Final Draft
of the original manuscript:

Wang, Z.; Xie, Z.; Moeller, A.; Mi, W.; Wolschke, H.; Ebinghaus, R.:

Atmospheric concentrations and gas/particle partitioning of neutral poly- and perfluoroalkyl substances in northern German coast

Atmospheric concentrations and gas/particle partitioning of neutral poly- and perfluoroalkyl substances in northern German coast

Zhen Wang[a,b], Zhiyong Xie[a]*, Axel Möller[a], Wenying Mi[a], Hendrik Wolschke[a], Ralf Ebinghaus[a]

[a]Helmholtz-Zentrum Geesthacht, Institute for Coastal Research, 21502 Geesthacht, Germany

[b]National Marine Environmental Monitoring Center, Dalian 116023, China

Abstract

Total 58 high volume air samples were collected in Büsum, Germany, from August 2011 to October 2012 to investigate air concentrations of 12 per- and polyfluoroalkyl substances (PFASs) and their gas/particle partitioning. The ΣPFASs concentration (gas + particle phases) ranged from 8.6 to 155 pg/m^3 (mean: 41 pg/m^3) while fluorotelomer alcohols 8:2 (FTOH 8:2) dominated all samples accounting for 61.9% of ΣPFASs and the next most species were FTOH 10:2 (12.7%). Air mass back trajectory analysis showed that atmospheric PFASs in most samples were from long range atmospheric transport (LRAT) processes and had higher ratios of FTOH 8:2 to 6:2 compared to the data obtained from urban/industrial sources. Small portion of particle PFASs in the atmosphere was observed and the average percent to ΣPFASs was 2.0%. The particle-associated fractions of different PFASs decreased from perfluorooctane sulfonamidoethanols (FOSEs) (15.5%) to fluorotelomer acrylates (FTAs) (7.6%) to perfluorooctane sulfonamides (FOSAs) (3.1%) and FTOH (1.8%), indicating the

*Corresponding author. Tel./fax: +49-4152872330, E-mail address: zhiyong.xie@hzg.de (Z. Xie).

functional group obviously influenced their gas/particle partitioning. For neutral compounds with acid dissociation constant (pK_a) > 7.0 (i.e., FTOH, FOSE and FOSA), a significant log-linear relationship was observed between their gas/particle partition coefficients (K_{SP}) and vapor pressures ($p_L^°$), suggesting the gas/particle partitioning of neutral PFASs agreed with the classical $\log K_{SP}$ - $\log p_L^°$ relation. Due to the pK_a values of FTA 6:2 and 8:2 below the typical environmental pH conditions, they mainly exist as ionic form in aerosols, and the corrected $\log K_{SP}$ (neutral form) were considerably lower than those of FTOH, FOSE and FOSA with similar vapor pressures. Considering the strong partitioning potential to aqueous phases for ionic PFASs at higher pH values, a need exists to develop a model taking account of the ad/absorption mechanism to the condensed phase of aerosols for ionizable PFASs (e.g., FTAs).

Keywords: polyfluoroalkyl substances (PFASs); gas/particle partitioning; long range atmospheric transport (LRAT)

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) have been widely produced and used worldwide in high volume for several decades in a variety of consumer and industrial products (Paul et al., 2009). They have attracted scientific and regulatory scrutiny due to their potential for environmental persistence, bioaccumulation and possible adverse effects on humans and wildlife (Gewurtz et al., 2012). PFASs comprise a wide range of chemicals with different fluorocarbon chains ($CF_3[CF_2]_n$-). Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are the most well-known PFASs because of their presence in global environments and adverse effects.

49   Ellis et al. (2004) pointed out one of important sources of PFOS and PFOA in the

50   environment is the degradation of neutral precursors, such as fluorotelomer alcohols

51   (FTOHs), fluorotelomer acrylates (FTAs), perfluorooctane sulfonamides (FOSAs) and

52   perfluorooctane sulfonamidoethanols (FOSEs). These precursors are more volatile

53   than PFOA and PFOS and are believed to be more importantly by diffuse sources

54   during their manufacture, use and disposal (Paul et al., 2009). Therefore, they are

55   more likely to release into the atmosphere and undergo long range atmospheric

56   transport (LRAT). During the LRAT, they are degraded to PFOA and PFOS by ·OH

57   radicals initiated oxidation (Ellis et al., 2004; Martin et al., 2006). These precursors

58   have been detected in many field studies in the atmosphere of the North America,

59   Europe, Asia, and the Polar areas (Butt et al., 2010; Ahrens, 2011; Li et al., 2011;

60   Ahrens et al., 2012; Vento et al., 2012).

61   Previous studies showed that the reaction rates with hydroxyl radicals are quite low

62   for these neutral PFASs and their atmospheric residence time of FTOHs can be more

63   than 50 d (Piekarz et al., 2007). These provide the possibility of regional and global

64   atmospheric transport of PFASs. Some typical precursors, such as FTOFs, have been

65   detected in ice caps from the high Arctic, where they are solely from atmospheric

66   sources (Young et al., 2007). This finding supports the oxidation of volatile precursors

67   in the atmosphere as a major source of PFOA and PFOS. Thus, the atmospheric

68   partitioning of these precursors between the gas and particle phases plays a key role

69   on their abilities to undergo LRAT and global distribution.

70   Arp and co-workers (Arp et al., 2008a,b; Arp and Goss, 2009a,b) discussed the

71   gas/particle partitioning behavior of apolar, polar and ionizable organic compounds

72   including perfluorocarboxylic acids and developed a model taking into account the

73   ambient relative humidity (RH) and acid dissociation constant (pK_a). A key factor of

74 gas/particle partitioning for PFASs is that they are ionizable, which may cause the

75 dissociation into ionic forms under typical environmental pH condition and the

76 enhanced partitioning to the particle, especially on the wet particles (aqueous

77 aerosols). Thus, the dissociation and partitioning extent of PFASs to the atmospheric

78 particles rely on the pK_a and the pH condition. Arp and Goss (2009b) pointed out that

79 the gas/particle partition coefficient (K_{SP}) can be estimated by their molecular

80 structure descriptors. Pankow (2003) proposed a unified modeling framework for

81 gas/particle partitioning of neutral and ionizing compounds to single and multi-phase

82 aerosol particles, which involved the vapor pressure of compound as a pure liquid

83 (sub-cooled if necessary) at the temperature of interest (p°_L). The K_{SP} and p°_L do agree

84 with the classical Junge-Pankow model for nonpolar, nonionizable semi-volatile

85 organic compounds (SVOCs) (Wang et al., 2013). For PFASs, previous studies

86 indicated that the variation of the particle phase percentages for different species was

87 likely owing to the changes of vapor pressure with different chain length for the

88 neutral forms (Vierke et al., 2011; Ahrens et al., 2011; Ahrens et al., 2012). However,

89 few data are available for atmospheric PFASs, in particular for data on their

90 gas/particle partitioning. Therefore, robust data sets of polar/ionizable compounds

91 (e.g., PFASs) were needed to verify and improve the existing gas/particle partitioning

92 models, which will promote the understanding of the LRAT, deposition, and overall

93 fates of PFASs in the atmospheric environment.

94   In the present study, the gas and particle phase samples were collected

95 simultaneously for one year at the weather station in Büsum, a seaside village in

96 northern Germany. The concentrations of four PFAS classes (i.e., FTOHs, FTAs,

97 FOSAs and FOSEs) were determined separately for gas and particle phase . Their

98 gas/particle partitioning behavior and the relation to their p°_L were investigated and

99   discussed. This will contribute new information to help address the partitioning of

100   PFASs to particle and yield new insights into their environmental fates.

101   **2. Materials and methods**

102   **2.1 Air sampling**

103   Sampling campaign was conducted from August 3, 2011 to October 2, 2012 at the

104   seaside village Büsum (54.13ºN, 8.88ºE), Germany (see Fig. S1), and a total of 58

105   samples were collected. Air sample (about 2800 m^3 over 7 day periods) was collected

106   using a high-volume air sampler. A glass fiber filter (GFF, pore size: 0.7 μm) and a

107   self-packed polyurethane foam (PUF)/XAD-2 cartridge (PUF: φ5.0 cm $\times$ 2.5 cm; 35 g

108   XAD-2, particle size: 0.3-1.0 mm) were simultaneously employed to collect partical

109   and gas phase separate. Field blanks of GFFs and PUF/XAD-2 cartridge were

110   collected by exposure them for 1 min at the sampling site and treated in the same way

111   as real samples. Both PUF/XAD-2 cartridge and filters were stored until analysis at

112   -20ºC. Detailed information on the sampling dates, air volume, total suspended

113   particulate (TSP) and the average temperature for each sample are listed in Table S1.

114   **2.2 Sample preparation and analysis**

115   Prior to extraction, PUF/XAD-2 cartridge and GFFs were spiked with 2.5 ng of

116   mass-labeled surrogate standards (FTOH (M+5) 6:2, 8:2 and 10:2, MeFOSA D3,

117   EtFOSA D5, MeFOSE D7 and EtFOSE D9). PUF/XAD-2 was extracted with a

118   modified Soxhlet apparatus (MX extractor) for 16 h using dichloromethane (DCM).

119   Particle samples (GFF) were extracted using a MX extractor using DCM for 16 h.

120   Extracts were concentrated to approximately 2 mL using hexane as keeper and passed

121   over 3 g Na_2SO_4 to remove residual water. Samples were further evaporated to 200 μL

122   and spiked with 10 μL of 100 pg/μL FTOH 9:1 as recovery standard.

123   The instrumental analysis was described in detail elsewhere (Dreyer et al., 2008).

124 Briefly, analysis was performed using an Agilent 6890 gas chromatograph coupled

125 with an Agilent 5973 mass spectrometer in selective ion monitoring (SIM) mode with

126 positive chemical ionization mode with methane as reagent gas (PCI). Analytes were

127 separated on 60 m SUPELCO WAX$^®$ 10 column (60 m × 0.25 mm × 1.0 μm). Helium

128 was used as carrier gas at a flow rate of 1.3 mL/min and the injection volume was 2.0

129 μL in the pulse splitless mode. The temperature program was as follows: initial

130 temperature 50ºC hold for 2 min, increased to 70ºC at a rate of 3ºC/min, then

131 increased at a rate of 10ºC/min to 130ºC, 20ºC/min to 220ºC and 120ºC/min to 275ºC,

132 then held for 5 min. Finally, the temperature changed to 270ºC at the rate of 10ºC/min

133 and held for 10 min. The full names, abbreviations and their other detailed

134 information of the 12 compounds determined in this study are summarized in Table 1.

135 The response factors were calculated from the calibration curves based on the ratio

136 between the target compound and the corresponding surrogate.

137 **2.3 Quality assurance and control**

138 All PUF and XAD-2 were pre-cleaned with solvents and GFFs were baked at

139 450 °C for 12 h prior to their usage. The cartridges were protected against

140 UV-sunlight during sampling using aluminum foil in order to avoid the degradation of

141 the target compounds. Details of the breakthrough tests were given elsewhere (Xie et

142 al., 2013). Method detection limits (MDLs) were derived from mean blank values plus

143 three times the standard deviation (Table 1).

144 **3. Results and discussion**

145 **3.1 PFASs concentrations in gas and particle phases**

146 The summarized data of PFASs concentrations in both gas- and particle-phases are

147 listed in Table 1. Overall, all of the 12 compounds were detected in both phases,

148 however, the concentrations and composition of different species varied between gas-

149 and particle-phases. The total concentration (vapor plus particle phases) of the 12

150 PFASs (ΣPFASs) in the atmosphere ranged from 8.6 to 155 pg/m^3, and the average

151 value was 41 pg/m^3 with a standard deviation of 26 pg/m^3. The gas- and particle-phase

152 concentrations of PFASs for individual samples are presented in Fig. 1. For all 58

153 samples, the predominance of gaseous PFASs in the atmosphere was observed and a

154 small portion was presented in the particle phase (Fig. 1). The average percent of the

155 particle phase compounds to ΣPFASs was 2.0%, and the particle proportions of

156 different PFASs were: FTOHs (1.8%), FTAs (7.6%), FOSAs (3.1%) and FOSEs

157 (15.5%) (Table 1). Obviously, the proportions of particle associated FOSEs were

158 higher than those of FTOHs and FOSAs.

159

160   Fig. 1 Concentrations (pg/m^3) of gas- and particle-phase PFASs in air samples collected from

161   Büsum during August 3, 2011 to October 2, 2012

162

163   Table 1 Full names, acronyms, Chemical Abstract System (CAS) numbers of the 12 PFASs, the

164   minimum, maximum, average concentrations of gas, particle phases PFASs in air (pg/m^3), the

165   percent of each compounds and particle phase compounds to ΣPFASs

166

167   The total concentrations of FTOHs (sum of FTOH 6:2, 8:2, 10:2 and 12:2) (ΣFTOH)

168 varied from 7.3 to 146 pg/m^3 with a mean value of 37 pg/m^3, which was comparable

169 to the levels of the Atlantic and Southern Oceans (0.3-47 pg/m^3) (Dreyer et al., 2009b),

170 and slightly lower than the concentrations detected in the semi-urban location in

171 Toronto (79.5 pg/m^3) (Ahrens et al., 2012), in Hamburg (from 32 to 204 pg/m^3)

172 (Dreyer et al., 2009a), and in the North Sea (84 pg/m^3) (Xie et al., 2013) (Table 2).

173 FTOH 8:2 was the most abundant compound among the 12 PFASs in the atmosphere

174 (5.0-85 pg/m^3), representing 61.9% of ΣPFASs, and the next most species were FTOH

175   10:2 (0.9-17 pg/m^3) and FTOH 6:2 (0.8-40 pg/m^3), which accounted for 12.7% and

176   10.6% of ΣPFASs, respectively. The average ratios of FTOH 8:2 to 10:2 to 6:2 to 12:2

177   obtained in this study were 5.8:1.2:1.0:0.4. Similar ratios were observed in some

178   "background" sites, such as in the Mount Bachelor Observatory (Piekarz et al. 2007),

179   the Canadian Arctic (Ahrens et al. 2011) and the North Sea (Xie et al., 2013), while in

180   some urban/suburban areas lower proportions of FTOH 8:2 were observed, for

181   example, 1.1:0.2:1.0 for FTOH 8:2 to 10:2 to 6:2 was observed in semi-urban location

182   in Toronto, Canada (Ahrens et al., 2012), and 1.8:0.6:1.0 in the southeast of Hamburg,

183   Germany (Dreyer et al., 2009c). The variation of the ratios between background sites

184   and urban/suburban areas can be explained with the relative rates of removal of

185   different FTOHs from the atmosphere. Piekarz et al. (2007) estimated the atmospheric

186   residence times for FTOH 8:2 (80 d), FTOH 10:2 (70 d) and FTOH 6:2 (50 d), and

187   suggested that the higher ratios may be an indicator of atmospheric transport. Thus,

188   the observed enhancement of FTOH 8:2 and 10:2 (relative to FTOH 6:2) in this study

189   implied that atmospheric PFASs in Büsum were mainly from LRAT processes.

190

191   Table 2 Comparison of FTOHs and FOSA(E)s concentrations (pg/m^3) in air samples collected

192   from different sites

193

194   The concentrations of two fluorotelomer acrylates, FTA 6:2 and FTA 8:2, were

195   generally lower than those of other compounds. The levels of FTA 6:2 and 8:2 ranged

196   from < 0.2-1.3 pg/m^3 and 0.2-2.5 pg/m^3, respectively (Table 1). The results were

197   compared to those reported in the North Sea, however, they were considerably lower

198   than the levels at urban site of Hamburg, Germany (Dreyer et al., 2009c) and the

199   semi-urban location in Toronto, Canada (Ahrens et al., 2012). Although FTAs are the

200   second most abundant precursor class after the FTOHs (Ahrens et al., 2012), the

201   relatively short atmospheric lifetimes (about several days) make them subject to

202   degradation during their LRAT (Butt et al., 2009). Thus, lower levels were observed

203   in Büsum compared with some source regions.

204   ΣFOSAs and ΣFOSEs ranged from 0.5 to 13 pg/m^3 (mean: 3.3 pg/m^3) and 0.7 to

205   4.1 pg/m^3 (mean: 1.7 pg/m^3), respectively. Their concentrations were higher than the

206   levels observed in Toronto (mean: 0.75 and 1.47 pg/m^3) (Ahrens et al., 2012) and

207   slightly lower than those in the North Sea, the Canadian Arctic, the Atlantic and

208   Southern Ocean atmosphere, however, their values were in the range of several to ten

209   of pg/m^3 (Dreyer et al., 2009b; Ahrens et al., 2011; Xie et al., 2013) (Table 2). The

210   average concentration patterns of the three FOSAs were: MeFBSA (2.3 pg/m^3) >

211   MeFOSA (0.6 pg/m^3) > EtFOSA (0.4 pg/m^3), and FOSEs possessed a similar profile

212   (Table 1), which were agreement with the results reported by Dreyer et al. (2009c).

213   High levels of FOSAs and FOSEs compared to FTOHs reported in other studies

214   (Barber et al., 2007; Piekarz et al., 2007; Shoeib et al., 2010) were not observed in the

215   present study. For example, in the atmosphere of Bermuda and Sable Island, MeFOSE

216   exceeded the levels of FTOHs (Shoeib et al., 2010). The variation of PFAS

217   composition profiles among different sites is likely be explained by the phase-out of

218   PFOS-based chemistry in the atmosphere, and/or a shift to shorter chain PFASs and

219   new fluorinated chemicals during manufacture (Paul et al., 2009; Ahrens et al., 2012).

220   Wang et al. (2009) reported that the C$_4$-based fluorinated chemicals were the main

221   replacement compounds of the C$_8$-based products (i.e., PFOA and PFOS), which

222   would change the levels and composition patterns of different PFASs in various

223   environmental media. Moreover, the concentrations of MeFBSA, MeFOSA and

224   EtFOSA represented about 2 times higher than MeFBSE, MeFOSE and EtFOSE. The

225   results confirmed the findings of D'eon et al. (2006), who reported the stable

226 intermediate MeFBSA can be produced during the reaction of MeFOSE with ·OH

227 radicals, and the atmospheric lifetime of MeFBSA (> 20 days) is much longer than

228 that of the parent compound, MeFBSE. Accordingly, MeFOSA and EtFOSA are

229 expected be more stable than MeFOSE and EtFOSE (D'eon et al., 2006).

230 **3.2 Air mass back trajectory analysis**

231 For further insight into the relation of sources to the concentrations of atmospheric

232 PFASs, air mass back trajectories were performed by going back 6 days at 50 m and

233 100 m above sea level (asl) for Büsum using NOAA's HYSPLIT model

234 (http://www.arl.noaa.gov/HYSPLIT_info.php). Air mass back trajectory analysis

235 results showed that samples with higher air concentrations of PFASs mainly

236 originated from land-based sources, whereas most samples with relatively constant

237 PFAS concentrations were consistent with the back trajectories for the site that air

238 mass from the ocean during the sampling period (see Fig. S2). This can further

239 confirm that atmospheric PFASs in most samples were from LRAT processes and had

240 higher ratios of FTOH 8:2 to 6:2 compared to the data obtained from urban/industrial

241 sources.

242 Furthermore, ΣPFASs and ΣFTOHs did not exhibit statistical correlation with the

243 sampling temperature, also suggesting that temperature related volatilization of

244 PFASs near the sampling site displayed negligible influence on PFAS levels and the

245 LRAT process governed the atmospheric concentrations of PFASs. The fluctuation of

246 concentrations in dependence of air mass origin indicated that it was a key factor

247 governing atmospheric PFAS concentrations at the sampling site. Varying

248 concentrations of other organic micropollutants relying on air mass origin were

249 reported around Büsum, for example, atmospheric levels of organophosphorus flame

250 retardants were much higher in air from continental Europe and the UK than in air

251 from northern and northwestern directions (Möller et al., 2011).

3.3 Gas/particle partitioning of neutral PFASs

253 Particle-phase percentages of individual compounds to ΣPFASs are summarized in

254 Table 1. Of the target PFASs, FTOH demonstrated the smallest particle percentages

255 that were typically less than 8% and FTOH 8:2 possessed the lowest particle bound

256 fraction (1.1%), while FOSE had the highest particle associated fractions with average

257 15.5% and the percentage of EtFOSE (30.6%) was the highest among the 12 target

258 compounds. This profile is believed to be due to the decrease in vapor pressure with

259 increasing chain length for the neutral forms of PFASs (Vierke et al., 2011).

260 Compared with the vapor pressures of classical POPs, such as polycyclic aromatic

261 hydrocarbons, PFASs are expected to be almost entirely in the gas-phase given their

262 higher vapor pressures (Goss and Bronner, 2006; Lei et al., 2004). However, many

263 previous studies have reported the presence of PFASs on particles (Dreyer and

264 Ebinghaus, 2009; Dreyer et al., 2009a, b; Shoeib et al., 2010). It is an important issue

265 that needs further investigation.

266 The particle-associated fractions of different PFASs in Büsum decreased from

267 FOSE (15.5%) to FTA (7.6%) to FOSA (3.1%) and FTOH (1.8%), indicating that the

268 functional group obviously influenced the gas/particle partitioning of PFASs. Similar

269 profiles were also observed in the atmosphere of Germany (Jahnke et al., 2007) and

270 Canada (Ahrens et al., 2011). Furthermore, the particle-associated fraction of PFASs

271 increased slightly with increasing chain length (and substituent changed from methyl

272 to ethyl).

273 Ionizable compounds, such as FTA 6:2 and 8:2, can exist in the neutral form in the

274 gas phase, while they may dissociate to the ionic form in aqueous film of aerosols.

275 The degree of dissociation relies on their acid dissociation constant (pK_a) and the pH

11

276 value of the condensing media (Ahrens et al., 2012). pH values of aerosol are well in

277 general known to be weakly to strongly acidic, for example, diurnal variations in

278 aerosol pH from 0 to 4.5 for Pittsburgh aerosols (Zhang et al., 2007), and about 4.5 for

279 aerosols in Toronto (Ahrens et al., 2012). To investigate the dissociation degree of

280 different PFASs under the normal circumstances, the values of pK_a for individual

281 compounds were calculated using software SPARC (October 2011 release

282 w4.6.1691-s4.6.1687) in this study (Table 3). pK_a values of FTOH, FOSE and FOSA

283 were higher than 7.0, indicating they were neutral at an environmentally relevant pH

284 range ($\leq$ 7), whereas the values of FTA 6:2 and 8:2 were below the pH range, thus

285 they would mainly exist as anions in aerosols.

286

287   Table 3 Values of pK_a, logK_{SP}, logK_{SP} and logp_L°. Values of pK_a and logp_L° were calculated using

288   software SPARC (October 2011 release w4.6.1691-s4.6.1687) at the average temperature during

289   sampling (10.4ºC)

290

291   Based on Arp et al. (2008), the particle-phase concentrations of neutral compounds

292 (C_P, pg/m^3) can be calculated using the following equation:

293                    $$C_P = C'_P /(1 + 10^{\text{pH - p}Ka})$$ (1)

294 where C'_P is the measured concentration of compounds (neutral plus ionic) in the

295 particle-phase (pg/m^3). The gas/particle partition coefficient, K_{SP}, for the neutral form

296 can be derived as:

297                    $$K_{SP} = (C_P/\text{TSP})/C_A$$ (2)

298 where TSP is the total suspended particulate (μg/m^3), and C_A is the concentration of

299 target compound in the gas-phase (pg/m^3).

300   The corrected values of logK_{SP} by pK_a are listed in Table 3. It is noted that the

301 correction was not required for FTOHs, FOSEs and FOSAs because their pK_a were

302 higher than the environmentally relevant pH values as stated above. Thus, the

303 measured $\log K'_{SP}$ and the corrected $\log K_{SP}$ were not different for FTOHs, FOSEs and

304 FOSAs, however, the corrected K_{SP} (neutral form) were 9.8 log units lower than the

305 measured K'_{SP} (neutral plus ionic) (under the condition of the aerosol pH value = 4.5)

306 for FTA 6:2 and FTA 8:2 (Table 3). Based on Eq (1), the partitioning extent of

307 ionizable PFASs to particle in the atmosphere is up to their pK_a and the effective pH

308 properties of aerosol (aqueous phase), and as a result, the partitioning to particle will

309 be enhanced at higher pH environment (presenting more anionic species) as long as

310 pH exceeds pK_a value of the target compound. The apparent enhancement of FTA 6:2

311 and FTA 8:2 in partitioning to the particle phase obtained in this study confirmed the

312 fact of the strong partitioning potential to aerosol (aqueous phase) of ionizable

313 chemicals under the condition of higher pH.

314   Table 3 also showed that the partitioning extent of PFASs to the particle phase

315 relied on the functional group and fluorinated chain length. The K_{SP} values of FOSEs

316 were 0.5-0.8 log units higher than those of FOSAs, and 1.3-1.6 log units higher than

317 K_{SP} of FTOHs with the same fluorinated chain length. Among the same group, K_{SP}

318 increased with adding additional fluorinated chains and/or substituents as stated above,

319 for example, the $\log K_{SP}$ increased from -2.8 (FTOH 6:2, 6 chains) to -2.3 (FTOH 12:2,

320 12 chains). In fact, the changes of fluorinated chains and/or substituents for PFASs

321 will lead definitely to the substantial influence on their physicochemical properties,

322 such as vapor pressure, and chemicals with longer fluorinated chain (or methyl

323 substituents) possess lower vapor pressures comparing to their shorter chain (or ethyl-)

324 counterparts. Thus, the variation of particle-phase percentages for different PFASs in

325 the atmosphere is expected to be related to their vapor pressures.

326   To verify the above hypothesis, the linear relationship between $\log K_{SP}$ and $\log p^{\circ}_L$

327 for each sample collected in this study was investigated. The values of p°_L of

328 individual PFASs at different sampling temperature were calculated employing the

329 physicochemical calculator SPARC v4.6 (October 2011 release w4.6.1691-s4.6.1687)

330 (Table 3). The regression results showed that the relations of $\log K_{SP}$ to $\log p^{\circ}_L$ were

331 scattered ($p > 0.05$ for most samples). The reason of scattering was attributed to the

332 low values of the corrected $\log K_{SP}$ (neutral form) for FTA 6:2 and FTA 8:2. The

333 regression results of $\log K_{SP}$ versus $\log p^{\circ}_L$ with FTA 6:2 and FTA 8:2 were not

334 considerably improved when the aerosol pH values adjusted from 0 to 7 based on the

335 corrected pK_a values and Eq (1). However, after excluding the two compounds FTA

336 6:2 and FTA 8:2, $\log K_{SP}$ displayed significant correlation with $\log p^{\circ}_L$ (Fig. 2). The

337 regression data (slopes, intercepts, relationship coefficients and significant levels) for

338 all samples are listed in Table S2. The regression slopes and intercepts ranged from

339 -0.45 to -0.15 (mean: -0.29) and from -3.29 to -1.46 (mean: -2.39), respectively. The

340 results indicated that the partitioning of neutral PFASs (e.g., FTOHs, FOSAs and

341 FOSEs) between gas and particle phases agreed with the classical $\log K_{SP}$ - $\log p^{\circ}_L$

342 relation which was usually used to estimate the gas/particle partitioning of

343 nonionizable semi-volatile organic compounds (SVOCs).

344 As stated above, the partitioning extent depends on the functional group of PFASs,

345 thus the relation of $\log K_{SP}$ to $\log p^{\circ}_L$ can be estimated by dividing different groups.

346 Ahrens et al. (2012) performed the correlations of $\log K_{SP}$ versus $\log p^{\circ}_L$ by grouping

347 PFASs into different classes and obtained significant linear correlation between

348 $\log K_{SP}$ and $\log p^{\circ}_L$ for individual classes. However, considering the complexities of the

349 gas/particle partitioning for ionic PFASs and their strong partitioning potential to

350 aqueous phases at higher pH values, a demand exists to improve the aerosol sorption

351 model taking account of the ad/absorption mechanism to the condensed phase of

352 aerosols for ionizable PFASs (e.g., FTAs) at typical atmospheric pH values.

353

354 Fig. 2 Significant correlation between $\log K_{SP}$ and $\log p_L^\circ$ (excluding FTA 6:2 and 8:2)

355

4. Conclusions

357 The average ΣPFASs concentration (gas + particle phases) was 41 pg/m^3, and the

358 gaseous PFASs were dominated in all samples. FTOH 8:2 and 10:2 were two most

359 abundant compounds in the atmosphere, which accounted 61.9% and 12.7% of

360 ΣPFASs, respectively. Both the higher ratios of FTOH 8:2 to 6:2 and air mass back

361 trajectory analysis showed the atmospheric PFASs in most samples were from the

362 LRAT processes. For neutral compounds with pK_a > 7.0 (i.e., FTOH, FOSE and

363 FOSA), significant linear correlations between $\log K_{SP}$ and $\log p_L^\circ$ indicated the

364 gas/particle partitioning of neutral PFASs can be described by the classical J-P model.

365 However, due to lower pK_a values of FTA 6:2 and 8:2, they mainly exist as ionic form

366 in aerosols and display different gas/particle partitioning behavior compared with

367 FTOHs, FOSEs and FOSAs. Thus, it is necessary to develop a model taking account

368 of the ad/absorption mechanism to the condensed phase of aerosols for ionizable

369 PFASs considering their strong partitioning potential to aqueous phases.

370

377 **References**

378 Ahrens, L., 2011. Polyfluoroalkyl compounds in the aquatic environment: a review of

379   their occurrence and fate. Journal of Environmental Monitoring 13, 20–31.

380 Ahrens, L., Harner, T., Shoeib, M., Lane, D.A., Murphy, J.G., 2012. Improved

381   characterization of gas−particle partitioning for per- and polyfluoroalkyl substances

382   in the atmosphere using annular diffusion denuder samplers. Environmental

383   Science & Technology 46, 7199–7206.

384 Ahrens, L., Shoeib, M., Harner, T., Lee, S.C., Guo, R., Reiner, E.J., 2011. Wastewater

385   treatment plant and landfills as sources of polyfluoroalkyl compounds to the

386   atmosphere. Environmental Science & Technology 45, 8098–8105

387 Ahrens, L., Shoeib, M., Vento, S.D., Codling, G., Halsall, C., 2011. Polyfluoroalkyl

388   compounds in the Canadian Arctic atmosphere. Environmental Chemistry 8, 399–

389   406.

390 Arp, H.P.H., Goss, K.U., 2009a. Gas/particle partitioning behavior of

391   perfluorocarboxylic acids with terrestrial aerosols. Environmental Science &

392   Technology 43, 8542−8547.

393 Arp, H.P.H., Goss, K.U., 2009b. Ambient gas/particle partitioning. 3. estimating

394   partition coefficients of apolar, polar, and ionizable organic compounds by their

395   molecular structure. Environmental Science & Technology 43, 1923−1929.

396 Arp, H.P.H., Schwarzenbach, R.P., Goss, K.U., 2008. Ambient gas/particle

397   partitioning. 1. Sorption mechanisms of apolar, polar, and ionizable organic

398   compounds. Environmental Science & Technology 42, 5541−5547.

399 Arp, H.P.H., Schwarzenbach, R.P., Goss, K.U., 2008a. Ambient gas/particle

400   partitioning. 1. Sorption mechanisms of apolar, polar, and ionizable organic

401   compounds. Environmental Science & Technology 42, 5541−5547.

402   Arp, H.P.H., Schwarzenbach, R.P., Goss, K.U., 2008b. Ambient gas/particle

403   partitioning. 2: The influence of particle source andtemperature on sorption to dry

404   terrestrial aerosols. Environmental Science & Technology 42, 5951−5957.

405   Barber, J.L., Berger, U., Chaemfa, C., Huber, S., Jahnke, A., Temme, C., Jones, K.C.,

406   2007. Analysis of per- and polyfluorinated alkyl substances in air samples from

407   Northwest Europe. Journal of Environmental Monitoring 9, 530–541.

408   Butt, C.M., Berger, U., Bossi, R., Tomy, G.T., 2010. Levels and trends of poly- and

409   perfluorinated compounds in the Arctic environment. Science of the Total

410   Environment 408, 2936–2965.

411   Butt, C.M., Young, C.J., Mabury, S.A., Hurley, M.D., Wallington, T.J., 2009.

412   Atmospheric chemistry of 4:2 fluorotelomer acrylate

413   [C4F9CH2CH2OC(O)CH=CH2]: kinetics, mechanisms, and products of

414   chlorine-atom- and OH-radical-initiated oxidation. Journal of Physical Chemistry A

415   113, 3155–3161.

416   D'eon, J.C., Hurley, M.D., Wallington, T.J., Mabury, S.A., 2006. Atmospheric

417   chemistry of N-methyl perfluorobutane sulfonamidoethanol,

418   C4F9SO2N(CH3)CH2CH2OH: Kinetics and mechanism of reaction with OH.

419   Environmental Science & Technology 40, 1862–1868.

420   Dreyer, A., Ebinghaus, R., 2009c. Polyfluorinated compounds in ambient air from

421   ship- and land-based measurements in northern Germany. Atmospheric

422   Environment 43, 1527–1535.

423   Dreyer, A., Matthias, V., Temme, C., Ebinghaus, R., 2009a. Annual time series of air

424   concentrations of polyfluorinated compounds. Environmental Science &

425   Technology 43, 4029–4036.

426   Dreyer, A., Weinberg, I., Temme, C., Ebinghaus, R., 2009b. Polyfluorinated

427 compounds in the atmosphere of the Atlantic and Southern oceans: evidence for a

428 global distribution. Environmental Science & Technology 43, 6507–6514.

429 Ellis, D.A., Martin, J.W., De Silva, A.O., Mabury, S.A., Hurley, M.D., Sulbaek

430 Anderson, M.P., Wallington, T.J., 2004. Degradation of fluorotelomer alcohols: A

431 likely atmospheric source of perfluorinated carboxylic acids. Environmental

432 Science & Technology 38, 3316−3321.

433 Gewurtz, S.B., De Silva, A.O., Backus, S.M., McGoldrick, D.J., Keir, M.J., Small, J.,

434 Melymuk, L., Muir, D.C.G., 2012. Perfluoroalkyl contaminants in Lake Ontario

435 Lake Trout: detailed examination of current status and long-term trends.

436 Environmental Science & Technology 46, 5842−5850.

437 Goss, K.U., Bronner, G., 2006. What is so special about the sorption behavior of

438 highly fluorinated compounds. Journal of Physical Chemistry A 110, 9518-9522.

439 Jahnke, A., Ahrens, L., Ebinghaus, R., Temme, C., 2007. Urban versus remote air

440 concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances

441 in Germany. Environmental Science & Technology 41, 745–752.

442 Lei, Y.D., Wania, F., Mathers, D., Mabury, S.A., 2004. Determination of vapor

443 pressures, octanol-air, and water-air partition coefficients for polyfluorinated

444 sulfonamide, sulfonamidoethanols, and telomer alcohols. Journal of Chemical

445 Engineering Data 49, 1013–1022.

446 Li, J., Del Vento, S., Schuster, J., Zhang, G., Chakraborty, P., Kobara, Y., Jones, K.C.,

447 2011. Perfluorinated Compounds in the Asian Atmosphere. Environmental Science

448 & Technology 45, 7241–7248.

449 Martin, J.W., Ellis, D.A., Mabury, S.A., Hurley, M.D., Wallington, T.J., 2006.

450 Atmospheric chemistry of perfluoroalkanesulfonamides: Kinetic and product

451 studies of the OH radical and Cl atom initiated oxidation of N-ethyl

452   perfluorobutanesulfonamide. Environmental Science & Technology 40, 864–872.

453   Möller, A., Xie, Z., Caba, A., Sturm, R., Ebinghaus, R., 2011. Organophosphorus

454   flame retardants and plasticizers in the atmosphere of the North Sea. Environmental

455   Pollution 159, 3660–3665.

456   Pankow J.F., 2003. Gas/particle partitioning of neutral and ionizing compounds to

457   single and multi-phase aerosol particles.1.Unified modeling framework.

458   Atmospheric Environment 37, 3323–3333.

459   Paul, A.G., Jones, K.C., Sweetman, A.J., 2009. A first global production, emission,

460   and environmental inventory for perfluorooctane sulfonate. Environmental Science

461   & Technology 43, 386−392.

462   Piekarz, A.M., Primbs, T., Field, J.A., Barofsky, D.F., Simonich, S., 2007.

463   Semivolatile fluorinated organic compounds in Asian and western US air masses.

464   Environmental Science & Technology 41, 8248–8255.

465   Piekarz, A.M., Primbs, T., Field, J.A., Barofsky, D.F., Simonich, S., 2007.

466   Semivolatile fluorinated organic compounds in Asian and western U.S air masses.

467   Environmental Science & Technology 41, 8248–8255.

468   Shoeib, M., Vlahos, P., Harner, T., Peters, A., Graustein, M., Narayan, J., 2010.

469   Survey of polyfluorinated chemicals (PFCs) in the atmosphere over the northeast

470   Atlantic Ocean. Atmospheric Environment 44, 2887–2893.

471   Shoeib, M., Vlahos, P., Harner, T., Peters, A., Graustein, M., Narayan, J., 2010.

472   Survey of polyfluorinated chemicals (PFCs) in the atmosphere over the northeast

473   Atlantic Ocean. Atmospheric Environment 44, 2887–2893.

474   Vento, S.D., Halsall, C., Gioia, R., Jones, K., Dachs, J., 2012. Volatile per- and

475   polyfluoroalkyl compounds in the remote atmosphere of the western Antarctic

476   Peninsula: an indirect source of perfluoroalkyl acids to Antarctic waters?

477   Atmospheric Pollution Research 3, 450–455.

478   Vierke, L., Ahrens, L., Shoeib, M., Reiner, E.J., Guo, R., Palm, W.U., Ebinghaus, R.,

479   Harner, T., 2011. Air concentrations and particle–gas partitioning of polyfluoroalkyl

480   compounds at a wastewater treatment plant. Environmental Chemistry 8, 363–371.

481   Wang, T., Wang, Y., Liao, C., Cai, Y., Jiang, G., 2009. Perspectives on the inclusion of

482   perfluorooctane sulfonate into the Stockholm Convention on persistent organic

483   pollutants. Environmental Science & Technology 43, 5171–5175.

484   Wang, Z., Na, G.S., Ma, X.D., Fang, X.D., Ge, L.K., Gao, H., Yao, Z.W., 2013.

485   Occurrence and gas/particle partitioning of PAHs in the atmosphere from the North

486   Pacific to the Arctic Ocean. Atmospheric Environment 77, 640–646.

487   Xie, Z., Zhao, Z., Möller, A., Wolschke, H., Ahrens, L., Sturm, R., Ebinghaus, R.,

488   2013. Neutral poly- and perfluoroalkyl substances in air and seawater of the North

489   Sea. Environmental Science and Pollution Research 20, 7988–8000.

490   Young, C.J., Furdui, V.I., Franklin, J., Koerner, R.M., Muir, D.C.G., Mabury, S.A.,

491   2007. Perfluorinated acids in Arctic snow: new evidence for atmospheric formation.

492   Environmental Science & Technology 41, 3455–3461.

493   Zhang, Q., Jimenez, J.L., Worsnop, D.R., Canagaratna, M., 2007. A case study of

494   urban particle acidity and its influence on secondary organic aerosol.

495   Environmental Science & Technology 41, 3213–3219.

496