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Distribution and long-range transport of polyfluoroalkyl substances in the Arctic, Atlantic Ocean and Antarctic coast

1 # *Distribution and long-range transport of polyfluoroalkyl*

2 # *substances in the Arctic, Atlantic Ocean and Antarctic coast*

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15 **Abstract**

16 The global distribution and long rang transport of perfluorinated compounds (PFCs) were

17 investigated with marine surface water samples collected from Greenland Sea, east Atlantic

18 Ocean and Southern Ocean (80°N to 71°S) in 2009 to 2010. 76 samples were solid-phase

19 extracted using Oasis WAX cartridges and concentrations of 15 perfluoroalkyl carboxylic acids

20 (PFCAs) and perfluoroalkyl sulfonates (PFSAs) were determined by liquid chromatography-

21 electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS). Temporal tends of PFCs in

22 Atlantic Ocean were discussed in 2008, 2009 and 2010. The decreasing trend of $\sum$PFCs

23 concentration was attributed to the phased out of perfluorooctane sulfonyl fluoride (POSF) and

24 perfluorooctanoic acid (PFOA) in global area, while since the short chain compounds which were

25 substitutes of C8 compounds were widely produced and used, the increasing trends in the marine

26 water could be found in North and Middle Atlantic Ocean. PFOA and PFOS undergo long range

27 transport via atmospheric and hydrospheric paths from emission area to Polar Regions. The snow

28 and ice melting elevated the PFOA level in Greenland Sea implying the climate change could

29 strengthen the release from Arctic region. The marine current transport played a major role in

30 Atlantic Ocean while the atmospheric deposition was the main dynamic in Southern Ocean.

Introduction

Perfluorinated compounds (PFCs) include a large number of chemicals which are resistant to general environmental degradations. Because of their combination characteristics of lipophobic and hydrophobic, PFCs have been widely used as adhesives; water repellent coatings and fire fighting foams for over 50 years[1, 2]. The annual production of neutral fluorotelomer alcohols (FTOHs) was estimated to 11 000 ~ 14 000 t after 2002, and the global historical production was 44000 ~ 8000 t for perfluoroalkyl carboxylic acids (PFCAs) (1951-2004) and 96 000 t for perfluorooctane sulfonyl fluoride (POSF) (1970-2002), respectively [3-5]. Due to their large amount manufacture and application, PFCs have been detected ubiquitously in air, water, sediment, wildlife and human beings all around the world [6-11].

Different chemicals present distinguishing environmental behaviors. The volatile precursors, such as fluorotelomer alcohols (FTOHs) could undergo long-range atmospheric transport (LRAT) and degraded via abiotic and biotic mechanisms [12, 13]. The detection of FTOHs in Arctic and Antarctic air agreed with the model prediction and conclusion [4, 14], which supported the hypothesis of the atmospheric pathway to remote area. The ionic PFCAs and perfluoroalkyl sulfonates (PFSAs), which have higher solubility, mainly distributed in surface water. PFCAs and PFSAs have been detected in all of the oceans as well as some remote lakes[15, 16]. The global transport by marine current was suggested to be the major path to delivery PFCs to nonemission region by both monitoring and modeling results [17, 18]. As the bioaccumulation potential of PFCs, especially some long-chain PFCs, the possible adverse effects to creatures were suggested.

The polar areas receive PFCs via atmospheric and marine current transport. Armitage et al estimated the flux of PFO to Arctic region was 8-23 t/a from direct emissions, and Prevedouros et al calculated the amount of PFO transported by ocean water to 2-12 t/a employing the water

55   inflow to Arctic Ocean[5, 19]. Hydrospheric transport was stressed because of the larger amount

56   in water, even though higher concentrations were measured in Arctic snow than seawater [20].

57   As the circulation of marine water in Arctic Ocean, the PFCs in water could be imported out of

58   the polar area. During the melting seasons, the floating ice and the ice cap at Greenland and

59   Canadian Archipelago input PFCs from atmospheric deposition and sea-spray to the water

60   body[21]. Since the climate became warmer in the last 50 years, the influence to POPs transport

61   and fate was concerned by chemists. Rapid ice melting in Arctic area possibly accelerates the

62   release of POPs stored in the ice and snow.

63   In this study, the levels and distribution of PFCs in surface water in Greenland Sea (GS),

64   Atlantic Ocean (AO) and Southern Ocean (SO) were investigated. The occurrence of

65   perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) at Antarctic Peninsula coast

66   were reported. We argued the influence of snow and ice melting to the PFCs transport to Arctic

67   region, investigated the temporal trend of PFCs in AO and discussed long rang transport

68   pathways in three open seas.

69

70   **Materials and method**

71   **Sampling campaign.** A total of 76 marine surface water samples were collected with *Research*

72   *Vessel Polarstern* (Alfred-Wegener-Institute (AWI), Bremerhaven) in two cruises (See Table

73   S1). The first cruise ARK XXIV/3 was performed in GS, from 68.9 to 80.2°N in August 7th to

74   September 16th, 2009, and the second cruise ANT XXVII was performed in east AO from

75   50.2°N to 59.2°S and the SO from 61.4 to 70.9°S during October 27th 2010 to January 1st 2011.

76   2 liter water samples were taken in brown glass bottles onboard by the stainless intake systems at

77   approximately 11m below the surface. The filtration was operated onboard using glass fiber

78   filters (GF/C, Whatman, Ø47 mm, >1.2 μm). The filtrates were stored at 4°C prior to solid-phase

79 extraction (SPE) on ship. In previous studies, the mass of particles collected at filters from 2 liter

80 open sea water was too small and no PFCs was detected, so the filters in these two cruises were

81 not analyzed. 100 mL Millipore water was treated as dissolved phase field blank.

82 **Chemicals.** 15 PFCs were involved including C4-C10 PFSAs, and C5-C6, C8-C16 PFCAs. 8

83 mass labeled PFCs were used as Internal Standards (IS) i.e. carbon labeled ionic PFCs and

84 oxygen labeled perfluorohexanesulfonate (PFHxS). 2H-perfluoro-[1,2-^{13}C2]-2-decenoic

85 acid(MFOUEA) was used as the injection standard (InjS) (See Table S2). Methanol (Suprasolv)

86 and ammonium hydroxide (25%, Suprapur) were purchased from Merck (Darmstadt, Germany).

87 Millipore Water was produced by a Milli-Q Plus 185 system by Millipore (Zug, Germany). The

88 methanol was distilled in a glass apparatus before using, and the water was cleaned through

89 cartridges as real samples (see Extraction and analysis) to remove PFCs in it.

90 **Extraction and analysis.** The extraction was performed onboard using glass funnels and

91 polymer cartridges. 400 pg (20 µL, 20 pg/µL) IS mixture were spiked into the filtrate before

92 extraction and Oasis WAX cartridges (Waters, 150 mg, 6 cm3, 30 µm) were employed for SPE.

93 The pre-treatment of the cartridges and the extraction processes were described elsewhere with

94 some modification(22). Briefly, the cartridges were first preconditioned by 10 mL methanol and

95 Millipore water, then loaded with samples at a speed of 2 drops per second and after that, they

96 were stored at -20°C sealed by aluminum bags until eluted in a clean laboratory. In the clean

97 laboratory(class 10 000), the cartridges were first washed by 15 mL precleaned Millipore water to

98 remove the salt which could affect the instrument and then dried by a vacuum pump with another

99 preconditioned cartridge on top to remove the PFCs in the air that flowed though the cartridges.

100 The dried cartridges were eluted with 10 mL 0.1% ammonium hydroxide in methanol and the

101 elutes were reduced to 150 µl under a soft nitrogen (>99.999%) flow. Before injection into the

102 instrument, 1000 pg (50 µL, 20 pg/µL) MFOUEA were spiked into the vials.

103　The instrument analysis was performed using a high performance liquid chromatography-

104　negative electrospray ionisation-tandem mass spectrometry system (HPLC-(-) NEI-MS/MS) with

105　a HP 1100 HPLC system (Agilent Technologies) coupled to an API 3000 triple-quadrupole

106　(Applied Biosystems/MDS SCIEX). The instrument programme was described elsewhere(22).

107　Internal standards method was applied in quantification with an external 8 point calibration (0,

108　0.5, 1, 2.5, 5, 7.5, 10, 13 pg/μL).

109　**QA/AC.** Instrument detect limits (IDLs) were determined at a signal to noise (S/N) ratio of

110　three ranging from 3.9 pg (PFHxA) to 31 pg (PFBS). The method detect limits (MDLs) were

111　determined in two ways. When the mass of the compounds in blank samples were below the

112　IDLs, the MDLs were replaced by method quantification limits (MQLs), which were determined

113　at a signal to noise (S/N) ratio of ten, otherwise, the MDLs were determined at a 98% confidence

114　interval level multiply the standard deviation plus the average blank. ? field blank were involved

115　in the two cruises, and another 5 blank were taken in the clean lab to supervise the extraction

116　process. PFPA, PFHxA, PFOA and PFOS could be detected in blank samples at pikogram per

117　liter. The MDLs ranged from 5.9 pg/L (PFHxA) to 51 pg/L (PFBS). Three break though tests

118　were taken during the ARK XXIV/3 cruise and the mass of PFCs were all below the IDLs in the

119　second cartridges. Duplicated samples showed the deviation in ±15% range. 10 mL methanol and

120　0.1% ammonium hydroxide in methanol were reduced to 200 μL for injection to check the

121　solvent blank and no PFCs were detectable. In the calibration curve, the point of 0 pg/μL was

122　prepared by only spiking IS mixture and InjS in methanol, and only the peak IS and InjS could be

123　integrated indicating no native PFCs were introduced during the preparation of calibration. The

124　instrument modification was described elsewhere (23, 24). The recoveries ranged from

125　32%±15% (^{13}C-PFDoDA) to 76%±13 % ($^{18}O_2$-PFHxS) in cruise ARK XXIV/3, and 38%±14%

126　($[^{13}C_2]$-PFDA) to 66% ± 22% ($[^{13}C_4]$-PFOA) in cruise ANT XXVII (See Table S3).

127   **Result and Discussion**

128   **Concentrations of PFCs in marine surface water.** In the 76 marine surface water samples, 8

129   out of 15 PFCs were quantified in GS, AO and SO (i.e. PFPA, PFBS, PFHxA, PFHxS, PFHpS,

130   PFOA, PFOS and PFNA, see Table S4). The ∑PFCs concentrations varied from <MDL to 650

131   pg/L, and the average concentrations declined in the following order in three sea/oceans: AO

132   (260 pg/L)> GS (140 pg/L) > SO (30 pg/L).

133   In GS, the ∑PFCs concentrations ranged from 48 to 270 pg/L. The five most frequently

134   detected compounds were PFOA, PFHxS, PFHxA, PFOS and PFBS (See Figure 1.). PFOA was

135   detected in all 25 samples with a concentration range from 45 to 160 pg/g, accounting for 42% to

136   94% of total PFCs. Caliebe et al reported similar concentration range in GS in 2005, indicating

137   the level didn't changed very much(*25*). The perfluorooctanoate (PFO) concentration in northern

138   polar zone were predicted to increase until 2030 and decrease afterwards (*19*). The quite

139   consistent levels in 2005 and 2009 might imply the shorter time to reach to the extreme values.

140   Comparing with the concentration in Canada Arctic water, the level of PFOA in GS was two

141   times lower, while the concentrations of PFOS were quite comparable. Young et al reported the

142   PFCs concentration in Canadian caps (*21*). The concentration of PFOA was at the same range,

143   while PFNA could not be detected in most samples in this study. The short chain PFCs, i.e. PFBS

144   and PFHxA were quantified in 24% and 56% total samples with the concentrations ranging from

145   <51 to 65 pg/L and <5.9 to 38 pg/L, respectively. That could attribute to the shift of usage from

146   C8 to C4-6 PFCs after the voluntary phase-out of POSF and PFOA from 2000(*16, 26*). PFHxS

147   could be frequently quantified in 88% samples at a low level of <6.5 to 45 pg/L. Stock et al.

148   reported elevated level of PFHxS in Resolute Lake, Canada, and the local input was suggested as

149   the source(*27*). In GS, the concentration was two to three orders of magnitude lower than that in

150   Canada Arctic region. Because of no industrial source located nearby, the PFHxS probably came

151   from the emission areas. J. Busch., et al collected water samples in the same cruise(28). The

152   result agreed well with this study except the PFOSA, which was not included in this study. They

153   reported PFOSA was the predominant PFCs in Arctic water but it was unexpected in remote

154   marine water although higher concentration had been reported in ice cores (29).

155   In AO, PFCs were mainly detected in north hemisphere (See Figure 2.). From 50°N to 20°N,

156   the concentration of ∑PFCs ranged from 250 to 650 pg/L, it decreased to 11 to 140 pg/L in 20°N

157   to 15°S, and in 15°S to 60°S, the concentrations were all below the MDL. The highest

158   concentration was detected in English Channel and the second highest concentration was found in

159   the Bay of Biscay, which agreed with former study(22). Mclachlan et al investigated the riverine

160   discharge of PFCAs in Europe(30). The concentration of ∑PFCs was quantified to be 60 ng/L in

161   Thames River, 27 ng/L in Seine River and 8.1 ng/L in Loire River, respectively, suggesting the

162   local discharge could be the possible source. Comparing with other sites near the European coast,

163   the elevated level could attribute to the abundance of PFPA and PFHxA. The dominant

164   compound in the Bay of Biscay was PFPA (29%) followed by PFOA accounting for 27% of

165   ∑PFCs, while it was the third abundant one (19%) in English Channel following PFOA (21%)

166   and PFOS (20%). PFPA was usually detected in urban rivers and waste water treatment plant

167   effluent, and it could not be effectively removed by common treatment techniques as well as

168   filtration through activated carbon. The abundance of PFPA could be attributed to the direct

169   release from the urban and industrial region and the defected water treatment processes (Wilhelm

170   et al.; Ahrens et al., 2009b). The Pearson analysis (See Table S6) suggested the sources of

171   detectable PFCs were positively related which were the direct emissions.

172   PFOA and PFOS could only be detected in 1 and 3 SO samples, respectively (See Figure 3.).

173   The concentrations of PFOS were higher than PFOA in detectable samples which could be

174   explained by the rapid transport of PFOS precursors via atmosphere(16, 31).. Ahrens et al and

175   Wei et al reported the PFOS concentration in the similar range at the coast, and no PFCs could be

176   detected at more open area *(16, 32)*. The occurrence in Antarctic biota samples strongly

177   supported the long rang transport, although only trace concentration could be quantified in water

178   samples*(33-35)*. Local input was another possible source of PFCs in Antarctica. The Peninsula

179   that supports 19 stations and around 1000 people in the warm season was a hot spot*(14)*. Whilst,

180   PFCs were all under the MDL along the west coast of Peninsula so that it was not confidential

181   enough to confirm the importance of local source hypothesis.

182   **Temporal trends of PFCs in Atlantic Ocean.** With the studies conducted by Ahrens et al in

183   2007 and 2008, the comparison in Atlantic Ocean (AO, from 46°N to 60°S) was credible due to

184   the same sampling vessel and similar laboratory conditions and treatment method*(16, 22)*(See

185   Table 1. and Figure S2). The ∑PFCs concentration decreased from 2007 to 2010 (96 to 824 pg/L

186   in 2007, 289 to 468 pg/L in 2008 and 120 to 380 pg/L in 2010) in North Atlantic Ocean (NAO,

187   46° to 20° N, the sites in the Biscay Bay were excluded) which could explained by the phased out

188   of POSF and PFOA by Europe and global. In Middle Atlantic Ocean (MAO, 20°N to 0°), the

189   concentration of ∑PFCs increased from 2007 to 2008 while decreased from 2008 to 2010. PFDA,

190   PFUnDA and PFDoDA were only detected in 2008 at a range of tens of pikogram per litre.

191   PFHxS and PFPA could be found in 2008 and 2010 and the concentration of PFHxS increased

192   from 2008 to 2010, while PFPA were quite consistent (See Figure S2). PFBS, PFOS, PFHxA,

193   PFOA and PFNA could be quantified in all involved years. PFBS and PFHxA were mainly

194   distributed in NAO and MAO with an increasing trend from 2008 to 2010. In NAO, PFHxA

195   accounted for 9% to 14% of ∑PFCs concentration in 2008 while the percentage increased to 17%

196   to 35% in 2010. PFBS had been found in European rivers and coast in previous studies *(1, 23, 36-*

197   *38)*. In this study, it was only reported in two sites but at higher level comparing with those in

198   2007 and 2008. The less frequent detection was partly due to the high MDL. These increasing

199   trends of PFHxA and PFBS could be attributed to the usage shift to shorter chain compounds as

200   well as the substitute of volatile PFCs, i.e. MeFBSE which could degraded to PFBS in

201   atmosphere *(39)*. PFOS were reported in only four sampling sites in 2007, while, in 2008, it

202   could be detected from 45°N to 60°S. The frequent occurrence didn't continue to 2010, and the

203   concentrations were all below MDL from 5° to 60°S. The concentration of PFOA didn't change a

204   lot near European coast from 46° to 40°N, but it increased from 2007 to 2008, and decreased in

205   2010 to the similar level as that in 2007 from 40° to 20°N. Same to PFOS, PFOA could only be

206   detected in South Atlantic Ocean (SAO) in 2008. The frequent detection and relatively high

207   concentration in 2008 implied an intensive release of PFOA and PFOS between 2007 and 2008.

208   PFNA was more frequently detected than PFOA (71% for PFNA, 57% for PFOA) in 2007, and

209   the concentration were higher than those in 2008 and 2010. Different from other long chain

210   PFCs, PFNA showed quite consistent level in 2008 and 2010, and it was mainly detected in

211   NAO.

212   **Large scale long range transport.** The global transport of PFCs was confirmed in two ways:

213   the atmospheric delivery of volatile precursors followed by the oxidizing degradation and the

214   marine current transport of ionic compounds in the oceans. Both of these two ways could result in

215   the detection of PFCs in remote and polar areas. Some modelling and monitoring result supported

216   the more important role of marine current transport due to the larger amount of flux and the

217   consistent variation pattern to the current direction change. PFOA and PFOS are representative

218   for the long range transport research *(19, 40)*.And in this study, they were the only two

219   compounds which could be detected in all the targeted sea and oceans.

220   As the intensive production and usage in European countries, the emissions of PFOA and

221   PFOS to the sea were estimated to ~31t/a and ~20 t/a, accounting for ~41% and ~25% of global

222   emission, respectively *(19, 41)*. The released PFCs from 45°N northward of European countries

10

223   combined with the PFCs delivered by the NAC form North America go on to transport to Arctic

224   region with the North Atlantic Current (NAC). The concentrations of PFOA near the bay of

225   Biscay and English Channel were comparable with those at North American coast and on way of

226   NAC to north, all of which could be the source in Arctic Ocean(22). The atmospheric transport to

227   Arctic region has been confirmed by monitoring work on air ice and snow, water and sediment in

228   remote lakes and the mechanism was argued in several models involving FTOHs and their major

229   degraded compound, i.e. PFOA(42).

230   Aksenov et al modelled the inflow and outflow of Arctic Ocean water (43, 44). Half of the

231   North Atlantic Water (NAW) inflow (1.2×10^6 m^3/s) into the Arctic Ocean through the Fram

232   Strait, and the other half through the Barents Sea (BS). Two opposite direction marine currents

233   run though the Fram Strait (See Figure 1.). In the east part, one branch of the Norwegian Current

234   (NC) delivery the warm marine water to high Arctic region, and in the west part, the East

235   Greenland Current (EGC) transports the recirculating Atlantic water, the Arctic Ocean water

236   masses and >90% Arctic Ocean ice to the south(45). In this study, we take part of the Greenland

237   Sea, 76°-81°N and 15°W ot 8°E covering the whole Fram Strait, and simply divided it into two

238   longitudinally average parts by 3°W. The PFOS concentrations were all below the MDL, while

239   the average concentration of PFOA in the west part (100 pg/L±27 pg/L, n=7) was twice as that in

240   the east (57 pg/L±16 pg/L, n=5). The concentration inputting to high Arctic agreed with previous

241   monitoring and modelling studies(19). The input mass of PFOA through the strait was estimated

242   to ~2.1 t/a. Ahrens et al investigated the PFCs concentrations in open North Sea, and Norwegian

243   Coast which have the potential to be transported to BS. PFOS could not be detected northern than

244   56°N, which is consistent to this study. The concentration of PFOA was from 0.03±0.005 to 0.07

245   ng/L, and the mass flow was calculated to ~2.6 t/a under the assumption that same concentration

246   could be found in Barents Sea. The total inflow of PFOA to high Arctic (80°N northward) was

247 4.7 t/a. This was underestimated comparing with previous studies conducted by Macdonal et al

248 (4.9×106 m3/s), but the flux was in the range of the result (2-12 t/a)from Pervedouros et al*(46)*.

249 Stemmler et al estimated 10~30 t/a PFOA imported to Arctic Ocean via Norwegian coastal

250 current and Armitage et al suggested 8~23 t/a from direct sources*(17, 19)*. The gap between

251 different modelling and between the modelling and monitoring was obvious. The fluxes

252 calculated from emission were much higher than that from on site monitoring concentration

253 multiplying the modelled water mass. Basically, the monitoring work focused on smaller scale,

254 and more details could be involved, but since the limit of sampling work, deeper water could not

255 be involved which might lead to the underestimation. On the other hand, for modelling, the large

256 scale concern reduces the resolution, so that not every factor could be included.

257 In all of the 25 surface water samples in Greenland Sea, the PFOA concentration was slightly

258 higher than the modelled result(25 to 90 pg/L), but quite comparable with that of Canadian Arctic

259 ice(12 to 150 pg/L). Significant correlationship could be found between salinity and the

260 concentration of PFOA (r^2=0.46, n=25, p<0.001), suggesting the fresh water enriched the PFOA

261 in this area (See Figure S1a). Moreover, with the exception of G4, the temperature also

262 significantly related to the concentration of PFOA (r^2=0.57, n=24, p<0.001), meaning the cooler

263 water presented higher level of PFOA (See Figure S1b). Considering the warm sampling season,

264 the elevated PFOA concentration in surface water could be attributed to the release of stored

265 mass in the ice and snow. Besides the melted ice and snow transported by EGC from high Arctic,

266 the melted cap on the Greenland could also enrich PFOA in GS. While, the slightly higher

267 concentration could be found at the coast than open sea indicating the local input was moderate

268 comparing with other sources. Young et al draw a conclusion that the Arctic perfluorinate acids

269 (PFAs) mainly came from the atmospheric transport and the flux of PFOA from Canadian caps to

270 Arctic region was estimated to 0.1 ~0.6 t/a, which was considered to be small comparing with

271 hydrospheric transport from modelling studies. The PFOA input from the fresh water could not

272 be considered as the atmospheric transport because the moving ice in Arctic Ocean might get

273 PFOA through sea spray. With the influence of fresh water, the outflow of PFOA though Fram

274 Strait was calculated to be 3.9 t/a, which was higher than the inflow. Two fifth of the Arctic water

275 outflow (1.2×10^6 m^3/s) through the strait towards south suggesting around 9.6 t/a PFOA were

276 transported southward to NAO and Canadian Archipelago(43).

277 　From 45° to 15°N, the major direction of surface water movement is to south, where the

278 Canary Current (CC) transports European emission southward (See Figure 2a). The PFOA

279 concentrations were quite consistent between 46° to 20°N, but they decreased below the MDL

280 between 20° to 10°N when the CC turn to the west and joins into the North Equatorial Current

281 (NEC). PFOS showed the similar distribution pattern between 40° to 20°N. The concentration

282 decreased from 30°N, after cross the Equator, it dropped to half of that at northern locations and

283 decreased below the MDL at 3°S southward. The Equatorial Current (EC) controlled the surface

284 water movement between 20°N to 0° where the PFOS concentration presented very slight

285 variation. EC is fed by water from NAC and African Coast, so that the PFOS in equator area

286 might origin from both the European emission and the African local input. Due to the

287 precipitation in Middle Atlantic region, the salinity presents the low value (34.0%) at station W16

288 but both the PFOA and PFOS didn't show outstanding increase indicating the limit influence of

289 wet deposition. Benguela Current (BC) brings Southern Ocean water and Pacific Ocean water

290 from south to north. No direct source were reported from African coast between 3° and 35°S and

291 the volatile precursors, i.e. 8:2 FTOH were at a low concentration which could not elevated the

292 level in marine water very much (47).

293 　In SO, both the surface and deep marine current could transport PFOA and PFOS from their

294 emission region, but with the long timescale, the hydrosphere delivery obviously could not catch

13

295　up the rapid wind transport*(14)*. Moreover, as the long distance and the powerful dilution effect,

296　the marine current transport might not be as effective as it was in Arctic region. At the tip of

297　Peninsula where PFOS and PFOA was detected, the Antarctic Circumpolar Current (ACC) runs

298　from the west to the east around the continent (See Figure 3.). The ACC gave a chance for PFCs

299　to distribute all around the Antarctic coast. It was predicted that when the PFCs accumulate to a

300　high level and the dilution function became week, they could be detected everywhere around

301　Antarctica.

302　　**PFCs release from polar region**. Covering the open sea area where the EGC influenced in this

303　study (3°W westward, n=15), the concentration of PFOA was 44 to 160 pg/L. The outflow of

304　high Arctic water through Fram Strait was estimated to be 1.7- 5.9 t/a. That was the source in

305　west GS where few direct input occurred and could elevate the level in west Greenland coast.

306　Almost half of the mass could be transported to the NAO which was two to four orders of

307　magnitude lower comparing with the total inventory in the AO water *(5)*. Three fifth ocean

308　outflow run out of Arctic Ocean though the Canadian Archipelago carrying 2.6- 8.9 t/a PFOA,

309　which could be the source in the ice because of the sea spray. The global surface temperature

310　increased by 0.13°C ± 0.03°C per decade in the last 50 years, and the Arctic was predicted to be

311　ice-free ($<10^6 km^2$) by 2037 according to Wang et al*(48-50)*. Valle et al suggested that the rising

312　temperature probably strengthened the ability of PCB and PCDD/F for the long rang atmospheric

313　transport*(51)*. Considering the climate change, the PFCs accumulated in the last 50 years could

314　be released to the water body in a short time, and elevated the level all around the Arctic Ocean.

315　Because of the lack of concentration in Arctic floating ice and Greenland caps, it was difficult to

316　estimate the increased flux resulted from climate change. Long-term monitoring should be

317　conducted in the future.

318   In Antarctica, Trevena et al reported elevated dimethylsulphide (DMS) concentration was

319   associated with the release of sea ice in melting season(52). It was reasonable that the PFCs

320   deposited from the air to the ice could be released in summer and spring. But since the trace

321   concentration and small amount, the influence could not be detected at farther area.

322   **Acknowledgement**

327   **Supporting Information Available**

328   Tables and Figures on the sampling locations, target analysts, recoveries of internal standards,

329   individual concentrations, global comparison of PFCs in surface water, coefficient of Pearson's

330   2-tailed analysis, correlations between PFOA concentration and salinity and water temperature,

331   temporal and latitudinal distribution of PFCs.

332   **Reference**

333

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Table 1. Temporal comparison of individual PFC concentrations in surface water from Atlantic Ocean (ng/L)

Location	Year	n	PFBS	PFHxA	PFHxS	PFOS	PFPA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	FOSA	ΣPFCs
NAO[a]	2007	40	<1.6-60	<5.7-127	nd	<10-291	nd	<4.0-229	<5.1-107	nd	nd	nd	<17-307	nd-1115
	2008	21	<4.4-50	38-117	8.3-53	45-232	28-100	<85-223	<3.0-39	8.5-37	21-66	<5.9-48	<3.0-65	259-1004
	2010	13	<51-84.3	40-85	<6.5-61	<20-100	16-170	<13-160	13-39	<21	<13	<25	<83	130-650
MAO[b]	2007	10	<1.6	<5.7	nd	<10-60	nd	<4.0-87	<5.1-35	nd	nd	nd	<17-60	27-187
	2008	5	<4.4-17	20-31	8.1-14	62-77	21-35	49-70	4.4-25	19-35	26-30	<5.9	<3.0	161-266
	2010	5	<51	33-38	<6.5-12	40-59	<13-32	<13	<12-16	<21	<1	<25	<83	83.0-140
SAO[c]	2007	10	<1.6	<5.7	nd	<10	nd	<4.0	<5.1	nd	nd	nd	<17-53	nd-53
	2008	13	<4.4-13	<3.0-26	<4.1-17	<11-72	<14-24	<5.2-62	<3.0	<5.5-27	<11-28	<5.9	<3.0	n.d-266
	2010	16	<51	<5.9	<6.5	<20-45	<13	<13-15	<12	<21	<13	<25	<83	n.d.-45

[a] NAO:North Atlantic Ocean; [b] MAO:Middle Atlantic Ocean; [c] SAO:South Atlantic Ocean
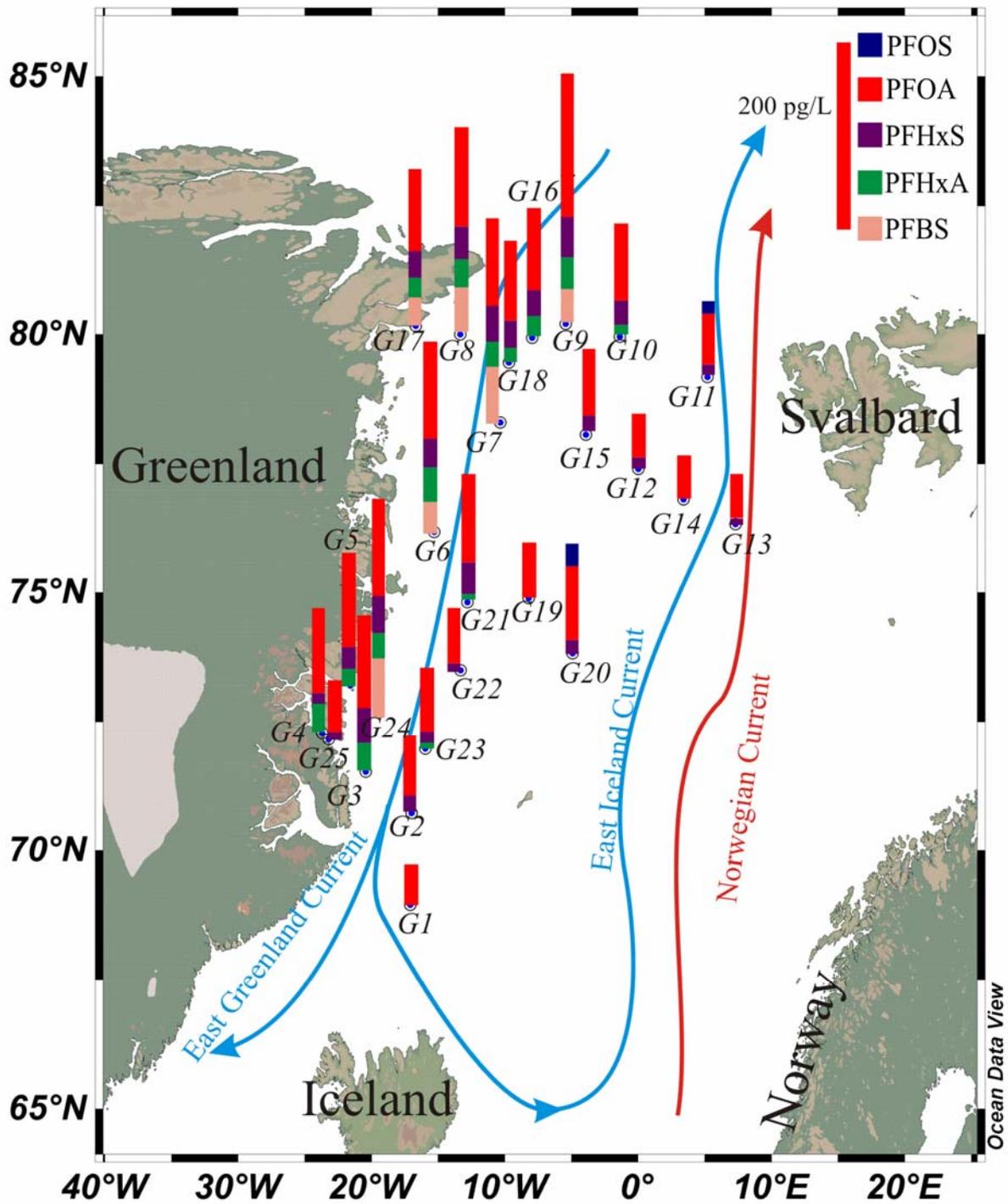
Figure 1. Sampling locations and concentrations of PFHxA. PFHxS. PFOA and PFOS (pg/L) in surface water of Greenland Sea. The red line with arrow represents the warm current. The blue lines with arrow represents the cold current.
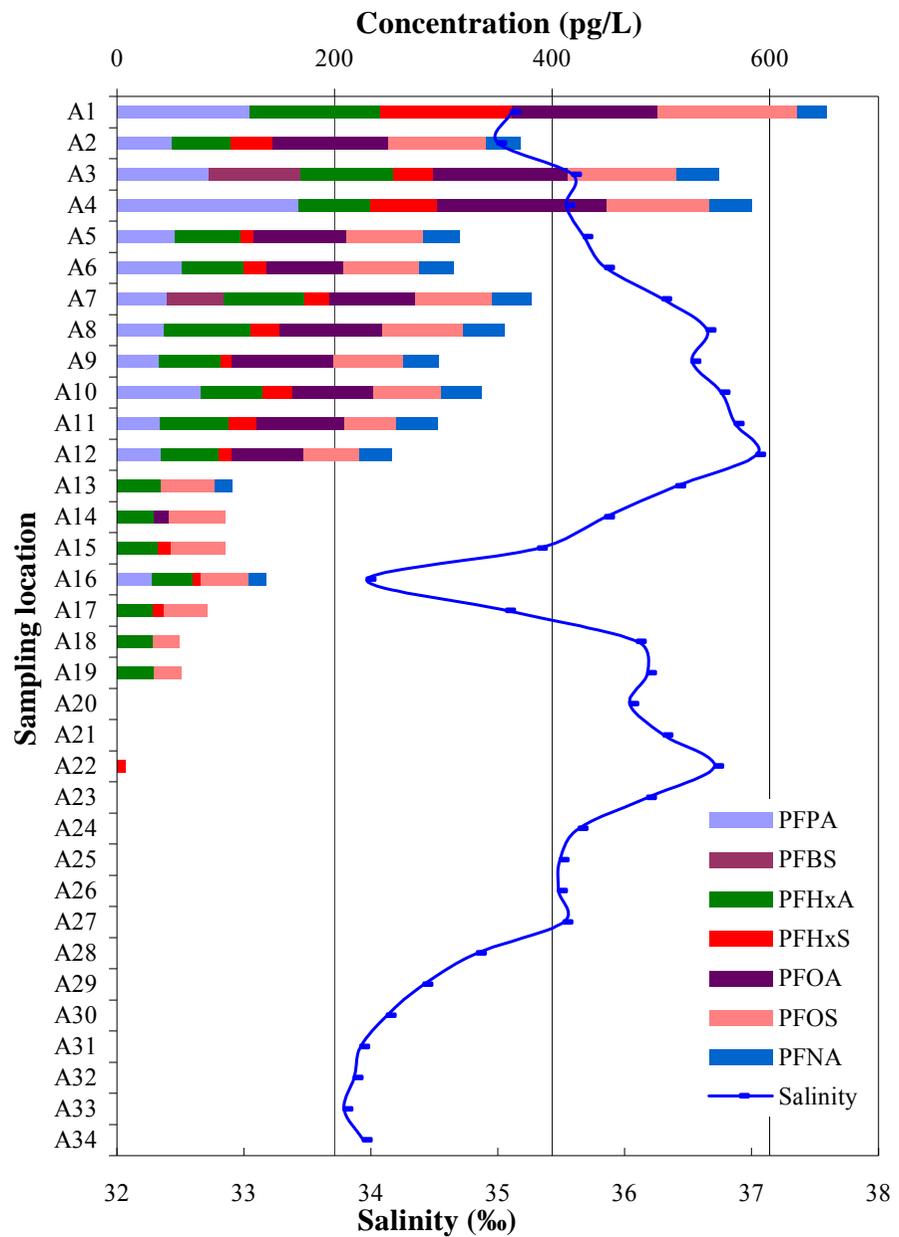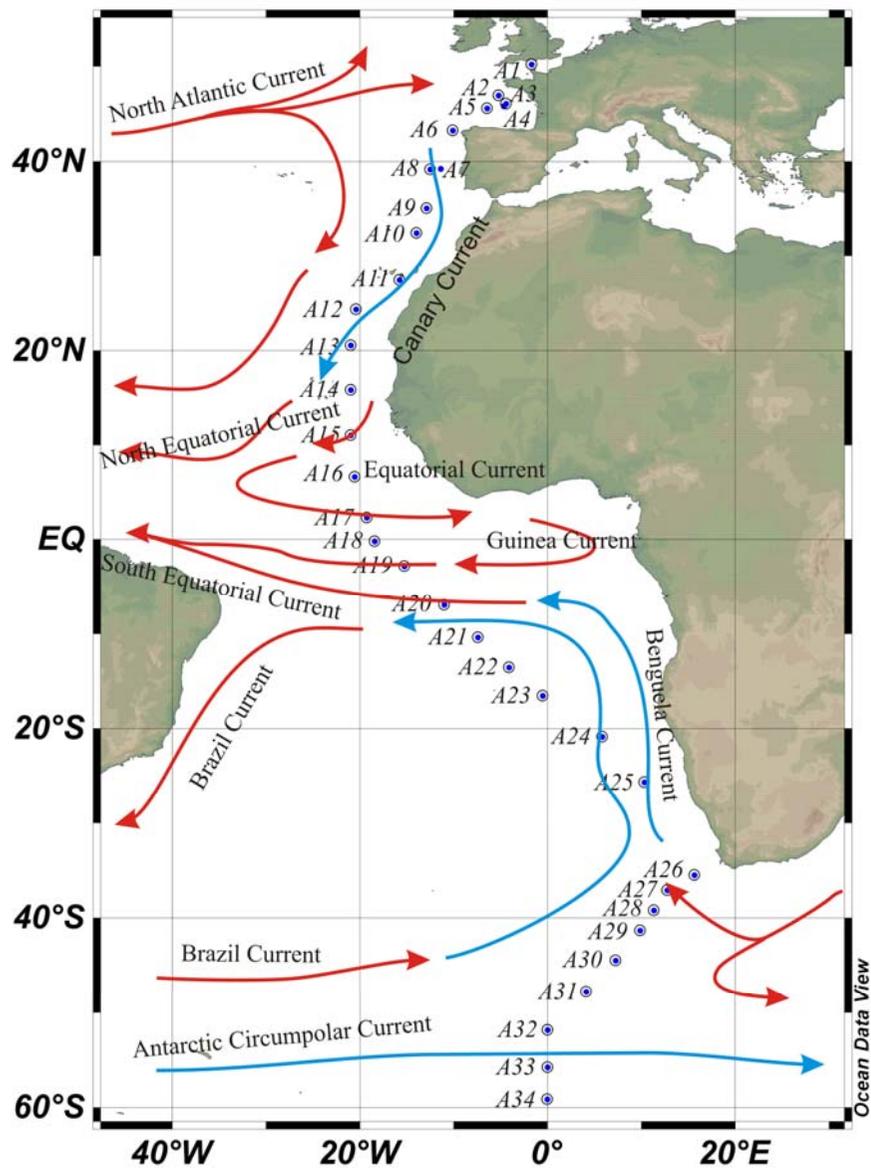
Figure 2a. Sampling locations in Atlantic Ocean. The red and blue lines with arrows represent the warm and cold current, respectively. **2b.** Concentrations of PFCs (pg/L) and water salinities (‰)in Atlantic Ocean.
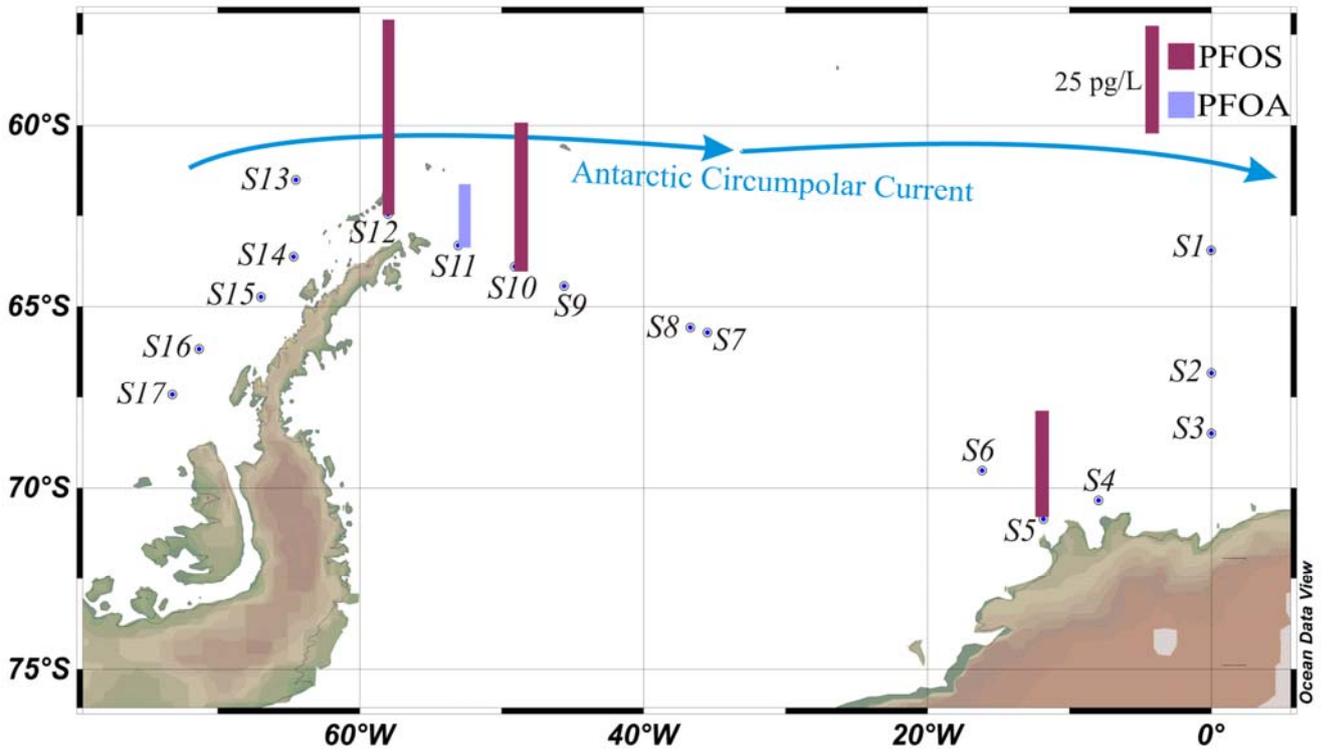
Figure 3. Sampling locations and concentrations of PFOS and PFOA (pg/L) in surface water of Sourthern Ocean. The bule lines with arrow represents the cold current.