Occurrence of Perfluoroalkyl Compounds in Surface Waters from the North Pacific to the Arctic Ocean

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Ⓢ Supporting Information

ABSTRACT: Perfluoroalkyl compounds (PFCs) were determined in 22 surface water samples (39−76°N) and three sea ice core and snow samples (77−87°N) collected from North Pacific to the Arctic Ocean during the fourth Chinese Arctic Expedition in 2010. Geographically, the average concentration of $\sum$PFC in surface water samples were 560 ± 170 pg L^{-1} for the Northwest Pacific Ocean, 500 ± 170 pg L^{-1} for the Arctic Ocean, and 340 ± 130 pg L^{-1} for the Bering Sea, respectively. The perfluoroalkyl carboxylates (PFCAs) were the dominant PFC class in the water samples, however, the spatial pattern of PFCs varied. The C_5, C_7 and C_8 PFCAs (i.e., perfluoropentanoate (PFPA), perfluoroheptanoate (PFHpA), and perfluorooctanoate (PFOA)) were the dominant PFCs in the Northwest Pacific Ocean while in the Bering Sea the PFPA dominated. The changing in the pattern and concentrations in Pacific Ocean indicate that the PFCs in surface water were influenced by sources from the East-Asian (such as Japan and China) and North American coast, and dilution effect during their transport to the Arctic. The presence of PFCs in the snow and ice core samples indicates an atmospheric deposition of PFCs in the Arctic. The elevated PFC concentration in the Arctic Ocean shows that the ice melting had an impact on the PFC levels and distribution. In addition, the C_4 and C_5 PFCAs (i.e., perfluorobutanoate (PFBA), PFPA) became the dominant PFCs in the Arctic Ocean indicating that PFBA is a marker for sea ice melting as the source of exposure.
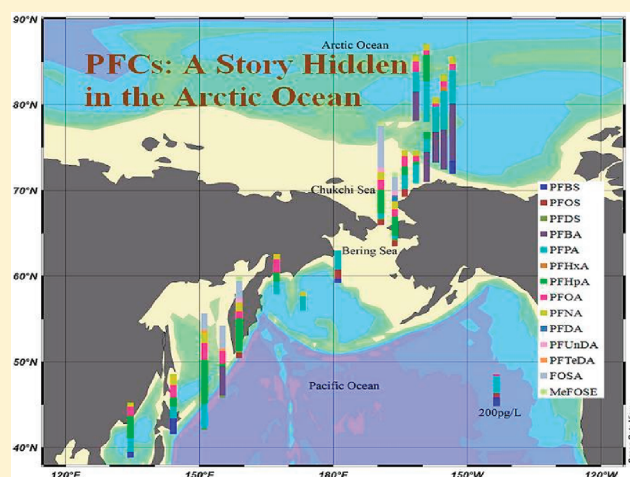
■ INTRODUCTION

Perfluoroalkyl compounds (PFCs), such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), have emerged as a new class of global environmental pollutants. PFCs are persistent against typical environmental degradation processes and have been found ubiquitously in water,[1,2] air,[3] food,[4] wildlife,[5] and humans.[6] PFCs are used in numerous products, such as fire-fighting foams, pesticides, and consumer applications including surface coatings for carpets, furniture, and paper products.[7] During production and usage of these products, PFCs can be released into the environment, where they can bioaccumulate and have potentially adverse effects on humans and wildlife.[5] As a result, PFOS has been added to the persistent organic pollutants (POPs) list of the Stockholm Convention in May 2009 resulting in global restriction of its production.[8] However, their homologues and neutral precursor compounds continue to be produced.[9]

In recent years, the occurrence and fate of PFCs in the aquatic environment has been recognized as one of the emerging issues in the environmental chemistry.[9] The extent of PFC pollution in the aquatic environment has previously been monitored in freshwaters,[10,11] coastal waters,[12,13] oceans,[1,2] and water, snow, and ice in the remote Arctic regions.[14−17] Previous studies examined the release of PFCs into the aqueous environment by runoff from contaminated soil,[18] industrial or municipal wastewater treatment plant (WWTP) effluents,[19] accidental spills or by the release of non treated discharges,[20] landfills,[21] and precipitation.[22] The PFCs can be further transported to the ocean via rivers[23] or through the air.[3]
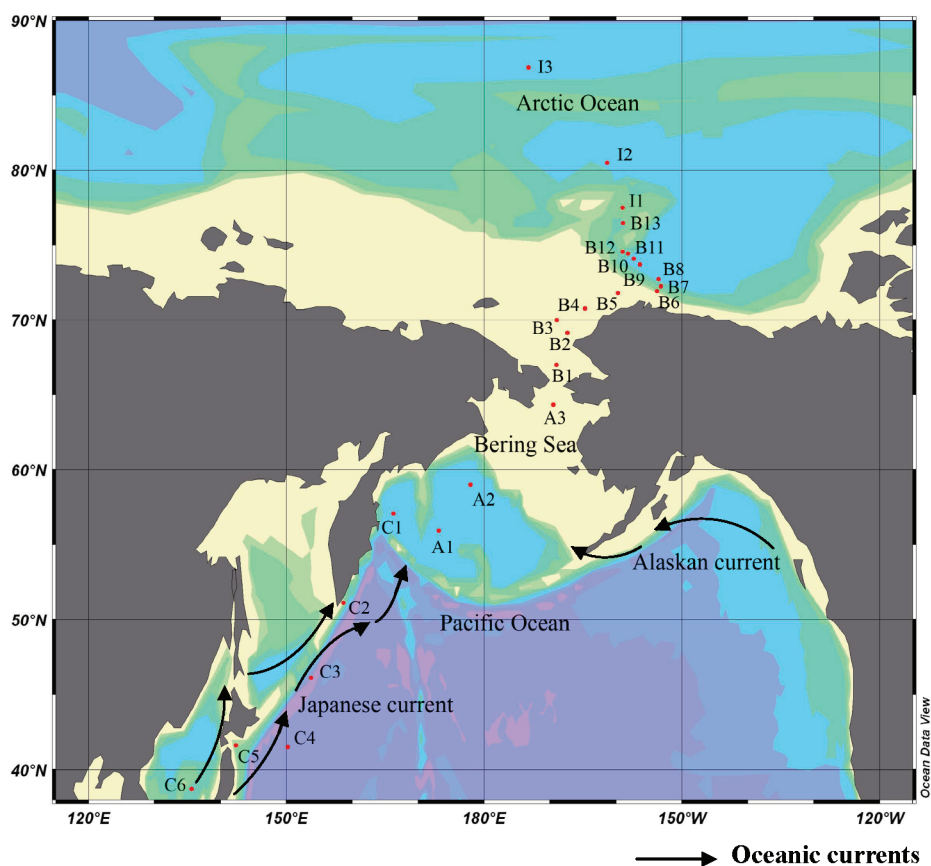
Figure 1. Sampling locations for surface water (A1−A3, B1−B13, and C1−C6) and glacial ice core samples (I1−I3) from the North Pacific to the Arctic Ocean. Note: Japan Sea: C6; North Pacific Ocean: C2−C5; Bering Sea: C1, A1−A3; Arctic Ocean: B1−B13, I1−I3.

The transport pathways of PFCs to remote regions have not been conclusively characterized to date. Two main hypotheses were proposed for the global transport of PFCs, namely long-range atmospheric transport of volatile precursor compounds[24−26] or direct transport of ionic PFCs via oceanic currents or by means of sea spray.[27,28] The first hypothesis is supported by the determination of precursor compounds (e.g., fluorotelomer alcohols (FTOHs), perfluorooctane sulfami-doethnols (FOSEs)) in remote regions.[29] FTOHs have been observed to undergo atmospheric oxidation to form perfluor-oalkyl carboxylates (PFCAs) under low NO_x conditions, such as those found in remote Arctic regions.[24,30] Analogously, the source of PFOS to the Arctic could be atmospheric oxidation of FOSEs.[25,31] The second hypothesis is supported by the fact that ionic PFCs such as shorter-chained PFCAs and perfluoroalkyl sulfonates (PFSAs) have high water solubilities and low pK_a values and therefore dissociated at environmentally relevant pH values.[7] The ocean currents were calculated to be the major transportation pathway of PFCAs to remote regions in comparison to atmospheric transportation.[28,32] However, PFCAs and PFSAs were also determined in snow samples of high Arctic which originated solely from atmospheric sources, confirming the indirect precursor-based atmospheric transport and deposition of these compounds.[14] However, the measure-ments of PFCs in the aqueous environment are limited, and further research is needed to determine the global fate and transport pathways of PFCs.

The objective of this study was to investigate the occurrence, spatial distribution, pattern of PFCs in the aquatic environment. This study provides the first evidence for the presence of C_4 and C_{10} PFSAs, $C_4−C_7$, C_{10}, C_{11} and C_{14} PFCAs, perfluorooctane sulfonamide (FOSA) and *N*-methyl perfluor-octane sulfonamidoethanol (MeFOSE) in the Pacific Ocean, and new information on the occurrence of PFCs in the Arctic Ocean.

■ MATERIALS AND METHODS

Chemicals and reagents. The standards used in this study are described elsewhere[2] (for details see Supporting Information (SI) Table S1. Methanol (pesticide residues grade) were purchased from LGC Standards GmbH, Germany, and ammonium hydroxide (25% for analysis) were purchased from Merck (Darmstadt, Germany). The methanol was distilled and the Millipore water (Millipore, Elix 5) was cleaned prior to use. Oasis WAX cartridge (6 cm^3, 150 mg) was purchased from Waters Co. (Made in Ireland).

Sample Collection and Sample Pretreatment. Surface water samples were taken onboard the research vessel *Snow Dragon* at 22 stations from the North Pacific to Arctic Ocean (39−76°N) from July to September in 2010 (Figure 1, A1−A3, B1−B13, C1−C6). One liter of surface water was collected from each sampling station by using a stainless steel bucket. Water samples were stored in 1 L polypropylene (PP) bottles. All the equipment including the stainless steel bucket and PP bottles were precleaned by rinsing with methanol, distilled water, and then seawater from the specific locations before sampling. The seawater samples were stored at 4 °C in darkness before extraction.

Three sea ice core samples were collected using Mark II ice core driller in the Arctic Ocean (77−87°N) from July to August
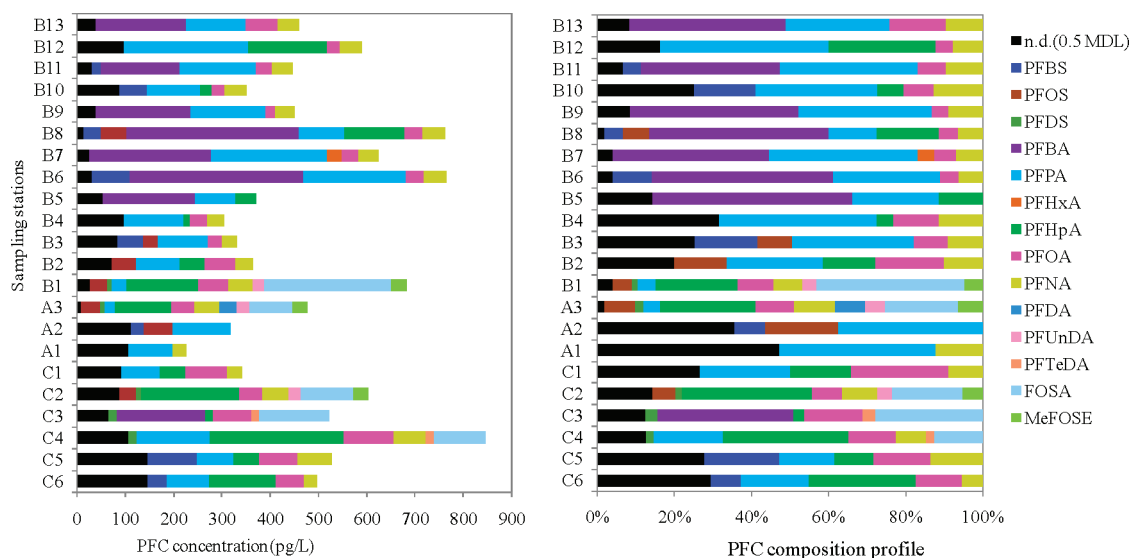
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Figure 2. Spatial distribution and composition profiles of individual PFCs in surface water samples from the North Pacific to the Arctic Ocean. Note: PFCs, which were not detected, are shown as the sum of the half values of the method detection limit (black bar).

in 2010 (Figure 1, I1−I3), as well as covered snow samples were collected from the same location by using a stainless spade and stainless steel bucket. Sea ice core samples (length: 140−160 cm) were divided into three parts (i.e., surface layer (0−15 cm), middle layer (70−85 cm) and bottom layer (130 cm−bottom)). All the divided sea ice samples, together with snow samples were melted in a dark room at 4 °C in order to get water samples for analyses. Details of the sampling date, location, and sampling parameter during the sampling can be found in SI Table S2 and S3.

The water samples were filtered using glass fiber filters (GFF, Whatman, O.D. 47 mm, 0.7 μm). Five field blanks (FB) were stored and transported to test for possible external contamination. For the FB, 1 L Millipore water was cleaned by passing the water through a WAX cartridge and the precleaned water was subsequently collected in a PP bottle. Finally, the FB were stored and extracted in the same manner as "real samples".

Sample Extraction. The filtrated sample was extracted by solid phase extraction (SPE) using Waters Oasis WAX cartridges in a clean lab, similar as described elsewhere.[2] Prior to extraction, the samples were spiked with 400 pg absolute of an internal standard (IS) mix (see SI Table S1). Briefly, after preconditioning with 10 mL methanol and 10 mL distilled Millipore water, the cartridge was loaded with the water samples at approximately 1−2 drops per second. The cartridge was then dried for 30 min under vacuum by which time another WAX cartridge was connected on the top of the sample cartridge to clean the air passed through. Elution was performed using 10 mL methanol with 0.1% ammonium hydroxide. The extracts were concentrated to 200 μL by nitrogen.

Instrumental Analysis. Analytical method has been described in elsewhere.[2] Briefly, an HP 1100 HPLC-system (Agilent Technologies) was used with a Synergi Hydro RP 80A column (150 × 2 mm, 4 μm, by Phenomenex), combined with a suitable guard column (Synergi 2 μ Hydro RP Mercury, 20 × 2 mm, 2 μm). Modifications of the HPLC system were made as described elsewhere[2] to eliminate instrumental blank contamination. The triple-quadrupole mass spectrometer, supplied by Applied Biosystems/MDS SCIEX (API 3000), used an

electrospray ionization (ESI) interface in negative ionization mode.

Quantification was performed by the internal standard method. An 8-point calibration curve (0, 0.5, 1, 2.5, 5, 7.5, 10, 15 pg/μL) was used for quantification. For peak integration only the main peak of a compound was used. The isomers were not included in the peak integration, because of the lack of standards.

Quality Control. Recovery of each spiked sample, instrument detection limit (IDL), method quantification limit (MQL), field blank, matrix spike recoveries and duplicate samples were measured (for details see SI Table S4 and S5). All results were recovery corrected for PFCs. The IDL and MQL were calculated at a signal-to-noise ratio (S/N) of 3 and 10, respectively. The MQL ranged from 6.3 pg/L for perfluorodecatane sulfonate (PFDS) to 130 pg/L for perfluorobutanoate (PFBA). In field blank samples, perfluorobutane sulfonate (PFBS), perfluoroheptane sulfonate (PFHpS) and perfluorooctanoate (PFOA) were found above the MQL (68 pg/L for PFBS, 23 pg/L for PFHpS and 43 pg/L for PFOA), and therefore the concentrations were blank corrected afterward. The matrix spike recoveries were determined at 400 pg/L and they ranged between 38 ± 44% for d9-EtFOSE and 100 ± 84% for [^{18}O$_2$]-PFHxS.

■ RESULTS AND DISCUSSION

Concentration of PFCs in the Oceans. In the present study, overall 14 of 24 PFCs were quantified in surface water samples at the 22 sampling sites (for details see SI Table S6 and S7). The quantified PFCs included C_4−C_{11} and C_{14} PFCAs (i.e., perfluorobutanoate (PFBA), perfluoropentanoate (PFPA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), perfluorotetradecanoate (PFTeDA)), C_4, C_8, and C_{10} PFSAs (i.e., PFBS, PFOS, perfluorodecane sulfonate (PFDS)), FOSA, and MeFOSE. To elucidate the spatial distribution of PFCs in the surface water samples, sampling sites were geographically separated into three groups: Northwest Pacific Ocean (C1−C6), Bering Sea (A1−A3), and Arctic Ocean (B1−B13). Concentrations of ∑PFCs
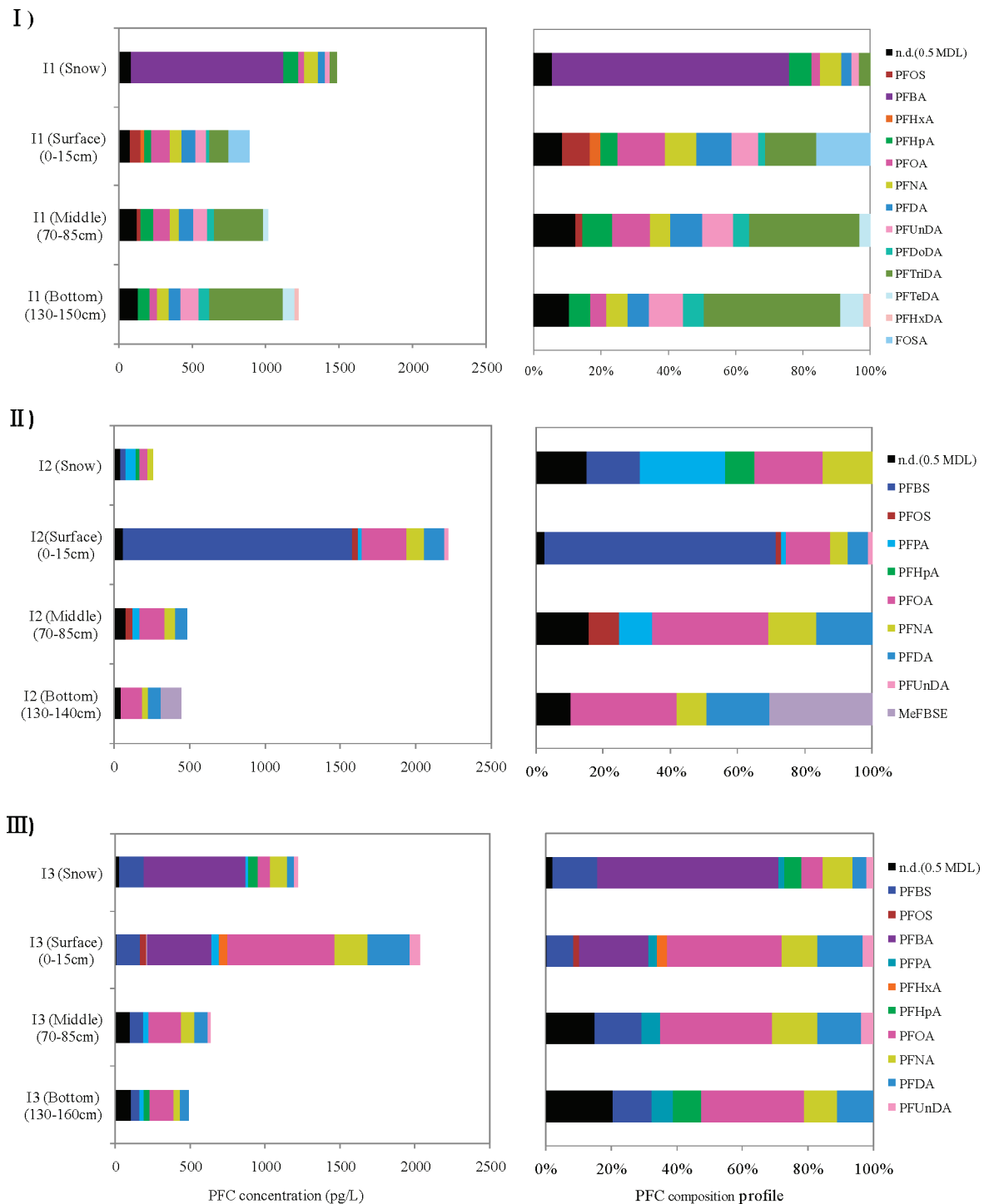
Figure 3. Concentration and composition profiles of PFCs in snow and ice core samples. Note: PFCs, which were not detected, are shown as the sum of the half values of the method detection limit (black bar).

during the whole cruise ranged from 230 to 840 pg L^{-1} (Figure 2). Higher concentrations were observed in the Arctic Ocean (site B1, B6, B7, and B8), and near the east coastline of Japan (site C4). Geographically, the average concentrations of $\sum$PFCs from high to low were in the following order: Northwest Pacific Ocean (560 ± 170 pg L^{-1}), Arctic Ocean (500 ± 170 pg L^{-1}), and Bering Sea (340 ± 130 pg L^{-1}).

In the Northwest Pacific Ocean, the $\sum$(PFOA+PFOS) concentrations (82 ± 14 pg L^{-1}) were lower in the present study than the monitoring data collected in the same oceanic

area (i.e., 200 ± 21 pg L^{-1}, $n = 2$),[1] and this mainly is ascribed to the voluntary phase-out of perfluoroctanesulfonyl fluoride (POSF)-based compounds, which caused decreasing emission of PFOS. On the other hand, the PFC concentrations of the present study were lower than those for coastal sites of northern Bohai Sea, China (15 ± 26 ng L^{-1}, $n = 34$)[33] and Tokyo Bay, Japan (190 ± 22 ng L^{-1}, $n = 3$).[34] The dominant PFC in the Northwest Pacific Ocean was PFHpA, followed by PFOA and PFPA (Figure 2), contributing 20.5% (3.0−33.7%), 14.6% (7.8−25.4%), and 12.3% (0−23.5%) of the total PFCs,

respectively. A similar PFC pattern was reported in water samples collected in Bohai (China), where PFOA and PFHpA were the dominant compounds.[33] In contrast, previous studies in oceanic waters reported that PFOA and PFOS were the dominant compounds in Atlantic Ocean,[1,2,34] Indian Ocean,[35] Pacific Ocean, South China Sea, and Sulu Sea,[1,34] while in East Greenland Arctic Ocean FOSA and PFOA,[16] and in Tokyo Bay, Japan, PFBA was the predominated PFC.[36] The different composition pattern indicates the regions were influenced by different sources. The composition profile of samples from coastal area near Japan (sites C5 and C6) were similar (dominated by PFPA, PFHpA and PFOA) which suggest that the PFCs originated from the same potential source.

In the Bering Sea, a relatively large proportion of total PFC concentration was contributed by PFPA (average of 27.5%), while the concentration profiles of samples were different from each other at the three sites (A1−A3), which suggest unrelated sources. Interestingly, the concentration of $\sum$PFCs was much higher at site A3 (480 pg L^{-1}) compared to that at site A1 (230 pg L^{-1}) and A2 (320 pg L^{-1}), which suggest the influence of different sources at site A3.

In the Arctic Ocean, PFPA (average of 28.9%) and PFBA (average of 23.6%) were the dominant PFCs. There are very limited measurements of PFCs in the Arctic seawater focusing primarily on the Canadian Arctic, the Labrador and Greenland Seas. In general, the concentration of PFCs from this study was comparable to that in Labrador Sea and East Greenland Arctic Ocean, especially for PFOA and PFOS,[16,37,38] while lower than that in the Canadian Arctic.[15] However, the PFC composition patterns in these Arctic waters varied depending on the location. For example, PFBS and PFOA were the dominant compounds in Labrador Sea, PFOA and PFOS for the Canadian Arctic, and FOSA and PFOA for East Greenland Arctic Ocean.[15,16,37] This suggests the sources and transport pathways of PFCs in the Arctic are complex (see section "Potential Sources and Transport Pathways of PFCs").

Concentration of PFCs in the Arctic Snow and Ice. Surface snow and three layers (surface, middle and bottom) of ice core samples were analyzed for PFCs. Sixteen PFCs were quantified including C_4−C_{14}, C_{16} PFCAs (i.e., PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, perfluorododecanoate (PFDoDA), perfluorotridecanoate (PFTriDA), PFTeDA, perfluorohexadecanoate (PFHxDA)), C_4 and C_8 PFSAs, FOSA and N-methylperfluorobutane sulfonamidoethanol (MeFBSE) (for details see SI Table S8). Highest concentration of $\sum$PFCs was detected in the surface ice layer at site I2 (i.e., 2200 pg L^{-1}). Lower $\sum$PFC concentrations were observed in the snow sample at site I2 (i.e., 260 pg L^{-1}, Figure 3). In snow samples, the concentration of $\sum$PFCs ranged from 260 to 1500 pg L^{-1} (average of 990 pg L^{-1}). The dominant PFCs were PFBA (<130−1000 pg L^{-1}), followed by PFNA (38−110 pg L^{-1}), PFOA (39−82 pg L^{-1}), PFBS (<17−170 pg L^{-1}), PFPA (<20−66 pg L^{-1}), and PFHpA (23−99 pg L^{-1}), contributing 42%, 10%, 9.9%, 9.9%, 9.1%, and 6.8% of total PFCs, respectively. The composition pattern of PFCs in snow samples was similar with that in the European Arctic,[39] dominated by PFBA. However, it was not consistent with that in the Canadian Arctic and North Russia.[14,17]

Vertical profiles of PFC concentrations in three sea ice cores differed from each other (Figure 3). The reasons for the differences among the three ice cores may be attributed to their different locations, climate, contamination sources and also melting and refreezing processes. An ice core represents the accumulation of snow and ice over several years, and they have been used to reconstruct long-term temporal trends and inputs of PFCs from the atmospheric environment.[14] For sea ice core at site I1, the concentration of $\sum$PFCs in the snow was higher than that in ice layers, and this attributed to the relatively high concentration of PFBA (1000 pg L^{-1}). The concentration of PFCs increased slightly from surface to bottom layer in the sea ice core at site I1 while the composition pattern nearly did not change, suggesting similar sources over the years. Regarding sea ice core at site I2, high concentration of $\sum$PFCs was detected in the surface layer of the ice core, which was mainly due to the high concentration of PFBS (1500 pg L^{-1}). However, the relative PFC concentration profiles were quite different among the layers. PFBS was only detected in snow and the surface ice core layer. This could be attributed to the increasing production of PFBS, its precursor compound MeFBSE and related products with four perfluorinated carbon chain, which was introduced after the voluntary phase-out of perfluorooctanesulfonyl fluoride (POSF)-based compounds by the 3M Company in 2000.[31] Interestingly, the concentration of PFBS in the surface ice layer was ∼38 times higher than that in the snow. The ice core at I2, which was collected in summer, showed signs of melting progresses in the surface layer. Because of this melting, it is possible that some PFCs migrated down the snow profile. However, no melting signs were observed in the middle and bottom layer which is in agreement with the similar PFC levels and pattern in these layers. If water freezes sufficiently to form an ice layer, further meltwater will accumulate on the impermeable layer, preventing soluble species from moving down the snowpack.[14] Thus, it is likely that the PFCs would have accumulated on the thick ice layer and the concentration of PFCs in the surface ice layer may be inflated. Looking at glacial ice core at site I3, high concentration of $\sum$PFCs was detected in the surface ice core layer, which was ∼2, ∼3, and ∼4 times higher than that in the snow, middle and bottom ice core layers, respectively. The vertical profiles of $\sum$PFC concentrations in the sea ice core were consistent with that at site I2 with maximum PFC concentrations in the surface ice layer, suggesting this ice core was also influenced by melting processes like for ice core I2. The higher concentration of PFCs in the snow and surface ice layer, especially for PFBS and PFBA, may also be attributed to the increasing usage of substitute chemicals like MeFBSE and related products with C_4-based compounds (i.e., PFBS and PFBA) in recent years.[31] Ultimately, higher concentrations of PFOA, PFNA, and PFDA indicates increasing production of these chemicals or their precursors such as FTOHs over the time.[14,32]

Potential sources and Transport Pathways of PFCs. As the water samples were collected in the Northwest Pacific Ocean (C1−C6) and Bering Sea (A1−A3) close to the coast of the Eurasian continent, industrial inputs and ocean currents may affect the spatial distributions of PFCs. Generally, PFC concentrations measured in the Northwest Pacific Ocean were higher (560 ± 170 pg L^{-1}, n = 6) compared to those in the Bering Sea (340 ± 130 pg L^{-1}, n = 3). However, the difference was not significant which can be attributed to the influence of the different ocean currents in this area. The higher PFC concentrations in the Northwest Pacific Ocean can be explained by the influence of the industrial regions, such as Japan and China, in which area high concentrations of PFCs in nanogram per liter range have been detected.[33,40] For Example, sampling site C4 in the Pacific Ocean with high PFC concentrations, was probably influenced by potential sources

from industrial regions in Japan. During the sampling periods (in summer), the water mass is driven by the prevailing southwesterly winds moving along the Chinese shore from southwest to northeast.[12] This can explain the decreasing PFC concentration from the Northwest Pacific Ocean to the Bering Sea because of dilution by seawater and less influence by industrial areas. Interestingly, there was an increase trend of $\sum$PFC concentrations in the Bering Sea from sampling site A1–A3. This can be attributed to the Alaskan current, which causes runoff from the Northern American regions (urbanized and industrialized areas) to move toward the Bering Sea, and the contaminant volumes probably overwhelmed the dilution effect from A1 to A3.

In the Arctic Ocean, the sampling region was further divided into two subgroups: the Chukchi and Beaufort Seas (B1–B5) characterized by open water with a higher temperature ranging from 2.9 to 5.9 °C, and the central Arctic Ocean (B6–B13, I1–I3) covered by seasonal or multiyear sea ice with a lower temperature ranging from −2.8 to 1.6 °C. In the Chukchi and Beaufort Sea, the PFC concentration decrease from B1 to B4, which can be caused by the dilution effect from the Bering Sea. Interestingly, the concentration of $\sum$PFCs at B1 was higher than that at A3 in the Bering Sea, while the composition profiles of PFCs were similar between site B1 and A3 (except for FOSA). This suggests that the sampling sites B1 and A3 were influenced by similar potential sources and confirms the conclusion that PFCs can reach the Arctic regions through oceanic currents.

The ice cores in the central Arctic Ocean (sites I1–I3) receive PFCs contamination solely from atmospheric deposition. PFC contamination could come from direct deposition or atmospheric oxidation of volatile precursors, followed by wet or dry deposition onto the ice cap. The presence of the long chain PFCAs, PFDA, and PFUnDA on High Arctic ice caps is an indication that they originated from atmospheric oxidation of volatile precursors such as 10:2 FTOH.[14,24] In this study, PFDA and PFUnDA were mainly detected in ice samples, except for a few water samples, indicating the existence of atmospheric transport into the Arctic regions. A previous study found strong correlation between the concentrations of PFOA and PFNA in Canadian Arctic ice cap samples and suggest these two compounds come from a similar source (i.e., atmospheric transport via FTOHs).[14] Similarly, in this study, a graph of PFOA versus PFNA concentrations shows a positive correlation in ice core samples ($n = 9$, $R^2 = 0.88$) (SI Figure S1), whereas no correlation was observed in seawater samples from the Northwest ($n = 6$, $R^2 = 0.05$) and Arctic Ocean ($n = 12$, $R^2 = 0.06$). This supports the conclusions of atmospheric transport to the Arctic. Alternately, PFCs could come from marine aerosols, which are known to be coated with a layer of organics that can contain enriched concentrations of organic pollutants.[41] For example, PFOA can enrich by a factor of up to 3 in foam produced from bubbling through a dilute PFOA solution.[42] Thus, it is possible that these aerosols could transport PFCs from marine environments to the ice cap. In this study, the concentration of PFOA in the North Pacific Ocean (C1–C6, A1–A3) ranged from <20 to 100 pg L^{-1} (average of 56 pg L^{-1}), while the PFOA concentration in the three sea ice cores (I1–I3) was ~3 times higher ranging from 52 to 710 pg L^{-1} (average of 180 pg L^{-1}). This is in good agreement of the theoretical enrichment factor of 3 calculated by Kaiser et al (2006) which suggests that marine aerosol transport can be a source of PFCs for the Arctic ice caps.

The ice core samples (I1–I3) had relatively higher $\sum$PFC concentrations (220–2200 pg L^{-1}, average of 960 pg L^{-1}) in comparison with that in the water samples (B1–B13) in the central Arctic regions (210–750 pg L^{-1}, average of 450 pg L^{-1}). This indicates that a significant amount of PFCs were transported by the atmosphere to the Arctic regions. This is consistent with a previous study on Arctic ice cores,[14] whereas modeling studies have identified the ocean currents as the dominant transport pathway into the Arctic.[27,28] However, individual PFCs may have different long-range transport pathways. For example, the concentration of PFPA ranged from 31 to 260 pg L^{-1} (average of 140 pg L^{-1}) in water samples in Arctic region (B1–B13), while the concentration of PFPA was lower in the ice samples (I1–I3), ranging from <20 to 65 pg L^{-1} (average of 24 pg L^{-1}). This indicates the transport pathways of PFPA were dominated by oceanic currents in the Arctic regions.

Sea ice may also play an important role on the spatial distribution of PFCs in the Arctic Ocean. In this study, the levels of PFCs in the Arctic Ocean showed high variations. The concentration of PFCs in water samples from B6 to B8 (average of 720 pg L^{-1}) was higher than that from B9 to B13 (average of 460 pg L^{-1}), and this may be ascribed to the sea ice. It is known that precipitation in the form of snow results in the accumulation of contaminants in the seasonal snowpack and sea ice.[43] Because of sea ice melting, the PFCs can move into water. The area at the sampling sites B6–B8 was covered by seasonal ice ("float sea ice"), while at higher latitudes (B9–B13) the ocean was covered with multiyear sea ice ("pack ice region") during the sampling cruise (in summer). In the areas of float sea ice (B6–B8), the melting ice might lead to elevated PFC concentrations. Lower PFC concentrations were observed at higher latitudes where pack sea ice dominated (B9–B13). The reduced ice−water exchange could be responsible for the lower PFC concentrations at sampling sites B9–B13 in comparison to sampling sites B6–B8. It is also interesting to note the different composition profile of sampling sites B5–B13 (dominated by PFBA and PFPA) in comparison to sampling sites B2–B4 in Chukchi and the Beaufort Seas (dominated by PFPA). This could be caused by sea ice melting and PFBA might be a marker for sea ice melting.

In summary, this study demonstrates the transport of PFCs from the North Pacific Ocean to the Arctic Ocean by the ocean currents and long-range atmospheric transport. The presence of PFCs in the snow and ice core samples indicates an atmospheric deposition of PFCs in the Arctic. Our results show that the ice melting had an impact on the PFC levels and distribution in surface water in the Arctic Ocean. The influence of ice melting might be enhanced in the future due to climate warming. Overall, further studies are necessary focusing on transport pathways and seasonal trends of PFCs in Arctic water and atmosphere using, for example, dated ice core samples or by long-term monitoring studies to improve our knowledge about the air−water interactions of PFCs in the Arctic.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Additional information about the analytes, instrumental detection limit, method quantification limit, recoveries and overview of PFC concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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