



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

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ABSTRACT

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 Σ PFASs were detected in the North Atlantic Ocean with the concentrations ranging from 130 to 650 pg/L. In the Greenland Sea, the Σ PFASs concentrations ranged from 45 to 280 pg/L, and five most frequently detected compounds were perfluorooctanoic acid (PFOA), perfluorohexanesulfonate (PFHxS), perfluorohexanoic acid (PFHxA), perfluorooctane sulfonate (PFOS) and perfluorobutane sulfonate (PFBS). PFOA (15 pg/L) and PFOS (25–45 pg/L) were occasionally found in the Southern Ocean. In the Atlantic Ocean, the Σ PFASs 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 lipophobicity and hydrophobicity, PFASs have been widely used as adhesives, water-repellent coatings, and fire-fighting foams for over 50 years (Kissa, 2001; Prevedouros et al., 2006). The annual production of neutral fluorotelomer 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 (POSF) (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 (PFSAs), 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. Hydrospheric transport was stressed due to the larger amount of PFASs in marine water than in air, although higher concentrations were measured in

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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-Institute (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

Fifteen PFASs including C₄–C₁₀ PFSAs, and C₅, C₆, and C₈–C₁₆ PFCAs were analyzed. Eight mass labeled PFASs, i.e., ¹³C labeled ionic PFASs and ¹⁸O labeled perfluorohexanesulfonate (PFHxS) were used as Internal Standards (IS). 2H-perfluoro-[1,2-¹³C₂]-2-decanoic acid (8:2FTUCA) was used as injection standard (InjS) (Table S2). Methanol (Suprasolv) and ammonium hydroxide (25%, Suprapur) were purchased from Merck (Darmstadt, Germany). Millipore water was produced using a Milli-Q Plus 185 system by Millipore (Zug, Germany). The methanol was distilled in a glass apparatus before be used, and the Millipore water was precleaned by passing it through Oasis WAX cartridges similar to the real samples (Extraction and analysis section) to remove PFASs.

2.3. Extraction and analysis

Extraction of the filtrated water samples was performed on board using glass funnels and SPE cartridges. Prior to the extraction, 400 pg (20 µL, 20 pg/µL) IS mixture were spiked into the filtrate. Oasis WAX cartridges (Waters, 150 mg, 6 cm³, 30 µm) were used for SPE. The pretreatment of the cartridges and the extraction processes were described elsewhere but with minor modifications (Ahrens et al., 2009a). Briefly, the cartridges were first preconditioned by 10 mL methanol and 10 mL precleaned Millipore water, and were then loaded with samples at a speed of two drops per second. Subsequently, they were sealed in aluminum bags and stored at –20 °C until eluted in a clean laboratory. In the clean laboratory (class 10,000), the cartridges were first washed with 15 mL precleaned Millipore water to remove the salt, which could affect the performance of the instrument, and then dried using a vacuum pump with another preconditioned cartridge on top to remove the PFASs in the air that passed through the cartridges. The dried cartridges were eluted with 10 mL of 0.1% ammonium hydroxide in methanol. The eluates were reduced to 150 µL under a gentle stream of nitrogen (>99.999%). Before being injected into the instrument, 1000 pg (50 µL, 20 pg/µL) mass labeled 8:2 FTUCA were spiked into the vials and used as InjS.

The instrumental analysis was performed using a high performance liquid chromatography-negative electrospray ionization-tandem mass spectrometry

system (HPLC(–)ESI-MS/MS) with an HP 1100 HPLC system (Agilent Technologies) coupled to an API 3000 triple-quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX). The instrumental setup was described elsewhere (Ahrens et al., 2009a).

2.4. Quality assurance and quality control

Instrument detection limits (IDLs) were determined at a signal to noise (S/N) ratio of three, ranging from 3.9 pg perfluorohexanoic acid (PFHxA) to 31 pg perfluorobutane sulfonate (PFBS). The method detection limits (MDLs) were determined in two ways. When the mass of the compounds in blank samples were below the IDLs, the MDLs were replaced by the method quantification limits, determined at a signal to noise (S/N) ratio of 10, otherwise, the MDLs were determined at a 98% confidence interval level multiplied by the standard deviation plus the average of the blank. Five blanks were considered for comparison with the extraction process. Perfluoropentanoic acid (PFPA), PFHxA, PFOA, and PFOS can be detected in blank samples at a picogram-per-liter range. The MDLs ranged from 5.9 pg/L (PFHxA) to 51 pg/L (PFBS). Three breakthrough tests of WAX cartridges were performed during the ARK-XXIV/3 cruise, and the amounts of PFASs in the second cartridges were all below the IDLs. The duplicate samples showed a deviation of ±15%. The 10 mL methanol and 10 mL 0.1% ammonium hydroxide in methanol were reduced to 200 µL for injection to determine the solvent blank, respectively, but no PFASs were detected. The instrument modification process, done avoid contamination by the HPLC-MS/MS system, was described elsewhere (Ahrens et al., 2009b; Möller et al., 2010). The sample recoveries ranged from 32 ± 15% (¹³C-PFDoDA) to 76 ± 13% (¹⁸O₂-PFHxS) in cruise ARK-XXIV/3, and from 38 ± 14% (¹³C₂-PFDA) to 66% ± 22% (¹³C₄-PFOA) in cruise ANT-XXVII (Table S3). All concentrations were corrected by recoveries.

3. Results and discussion

3.1. Concentrations of PFASs in marine surface water

In the 76 marine surface water samples, 8 out of 15 PFASs were quantified in the Greenland Sea, AO and Southern Ocean (namely, PFPA, PFBS, PFHxA, PFHxS, PFHpS, PFOA, PFOS and PFNA; Table S4). The ∑PFAS concentrations varied from <MDL to 650 pg/L, and the average concentrations declined in three oceans in the following order: Atlantic (260 pg/L) > Greenland Sea (140 pg/L) > Southern Ocean (30 pg/L).

In the Greenland Sea, the ∑PFAS concentrations ranged from 45 to 280 pg/L. The five most frequently detected compounds were PFOA, PFHxS, PFHxA, PFOS, and PFBS (Fig. 1). PFOA was detected in all 25 samples within a concentration range of 45–160 pg/L, accounting for 42%–94% of ∑PFASs. Caliebe et al. (2005) reported that the total concentrations of PFOA and PFOS ranged from 20 to 120 pg/L in 2005, while in 2009, the concentrations were at a similar level from <MDL to 185 pg/L. Compared with the concentrations in the Canadian Arctic water (125–225 pg/L) in 2007 (Table S5), the PFOA level (45–150 pg/L) in the Greenland Sea in 2009 was two times lower, whereas the concentrations of PFOS (10–40 pg/L in the Canadian Arctic water and from <20 to 25 pg/L in the Greenland Seawater, respectively) were quite comparable (Rosenberg et al., 2008). Young et al. (2007) reported the PFASs concentration in the Canadian ice caps. Compared with their study, the PFOA concentration in the Greenland Sea surface water was at the same range as that in the Canadian ice caps (12–147 pg/L), whereas PFNA was not detected in most samples in our study. The short chain PFASs, i.e., PFBS and PFHxA, were quantified in 24% and 56% of all samples in the Greenland Sea, with concentrations ranging from <51 to 65 pg/L and from <5.9 to 38 pg/L, respectively. This result could attribute to the shift of usage from C₈ to C₄–C₆ PFASs after the voluntary phase-out of POSF and PFOA since 2000 (D'Eon et al., 2006; De Voogt et al., 2006). PFHxS were frequently quantified in 88% samples at a low level of from <6.5 to 45 pg/L Stock et al. (2007) reported elevated level of PFHxS in Resolute Lake, Canada, where local input was suggested as the source. In the Greenland Sea, the concentration (<6.5–45 pg/L) was two to three orders of magnitude lower than that in Canadian Arctic (from 19 pg/L to 24 ng/L in 2003 and from

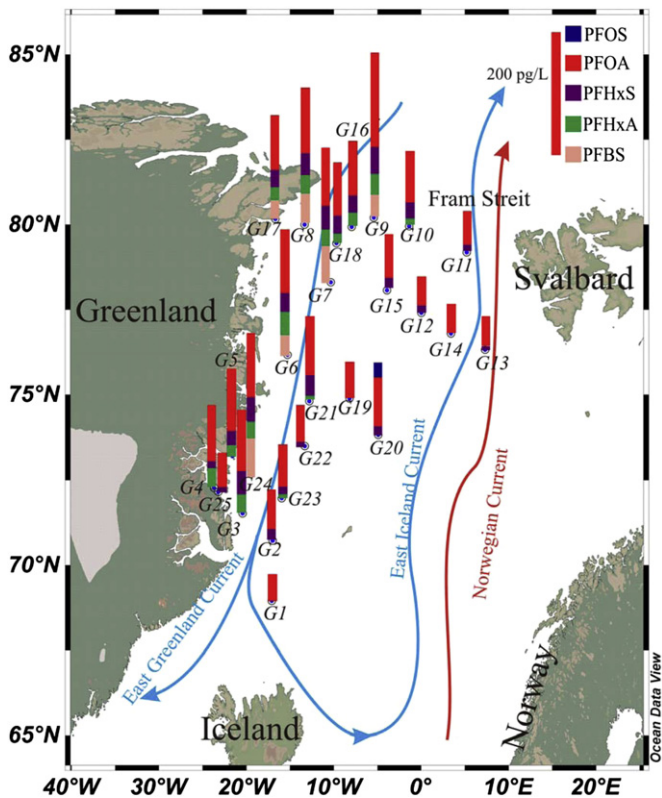


Fig. 1. Sampling locations and concentrations of PFHxA, PFHxS, PFOA, and PFOS (pg/L) in surface water of the Greenland Sea. The red lines with arrow represent the warm current. The blue lines with arrow represent the cold current.

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 Σ 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 Σ PFASs 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 Σ 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 A1 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 Σ 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

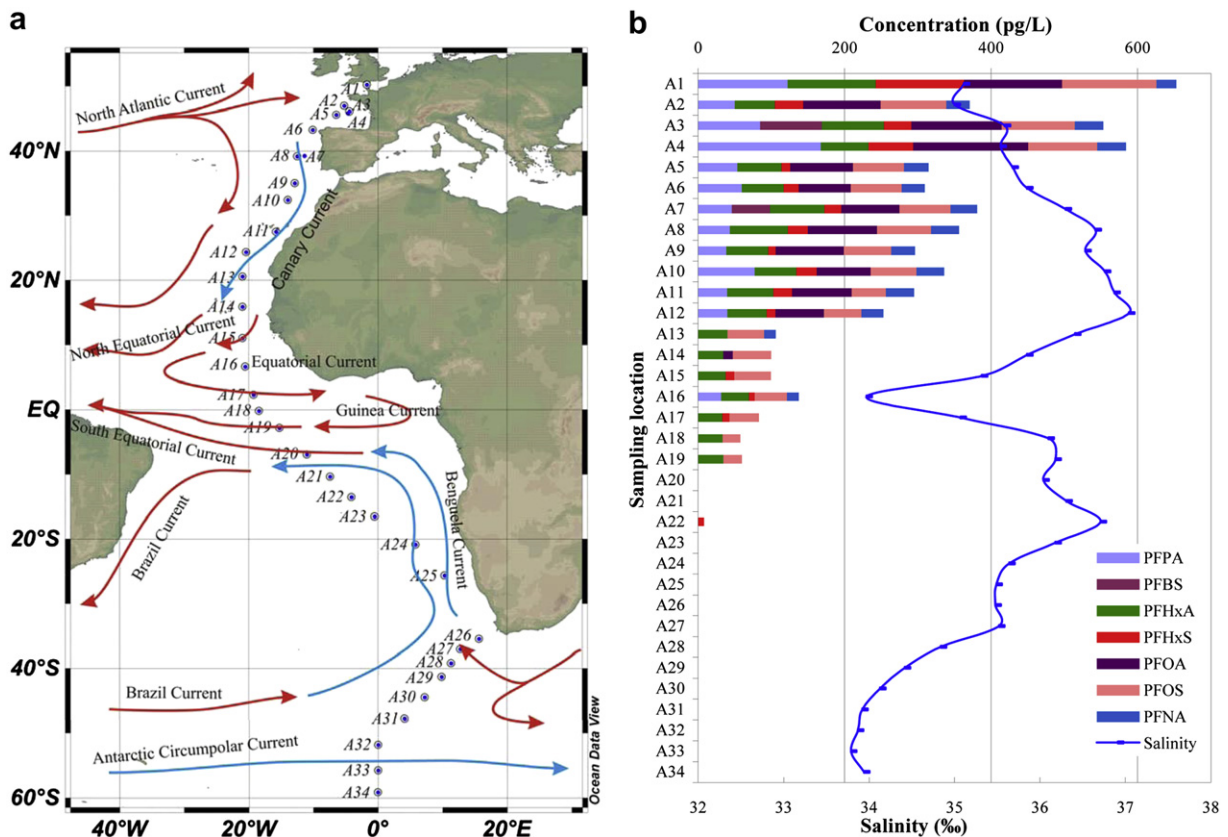


Fig. 2. a: Sampling locations in Atlantic Ocean. The red and blue lines with arrows represent the warm and cold currents, respectively (references). b: concentrations of PFASs (pg/L) and water salinities (‰) in Atlantic Ocean.

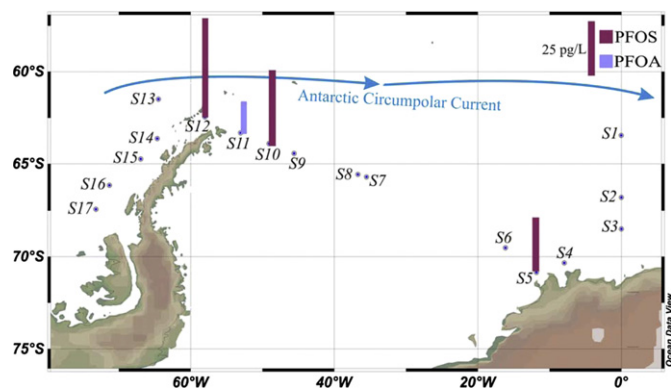


Fig. 3. Sampling locations and concentrations of PFOS and PFOA (pg/L) in surface water of Southern Ocean. The blue line with arrow represents the cold current.

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 PFOS were only detected in one and three samples in the Southern Ocean, respectively, and the PFOS concentrations (25–45 pg/L) were higher than that of PFOA (15 pg/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 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 evidential 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 \sum PFASs concentration decreased slightly from 2007 to 2010 (51–517 pg/L in 2007, 259–422 pg/L in 2008 and 120–380 pg/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 \sum 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, PFHxA, 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., PFOA (Butt et al., 2010).

Aksenov et al. (2010) modeled the inflow and outflow of Arctic Ocean water. Half of the volume of the North Atlantic Water ($1.2 \times 10^6 \text{ m}^3/\text{s}$) 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) (pg/L).

Location	Year	n	PFBS	PFHxA	PFHxS	PFOS	PFPA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	\sum PFASs
NAO ^a	2007	39	<1.6–45	<5.7–88	nd	<10–114	nd	<4.0–209	<5.1–100	nd	nd	nd	51–517
	2008	10	<4.4–20	38–54	13–27	54–116	30–74	87–154	24–39	12–37	20–39	<5.9–27	259–422
	2010	13	<5.1	40–79	<6.5–39	<20–90	16–77	<13–110	13–38	<21	<13	<25	120–380
MAO ^b	2007	10	<1.6	<5.7	nd	<10–60	nd	<4.0–87	<5.1–35	nd	nd	nd	27–152
	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	161–252
	2010	5	<5.1	33–38	<6.5–12	40–59	<13–32	<13	<12–16	<21	<1	<25	83.0–140
SAO ^c	2007	10	<1.6	<5.7	nd	<10	nd	<4.0	<5.1	nd	nd	nd	nd
	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	nd–252
	2010	16	<5.1	<5.9	<6.5	<20–45	<13	<13–15	<12	<21	<13	<25	nd–45

nd: not detect.

<x: below the method detect limit (MDL).

^a NAO: North Atlantic Ocean.

^b MAO: Middle Atlantic Ocean.

^c SAO: South Atlantic Ocean.

Strait (WPFS, G7–G9, G15, G16, and G18) and the East Part of Fram Strait (EPFS, G10–G14). The PFOS concentrations were all below the MDL, whereas the average PFOA concentration in WPFS (103 ± 31 pg/L, $n = 6$) was twice that in the EPFS (57 ± 16 pg/L, $n = 5$). The concentrations agreed with those in North Polar Zone in previous modeling studies (25–90 pg/L) (Armitage et al., 2006). The mass of PFOA transported from south to north through the strait was estimated to ~ 2.1 t/a using the concentration in EPFS (water flow of 1.2×10^6 m³/s cited from Aksenov et al. (2010) multiplied by the concentration of 56 pg/L from this study). Ahrens et al. (2010) investigated the PFASs concentrations in the open North Sea, and the Norwegian Coast, and stated that they can potentially transport to the Barent Sea. PFOS was not detected northern than 56° N, and the PFOA concentration ranged from 30 ± 5 –70 pg/L (average: 20 pg/L). The mass flow was calculated as ~ 0.6 t/a under the assumption that the same concentration could be found in the Barents Sea as in the open North Sea and Norwegian Coast (water flow of 1.2×10^6 m³/s from Aksenov et al. (2010); concentration of 20 pg/L from Ahrens et al. (2010)). The total PFOA inflow to the high Arctic region (80° N northward) was 2.7 t/a, which within the range of the result (2–12 t/a) estimated by Prevedouros et al. (2006). Stemmler and Lammel, (2010) estimated that 10–30 t/a PFOA is imported to the Arctic Ocean via the Norwegian coastal current, and Armitage et al. (2006) suggested 8–23 t/a from direct sources. The difference between the different modeling and between the modeling and monitoring data is obvious. The fluxes calculated from the emissions were much higher than those from on-site monitoring concentration multiplying the modeled water mass. Basically, monitoring studies were focused on smaller scale, and more details could be involved. However, due to the limitation in the sampling work, deeper water could not be involved, which might lead to underestimation. On the other hand, for the modeling, large-scale concern reduces the resolution; thus, not every factor can be included.

From 45° N to 15° N, the major direction of the surface water movement is to the south, where the Canary Current (CC) transports the European emission southward (Fig. 2a). The PFOA concentrations were quite consistent between 46° N and 20° N, but they decreased below the MDL between 20° N and 10° N when CC turns to the west and joins the North Equatorial Current (EC). PFOS showed a similar distribution pattern between 40° N and 20° N. The concentration decreased from 30° N, and after crossing the equator, it dropped to half of that at northern locations and decreased below the MDL at 3° S southward. EC controlled the surface water movement between 20° N and 0°, where the PFOS concentration displayed very slight variation. EC is fed by water from NAC and the African Coast, so that the PFOS in the equator area might origin from both the European emission and the African local input. The Benguela Current brings Southern Ocean and Pacific Ocean water from south to north. No direct sources were reported from the African Coast between 3° S and 35° S, and the volatile precursors, e.g., 8:2 FTOH, were at a low concentration, which could not elevate the marine water very much (Dreyer et al., 2009).

In the Southern Ocean, both the surface and deep marine ocean currents can transport PFOA and PFOS from their emission regions. Considering the long timescale and far distance from the source, the hydrospheric transport was slow compared with the atmospheric transport (Bengtson Nash et al., 2010). Trace gas-phase concentrations of 8:2 FTOH were reported in 2008 by Dreyer et al., and atmospheric transport was suggested as the significant contributor of PFCAs and PFSAs in the Southern Ocean (Dreyer et al., 2009). 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 Nash et al. (2010). PFOA has more volatile precursors than PFOS,

but it was not frequently detected in this study. Wei et al. (2007) reported PFOS 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 Nash 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 PFOS 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, PFOS 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 ice (12–150 pg/L) (Young et al., 2007). Significant inverse correlation can be found between salinity and the PFOA concentration ($r^2 = 0.46$, $n = 25$, $p < 0.001$), 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 ($r^2 = 0.57$, $n = 24$, $p < 0.001$), 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 get 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 hydrospheric 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) (Aksenov et al., 2010). In the open sea area where 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 (Aksenov 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 $0.13^{\circ}\text{C} \pm 0.03^{\circ}\text{C}$ per decade in the last 50 years, and that of the Arctic region was predicted to be ice-free ($<10^6 \text{ km}^2$) 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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Appendix A. Supplementary data

Supplementary data related to this article can be found online at <http://dx.doi.org/10.1016/j.envpol.2012.06.004>.

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