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Polyfluorinated compounds in the atmosphere along a cruise pathway from the Japan Sea to the Arctic Ocean

1 # Polyfluorinated compounds in the atmosphere along a cruise

2 # pathway from the Japan Sea to the Arctic Ocean

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19 **Abstract**

20 Neutral polyfluorinated alkyl substances (PFASs) were measured in high-volume air samples

21 collected on board the research vessel *Snow Dragon* during the 4th Chinese National Arctic

22 Expedition from the Japan Sea to the Arctic Ocean in 2010. Four volatile and semi-volatile

PFASs (fluorotelomer alcohols (FTOHs), fluorotelomer acids (FTAs), perfluoroalkyl sulfonamides (FASAs), and sulfonamidoethanols (FASEs)) were analyzed respectively in the gas and particle phases. FTOHs were the dominant PFASs in the gas phase (61−358 pg/m^3), followed by FTAs (5.2−47.9 pg/m^3), FASEs (1.9−15.0 pg/m^3), and FASAs (0.5−2.1 pg/m^3). In the particle phase, the dominant PFAS class was FTOHs (1.0−9.9 pg/m^3). The particle-associated fraction followed the general trend of FASEs > FASAs > FTOHs. Compared with other atmospheric PFAS measurements, the ranges of concentrations of ∑FTOH in this study were similar to those reported from Toronto, North America (urban), the northeast Atlantic Ocean, and northern Germany. Significant correlations between FASEs in the gas phase and ambient air temperature indicate that cold surfaces such as sea-ice, snowpack, and surface seawater influence atmospheric FASEs.

Keywords: Polyfluoroalkyl compounds; FTOHs; FTAs; FASE/FASAs; Arctic.

1. Introduction

In recent years, ionic per- or polyfluorinated alkyl substances (PFASs) have been detected globally (Giesy and Kannan, 2001). Among these ubiquitous compounds have been found perfluorooctane sulfonate (PFOS) and perfluorocarboxylates (PFCAs) such as perfluorooctanoate (PFOA), which are widespread and persistent environmental contaminants that have been detected in polar bears from the Canadian and European Arctic (Smithwick et al., 2005a, 2005b), dolphins in the Atlantic Ocean (Houde et al., 2005), seawater from the Pacific, Atlantic, and Arctic Oceans (Yamashita et al., 2005; Wei et al., 2007; Ahrens et al., 2009, 2010), and fur seal pups and penguin eggs in Antarctica (Schiavone et al., 2009).

The stability of PFOS and PFCAs precludes degradation or metabolism, which contributes to their global dispersion, persistence, and bioaccumulation. High water solubility and a low Henry's law constant render PFOS and PFCAs susceptible to wet deposition, making it

48 unlikely that they are transported long distances atmospherically in the vapor phase (Loewen

49 et al., 2008). It has been hypothesized that these chemicals are transported atmospherically as

50 volatile precursors to remote areas where their degradation products are then deposited

51 (Renner, 2001). Alternatively, long-range transport of PFCAs and PFOS to remote areas by

52 ocean currents has also been hypothesized (Prevedouros et al., 2006).

53 Atmospheric transport with subsequent degradation of volatile and semi-volatile precursor

54 compounds (e.g., fluorotelomer alcohols (FTOHs), perfluoroalkyl sulfonamides (FASAs), and

55 perfluoroalkyl sulfonamidoethanols (FASEs)) to persistent PFCAs and PFOS has been

56 hypothesized as a main transport mechanism (Ellis et al., 2004; Sulbaek Andersen et al., 2005;

57 D'Eon et al., 2006; Martin et al., 2006). Because of their slow reaction with hydroxyl radicals,

58 atmospheric lifetimes of more than 10−20 days for FTOHs and more than 20−50 days for

59 FASAs have been estimated in smog chamber studies (Ellis et al., 2003; Martin et al., 2006).

60 Field studies have indicated an atmospheric residence time of more than 50 days for FTOHs

61 (Piekarz et al., 2007). These data indicate the possibility of regional and long-range

62 atmospheric transport of FTOHs and FASAs. PFCAs and perfluoroalkyl sulfonates (PFSAs)

63 have also been detected in snow samples from the high Arctic, where contamination is solely

64 from atmospheric sources. This finding confirms the indirect precursor-based atmospheric

65 transport and deposition of these compounds (Young et al., 2007).

66 Several datasets are available for ambient air as well as for indoor air samples. 6:2 FTOH,

67 8:2 FTOH, 10:2 FTOH, *N*-ethyl fluorooctane sulfonamide (EtFOSA), *N*-methyl fluorooctane

68 sulfonamidoethanol (MeFOSE), and *N*-ethyl fluorooctane sulfonamidoethanol (EtFOSE) were

69 found to be widely distributed in the atmosphere of North America, Europe, and over an

70 Atlantic transect (Martin et al., 2002; Shoeib et al., 2004; Stock et al., 2004b; Boulanger et al.,

71 2005; Shoeib et al., 2005; Dreyer and Ebinghaus, 2009; Dreyer et al., 2009a, 2009b). PFASs

72 are manufactured by two main synthesis routes. Generally, the production of FASAs/FASEs is

associated with the electrochemical fluorination (ECF) process, which has been in use since the 1950s. FASAs/FASEs are predominantly used as paper protectors, as water- and dirt-proofing in carpets/leathers/textiles, as performance chemicals (e.g., in aqueous film-forming fire-fighting foams, AFFFs) (De Voogt and Saez, 2006), and as an insecticide (Sulfluramid). The second manufacturing process, telomerization, has been in use since the 1970s to produce exclusively linear compounds, including FTOHs. The production of FTOHs has continued to increase, particularly for use as precursors in the production of fluorinated polymers used in paper and carpet treatments, as well as in the production of paints, coatings, and adhesives (Dinglasan et al., 2006).

The aim of this study was to investigate the inter-hemispherical gradient of neutral (volatile and semi-volatile) precursors of PFOS and PFCAs in ambient air, starting from the Japan Sea, adjacent to urbanized regions, and then on a transect towards the Arctic Ocean. Data presented in this study yield new information on the spatial atmospheric distribution of PFASs on a regional scale, as well as the identification of their source regions in the Northern Hemisphere. The airborne PFAS data are compared with the results of previous studies. This study provides the first evidence of the occurrence of airborne PFASs in ambient air samples from the Japan Sea to the Arctic Ocean.

2. Materials and Methods

2.1. Chemicals and Standards

All solvents (Methanol, acetone, dichloromethane, and *n*-hexane) were residue-grade and additionally distilled in a full glass unit prior to use. Details of the analytical standards of FTOHs (FTOH 6:2, 8:2, 10:2, and 12:2), fluorotelomer acrylates (FTA 6:2, 8:2, and 10:2),

96　Me- and EtFOSA, Me- and EtFOSE, and mass-labeled internal standards are summarized in

97　Table S2 (Supplementary Materials).

98

99　**2.2 Sampling cruise**

100　Air samples were taken onboard the Arctic expedition of the *R/V Snow Dragon* from the

101　Japan Sea to the high Arctic (33.2–84.5 °N) during June–September 2010 (see Fig. 1). Air

102　samples (~500 m^3/sample, ~48 h) were taken using a high–volume air sampler placed in the

103　front of the ship's upper deck (20 m above sea level), with a glass fiber filter ([GFF], GF/F,

104　pore size: 0.7 μm) to trap airborne particles, and a self–packed PUF/XAD–2 glass column

105　(PUF: Ø 5.0 cm x 2.5 cm; 35 g XAD-2, particle size: 0.3-1.0 mm) for the gaseous phase. Both

106　air column and filters were stored at −20 °C until analysis. Sampling parameters, including

107　date, position, temperature, and wind speed, are listed in Table S1 in the Supplementary

108　materials.

109

110　**2.3 Sample preparation and instrumental analysis**

111　Extraction and clean–up of the samples was done in a clean laboratory (class 10000). All

112　solvents were residue–analysis grade and were distilled prior to use. Samples were spiked with

113　2500 pg of mass labeled internal standards (Wellington Laboratories) prior to extraction. Air

114　columns were extracted in a modified Soxhlet apparatus for 16 h using

115　dichloromethane/hexane (1/1), and air filter samples were Soxhlet extracted using

116　dichloromethane for 16 h, respectively. Extracts were evaporated to 1−2 mL with rotary

117　evaporator and then passed a glass column (i.d. 1 cm, length: 15 cm) packed with 3 g Na$_2$SO$_4$

118   to remove residual water. The extracts were further concentrated down to 150 µL and spiked

119   with 1000 pg ^{13}C–HCB as injection standard.

120   Detailed analysis methods have been described elsewhere (Dreyer et al., 2008). In brief,

121   analysis was performed using gas chromatography–mass spectrometry (GC–MS) using an

122   Agilent 6890 gas chromatograph and an Agilent 5973 mass spectrometer, Agilent

123   Technologies) in selective ion monitoring (SIM) mode with positive chemical ionization

124   (PCI). The ion masses are summarized in Table S2 in the Supplementary Materials. The

125   response factors were derived from the calibration curves (6-points) made for response ratio

126   between targets compounds (0–250 ng/mL) and mass labeled internal standards (12.5

127   ng/mL)."

128

129   **2.4 Quality assurance and control**

130   All air columns were pre-cleaned with organic solvents (methanol, acetone, and

131   hexane/acetone in turn for 96 h) and GFFs were heated at 450 °C for 12 h prior to use. Na_2SO_4

132   was cleaned with dichloromethane for 12 h and heated at 450 °C for 12 h prior to use. To

133   avoid degradation of the target compounds, air columns were protected against UV–sunlight

134   during sampling using aluminum foil. Breakthrough of the target analytes using these

135   sampling methods has been checked previously on board the German icebreaker *R/V*

136   *Polarstern*. Three field blanks were run for each sample type, with blanks showing very low

137   values ranging from 0.01 to 0.2 pg/m^3 (12:2 FTOH). Method detection limits (MDLs) were

138   derived from mean blank values plus three times the standard deviation (σ) (for compounds

139 showing no blanks, a peak area of 100 was adopted as background response), which ranged

140 from 0.1 to 0.3 pg/m^3 for both gas and particle phases.

141

142 **2.5 Air Mass Back-Trajectories**

143   Air mass origins of the individual air samples collected during the cruise segments were

144 calculated using NOAA's HYSPLIT model. Air mass back-trajectories (BTs) were calculated

145 in 6-h steps tracing back the air masses for 5 days using the sampling height as arrival height.

146

147 **3. Results and discussion**

148 *3.1. Concentrations of Airborne PFASs*

149   Total air concentrations of target compounds at various points sampled along the cruise

150 route are presented in Figure 1 and summarized in Table 1 (for details, see Table S3,

151 Supplementary Materials). PFASs were detected in all air samples, with FTOHs/FTAs and

152 FASAs/FASEs ubiquitous at the sites sampled, except for MeFOSA, which was not detected at

153 sample site A6.

154

155 *3.1.1. FTOHs, FTAs, FASEs, and FASAs in the gas phase*

156   The PFAS concentrations in the gas phase ranged from 77.9 to 416 pg/m^3, and the highest

157 gas-phase total concentrations of PFASs (416 pg/m^3) were measured in sample A2 in the

158 Okhotsk Sea, followed by sample A1 (346 pg/m^3) in the Sea of Japan. The lowest total PFAS

159 concentrations were found in samples A4 (78 pg/m^3) in the Bering Sea and A9 (118 pg/m^3) in

160 the Beaufort Sea.

161   Generally, the FTOH concentrations were about 10 times higher than those of FTAs and

162 about 24 times those of FASAs/FASEs. The dominant FTOH was 8:2 FTOH (44.6−286 pg/m^3),

163   followed by 10:2 FTOH (6.1−47 pg/m^3), 12:2 FTOH (4.2−16 pg/m^3), and 6:2 FTOH (0.8−12

164   pg/m^3). This distribution pattern was the same at almost all sampling sites. Interestingly, 12:2

165   FTOH was detected in north Germany in a previous study, with the concentration ranging from

166   1.3 to 8.0 pg/m^3 (Dreyer and Ebinghaus, 2009).

167   The chemical pattern of FTOHs in the present study was, in order, 8:2 FTOH > 10:2 FTOH

168   > 6:2 FTOH from the Japan Sea to the Arctic Ocean, a pattern similar to that reported for the

169   Arctic (Shoeib et al., 2006), northeast Atlantic Ocean (Shoeib et al., 2010), and the western

170   USA and Japan (Piekarz et al., 2007; Oono et al., 2008a, 2008b). The chemical pattern of

171   FTOHs was consistent with the estimated atmospheric residence times of FTOHs, with 80 d,

172   70 d, and 50 d for 8:2 FTOH, 10:2 FTOH, and 6:2 FTOH, respectively (Piekarz et al., 2007).

173   For the FTAs, 8:2 FTA was dominant (3.3−28.7 pg/m^3), followed by 10:2 FTA (1.8−19.0

174   pg/m^3) and 6:2 FTA (0.1−0.2 pg/m^3). FTAs were also detected in north Germany, with values

175   of 1.7−15 pg/m^3 for 8:2 FTA, 0.8−6.6 pg/m^3 for 10:2 FTA, and 4.2−5.7 pg/m^3 for 6:2 FTA

176   (Dreyer and Ebinghaus, 2009), closely similar to the chemical pattern of FTAs measured in the

177   present study. FTAs were not included in previous studies from Northwest Europe (Barber et

178   al., 2007), North America (Stock et al., 2004b), Western Canada (Loewen et al., 2008), the

179   Canadian Arctic (Stock et al., 2007), the northeast Atlantic Ocean (Shoeib et al., 2010), and the

180   Arctic atmosphere (Shoeib et al., 2006).

181   For the FASAs/FASEs, MeFBSE was dominant (1.7−15 pg/m^3), followed by MeFBSA

182   (0.2−1.3 pg/m^3), EtFOSE (0.1−0.7 pg/m^3), EtFOSA (0.1−0.9 pg/m^3), MeFOSE (0.1−0.6

183   pg/m^3), and MeFOSA (0−0.3 pg/m^3). The concentrations of FASEs were much higher than

184   those of FASAs. The atmospheric lifetimes of FASEs were shorter than those of FASAs (~2 d

185   in contrast to >20 d) (D'Eon et al., 2006; Martin et al., 2006), whilst MeFBSE has a lifetime of

186   2 days, much shorter than the 20−50 day lifetime of its parent compound MeFBSA. This result

187   suggests that FOSEs probably originated from nearby pollution sources or were transported by

188   mist aerosols, which arrived in the study regions without long-range atmospheric

189   transportation, especially for MeFBSE. Surprisingly, the concentration of MeFBSE was about

190   one order of magnitude higher than that of MeFBSA, even in the Arctic region, from sampling

191   sites A8 to A12. It is thought that the PFASs enriched in the sea surface microlayer may be

192   transported into the atmosphere as organic-rich particles via wave–wind interactions

193   (Cincinelli et al., 2001). Prevedouros et al. (2006) also indicated that PFASs concentrated in

194   the surface waters of oceans and rivers could be transported into the air as marine aerosols,

195   and that they could partition onto particle surfaces when spray droplets evaporated, and thus

196   be transported long distances in the atmosphere. The MeFOSE measured in this study

197   probably reached the Arctic region through marine aerosol transportation, suggesting that this

198   transmission mode is possible for other FASEs.

199

200   *3.1.2. FTOHs, FTAs, FASEs, and FASAs in the particle phase*

201   All FTOHs, FTAs, FOSAs, and FOSEs were quantified in the particle phase of ambient air

202   from the Japan Sea to the Arctic Ocean. The ∑FTOH/FTA/FASA/FASE concentrations in the

203   particle phase ranged between 2.2 and 13.1 pg/m^3 and were hence about 35 times lower than in

204   the gas phase. The highest ∑FTOH/FTA/FASA/FASE concentrations were found in the Bering

205   Sea and Beaufort Sea (13.1 and 11.3 pg/m^3, respectively); the lowest concentrations were

206   found in the Arctic Ocean and East China Sea (2.2 and 2.4 pg/m^3, respectively). The dominant

207   PFAS classes were FTOHs (1.0−9.9 pg/m^3) with 8:2 FTOH as the dominant compound

208   (0.2−8.2 pg/m^3), followed by FASEs (0.44−4.9 pg/m^3) with MeFBSE (0.1−4.5 pg/m^3). The

209   concentrations of individual FTA and FASA compounds were below 0.3 pg/m^3, while the

210   ∑FTOH concentrations were about 14 and 23 times higher than the ∑FTA and ∑FASA

211   concentrations, respectively, and the ∑FASE concentrations were about 7 and 11 times higher

212   than those of ∑FTAs and ∑FASAs, respectively.

213

3.1.3. Gas/particle partitioning

The distribution ratio of the particle and gas phases of a chemical will influence its fate and transport in the atmosphere. While the FTOHs, FTAs, FASAs, and FASEs were dominantly distributed in the gas phase, individual compounds showed a different partitioning profile (see Fig. 2). The particle-associated fraction (φ, $\varphi = c_{particulate}/(c_{particulate} + c_{gaseous})$) represents the fraction of particles ($c_{particulate}$) in relation to the gas phase ($c_{gaseous}$) in air. In the present study, a significant proportion of FASEs/FASAs were in the particulate phase in the samples, with an average of 53% for EtFOSE, 48% for MeFOSE, 21% for MeFBSE, 21% for MeFOSA, 17% for EtFOSA, and 2% for MeFBSA. The functional group has the greatest influence on the portioning of PFCs; the highest particle-associated fraction was observed for FASEs (~26%), followed by FASAs (12%), FTOHs (2.7%), and FTAs (1.8%). A similar pattern was observed in previous studies from other regions, such as the Atlantic Ocean (Shoeib et al., 2010), North Atlantic and Canadian Archipelago, the Arctic (Shoeib et al., 2006), Toronto, Canada (Shoeib et al., 2006), Germany (Jahnke et al., 2007a), the UK (Barber et al., 2007), and northwest Europe (Barber et al., 2007). Interestingly, the particle-associated fraction of ethyl FOSE and FOSA (53% and 17%, respectively) was comparable to the methyl FOSE and FOSA (48% and 21%, respectively), suggesting that the length of alkyl carbon chain had little influence on the gas/particle partition of FASEs/FASAs. Furthermore, the particle-associated fraction for FTOHs was, in order, 12:2 FTOH > 6:2 FTOH > 10:2 FTOH > 8:2 FTOH, which was not consistent with the thermodynamic law that the vapor pressure of the longer-chain FTOHs is lower than in the shorter-chain FTOHs (e.g., 144 Pa for 10:2 FTOH; 254 Pa for 8:2 FTOH; 713 Pa for 6:2 FTOH; Stock et al., 2004a). The reasons for this are not clear, but may be related to differences in particulate matter, a potential contribution of sea spray, and/or mist aerosols (Prevedouros et al., 2006) in the cruise samples that may absorb to the GFF and

238   contain FTOHs, or differences in atmospheric residence times.

239

240   *3.1.4. Correlation analyses*

241   Of the sum concentrations of all substance classes in the cruise samples, $\sum$FTOH and $\sum$FTA

242   showed a highly significant positive correlation (Spearman correlation: $p < 0.01$, $r_s = 0.729$).

243   FTOHs were used as precursors to produce FTAs for fluorotelomer-based polymers

244   (Prevedouros et al., 2006), which suggests the possible FTOHs and FTAs contamination

245   originated from the similar sources. $\sum$FASAs and $\sum$FASEs were positively correlated ($p < 0.05$,

246    $r_s = 0.575$), indicating that the sources of these compounds are related. For individual PFASs

247   (Table S4, Supplementary Materials), the concentrations of FTOHs were significantly

248   correlated with each other ($p < 0.05$), except 6:2 FTOH. The concentration of 8:2 FTA

249   correlated significantly with that of 10:2 FTA ($p < 0.01$, $r_s = 0.973$). Significantly positive

250   correlations were also observed between MeFBSA and MeFBSE ($p < 0.01$, $r_s = 0.725$), and the

251   concentrations of the two compounds were higher than that of other FASAs/FASEs. This result

252   suggests the sources of MeFBSA and MeFBSE are related, and probably were derived from

253   sources different than those of other FASAs/FASEs. Furthermore, the concentrations of

254   MeFOSE and EtFOSE were significantly correlated ($p < 0.01$, $r_s = 0.918$). Interestingly,

255   MeFOSA and EtFOSA were not significantly positively correlated with other PFAS ($p > 0.05$),

256   which points to a variability in the source and/or differences in atmospheric persistence among

257   these chemicals.

258

259   *3.2. Comparison with other reported airborne PFASs*

260   Figure 3 provides an overview of $\sum$FTOH and $\sum$FASA/FASE concentrations determined in

261   this study and reported by other research groups. However, it should be noted that analyzed

262   substances in the previous studies differed to some extent (Stock et al., 2004b; Shoeib et al.,

263 2006; Barber et al., 2007; Stock et al., 2007; Oono et al., 2008a, 2008b; Dreyer et al., 2009a,

264 2009b; Dreyer and Ebinghaus, 2009; Shoeib et al., 2010). In general, the concentrations of

265 ∑FTOHs in this study were in the same ranges as seen in studies of Toronto, North America

266 (urban), the Northeast Atlantic Ocean, and Northern Germany, higher than those of the North

267 Atlantic and Canadian Archipelago, Arctic (Stock et al., 2004b; Dreyer and Ebinghaus, 2009;

268 Shoeib et al., 2006, 2010), but lower than those of urban and traffic-influenced areas in

269 England, Germany, Northwest Europe, and Japan (Barber et al., 2007; Jahnke et al., 2007a;

270 Oono et al., 2008a, 2008b). This result indicates that the industrialized regions are potential

271 sources of ∑FTOHs.

272 Compared with data published for other regions, ∑FTOH levels were significantly higher in

273 Japan, probably suggesting point sources, which is consistent with the higher ∑FTOHs at

274 sampling sites A1 (Sea of Japan), A2 (Bering Sea), and A13 (East China Sea) in this study. As

275 for ∑FASAs/FASEs, the concentrations were lower than in all regions studied previously,

276 except the Southern Hemisphere (Jahnke et al., 2007b). Similarly, the higher concentrations of

277 ∑FASAs/FASEs were also correlated with industrialized regions, and ∑FASA/FASE levels

278 were significantly higher in North America, suggesting possible point sources.

279 The ∑FTOH/FASA/FASE concentrations (2.0−13 pg/m^3) in the particle phase were similar

280 to those of Toronto, Canada (Shoeib et al., 2006), Waldhof (rural area), Germany (Jahnke et al.,

281 2007a), Hazelrigg, UK (Barber et al., 2007), and Kjeller, Norway (Barber et al., 2007), and

282 were about 2−3 times lower than those of the North Atlantic and Canadian Archipelago, Arctic

283 (Shoeib et al., 2006), Hambury (urban area), Germany (Jahnke et al., 2007a), Northern

284 Germany (Dreyer and Ebinghaus, 2009), and Manchester, UK (Barber et al., 2007). In addition,

285 the pattern of the PFAS classes in the particle phase followed the trend FASEs > FASAs >

286 FTOHs, which was in accordance with the general trends observed in other areas, such as

287 Northern Germany; Hazelrigg and Manchester, UK; Kjeller, Norway; and Hamburg and

288   Waldhof, Germany (Barber et al., 2007; Jahnke et al., 2007a; Dreyer and Ebinghaus, 2009).

289

290   *3.3. Identification of air mass sources and influence of ambient temperatures on FASEs*

291   *gas/particle partition*

292   Air mass back-trajectories were used to determine the source routes of PFASs, and all 13

293   sites were primarily oceanic in origin. The air mass back-trajectories (6-h steps) and altitudinal

294   profiles of the air mass parcels of five selected stations (A1 (120 h), A5 (120 h), A11 (96 h),

295   A13 (120 h), and A15 (120 h)) are shown in Fig. 4. As the analysis of air mass back-

296   trajectories shows, the air masses were mainly from oceanic source routes, even for the

297   samples taken in the Japan Sea. We therefore investigated the influence of ambient

298   temperature on the airborne concentration of volatile and semi-volatile PFASs, and their

299   distribution between the gaseous and particulate phases, to identify the probable influence of

300   sea/air exchange. FTOHs, FTAs, and FASAs showed no significant correlation with ambient

301   temperature in the gas/particle phase, which indicates that their presence is not associated with

302   a temperature effect. However, we found a significant correlation of FASE concentrations

303   (sum of gas and particulate phases) with ambient temperature ($p < 0.05$, $R^2 = 0.699$), and a

304   significant correlation was also found between FASE concentrations in the gas phase and

305   ambient temperature ($p < 0.05$, $R^2 = 0.740$) (see Fig. 5). Similar results were also observed in

306   Germany, and the North Atlantic and Canadian Archipelago (Shoeib et al., 2006; Jahnke et al.,

307   2007a). This phenomenon could be related partly to the significant revolatilization of particle-

308   bound compounds from the filter at higher temperatures (Gundel et al., 1995) or associated

309   with the process of sea/air exchange. Further investigations are needed, especially studies of

310   the concentrations of FASEs in the sea surface microlayer or sub-layer in these areas. In the

311   present study, although the influence from the continent is not that high, much higher

312   contaminations would be expected if the air had come directly from Asian countries. The data

313 with higher FTA concentrations (5.2−48 pg/m^3) presented in this study agree with the higher

314 concentrations reported in Japan, which confirmed an Asian origin (Oono et al., 2008a, 2008b);

315 fewer data have been reported from Europe and North America.

316

317 **4. Conclusions**

318 Generally, the concentrations of PFASs were higher in urban regions, and FTOHs were the

319 most dominant compounds of PFASs, followed by FTAs, FASEs, and FASAs. The relatively

320 high concentrations of FTOHs at sample sites A1 (Sea of Japan), A2 (Bering Sea), and A13

321 (East China Sea) were probably caused by the countries of East Asia, where ∑FTOH and

322 ∑FTA levels are much higher than in Europe and North America. The particle-associated

323 fractions of PFASs followed the general trend FASEs > FASAs > FTOHs. Given the

324 importance of particle-gas partitioning for determining the fate and transport pathways of

325 semi-volatile chemicals, further empirical studies are required. Ambient air temperature had a

326 significant influence on the partitioning behavior of FASEs, indicating that the atmospheric

327 behavior of these compounds was influenced by temperature-driven surface exchanges,

328 possibly including extensive areas of sea-ice, snow pack, and surface seawater.

329 In summary, this study documents the first measurements of FTOHs/FTAs and

330 FASAs/FASEs in ambient air sampled on a cruise transect from the Japan Sea to the Arctic

331 Ocean. Our study shows the wide distribution of FTOHs/FTAs and FASAs/FASEs in the

332 ambient atmosphere, not only in low-latitude urban regions but also in remote Arctic regions.

333 The findings confirm the hypothesis of long-range atmospheric transport of neutral, volatile

334 precursors of PFCAs and PFOS to remote regions.

335

343

Appendix A: Supplementary materials

345 Supplementary data associated with this article can be found in Appendix A: Supplementary

346 materials.

347

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Figure Captions

Figure 1. Total concentrations of PFASs in the atmosphere along the cruise track from the Japan Sea to Arctic Ocean.

Figure 2. Composition profile of PFASs in the gaseous phase (left) and particle phase (right) along the sampling transect.

Figure 3. Concentrations (minimum, maximum) of FTOHs and FASAs/FASEs in ambient air of different areas ((a) *Shoeib et al.*,2006, (b) *Loewen et al.*,2008, (c) *Stock et al.*,2004b, (d) *Shoeib et al.*, 2010, (e) *Barber et al.*, 2007, (f) *Dreyer and Ebinghaus*, 2009, (g) *Jahnke et al.*, 2007a, (h) *Oono et al.*, 2008b.)

Figure 4. Air mass back trajectories (6 h steps) and altitudinal profiles of the air mass parcels for the selected air samples A1 (120 h), A5 (120 h), A11 (96 h), A13 (120 h) and A15 (120 h). The black line indicates the cruise leg.

**Figure 5.** Correlations between FASEs concentrations and ambient temperatures in atmosphere of sampling stations.

Table 1 Gas- and particle-phase concentrations (pg m^{-3}) of volatile PFCs in ambient air from
the Japan Sea to Arctic Ocean

PFASs	Phase	MDL	Variation range	Arithmetic mean	Stardard deviation
6:2FTOH	c(g)	0.1	0.8−12	3.9	3.2
	c(p)		0−0.2	0.1	0.1
8:2FTOH	c(g)	0.2	45−286	139	65
	c(p)		0.2−8.2	2.2	2.1
10:2FTOH	c(g)	0	6.1−47	22	12
	c(p)		0.1−1.1	0.4	0.3
12:2FTOH	c(g)	0.3	4.2−16	9.2	4.1
	c(p)		0.2−2.5	0.9	0.8
∑FTOHs	c(g)		61−358	174	79
	c(p)		1−9.9	3.6	2.6
6:2FTA	c(g)	0.1	0.1−0.2	0.1	0.1
	c(p)		BDL−0.1	0.04	0.05
8:2FTA	c(g)	0.1	3.3−29	12	8.7
	c(p)		BDL−0.2	0.1	0.1
10:2FTA	c(g)	0.2	1.8−19	5.9	4.7
	c(p)		0.1−0.3	0.1	0.1
∑FTAs	c(g)		5.2−48	18	13
	c(p)		0.1-0.5	0.3	0.1
MeFBSA	c(g)	0	0.2-1.3	0.7	0.3
	c(p)		BDL−0.05	0.02	0.02
MeFOSA	c(g)	0.1	BDL−0.3	0.1	0.1
	c(p)		BDL−0.1	0.04	0.05
EtFOSA	c(g)	0.1	0.2−0.9	0.6	0.2
	c(p)		0.1	0.1	0.0
∑FASAs	c(g)		0.5−2.1	1.4	0.5
	c(p)		0.1−0.24	0.2	0.1
MeFBSE	c(g)	0.03	1.7−15	5.4	3.7
	c(p)		0.1−4.5	1.5	1.3
MeFOSE	c(g)	0.1	0.1−0.6	0.2	0.2
	c(p)		0.1−0.5	0.2	0.1
EtFOSE	c(g)	0.1	0.1−0.7	0.2	0.2
	c(p)		0.1−0.5	0.2	0.1
∑FASEs	c(g)		1.9−15	5.8	3.9
	c(p)		0.4−4.9	1.8	1.2
∑FTOHs+∑FTAs	c(g)		66−406	192	90
	c(p)		1.2−10	3.9	2.7
∑FASAs+∑FASEs	c(g)		2.7−17	7.2	4.1
	c(p)		0.55−5.1	2.0	1.2
∑neutral PFCs	c(g)		78−346	200	92
	c(p)		2.2−13	5.9	3.6

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Figure 1.
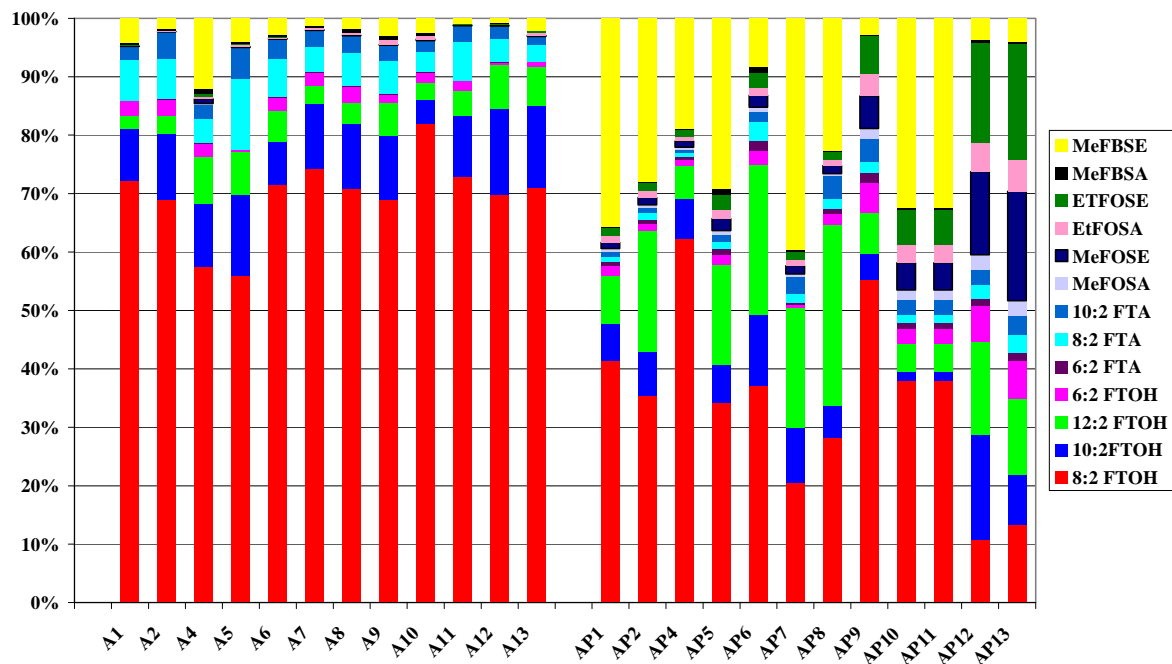
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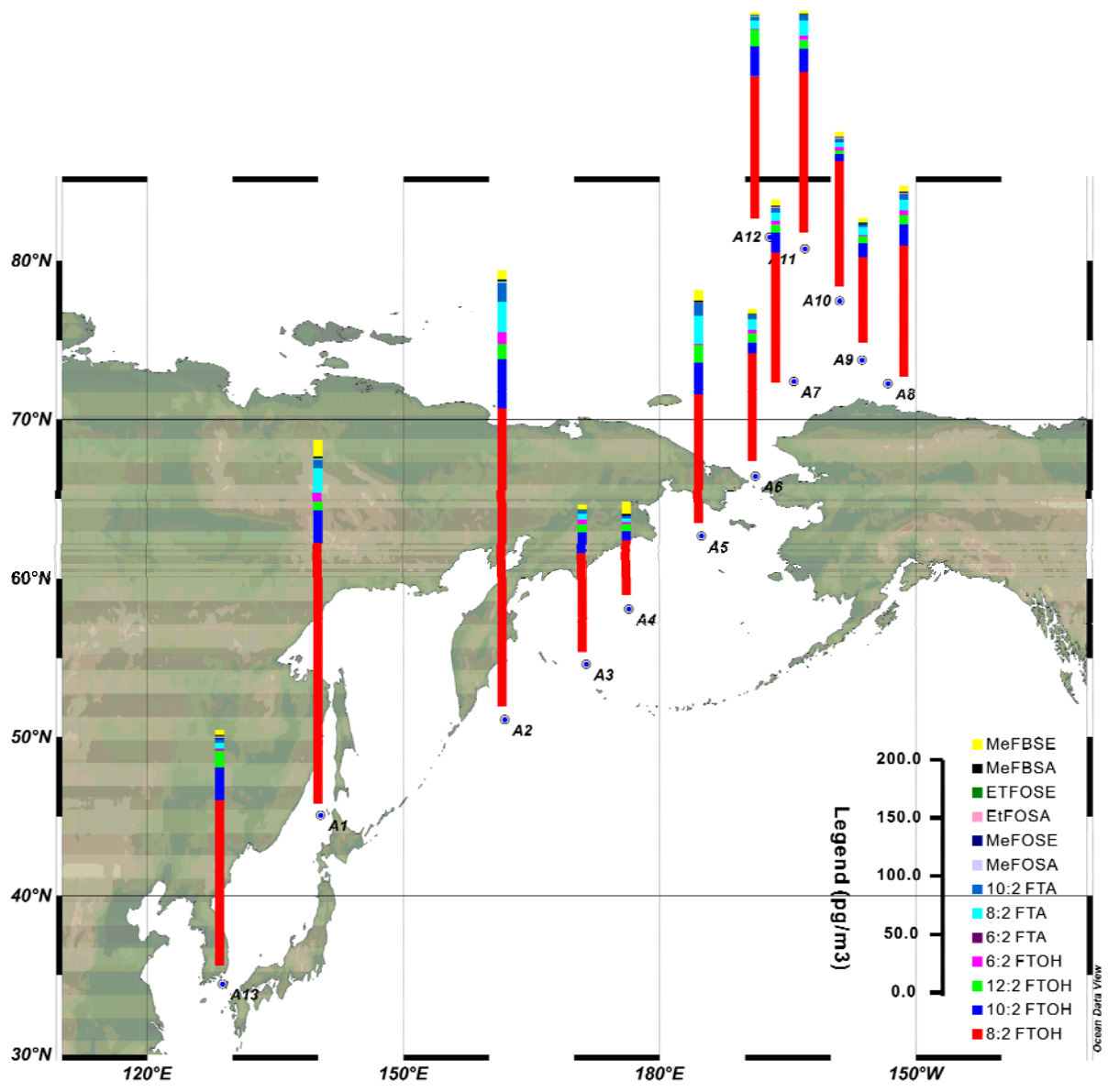
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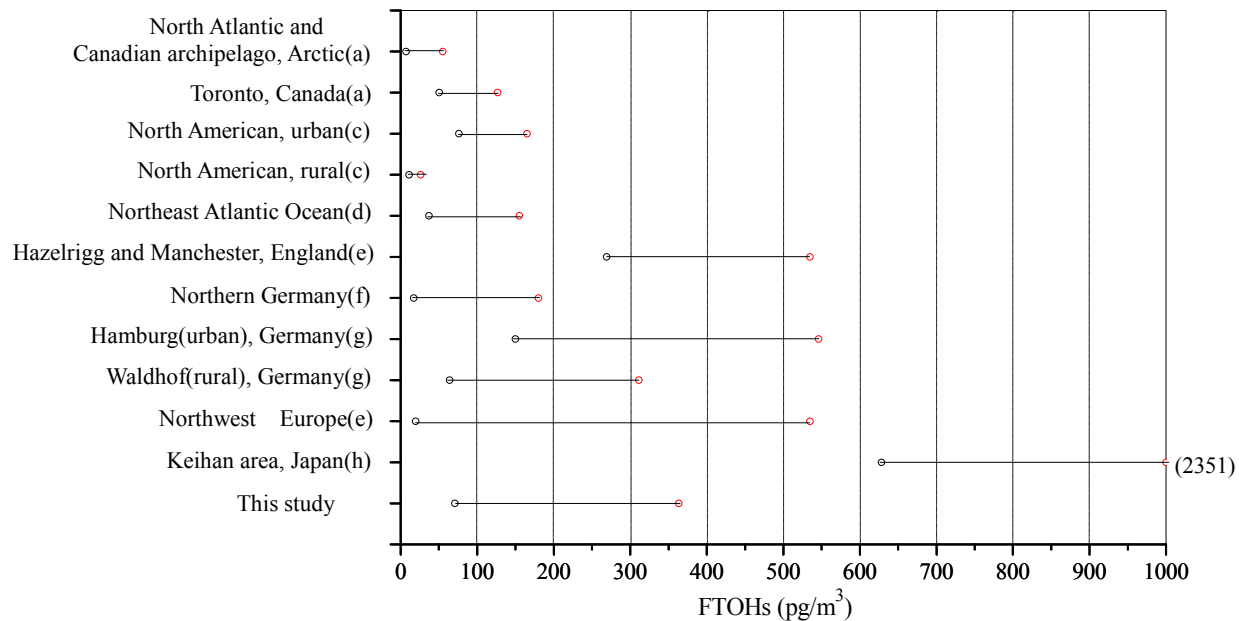
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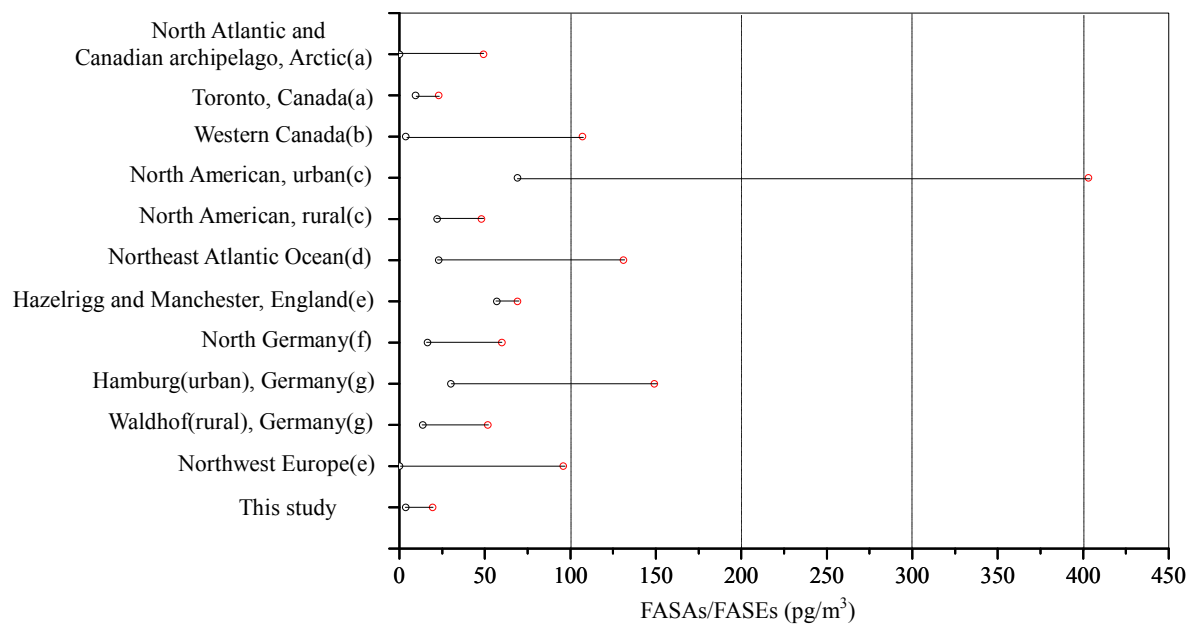

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504 **Figure 2.**

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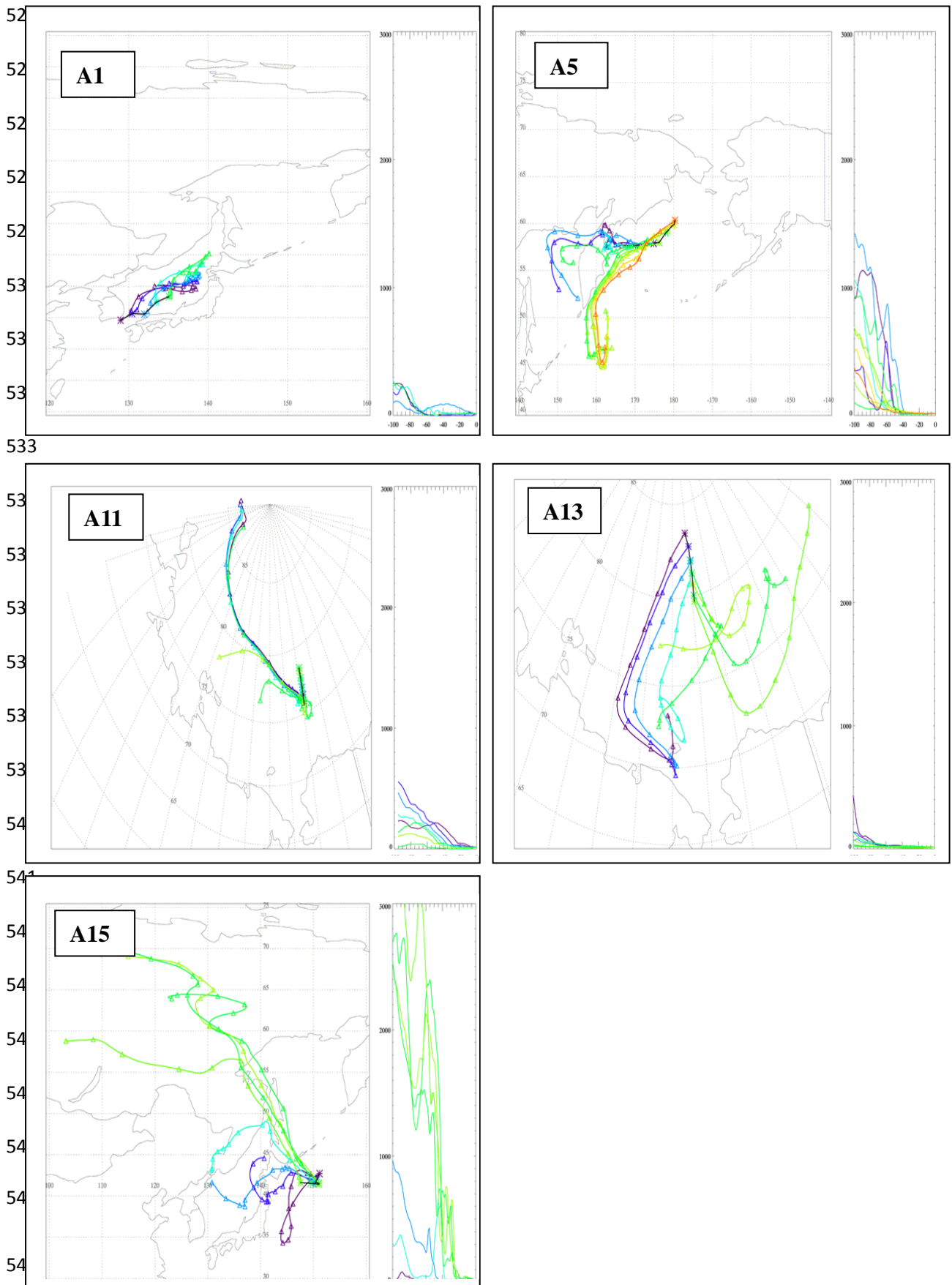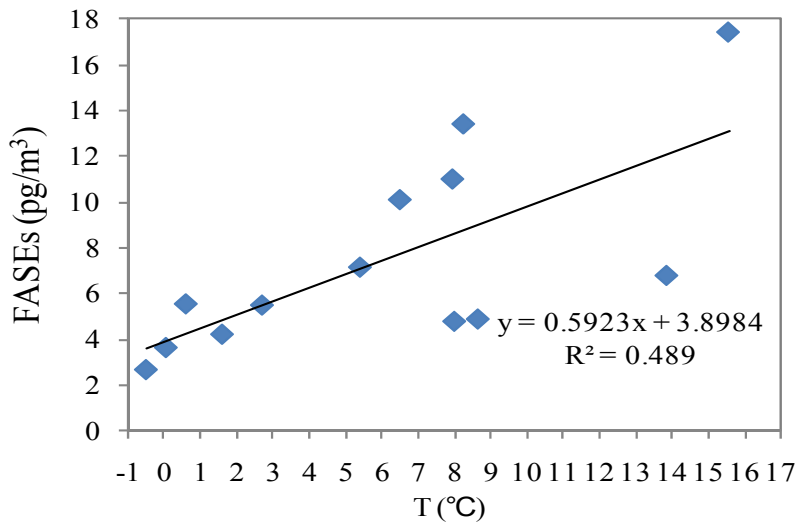
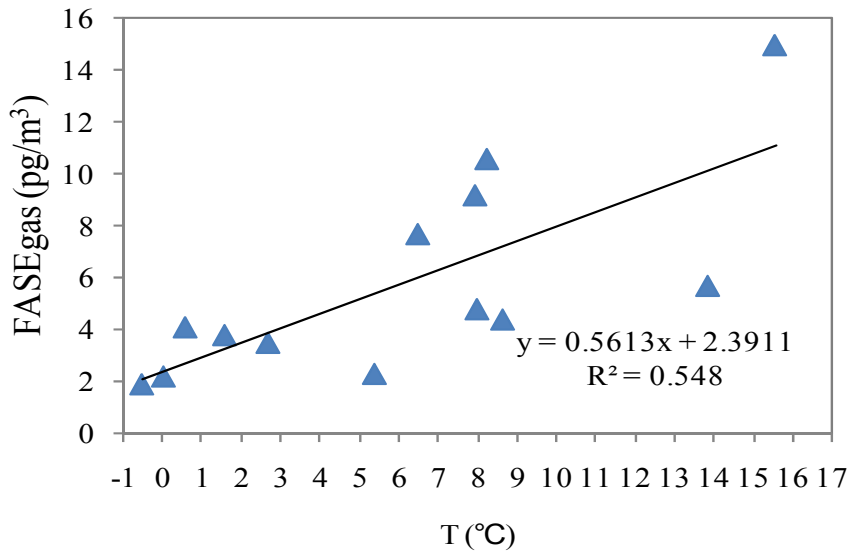515

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518 **Figure 3.**

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524 **Figure. 4**

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Figure 5.

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