Per- and polyfluoroalkyl substances in snow, lake, surface runoff water and coastal seawater in Fildes Peninsula, King George Island, Antarctica

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ARTICLE INFO

ABSTRACT

The multi-matrices samples from snow ($n = 4$), lake water ($n = 4$), surface runoff water (SRW) ($n = 1$) and coastal seawater ($n = 10$) were collected to investigate the spatial distribution and the composition profiles of per- and polyfluoroalkyl substances (PFASs) in Fildes Peninsula, King George Island, Antarctica in 2011. All samples were prepared by solid-phase extraction and analyzed by using high performance liquid chromatography/negative electrospray ionization-tandem mass spectrometry (HPLC/(−)ESI-MS/MS). 14 PFASs in snow, 12 PFASs in lake water, 9 PFASs in SRW and 13 PFASs in coastal seawater were quantified, including C_4, C_7, C_8, C_{10} PFSAs, C_4–C_9, C_{11}–C_{14}, C_{16} PFCAs, and FOSA. PFOA was detected in all samples with the highest concentration (15,096 pg/L) in coastal seawater indicating a possible influence of local sewage effluent. High concentration and mostly frequency of PFBA occurred in snow (up to 1112 pg/L), lake water (up to 2670 pg/L) and SRW (1431 pg/L) while detected in the range of method detection limited (MDL) in the coastal seawaters indicate that PFBA is mainly originated from atmospheric dust contamination and also affected by the degradation of their precursors. No geographical differences in PFOS concentrations ($n = 8$, 18 ± 3 pg/L) were measured in all snow and lake water samples also suggests that PFOS could be originated from the degradation of their precursors which can transported by long-range atmospheric route, but in a very low level.

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1. Introduction

Antarctic region often refers to the area around the South Pole, including Antarctica and Southern Ocean, which includes South Pacific Ocean, Indian Ocean and South Atlantic Ocean. Compared with other regions on Earth, Antarctic ecosystem is particularly sensitive to anthropogenic modifications and highly susceptible to human impact according to its remote location and harsh weather conditions. Anthropogenic contamination in Antarctic area is originated from both local and global sources. Local sources include scientific activities, garbage incineration, paints, fuel usage and sewage; while global source refers to long-range atmospheric transportation of pollutants from lower latitude area [1].

Recently, the occurrence of per- and polyfluoroalkyl substances (PFASs) in the global environment has been recognized as one of the emerging issues. PFASs were even detected in organisms

from remote locations such as biota in Arctic [2,3], dolphins in the Atlantic Ocean [4], as well as in the seawater from the Pacific, Atlantic and Arctic Oceans [5–7]. Furthermore, PFASs were also detected in Antarctic biological matrices [8].

The environmental fate of PFASs results from the interplay of numerous processes including physical transport and multimedia partitioning. Neutral PFASs such as perfluoroalkane sulfonamides (FASAs), perfluoroalkane sulfonamidoethanols (FASEs) and fluorotelomer alcohols (FTOHs) have a higher vapor pressure and lower water solubility in comparison to the perfluoroalkane sulfonates (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs), which make it possible for them to process the potential of long-range transportation [9–11]. Because of their slow reaction with hydroxyl radicals, estimation of atmospheric lifetime is more than 10–20 days for FTOH and more than 20–50 days for perfluorooctane sulfonamide (FOSA) in smog chamber studies [11,12] and atmospheric residence time is more than 50 days for FTOH in field studies [13]. All of these characters also indicate the possibility of regional or long-range atmospheric transport. Alternatively, long-range transport of PFSAs and PFCAs to remote areas by ocean currents has also been hypothesized [14,15]. But the specific circulation pattern of the Southern Ocean appears to

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be prolonging protection of Antarctic organisms from exposure to PFASs [16]. To date, the dominant transport pathways of PFASs to remote regions have not been conclusively characterized.

The aim of this paper is to study the contamination of PFASs in abiotic multi-matrices (snow, lake, surface runoff water and coastal seawater) in Fildes Peninsula, King George Island, Antarctica, to identify the possible local contamination of PFASs or the global transport of short-chained PFASs from low latitude areas. Data presented in this study yield new information on the spatial distribution of PFASs on an Antarctic regional scale and identifies knowledge gaps in the transportation of PFASs, especially for PFBA and PFOS.

2. Materials and methods

2.1. Site description

Fildes Peninsula, Ardley Island and the adjacent smaller islands form the south-western part of King George Island, one of the South Shetland Islands in the Maritime Antarctica. Fildes Peninsula is flat and stable, covers a total area of 30 km^2 and the highest altitude is only 70 m. More than 70–80% of the island is covered by the vegetation, especially lichen and moss grow all round. The average precipitation in this area is about 600–700 mm/year, mostly snow, and the average summer temperature is $\sim$0 °C. During the years since 1968, several countries (Chile, Russia, Uruguay, Germany and China) have established research stations and field huts there. In addition, in 1980, Chile built a hard runway capable of handling intercontinental and intracontinental flights for transporting cargo, station personnel, and visitors between stations in the South Shetland Islands and South America. Additional, supply, research, patrol and tourist vessels frequently anchor in Maxwell Bay. All of these activities affect the environment in that area.

2.2. Chemicals and reagents

The methods used in this study are described elsewhere [17] and the standards are listed in the Table S1 in the supplementary data. Methanol (pesticide residues grade) was purchased from LGC Standards GmbH, Germany, and ammonium hydroxide (25% for analysis) from Merck (Darmstadt, Germany). Oasis WAX cartridge (6 cm^3, 150 mg) was purchased from Waters, Milford, MA, USA.

2.3. Sample collection and sample pretreatment

Coastal surface seawater samples were taken on a rigid inflatable boat (*Zodiac*) along the Ardley Cove and Great Wall Cove between Peninsula and Ardley Island in January 2011 (Fig. 1). In this study, the sampling region was separated into the inner cove and deeper outer cove. Sampling sites A1 and G1 were chosen in the inner cove closer to land areas to show the influence of the surface runoff waters and regard as unmixed seawaters without influenced by sewage outlet waters (the depth is about 10–20 m). A2–A4 and G2–G4 were chosen near the sewage outlet to show the influence of the potential pollution sources of wastewater (the depth is about 30–50 m). A5 and G5 were chosen as the outer cove site (the depth is >100 m). Two liters of surface water were collected from each sampling station by using a stainless steel bucket. Water samples were stored in 2 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 sea water from the specific locations before sampling. The seawater samples were stored at 4 °C in darkness before extraction.
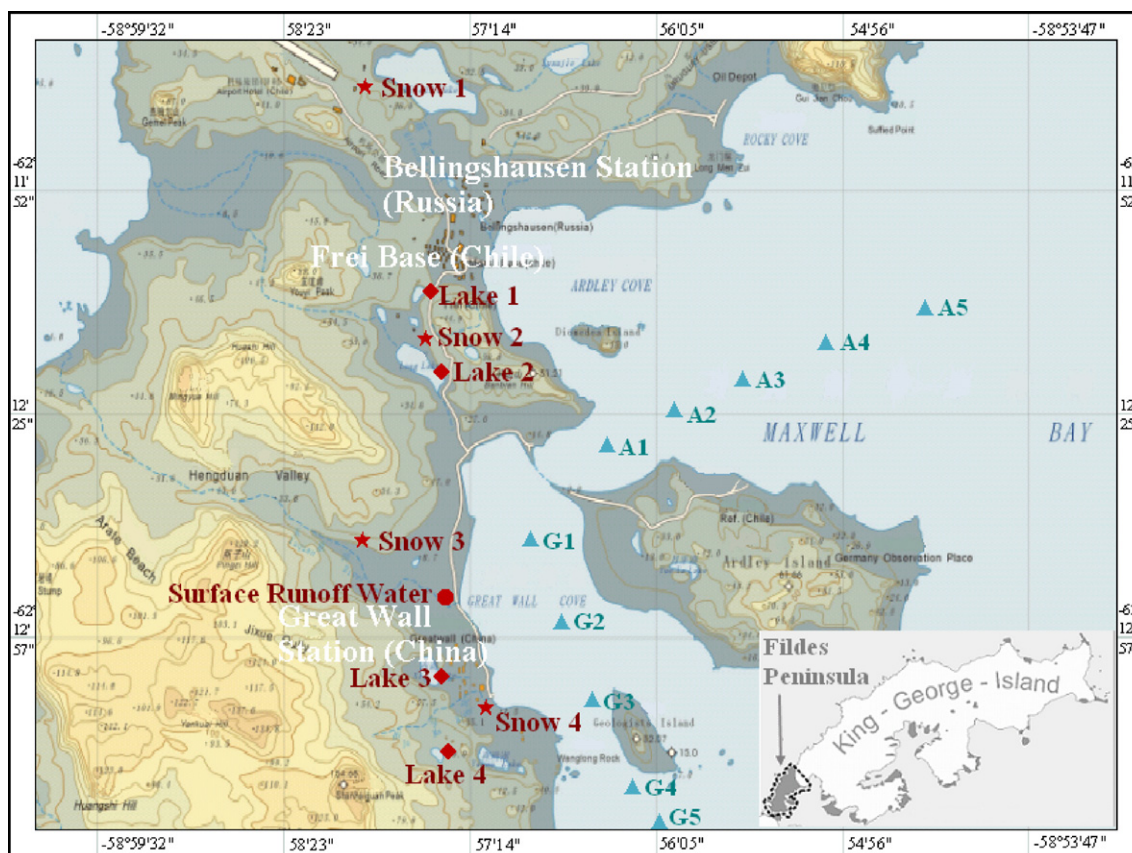

Fig. 1. Map showing the sampling locations of coastal seawater, snow, lake and surface runoff water samples from Fildes Peninsula, King George Island, Antarctica.

Between Frei Base (Chile) and Great Wall Station (China), we chose 4 lakes and 4 snow sites and one surface runoff water to determine the potential influence of human activities in Fildes Peninsula (Fig. 1). Lake water samples and surface runoff water sample were collected by using a stainless steel bucket and stored in 2 L PP bottles. Snow samples were also collected by using a 20 L stainless steel bucket with lid. The snow samples were melted at 4 °C in clean room and were transferred to 2 L PP bottles.

The water samples were filtered using glass fiber filters (GFF, Whatman, O.D. 47 mm, 0.7 μm, Banbury Oxon, UK). Five field blanks (FB) were stored and transported to test for possible external contamination. For the FB, 2 L of Millipore water (Millipore, Elix 5) were 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".

2.4. Sample extraction

The filtered sample was extracted by solid phase extraction (SPE) with Waters Oasis WAX cartridges in a clean laboratory, similar as described elsewhere [14,18]. Prior to extraction, the sample was spiked with 400 pg absolute of an internal standard (IS) mix (see Table S1). Briefly, after preconditioning with 10 mL distilled methanol and 10 mL Millipore water precleaned with Oasis WAX cartridge, the cartridge was loaded with approximately 1–2 drops/s. 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 150 μL under a nitrogen stream (N$_2$, purity >99.999%, Linde Gas, Pullach, Germany).

2.5. Instrumental analysis

The analytical method has been described elsewhere [14]. Briefly, an HP 1100 HPLC-system (Agilent Technologies, Vintage park, CA, USA) was used with a Synergi Hydro RP 80A column (150 mm × 2 mm, 4 μm, Phenomenex, Aschaffenburg, Germany combined with a suitable guard column; Synergi Hydro RP, 20 mm × 2 mm, 2 μm). Modifications of the HPLC system were made as described elsewhere [14,19] to eliminate instrumental blank contamination. The triple-quadrupole mass spectrometer, supplied by Applied Biosystems/MDS SCIEX (Agilent Technologies, Vintage park, CA, USA), used an electrospray ionization (ESI) interface in negative ionization mode.

2.6. Data analysis

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 injected) was used for calculation. 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.

2.7. Quality control

For quality assurance and 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 (Tables S2 and S3, supplementary data). The IDL and MQL were calculated at a signal-to-noise ratio (S/N) of 3 and 10, respectively. The MQL was calculated from 6 pg/L for perfluorodecane sulfonate (PFDS) to 128 pg/L for perfluorobutanoate (PFBA). In field blank samples, perfluorobutane sulfonate (PFBS), perfluoroheptane sulfonate (PFHpS) and perfluorooctanoate (PFOA) were found above the MQL (67.9 pg/L for PFBS,

23.1 pg/L for PFHpS and 42.6 pg/L for PFOA), and therefore the concentrations were blank corrected afterwards. As both methanol and Millipore water have been detected for certain PFASs (e.g. PFOA, PFBA, PFBS, PFNA, PFHpS, PFHpA) the methanol was distilled and the Millipore water was cleaned with Oasis WAX cartridge to eliminate the contamination. The matrix spike recoveries were determined at 400 pg/L and they ranged between $38 \pm 44\%$ for d$_9$-EtFOSE and $100 \pm 84\%$ for [$^{18}O_2$]-PFHxS. Breakthrough of PFASs was tested by using tandem Oasis WAX cartridges to extract 1 L seawater spiked with 400 pg internal standards. PFASs in the upper cartridge accounted for more than 80% of the sum determined from both cartridges. However, there were no internal standards detectable in the lower cartridge, indicating little breakthrough for PFASs with Oasis WAX cartridge. The recoveries of the internal standards were estimated by comparing the intensity of each internal standard in real sample and the average intensity in 8 calibration solutions (Table S3). It is noted that the matrix of the samples can significantly alter the response, that it is very important to use suitable isotope internal standards for individual target compounds.

3. Results and discussion

3.1. Concentrations of PFASs in snow, lake water, surface water runoff and coastal seawater

3.1.1. Snow and lake water

More than 15 of the 24 selected PFASs were found in the snow and lake water samples at 8 sampling stations (for details see Table S4, supplementary data). The quantified PFASs were C$_4$, C$_7$, C$_8$, C$_{10}$ PFSAs, C$_4$–C$_9$, C$_{11}$–C$_{14}$, C$_{16}$ PFCAs. The spatial distributions and composition profiles of PFASs along the sampling transect in snow and lake samples were shown in Fig. 2(a and b). All the snow and lake water samples contained detectable concentrations of PFOS, PFDS, PFBA, PFHxA, PFOA, PFNA, with a trend $\sum$PFBA > $\sum$PFHxA > $\sum$PFOA > $\sum$PFNA > $\sum$PFDS > $\sum$PFOS. The next frequently detected PFASs were PFPA (87.5%), PFTriDA (67.5%), PFTeDA (50%). Less than 50% of frequently detected PFASs were PFBS (37.5%), PFHpA (37.5%), PFUnDA (37.5%), PFDA (25%), PFHpS (12.5%), PFDoDA (12.5%). In all the snow and lake water samples, PFBA was detected with the highest concentration, with PFBA concentration from 1714 pg/L to 2670 pg/L (average of 2262 pg/L) in lake water samples and lower PFBA concentration (average of 522 pg/L) was found in snow samples. Additionally, PFTriDA and PFTeDA were detected below the detection limit in Lake 2 and Lake 3, and at high concentrations in Lake 1 (1560 pg/L for PFTriDA and 309 pg/L for PFTeDA) and Lake 4 (2811 pg/L for PFTriDA and 355 pg/L for PFTeDA), suggesting a potential point source contamination around the Lake 1 and Lake 4.

For snow samples, the $\sum$PFAS concentrations ranged from 1129 pg/L to 2491 pg/L in this study, which was higher than that in Greenland Arctic (~271 pg/L to 1082 pg/L) and Canadian Arctic (~22 pg/L to 80 pg/L) of remote Arctic regions, while lower than that in Albany, New York (910–23,900 pg/L) of urban region [20–22]. This indicated the lower $\sum$PFAS concentration in remote regions compared to urban regions with more industrial and commercial activities of PFASs. A relatively large proportion of total PFASs concentration was contributed by PFBA (average of 29%), followed by PFHxA (18%) and PFOA (12%), while PFAS concentrations were dominated by PFOA and PFNA in Canadian Arctic, PFOA and PFDA in Greenland Arctic, and PFOA in Albany, New York, respectively. This suggested PFAS concentration profiles depended on different regions and pollution sources, and PFCAs were always the predominant PFASs rather than PFSAs in snow samples.
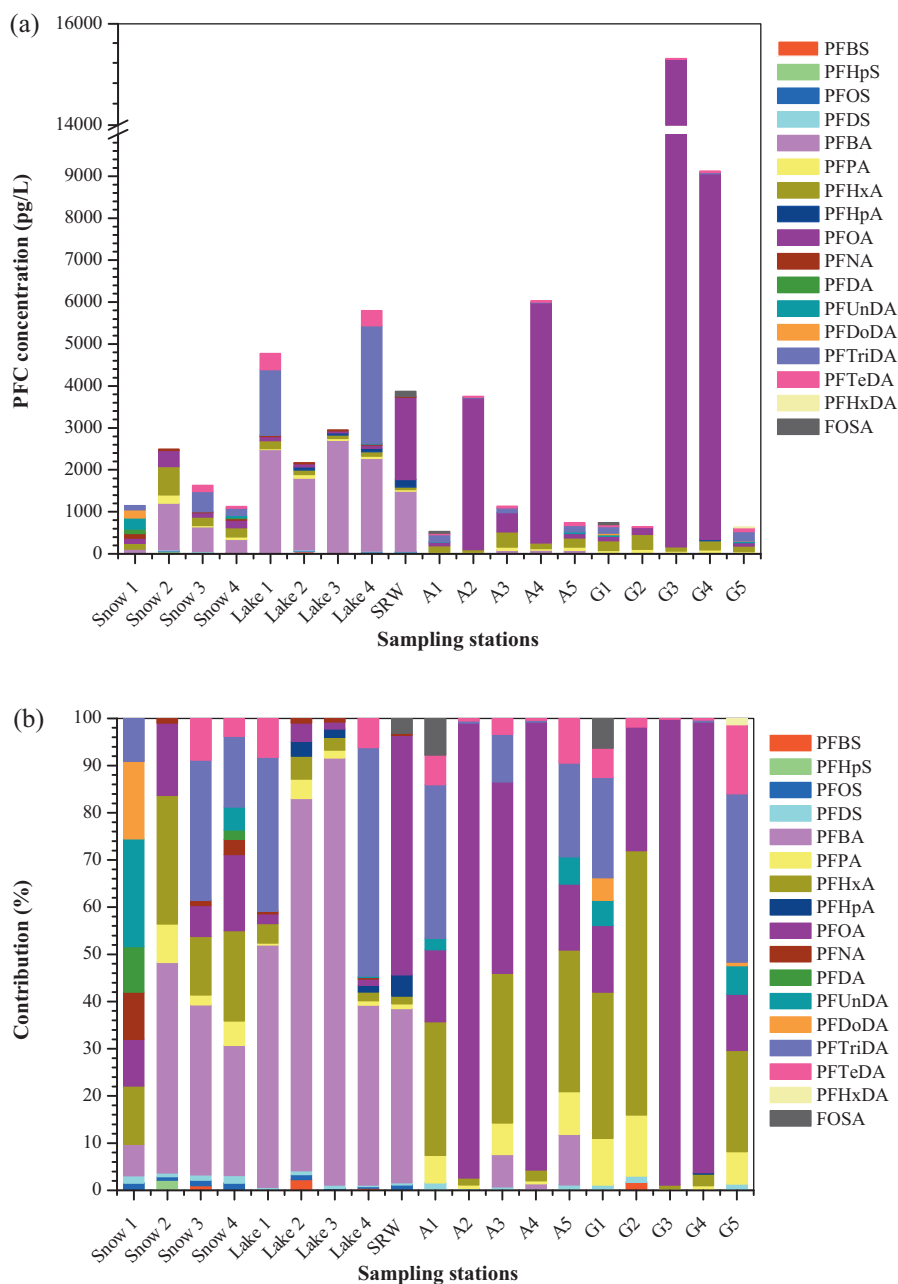
Fig. 2. (a) Spatial distribution of $\sum$PFASs and individual PFAS concentrations in the coastal seawater, snow, lake and surface runoff water samples from Fildes Peninsula, King George Island, Antarctica and (b) composition profile of individual PFAS in the coastal seawater, snow, lake and surface runoff water samples from Fildes Peninsula, King George Island, Antarctica.

Regarding lake water samples, $\sum$PFOA + PFOS concentrations (2–6 ng/L) were relatively lower in this study than the monitoring data for lakes in Canadian Arctic (3–70 ng/L), in New York State (16–805 ng/L), and Taihu lake in China (14–431 ng/L) [23–25]. In water of Lake 1 and Lake 4 of this study PFBA and PFTriDA were the dominant compounds, contributing 51% and 33% for Lake 1, 65% and 20% for Lake 4, respectively. PFBA was the predominant PFASs and contributed 78% and 91% for Lake 2 and Lake 3, respectively. This was not consistent with the general profile of PFAS concentrations usually dominated by PFOA and PFOS, such as the lakes in Canadian Arctic and New York State, Taihu lake in China, which could ascribe to the special geographic regions and different pollution sources in this study. Similarly, PFCAs were also the predominant PFASs in lake water samples.

3.1.2. Surface runoff water

More than 9 of the 24 selected PFASs were found in the surface runoff samples (for details see Table S4, supplementary data). The PFAS concentrations and the composition profiles of individual PFAS in SRW were shown in Fig. 2(a and b). The quantified PFASs were C_8, C_{10} PFSAs, C_4–C_9 PFCAs, PFOSA. $\sum$PFAS concentrations were 3874 pg/L, higher than that in snow samples and comparable to that in lake water samples. PFOA and PFBA were the predominant PFASs with a proportion of 51% and 37%, respectively. Among all the samples, highest PFOS concentrations (45 pg/L) were detected in SRW, which was ~2.5 times higher than that in snow and lake water samples, indicating point source contamination existing along the SRW. PFHpA was detected with concentrations of 175 pg/L in the SRW and of 51 pg/L on average in the lake water

samples, but below the detection limit in snow samples. This suggests that local pollutant discharge was the main source for PFHpA rather than the atmospheric transport and deposition of volatile precursor compounds. The concentration of PFOA (1966 pg/L) was about 1–2 order of magnitude higher than those in snow and lake water (46–383 pg/L), suggesting point source pollution along the SRW. Interestingly, for FOSA, which can degrade to PFSAs and PFCAs [11,26], was only found in SRW (120 pg/L). The source of this compound could probably contribute to the higher concentrations of PFOS, PFOA and PFHpA in SRW.

3.1.3. Coastal seawater

Overall 13 of the 24 selected PFASs were found in the coastal seawater samples at 10 sampling stations (for details see Table S4, supplementary data). The quantified PFASs were C_4, C_{10} PFSAs, C_4–C_8, C_{11}–C_{14}PFCAs, C_{16} PFCAs and FOSA. The spatial distribution and composition profile of individual PFAS along the sampling transect in coastal seawaters were shown in Fig. 2(a and b). The $\sum$PFAS concentration ranged between 532 pg/L and 15284 pg/L, and the highest concentrations of $\sum$PFAS were at location A2 (3751 pg/L), A4 (6025 pg/L), G3 (15284 pg/L), G4 (9123 pg/L), which was related the sewage effluent from Chile station, Russia Station and Great Wall Station. Concentrations of PFASs were generally low and at the same range at A1, G1, G2 and A5, G5, with the average concentration of 664 pg/L. A1, G1, G2 are in the inner cove of Ardley Cove and Great wall Cove, which prevents the inner seawater from mixing with sewage effluent, mostly PFASs may originate from SRWs, which contaminated both by atmospheric route and pollution emission. A5 and G5 are just outside the cove which is mainly affected by the current and the concentration of PFASs has a lower level.

All the seawater samples contained detectable concentrations of PFOA, PFHxA, PFPA, PFTeDA and PFDS, with a trend $\sum$PFOA > $\sum$PFHxA > $\sum$PFPA > $\sum$PFTeDA. PFOA have the greatest variability depending on location and the highest concentration is about 200 times higher than the lowest PFOA concentration. The next most frequently detected PFASs were PFTriDA (80%). Less than 50% of frequently detected PFASs were PFBS (30%), PFBA (30%), PFUnDA (30%), PFHpA (10%), PFDoDA (20%) and PFOSA (20%). A previous study found significantly low concentration of PFASs in Antarctic seawater, in which PFOS ($\sim$5–23 pg/L) and PFBS (BDL to 3 pg/L) were detected of 3 selected PFSAs, and only PFDoDA (BDL to 1 pg/L) was detected of 6 selected PFCAs [27], PFASs concentration did not vary to a great extent among locations, indicating direct discharge of industrial effluents into the Antarctic region is less important than non-point source pollution, such as atmospheric deposition. However, the present study found significant geographical differences in PFAS concentration, especially for PFOA (3431 ± 5092 pg/L) and PFTriDA (90 ± 83 pg/L). This suggested the presence of direct point source pollution to this Antarctic region. Interestingly, the concentration of PFOA (81–15,096 pg/L) was relatively higher than that in other open oceans, such as Atlantic Ocean (<4–229 pg/L), Pacific Ocean (15–142 pg/L), Indian Ocean (<5–11 pg/L) [7,14,27], and comparable to that in coastal waters nearby the industrial regions, such as Pearl River Delta, China (240–16,000 pg/L) and the German Bight, Germany (2670–7830 pg/L) [28,29]. This also indicated direct pollution input of PFASs to the area. Looking at PFBA, which was only detected at three locations of A3, A4 and A5, the concentrations were 78 pg/L, 64 pg/L and 80 pg/L, respectively. In the previous study on PFASs in seawater, the PFBA was detected at German coast (<105–4730 pg/L), in River Elbe (<105–400 pg/L), Baltic Sea (<105–440 pg/L) and Tokyo Bay, Japan ($\sim$20,000 g/L) [30,31], while not included in open ocean, such as Atlantic Ocean, Pacific Ocean, Indian Ocean and East Greenland Arctic Ocean [6,7,14,27]. The limited data available for PFBA confined comparisons among studies.

PFOS was not detectable in all seawater samples, which was not consistent with the general pattern that PFOS was the dominant PFASs in seawaters. This probably ascribed to the sources and the characteristics of PFOS. PFOS is the predominant PFASs in wildlife with high bioaccumulation [32], and has high sorption potential to sediment [33]. Therefore, PFOS could probably accumulate in marine food chain and adsorb to sediments, which needs further research.

3.2. Identification of sources of individual long-chain PFSAs

Among long-chain PFSAs, PFOS occurred in all the snow, lake and SRW samples. Its ubiquity could be due to two major sources: (i) the direct discharge from point sources or direct use of perfluorooctane sulfonic fluoride (FOSF)-related consumer products [34–36], and (ii) non-point sources via atmospheric transport of precursor compounds such as perfluoroalkane sulfonamide derivatives including FASEs and FASAs followed by their subsequent degradation [11,37]. In the present study, PFOS was not detected in all coastal seawater samples, but in all snow, lake and SRW samples. It should be noted that no geographical differences in PFOS concentrations ($n = 8$, 18 ± 3 pg/L) were measured in all snow and lake water samples, suggesting that PFOS could originate from non-point sources via atmospheric transport of precursor compounds, which is similar to the results of a previous study in the Antarctic region [27]. The concentrations of PFOS in snow, lake and SRW (12–45 pg/L) in this study were about 2–3 orders of magnitude lower than those in snow (<250–1930 pg/L), lake water (<250–9300 pg/L) and SRWs (<250–14,600 pg/L) from Albany York [20], and slightly lower than those in Canadian Arctic snow (2.6–86 pg/L) and Greenland Arctic snow (25–137 pg/L) [21]. Although the transport route in Antarctica and Arctic for PFASs should be different. Antarctica is shielded from PFASs originating from larger Northern Hemisphere sources. Oceanic transport would be hindered by the long exchange times between various southern ocean waters. But atmospheric transport of volatile precursors may be reasonable, consisting with the fact that the PFASs were determined in seal pubs and penguin's eggs in Antarctica [8]. This study possibly supports the hypothesis of atmospheric transport of precursor compounds of PFOS.

PFDS was found in all the samples of coastal seawater, snow and lake water as well as at a lower level in SRW. Similar to PFOS, no geographical differences in PFDS concentrations existed in snow, lake water and SRW samples ($n = 9$, 18 ± 0.1 pg/L), and in coastal seawater samples ($n = 10$, 8 ± 0.1 pg/L), suggesting atmospheric transport of volatile precursor compounds. The concentrations of PFDS in snow, lake and SRW samples were about 2 times than those in coastal seawater, which also indicated that PFDS could probably transfer to marine food chain and sediments in coastal seawater. A previous study found that PFDS was not detectable in water but in sediment (0.12 ± 0.01 ng/g (dw)) and fish (plasma: 9.4 ± 3.3 ng/g (ww)) from Orge River, France [38]. Additionally, PFDS has also been found in the municipal wastewater treatment plants receiving domestic wastewaters [39] and in the lake and rain in U.S. [20]. However, PFDS was not frequently detected in environmental multi-matrices. The occurrence, use and sources of PFDS have not been well known. Therefore, more research on their potential precursors and sources is needed.

3.3. Identification of point-sources of individual long-chain PFCAs

Among long-chain PFCAs, PFOA was detected in all samples having the highest concentration in coastal seawaters. Similar results for PFCAs were presented in other studies in coastal areas, such as coastal waters of NW Mediterranean coast [40], Korea [28,41], Tokyo Bay (Japan) [7], and Cantabrian Sea [42], German coast and the Baltic Sea [30,43]. The dominance of PFOA in coastal

waters might indicate that the contamination originated from riverine input where PFOA was one of the predominant PFASs [40,43,44]. The significant geographical differences in PFOA concentrations also indicated direct input of PFASs to this region, and the likely sources of PFOA could include sanitation discharges from buildings and sewage water, including personal care products (e.g., shampoos, conditioners and soaps), as well as wastewater and landfills [45–48]. Therefore more work is needed in future.

As for C_{10}–C_{16} PFCAs, all the coastal seawaters and 50% snow and lake samples were detected for PFTeDA, 80% coastal seawater samples were detected for PFTriDA, and 50% snow and lake samples were detected for PFHxDA. Particularly, Lake 1 and 4, which locate in the inner of Chilean Station and Great Wall Station, contaminated exceptional higher PFTeDA, indicate that there exist point sources account for the occurrence of these contamination. Usually, C_{10}–C_{16} fluorochemicals were used for textile impregnation spray for car interior in a concentration about 0.01 mg/kg, so vehicle traffic could be another potential contamination source identified in this study, as PFASs were detected in SRWs collected near parking lots and roadways [20]. PFAS concentrations in street runoff were found to be more than ten times higher than those in rainfall [49], suggesting that PFASs derived from street dust or motor vehicles. The importance of these sources has been supported by reports of PFASs in street dust [50]. Additionally, paints (containing Teflon Wax), which usually frequently are used to maintain the buildings the stations, aqueous film forming foams (AFFFs), which usually were frequently used at airports [35,36], should be accounted to the occurrence of long-chain PFASs in snow and lakes, but needed further study.

3.4. Correlations and concentration ratio between individual long-chain PFCAs in snow, lake, SRW and their potential source implications

A significant positive relationship between concentrations of PFOA and PFHxA were observed in snow and lake water samples ($R^2 = 0.949$, Fig. 3a). These results indicate that the sources of PFOA and PFHxA are similar in the sources. The results also showed that the concentration of PFPA was positively correlated with those of PFOA ($R^2 = 0.763$, Fig. 3b), which indicates that the sources of PFOA, PFPA, PFHxA are related, originating from the same point sources.

Young et al. [21] found a positive correlation between PFNA and PFOA with a slope of ~1 in snow samples from remote ice caps and Ahrens et al. found a slope of ~0.4 in the Atlantic Ocean and ~0.2 in Northern Europe, which can be partly explained by atmospheric deposition [5,14]. However, in the present study, PFNA showed poor correlation with PFOA in both snow and lake water samples, also indicating that the sources of PFOA mainly come from direct pollution discharge rather than atmospheric deposition.

Concentration ratios of PFOS to PFOA were calculated to assess possible sources of contamination as discussed elsewhere [20,28]. Previous studies have reported PFOS/PFOA ratios in a range of 4.4–26 in surface waters affected by effluents from sewage treatment plants [51] and a ratio of 2.3 was found in surface waters receiving industrial effluents [28]. Ratios less than one have been suggested to indicate the presence of a point source of PFOA, such as the ratio range of 0.2–0.5 reported in waters of the Tennessee River downstream of a fluorochemical manufacturing plant [34] and a ratio of 0.4 found near a carpet manufacturing site in the U.S. [52]. However, in our study, the concentration ratios of PFOS/PFOA were in a range of 0.05–0.17 for snow samples and 0.13–0.32 for lake water samples, respectively, mainly reflect the atmospheric transport of PFOS and direct point-source pollution input of PFOA in the this remote region.
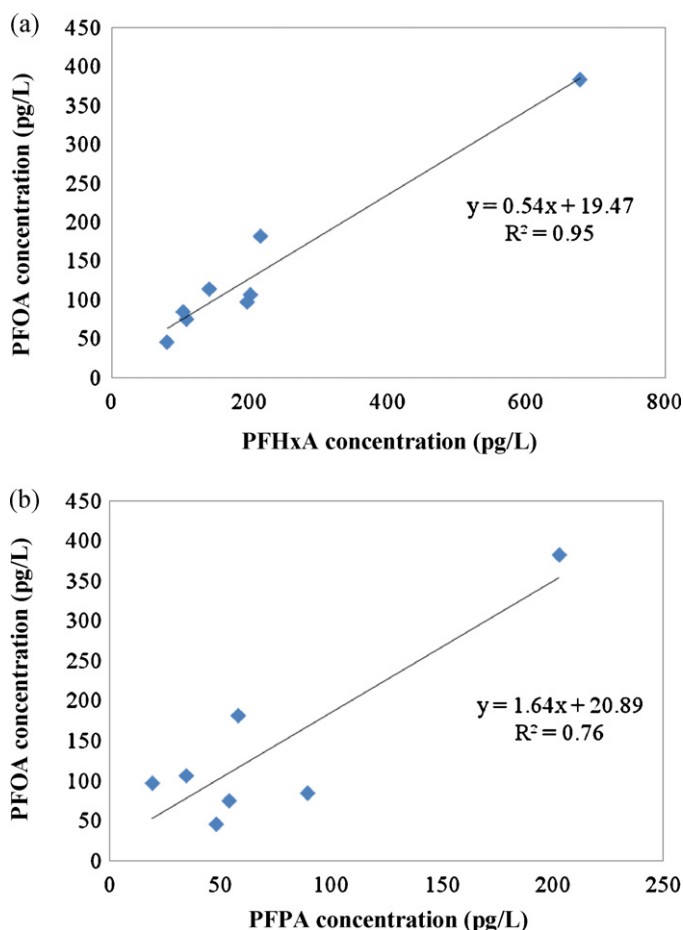

Fig. 3. (a) Correlation between PFOA and PFHxA concentrations in snow and lake water samples ($n = 8$) and (b) correlation between PFHxA and PFPA concentrations in snow and lake water samples ($n = 7$).

The calculation of PFHpA/PFOA ratio has been suggested to assess whether PFASs originate from atmospheric depositions [53]. In this study, the concentration ratios of PFHpA/PFOA for 3 lakes were 0.82, 1.13, 1.10 (PFHpA was not detected in Lake 1), less than the reported 6–16 in the remote regions and equal or slightly greater than 0.5–0.9 in urban areas [53]. Therefore, the sources of PFHpA and PFOA were dominated by point-source pollution in this region, this agrees with the conclusion in above analysis of this study.

3.5. Implication of occurrence of short-chain PFCAs in snow, lake and SRW in Antarctica

High concentration and mostly frequency of PFBA occurred in snow (average of 522 pg/L), lake (average of 2262 pg/L) and SRW (1431 pg/L) comparing with the lower composition and less frequency of those detected in coastal sea water, in which only A3, A4 and A5 were detected with PFBA ($n = 3$, 74 ± 8 pg/L), suggests PFBA in snow, lake and SRW have an important contaminating route by dust in the atmosphere and the degradation of their precursors. The significant variations of PFBA in snow, lake and SRW and the obvious difference of composition amounts and profiles of PFASs in these matrices indicate atmospheric dust contamination was the mainly pollution route. However, the degradation of their precursors are an important supplementary for the contamination of PFBAs. PFBA can be originated from the atmosphere route via the deposition of short-chain perfluorobutane sulfonyl-based precursors including *N*-ethyl perfluorobutane sulfonamide (EtFBSA), and

N-methyl perfluorobutane sulfonamidoethanol (MeFBSE) [10,11]. A previous study found that PFBA was the dominant PFASs in ice core samples from Svalbard Archipelago, European Arctic and also indicated the atmosphere sources of PFBA [54]. The precursors of PFBA are relatively new industrial chemicals used for surface-treated purposes. The industrial replacement of long-chain PFOS by C$_4$-based compounds was first introduced by the 3M Company in 2003 [55]. According to the Company, these C$_4$-based chemicals are not bioaccumulative and non-toxic [55]. Recently, PFBA and PFBS were found as dominant PFASs in European rivers and coast waters [43]. Additionally, FTOH precursors such as 4:2, 6:2 and 8:2 FTOHs, were shown to be the likely atmospheric sources of PFCAs including PFPA, PFBA, PFPrA (perfluoropropionic acid) and TFA [10,56]. Studies on transport of short-chain PFASs are important and can give a more complete view of the fate of PFASs in the global background. More investigation of short-chain PFASs in wet precipitation, SRWs, lakes in the global scale is needed.

4. Conclusions

Direct discharge of untreated sewage, as still practiced at most Antarctic research stations, together with the effects of the year-rounded operation of stations and activities of tourists and scientists, can result in the detectable levels of PFAS contaminants in most station areas in Antarctica. The PFASs in these areas mainly originated from the point sources, but also affected by the non-point sources, such as PFBA, which can be degraded by their precursors (such as FTOHs, EtFBSA, MeFBSE) with the potential ability of long-range atmospheric transportation. As for PFOS, no geographical differences were measured in all snow and lake water samples, suggesting a sole process of degradation of their precursors (such as FTOHs, EtFOSA, MeFOSE) which can transport by long-range atmospheric route, but in a very low level. The occurrence of PFASs in these remote locations suggests the widespread distribution of per- and polyfluoroalkane contamination, even in the pristine Antarctica. A global investigation and continual monitoring in future should be conducted for better understanding the fate of PFASs in the global scale environment.

Supplementary information

Additional information about the analytes, instrumental detection limit, method quantification limit, recoveries and overview of PFASs concentrations is available in the supplementary data.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.01.030.

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