et al., 2016).

211 Like the congener pattern in the present study, PFOA was found to be the predominant

212 PFCA in many other countries, such as Canada, Sweden, Spain or Australia (Eriksson

213 and Kärrman, 2015). The median concentration of PFOA (852 ng/g) in house dust here

214 was 1-2 orders of magnitude higher than that in house dusts from these countries (9-21

215 ng/g) (Eriksson and Kärrman, 2015) and was also 4 times higher than the mean PFOA

216 concentration (205 ng/g) in indoor dusts from ordinary houses without a nearby point

217 source in China (Zhang et al., 2010).
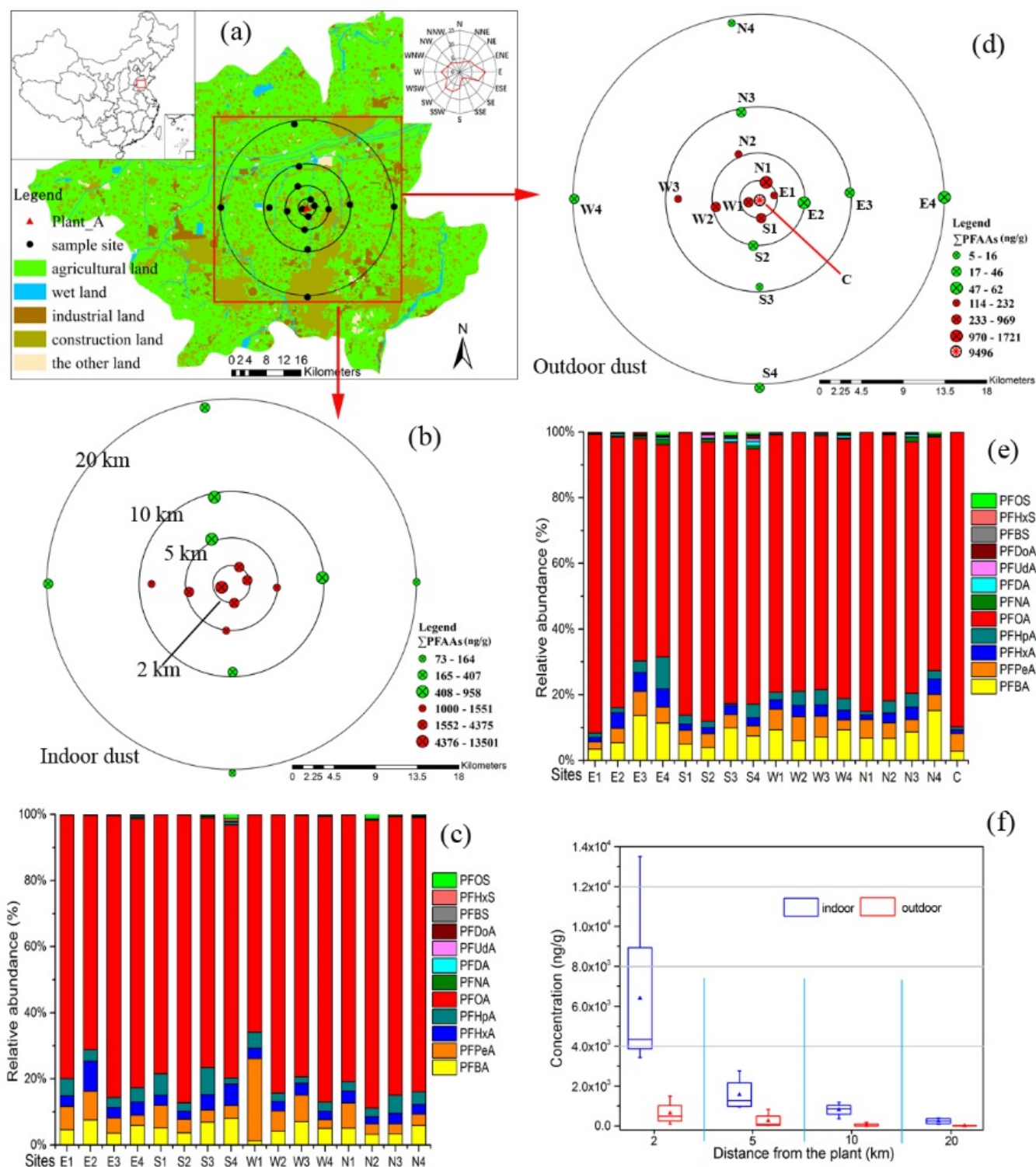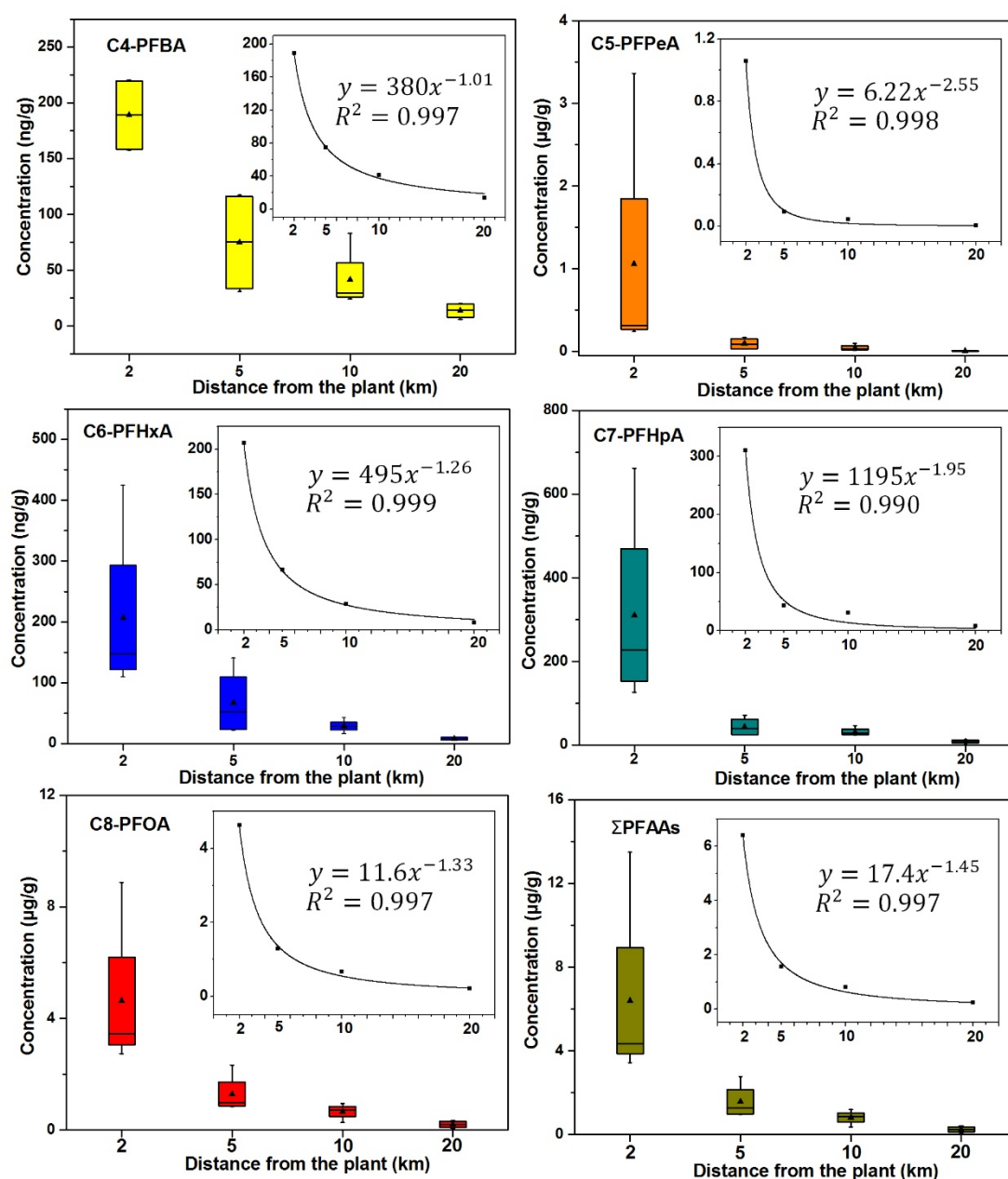
218   Fig. 1. (a) Map of the study area and sampling sites; (b) Spatial distribution of PFAAs

219   in indoor dusts; (c) Relative abundance of individual PFAA in indoor dusts; (d)Spatial

220   distribution of PFAAs in outdoor dusts; (e) Relative abundance of individual PFAA in

221   outdoor dusts; (f) Comparison of PFAAs concentration in indoor dust and outdoor dust.

222   The lower and upper ends of the box are the 25th and 75th percentiles of the data. The

223   horizontal solid line within the box is the median value and the symbol ▲ represents

224   the arithmetic mean value.

225   Fig. 2. Decline in C4-C8 PFCAs and ΣPFAAs concentrations in indoor dust samples

226   with the distance from the FIP. The decline curve was based on the arithmetic mean

227   concentration. The lower and upper ends of the box are the 25th and 75th percentiles of

228   the data. The horizontal solid line within the box is the median value and the symbol

229   ▲ represents the arithmetic mean value.

3.2 PFAAs in outdoor dusts

231   The concentrations of ΣPFAAs in outdoor dusts ranged from 5 to 9,495 ng/g (median:

232   62 ng/g) (Table S5). The highest ΣPFAAs concentration was found in the dust collected

233   from the road located in the FIP. Detection frequency of C4 to C9 and C12 PFCAs were

234   100% and that of C10 and C11 PFCAs were 94%, while the detection rate of PFBS and

235   PFOS was 88% and that of PFHxS was 41%. With the increase in distance from the FIP,

236   the concentrations of PFAAs in outdoor dusts decreased (Fig. 1d). Mean concentrations

237   of ΣPFAAs for 2, 5, 10 and 20 km from the FIP were 747, 319, 77.6 and 34.7 ng/g,

238   which were about 13-274 times lower than that in dusts from the FIP. The relative

239   contributions of individual PFAAs for indoor and outdoor dusts were similar (Fig. 1c,

240   1e). PFOA (4.29-8,511 ng/g) was the dominant PFAA and contributed 79.5% of

241   ΣPFAAs, followed by PFBA (0.53-255 ng/g, 7.7%), PFPeA (0.22-521 ng/g, 4.8%),

242   PFHxA (0.15-108 ng/g, 3.1%), PFHpA (0.03-82.2 ng/g, 3.1%) (Fig. 1e). Concentrations

243   of C9-C12 PFCAs and all PFSAs ranged from 0.17 to 16.6 ng/g.

244   Studies on PFAAs in outdoor dust are rare, although these dusts play an important

245   role in the global transportation of PFAAs (Yao et al., 2016). PFOA levels ranged from

246   1.2 to 11 ng/g in street dust including residential area and heavy traffic area in Japan

247   (Murakami et al., 2008), which were lower than PFOA concentrations (11-36 ng/g) in

248   outdoor dusts from 20 km away from the FIP. As for outdoor dust nationwide in China

249   (Yao et al., 2016), C4-C12 PFCAs as a whole accounted for 89% of the PFAAs, among

250   which PFOA was the predominant form as well. In their study, the highest PFOA

251 concentrations (65-100 ng/g) occurred in outdoor dusts from Shanghai, one of the most

252 urbanized cities in China (Yao et al., 2016), which were more than 2-6 times lower than

253 the mean concentrations of PFOA in dust samples from the 2 km (627 ng/g) and 5 km

254 (254 ng/g) circles, and higher than those from 10 km (59 ng/g) and 20 km (25 ng/g)

255 circles in our study.

256   For each site, the concentrations of PFAAs measured in indoor dust exceeded that

257 measured in outdoor dust (Fig. 1f). The same phenomenon has also been observed in

258 other organic contaminants, like Fipronil (Mahler et al., 2009), PBDEs (Yu et al., 2012),

259 or PCBs (Wang et al., 2013). Indoor dust particles have different properties from

260 outdoor such as in particle size, or organic content, potentially making them more

261 attractive sorbents fort PFAAs. Meanwhile, house dust is not subject to the same

262 environmental conditions as outdoor dust (e.g., wind and rain dispersal, runoff,

263 moisture, sunlight). Therefore, elimination or degradation of contaminants associated

264 with dust is assumed to be slower indoors than outdoors (Vorhees et al., 1999; Mahler

265 et al., 2009).

266 **3.3 Source identification of PFAAs in dust**

267 Associations among different PFAAs concentrations in dusts were explored using

268 Spearman Rank Correlations (Table S6, S7). PFCAs from C4 (PFBA) to C8 (PFOA)

269 were highly correlated ($p < 0.01$, correlation coefficients > 0.85) with each other.

270 Furthermore, a significant correlation ($p < 0.05$) was observed among the remaining

271 PFCAs, while associations within PFSAs as well as between PFCAs and PFSAs were

272 less significant. The associations among individual PFAAs indicated that these

273   congeners share similar origins or fate. A significant PFOA and PFOS correlation in

274   house dust which has been reported in many studies (Kato et al., 2009; Haug et al.,

275   2011a; Fraser et al., 2013) was not observed here. This might be due to different dust

276   PFAAs origins.

277   Correlation analysis of PFAA congeners between the central FIP (C) and the other

278   dust sampling sites (Table S8, S9) showed that they were similar in the signature

279   profiles ($p < 0.01$, correlation coefficients > 0.76). Based on our previous examination

280   of the area (Wang et al., 2014a), the FIP was the only point source in the study area,

281   which generated the PFAAs contaminants in dust samples. The FIP is a self-sufficient

282   manufacturer, so the PFCAs could be generated and released through their direct

283   production, the production of fluoropolymers or the production of many intermediates

284   (Wang et al., 2016). Global source inventories have also demonstrated that emissions

285   of PFCAs can be largely attributed to these processes (Wang et al., 2014b).

286   Spatially, PFAAs concentrations of dust samples in the west were higher than that in

287   other three directions, which were comparable to each other (Fig. 1b, 1d). Wind rose

288   plot for local area shows that the E (east) wind and the ESE (east-south-east) wind are

289   the primary wind directions in the study area (Fig. 1a, S1). Hence, the downwind

290   location may be the main reason for higher concentrations of PFAAs at the sites in the

291   west. So air transport and deposition was the most likely pathway for PFAAs from the

292   FIP to the households in the surrounding areas, which is similar to the APFO

293   transportation in environmental media near a fluorochemical manufacturing facility

294   (Davis et al., 2007).

295   Correlations of PFAAs in indoor and outdoor dusts at each sample site were also

296   investigated (Table S10). The total PFAAs in the indoor dust samples correlated well

297   with that in the corresponding outdoor dust samples ($p <0.01$, correlation coefficients

298   > 0.74), which implies similar sources. It is possible that outdoor dust is walked into

299   the houses by the residents (Mahler et al., 2012). Indoor air and outdoor to indoor air

300   transport may contribute to the organic contaminants in indoor dust as well (Mercier et

301   al., 2011). The clothing and skin of workers who live close to the FIP is possibly another

302   source of PFAAs in dusts (Fu et al., 2015). These sources of PFAAs in dusts around the

303   FIP (Fig. 3) are different from those in ordinary homes where the source is use, wear

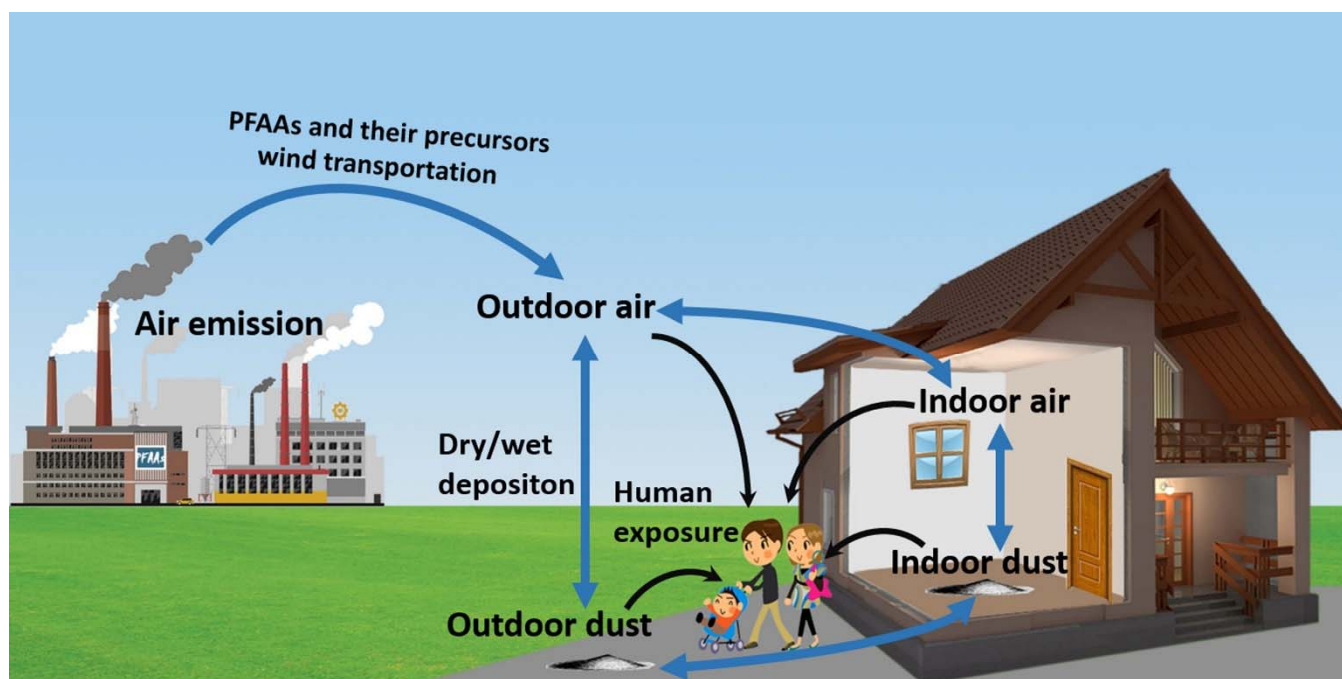304   and abrasion of consumer products inside the home (Moriwaki et al., 2003; Shoeib et

305   al., 2005).

306   Fig. 3. Schematic diagram of sources of PFAAs in dust around the FIP.

307   **3.4 Human exposure to PFAAs via dust ingestion and dermal absorption**

308   Humans can be exposed to PFAAs in dust via ingestion and dermal absorption. The

309   estimated daily intake (EDI, ng/kg.bw/day) of PFAAs through dust ingestion and

310   dermal absorption can be calculated by averaging the intake dose over body weight,

311   with equations and exposure/ingestion factors recommended by the Environmental

312   Protection Agency of the United States (USEPA, 2011) and Zhang et al (2010, 2015).

313   Considering that body weights and consumption rates vary by age, we estimated the

314   EDI of PFAAs for five age groups: infants (0-1 yrs), toddlers (2-5 yrs), children (6-10

315   yrs), teenagers (11-17 yrs), and adults (≥18 yrs). The details of the calculation and data

316   sources are shown in Table S11 and Table S12. As for the EDI calculation of each

317   sampling circle, arithmetic mean concentrations of PFAAs were used.

318   The EDIs of several main PFAAs in the study area via dust ingestion and dermal

319   absorption varied, depending on the age group and the distance of the residents from

320   the FIP (Table S13). The EDI of PFAAs through dust ingestion was approximately 4-

321   14 times higher than that through dermal absorption. The total exposure of PFBA,

322   PFPeA, PFHxA, PFHpA, PFOA, and ΣPFAAs via dust were 0.184, 0.997, 0.196, 0.293,

323   4.42 and 6.09 ng/kg.bw/day for adults who reside about 2 km away from the FIP, and

324   corresponding exposures were 1.10, 5.81, 1.14, 1.70, 26.0 and 35.9 ng/kg.bw/day for

325   toddlers, respectively (Table 1). As expected, the EDI for toddlers was higher than those

326   for other age groups in each sample circle (Fig. 4) due to more frequent hand-to-mouth

327   contact, indicating that the dust imposes more potential health risk on this age group.

328   Tolerable daily intake (TDI) values are only available for PFOS and PFOA. Compared

329   to current recommended TDI values of 100 to 1,500 ng/kg.bw/day for PFOA proposed

330   by several countries (Fig.4, Table S14), the EDI of PFOA via dust for residents in the

331 study area are less than these limits. However, it is important to note that there is an

332 ongoing discussion about the relevance of these TDIs. Some argue that these values are

333 insufficiently protective and may be several hundred fold too high (Grandjean and

334 Budtz-Jørgensen, 2013; Grandjean and Clapp, 2015). PTFE production has been

335 expanded in the FIP with an average annual growth rate of 25% since 2001, and without

336 suitable substitutes for PFOA in the production of most fluoropolymers (Wang et al.,

337 2016), high exposure is likely to continue for the local residents.

338 The EDIs of PFAAs via dust ingestion have been reported in the previous studies.

339 Zhang et al (2010) estimated PFOA intake via indoor dust collected from four cities in

340 China to be 0.87 ng/kg.bw/day for toddlers, about 3 times higher than that for children

341 and teenagers and adults, and a little lower than the EDI of PFOA for toddlers living

342 about 20 km away from the FIP. The EDI of PFOA was 0.43 ng/kg.bw/day for adults

343 and 5.3 ng/kg.bw/day for children in Birmingham, UK (Goosey and Harrad, 2011) and

344 was 0.20 ng/kg.bw/day for adult women in Norway (Haug et al., 2011b). The estimated

345 intake of PFAAs (PFOA) via dust ingestion by 2 years' children was between 2.5 (0.06)

346 and 7.0 (0.11) ng/kg.bw/day in Australia, Canada, the Faroe Islands and Japan, 0.3-0.8

347 (0.04-0.06) ng/kg.bw/day in Greece, Spain, and Sweden, and 0.02 (0) ng/kg.bw/day in

348 Nepal (Eriksson and Kärrman, 2015). Overall, the estimated intakes of PFOA/PFAAs

349 by residents about 2 km and 5 km from the FIP in our study were highest compared

350 with the values previously reported.

351 Table 1 Estimated Daily Intake (EDI) of PFAAs via dust (ng/kg.bw/day) for various

352 age groups

Distance (km)	objectives	PFBA	PFPeA	PFHxA	PFHpA	PFOA	∑PFAAs

2	Infants	0.53	2.86	0.56	0.84	12.6	17.4
	Toddlers	1.10	5.81	1.14	1.70	26.0	35.9
	Children	0.45	2.35	0.46	0.69	10.5	14.5
	Teenagers	0.23	1.24	0.25	0.37	5.52	7.62
	Adults	0.18	1.00	0.20	0.29	4.42	6.09
5	Infants	0.21	0.26	0.18	0.12	3.54	4.33
	Toddlers	0.44	0.54	0.38	0.25	7.34	8.99
	Children	0.18	0.22	0.15	0.10	2.97	3.64
	Teenagers	0.09	0.11	0.08	0.05	1.54	1.89
	Adults	0.07	0.09	0.06	0.04	1.23	1.51
10	Infants	0.11	0.12	0.08	0.09	1.80	2.21
	Toddlers	0.24	0.25	0.16	0.17	3.69	4.53
	Children	0.10	0.10	0.06	0.07	1.49	1.83
	Teenagers	0.05	0.05	0.03	0.04	0.79	0.97
	Adults	0.04	0.04	0.03	0.03	0.63	0.77
20	Infants	0.04	0.02	0.02	0.02	0.56	0.67
	Toddlers	0.08	0.04	0.05	0.05	1.14	1.37
	Children	0.03	0.02	0.02	0.02	0.46	0.56
	Teenagers	0.02	0.01	0.01	0.01	0.24	0.29
	Adults	0.01	0.01	0.01	0.01	0.19	0.23

353 Note: Infants (0-1 yrs); Toddlers (2-5 yrs); Children (6-10 yrs); Teenagers (11-17 yrs); Adults
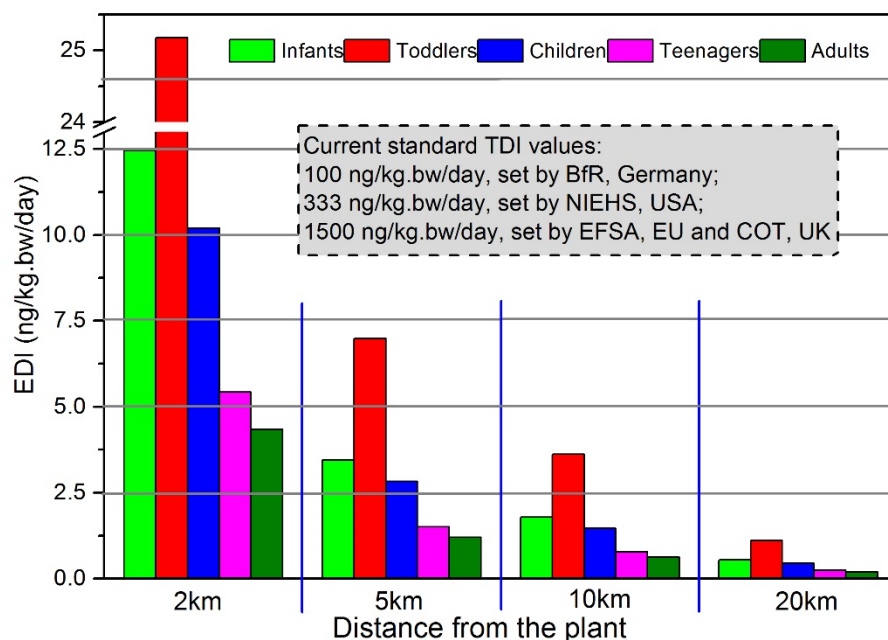354 (≥18 yrs)

355 Fig. 4. Estimated daily intake (EDI, ng/kg.bw/day) of PFOA via indoor dust for
356 residents around the FIP. Current standard Total Daily Intake (TDI, ng/kg.bw/day)
357 values are reported in Thayer and Houlihan, 2002; BfR, 2006; Benford et al., 2008;
358 COT, 2009

4 Conclusion

PFAAs in indoor and outdoor dusts were investigated around a mega fluorochemical industrial park (FIP). PFAAs generated from the FIP have diffused into the surrounding households and resulted in a zone of PFAAs contamination, at least 20 km in radius. The signature of the PFAAs in indoor and outdoor dust within this zone matches that within the FIP facility. The plume shape is consistent with air transport from the prevailing easterly winds from the FIP. PFOA and C4-C7 PFCAs were the predominant PFAAs in all dust samples with average contributions over 79% and 19%, respectively. The levels of PFAAs were significantly higher in indoor dusts than in outdoor dust. The entry of PFAAs contaminated dusts into resident's houses is most likely associated with entry via the window together with dusts being walked in.

The estimated daily ingestion dose of PFAAs for this area in China via contaminated dusts was higher than any previously recorded around the world, and the dusts impose more potential health risk on toddlers than any other age groups. Until new replacement products emerge, this high local exposure of residents to PFAAs via dust is likely to continue. In order to mitigate human exposure to fugitive gases and dusts heavily contaminated with PFOA and other PFAAs released from the FIP, scrubbers are suggested to be applied in smokestacks to capture smoke and toxic gases as well as fine particulates, and health risk awareness for the people (especially children) living in close proximity to the FIP should be enhanced to prevent them from exposures. This study identified primarily the sources of dust PFAAs and the possible transport pathways of PFAAs from the FIP to surrounding areas. Further investigation is needed

381   for health risk assessment and management.

382

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