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

Zhen Zhao a,b,c, Zhiyong Xie a,*, Axel Möller a, Renate Sturm a, Jianhui Tang b, Gan Zhang d, Ralf Ebinghaus a

a Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Institute of Coastal Research, Geesthacht, Germany
b Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research, CAS, Yantai 264003, China
c Graduate University of Chinese Academy of Sciences, Beijing 100049, China
d Guangzhou Geochemistry Institute, CAS, Guangzhou 510640, China

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The global distribution and long-range transport of polyfluoroalkyl substances (PFASs) were investigated using seawater samples collected from the Greenland Sea, East Atlantic Ocean and the Southern Ocean in 2009–2010. Elevated levels of ZPFASs were detected in the North Atlantic Ocean with the concentrations ranging from 130 to 650 pg/L. In the Greenland Sea, the ZPFASs concentrations ranged from 45 to 280 pg/L, and five most frequently detected compounds were perfluorooctanoic acid (PFOA), perfluorooctanesulfonate (PFOS) and perfluorooctane sulfonate (PFOS) and perfluorobutane sulfonate (PFBS). PFOA (15 pg/L) and PFOS (25 pg/L) were occasionally found in the Southern Ocean. In the Atlantic Ocean, the ZPFASs concentration decreased from 2007 to 2010. The elevated PFOA level that resulted from melting snow and ice in Greenland Sea implies that the Arctic may have been driven by climate change and turned to be a source of PFASs for the marine ecosystem.

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1. Introduction

Polyfluoroalkyl substances (PFASs) include a large number of chemicals resistant to degradation processes in the environment. Combining lipophobic and hydroophobic properties, PFASs have been widely used as adhesives, water-repellent coatings, and firefighting foams for over 50 years (Kissa, 2001; Prevedouros et al., 2006). The annual production of neutral fluoroelomer alcohols (FTOHs) was estimated as 11,000–14,000 t after 2002, and global historical production was 44,000–80,000 t for perfluoroalkyl carboxylic acids (PFCAs) (1951–2004) and 96,000 t for perfluorooctane sulfonyl fluoride (PFOS) (1970–2002), respectively (Prevedouros et al., 2006; Dinglasan-Panlilio and Mabury, 2006; Paul et al., 2008). PFASs have been detected ubiquitously in air, water, sediment, wildlife and human beings all around the world as a result of their decades-long manufacture and applications (Schiavone et al., 2009; Bao et al., 2010; Genualdi et al., 2010; Kato et al., 2011; Li et al., 2011; Meyer et al., 2011).

Atmospheric transport and global ocean currents were suggested as the pathways of the PFASs global transport. Volatile precursors, such as FTOHs, can undergo long-range atmospheric transport (LRAT) and can be possibly degraded via abiotic and biotic mechanisms (Ellis et al., 2004; Martin et al., 2005). The detection of FTOHs in the Arctic and Antarctic air agreed with the model prediction and conclusion, which supported the hypothesis of atmospheric transport toward remote regions (Paul et al., 2008; Dreyer et al., 2009; Bengtson Nash et al., 2010). Ionic PFCAs and perfluoroalkyl sulfonates (PFASs), which have higher water solubility, are mainly distributed in surface waters. PFCAs and PFSAs have been detected in global oceans as well as in some remote lakes (Yamashita et al., 2005; Ahrens, 2011). Global transport by marine ocean currents was indicated as the major pathway of PFASs delivery to non-emission regions by both monitoring and modeling results (Yeung et al., 2009; Stemmler and Lammel, 2010). Significant relationship had been reported between PFASs concentration and mortal disease in marine organisms, and world wide detection of PFASs in serum has been of utmost concern (Kannan et al., 2006; Bonefeld-Jorgensen et al., 2011; Shankar et al., 2011).

Armitage et al. (2006) estimated that the PFOA flux to Arctic region was 8–23 t/a from direct emissions, and Prevedouros et al. (2006) calculated the amount of perfluorooctanoic acid (PFOA) transported to the Arctic Ocean by water as 2–12 t/a. Hydropheric transport was stressed due to the larger amount of PFASs in marine water than in air, although higher concentrations were measured in...
Arctic snow, which resulted from atmospheric deposition (Theobald et al., 2007). Considering the marine water circulation of within the Arctic Ocean, PFASs in the water could be exported out of the polar area. During melting seasons, the floating ice and the ice cap at Greenland and Canadian Archipelago release PFASs from atmospheric deposition and sea-spray to the water body (Young et al., 2007). Inasmuch as the climate has become warmer in the last 50 years, the influence on persistent organic pollutants (POPs) transport and fate has become a concern for scientists (Macdonald et al., 2005). Rapid ice melting in the Arctic area could have possibly accelerated the release of POPs stored in ice and snow (Macdonald et al., 2005; Ma et al., 2011).

In this study, the levels and distribution of PFASs in surface water of the Greenland Sea, Atlantic Ocean (AO) and Southern Ocean were investigated. The occurrence of perfluorooctane sulfonate (PFOS) and PFOA at Antarctic Peninsula coast were reported. The influence of snow and ice melting on the PFASs transport to Arctic region were considered, the temporal trend of PFASs in the AO were investigated and the long-range transport pathways within the three oceans were discussed.

2. Materials and methods

2.1. Sampling

A total of 76 marine surface water samples were collected by the Research Vessel Polarstern (Alfred-Wegener-Institut (AWI), Bremerhaven) during two cruises (Table S1). The first cruise (ARK-XXIV/3) was performed in the Greenland Sea, from 68.9 to 80.2° N from August 7 to September 16, 2009, and the second cruise (ANT-XXVII/1 + 2) was performed in East Atlantic from 50.2° N to 59.2° S and in the Southern Ocean from 61.4 to 70.9° S from October 27, 2010, to February 1, 2011. Two liter water samples were collected in brown glass bottles via the ships intake seawater pump (stainless steel only) at approximately 11 m below sea level. The filtration was operated on board using glass fiber filters (GF/C, Whatman, Ø47 mm, >1.2 μm). The filtrates were stored at 4 °C prior to solid-phase extraction (SPE) on board the ship. In previous studies, the mass of the particles collected by the filters from the 2 L open seawater was very small, and no PFASs was detected in it (Busch et al., 2010); therefore, the filters in these two cruises were not analyzed. An amount of 100 mL Millipore water was treated as field blank for the dissolved phase.

2.2. Chemicals

In this study, the levels and distribution of PFASs in surface water of the Greenland Sea, Atlantic Ocean (AO) and Southern Ocean were investigated. The occurrence of perfluorooctane sulfonate (PFOS) and PFOA at Antarctic Peninsula coast were reported. The influence of snow and ice melting on the PFASs transport to Arctic region were considered, the temporal trend of PFASs in the AO were investigated and the long-range transport pathways within the three oceans were discussed.
1.5 pg/L to 17 ng/L in 2005, respectively) (Stock et al., 2007). The PFHxS could have been probably transported from the faraway direct source regions because no industrial source is located nearby. Busch et al. (2010) collected water samples from the same cruise, and showed comparable results (Table S5).

In the Atlantic, PFASs were mainly detected in the northern Atlantic (Fig. 2 and Table S4). From 50° N to 20° N (A1—A13), the ∑PFAS concentration ranged from 250 to 650 pg/L. It decreased to 8—140 pg/L in 20° N to 15° S (A14—A22). In 15° S to 60° S (A23—A34), the concentrations were all below the MDLs. The highest concentration (650 pg/L) was detected in the English Channel, and the second highest concentration (590 pg/L) was found in the Bay of Biscay, which agreed with a former study (Ahrens et al., 2010). McLachlan et al. (2007) investigated the riverine discharge of PFCAs in Europe. Their report indicated that the ∑PFAS concentration was quantified to be 60 ng/L in the Thames River and 27 ng/L in Seine River, respectively. Both rivers discharge water to the English Channel, which could be the PFASs sources. A ∑PFAS concentration of 8.1 ng/L was reported in the Loire River, one of the water sources of the Bay of Biscay suggesting a local discharge source. Compared with other sites near the European coast (A2 and A5—A8), the elevated levels at sampling sites A3 and A4 could attribute to the abundance of PFPA and PFHxA. The dominant compound in the Bay of Biscay (A4) was PFPA (170 pg/L, 29%) followed by PFOA, which accounted for 27% of ∑PFASs, whereas it was the third abundant compound (120 pg/L, 19%) in the English Channel (A1) next to PFOA (130 pg/L, 20%) and PFOS (130 pg/L, 20%). PFPA was usually detected in urban rivers and waste water treatment plant effluents, and it could not be effectively removed by common treatment techniques as well as filtration using activated carbon (Wilhelm et al., 2010). The abundance

Fig. 1. Sampling locations and concentrations of PFHxS, PFBS, PFOA, and PFOS (pg/L) in surface water of the Greenland Sea. The red lines with arrow represent the warm current. The blue lines with arrow represent the cold current.

Fig. 2. a: Sampling locations in Atlantic Ocean. The red and blue lines with arrows represent the warm and cold currents, respectively (references). b: concentrations of PFASs (pg/L) and water salinities (%) in Atlantic Ocean.
of PFPA could be attributed to the direct release from the urban and industrial regions and the defective water treatment processes (Ahrens et al., 2009c). The result of Pearson analysis (Table S6) suggested the sources of PFASs were related.

PFOA and PFOSs were only detected in one and three samples in the Southern Ocean, respectively, and the PFOS concentrations (25–45 ppb/L) were higher than that of PFOA (15 ppb/L) (Fig. 3). The profiles were different from those in the Greenland Sea, where PFOA showed higher concentration than PFOS. The occurrence of PFOA and PFOS in Antarctic seal and polar skua samples strongly supported the LRT, although only trace concentration were quantified in the water samples (Giesy and Kannan, 2001; Tao et al., 2006; Schiavone et al., 2009). Local input was considered to be the possible source of PFASs in Antarctica. The Antarctic Peninsula that supports 19 research stations and around 1000 people during warm season was found to be a hot spot (Bengtson Nash et al., 2010). Meanwhile, PFASs were below the MDL at most sites along the west coast of the Peninsula (i.e. S14–S17), and it was not evident enough to support the local source hypothesis.

From the studies conducted by Ahrens et al. in 2009a and 2010 which employed the same sampling vessel and similar laboratory conditions and treatment methods (Ahrens et al., 2009a), the PFASs in East AO (from 46° N to 60° S) were compared (Table 1 and Fig. S2). The ∑PFASs concentration decreased slightly from 2007 to 2010 (51–57 ppb/L in 2007, 259–422 ppb/L in 2008 and 120–380 ppb/L in 2010) in North AO (46° N to 20° N; the sites in the Biscay Bay were excluded), which could be explained by the phase out of POSF and PFOA. In Middle AO (20° N to 0°), the concentrations of ∑PFASs increased from 2007 to 2008, while it decreased from 2008 to 2010. For the individual PFASs, a decreasing trend of PFOA was detected in NAO from 2007 to 2010. In all the years involved, PFBS, PFOS, PFHxSA, PFOA, and PFNA were quantified, and they were mainly distributed in the NAO.

### 3.2. Large-scale long-range transport from European emission area

Two pathways were used to explain the global transport of PFASs: the atmospheric transport of volatile precursors followed by oxidizing degradation (Schenker et al., 2008; Dreyer et al., 2009) and the marine current transport of ionic compounds in the oceans (Ahrens, 2011). Both ways can result in the detection of PFASs in remote and polar areas. Some modeling and monitoring results supported the more important role of marine ocean current transport because of the larger amount of flux and the consistent variation pattern of the current direction change (Prevedouros et al., 2006; Armitage et al., 2006). PFOA and PFOS are representatives of the long-range transport research (Armitage et al., 2006; Yamashita et al., 2008), and in this study, they were the only two compounds detected in the Greenland Sea, AO and Southern Ocean.

As a result from the intensive production and usage in European countries, the emissions of PFOA and PFOS into the oceans were estimated as ~31 and ~20 t/a, accounting for ~41% and ~25% of global emissions, respectively (Armitage et al., 2006; Pistocchi and Loos, 2009). The PFASs released from 45° N northward of European countries can be transported to the Arctic region after combining with those delivered by the North Atlantic Current (NAC) from North America. The PFOA concentrations near the Bay of Biscay and English Channel were comparable with those at the North American coast and on the way from NAC to the north, all of which could be the source in the Arctic Ocean (Ahrens et al., 2009a). The atmospheric transport to the Arctic region was confirmed by monitoring data on air, ice and snow, water, and sediment in remote lakes and the mechanism has been argued in several models involving FTOHs and their major degraded compounds, e.g., PFOS (Butt et al., 2010).

Aksenen et al. (2010) modeled the inflow and outflow of Arctic Ocean water. Half of the volume of the North Atlantic Water (1.2 × 10⁶ m³/s) inflows into the Arctic Ocean through the Fram Strait, and the other half through the Barents Sea. Two major marine surface currents run through the Fram Strait (Fig. 1). In the eastern part, one branch of the Norwegian Current delivers warm marine water to the north, which could be recognized as the dynamic of transportation to the high Arctic Ocean. In the western part, the East Greenland Current (EGC) transports the recirculating Atlantic water, the Arctic Ocean water masses, and >90% of the Arctic Ocean ice to the south (Rudels et al., 1999). In this study, part of the Greenland Sea, 76°–81° N and 15° W to 8° E covering the whole Fram Strait, was considered and simply divided into two longitudinally average parts by 3° W, called the West Part of Fram

### Table 1

Temporal comparison of individual PFAS concentrations in surface water from Atlantic Ocean (46° N–60° S, sampling sites in the Bay of Biscay were excluded) (ppb/L).

<table>
<thead>
<tr>
<th>Location</th>
<th>Year</th>
<th>n</th>
<th>PFBS</th>
<th>PFHxA</th>
<th>PFHxS</th>
<th>PFOA</th>
<th>PFOS</th>
<th>PPGA</th>
<th>PFDA</th>
<th>PFUnDA</th>
<th>PFDoDA</th>
<th>∑PFASs</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAO&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2007</td>
<td>39</td>
<td>&lt;1.6–45</td>
<td>&lt;5.7–88</td>
<td>nd</td>
<td>&lt;10–114</td>
<td>nd</td>
<td>&lt;4.0–209</td>
<td>&lt;5.1–100</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>MAO&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2007</td>
<td>10</td>
<td>&lt;1.6</td>
<td>5.7</td>
<td>nd</td>
<td>&lt;10–60</td>
<td>nd</td>
<td>&lt;4.0–87</td>
<td>&lt;5.1–35</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2010</td>
<td>5</td>
<td>&lt;51</td>
<td>33–38</td>
<td>&lt;6.5–12</td>
<td>40–59</td>
<td>&lt;13–32</td>
<td>&lt;13</td>
<td>&lt;12–16</td>
<td>&lt;21</td>
<td>&lt;1</td>
<td>&lt;25</td>
<td>83.0–140</td>
</tr>
<tr>
<td>SAO&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2007</td>
<td>10</td>
<td>&lt;1.6</td>
<td>&lt;5.7</td>
<td>nd</td>
<td>&lt;10</td>
<td>nd</td>
<td>&lt;4.0</td>
<td>&lt;5.1</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2010</td>
<td>16</td>
<td>&lt;51</td>
<td>&lt;5.9</td>
<td>&lt;6.5</td>
<td>20–45</td>
<td>&lt;13</td>
<td>&lt;13–15</td>
<td>&lt;12</td>
<td>&lt;21</td>
<td>&lt;13</td>
<td>&lt;25</td>
<td>&lt;45</td>
</tr>
</tbody>
</table>

<sup>a</sup> NAO: North Atlantic Ocean.

<sup>b</sup> MAO: Middle Atlantic Ocean.

<sup>c</sup> SAO: South Atlantic Ocean.
Important role of marine transport was suggested by Bengtson et al. (2010). Trace gas-phase transport was slow compared with the atmospheric transport (Bengtson et al., 2006). PFOA has more volatile precursors than PFOS, and the hydrospheric transport was slow compared with the atmospheric currents can transport PFOA and PFOS from their emission regions. Consequently, occasional occurrence of PFOS was found in marine water in 2009 (Ahrens et al., 2010). By contrast, the more important role of marine transport was suggested by Bengtson et al. (2010). PFOA has more volatile precursors than PFOS, but it was not frequently detected in this study. Wei et al. (2007) reported PFOA concentrations in a range similar to this study, whereas PFOA levels were all below the quantification limit. Relatively low salinities were found at sites S7–S9 and S13–S15 (Table S1), and ice melting was observed during the sampling campaign. Meanwhile the concentrations were all below MDL and the fresh water influence could not be confirmed. Both PFOA and PFOS can transport through deep ocean water from NAO to the Southern Ocean (Yamashita et al., 2008; Bengtson et al., 2010). PFOA was assumed to stay at the surface water so that it was more easily detected in the Greenland Sea, whereas PFOS generally go deeper in the ocean, which resulted in their occurrence in the Southern Ocean. Multi-depth marine water monitoring work is required to test this hypothesis. At the tip of Antarctic Peninsula where PFOA and PFOA were detected, the Antarctic Circumpolar Current (ACC) runs from the west to the east around the continent (Fig. 3). ACC offered the chance for PFASs to distribute all around the Antarctic coast. It can be predicted that when the PFASs accumulated to a high level, and the dilution function became weak, and then they can be detected everywhere around Antarctica.

3.3. PFASs release from polar regions

In all 25 surface water samples from the Greenland Sea, PFOA was only detected in open sea area (G20) at a level around the MDL. The PFOA concentration was slightly higher than the modeled result (25–90 pg/L), but quite comparable with that of the Canadian Arctic (12–150 pg/L) (Young et al., 2007). Significant inverse correlation can be found between salinity and the PFOA concentration (r² = 0.46, n = 25, p < 0.001), suggesting that fresh water enriched the PFOA in this area (Fig. S1a). Moreover, except for station G4, the temperature was also significantly inversely correlated to the PFOA concentration (r² = 0.57, n = 24, p < 0.001), indicating that cooler water presented higher levels of PFOA (Fig. S1b). Considering the warm sampling season, the elevated PFOA concentration in the surface water could be attributed to the release of stored PFOA in the ice and snow. The PFOA input from the fresh water cannot be considered as only due to the atmospheric transport because the floating ice in the Arctic Ocean can also obtain PFOA through sea spray, and the melting mainly occurred at the bottom. In addition to the melted ice and snow transported by EGC from the high Arctic, the melted cap on Greenland can also enrich PFOA in the Greenland Sea. Meanwhile, slightly higher concentration can be found at the coast than in the open sea, indicating that the contribution from the Greenland glacier melting was moderate compared with other sources. Young et al. (2007) drew a conclusion that Arctic PFCAs mainly resulted from atmospheric transport, and the PFOA flux from the Canadian caps to the Arctic region was estimated at 0.1–0.6 t/a, considered to be small compared with hydropheric transport from the modeling studies (8–23 t/a from Armitage et al. (2006) and 2–12 t/a from Prevedouros et al. (2006), respectively).

In Section 3.2, the PFOA concentration was 103 ± 31 pg/L in the WPFS, and the outflow of PFOA through Fram Strait was calculated as 3.9 t/a, higher than the inflow (~2.1 t/a) (Ahrens et al., 2010). In the open sea area the EGC has influenced in this study (3°–W westward, n = 15), the PFOA concentration was from 44 pg/L to 160 pg/L. The outflow of the high Arctic water through the west Greenland Sea was estimated to be 1.7–5.9 t/a, which can elevate the level in the west Greenland coast (Ahrens et al., 2010). Almost half of the mass can be transported to the Northern Atlantic. The flow mass was two to four orders of magnitude lower compared with the total inventory in the Atlantic water (Prevedouros et al., 2006). The influence of the Arctic release was limited due to the large volume of emission from the source of the
Atlantic (Prevedouros et al., 2006). Three-fifth of the ocean outflow run out of the Arctic Ocean through the Canadian Archipelago, carrying 2.6–8.9 t/a PFOA, which could be the source of PFOA found in the ice due to the sea spray. The global surface temperature has increased by 0.13°C ± 0.03 °C per decade in the last 50 years, and that of the Arctic region was predicted to be ice-free (<10⁶ km²) by 2037, according to Wang et al. (Solomon et al., 2007; Lamon et al., 2009; Bader et al., 2011). Lamon et al. (2009) suggested that rising temperature probably strengthened the ability of PCBs and PCDD/Fs for the long-range atmospheric transport. Considering climate change, the PFASs accumulated in the last 50 years can be released to the water body in a short time and eventually elevate the PFAS levels all around the Arctic Ocean. Estimating the increased flux caused by climate change is difficult due to the lack of concentration in the Arctic floating ice and Greenland caps. Long-term monitoring should be conducted in the future.

In Antarctica, Trevena and Jones (2006) reported that the elevated dimethylsulphide concentration was associated with the release of sea ice during melting season. The PFASs deposited from air to the ice can be reasonably considered to be released during summer and spring. However, due to the trace concentrations of the precursors quantified in air as well as the strong dilution of ocean water, the significant elevation from the fresh water input was not detected in this study.

4. Conclusion

Generally, relatively high concentrations of PFASs were detected near the European continent. In the AO, the distributions were mainly influenced by the sources and surface marine currents. In the Greenland Sea, snow and ice melting elevated both the PFOA concentration and the mass, transported from high Arctic Ocean to the south. Moreover, the warming climate in the Arctic can accelerate the melting, and this may have resulted in the release of PFOA, which has been stored in the ice for decades. The PFOA and PFOS distributions in the Southern Ocean were different from those in the Greenland Sea, but the marine current transport is still considered to be more important than atmospheric transport. Snow and ice melting during summer in the Southern Ocean did not result in more release of PFASs. Further monitoring work should be conducted in the future for better understanding of the occurrence and distribution of PFASs in Antarctica.

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