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Occurrence of legacy and emerging organic contaminants in snow at Dome C in the Antarctic



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HIGHLIGHTS

- OPEs, PFASs and PAHs were detected in surface snow at Dome C in the Antarctic.
- HFPO-DA occurred in the Antarctic.
- Both global distillation and cold trapping play significant role for their occurrences.

GRAPHICAL ABSTRACT



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ABSTRACT

Concentrations of 9 organophosphate esters (OPEs), 16 perfluoroalkylated substances (PFASs) and 17 polycyclic aromatic hydrocarbons (PAHs) were investigated in surface snow samples collected at Dome C on the Antarctic Plateau in summer 2016. Tris(1-chloro-2-propyl) phosphate (TCPP), tris-(2-chloroethyl) phosphate (TCEP) and tri-n-butylphosphate (TnBP) were the dominant compounds of OPEs, with mean concentrations of 8157 ± 4860 , 1128 ± 928 and 1232 ± 1147 pg/L. Perfluorooctanoic acid (PFOA, mean: 358 ± 71 pg/L) was the dominant compound of PFASs, and following by perfluoro-n-hexanoic acid (PFHxA, mean: 222 ± 97 pg/L), perfluoro-n-heptanoic acid (PFHpA, 183 ± 60 pg/L) and perfluoro-n-pentanoic acid (PFPeA, 175 ± 105 pg/L). 2-(Heptafluoroproxy)propanoic acid (HFPO-DA, mean: 9.2 ± 2.6 pg/L) was determined in the Antarctic for the first time. Significantly positive correlations were observed between HFPO-DA and the short-chain PFASs, implying they have similar emission sources and long-range transport potential. High levels of 2-methylnaphthalene and 1-methylnaphthalene, as well as the ratios of PAH congeners indicated PAHs were attributable mostly to combustion origin. Occurrence and profiles of the indicators of OPEs, PFASs and PAHs, as well as air mass back-trajectory analysis provided direct evidences of human activities on Concordia station and posed obvious impacts on local environments in the Antarctic. Nevertheless, the exchange processes among different environmental matrices may drive the long-range transport and redistribution of the legacy and emerging Organic contaminants from coast to inland in the Antarctic.

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1. Introduction

Legacy and emerging organic contaminants, such as organophosphate esters (OPEs), perfluoroalkylated substances (PFASs) and polycyclic aromatic hydrocarbons (PAHs), have raised increasing concerns due to their persistence, transport potential and toxicity (Li et al., 2017; Wang et al., 2015). OPEs are a group of industrial chemicals that have been widely used in many industrial processes and household products as flame retardants and plasticizers (Li et al., 2017; Salamova et al., 2014a). The global consumption of OPEs has increased to 300,000 tons by 2011 (Castro-Jimenez et al., 2016) and to 680,000 tons in 2015 (Wang et al., 2019). As OPEs are added as plasticizers and/or flame retardants to the material without covalent binding, they can leach into the environment during the life-long process (Ma et al., 2017a, 2017b; Castro-Jimenez and Sempere, 2018). Moreover, OPEs have been shown to affect reproduction, development, and motor activity in a multitude of alternative animal models such as zebrafish, *Caenorhabditis elegans*, and *Planaria* (Blum et al., 2019; Cano-Sancho et al., 2017; Noyes et al., 2015; Oliveri et al., 2015). As the substitutes of polybrominated diphenyl ethers (PBDEs), OPEs exhibit lower persistence and long range atmospheric transport (LRAT) potential. However, OPEs were observed in multimedia in urban and rural areas, even in remote regions, such as the Arctic and Antarctic, proving their global distribution and high LRAT potential, (Castro-Jimenez et al., 2016; Cheng et al., 2013; Marklund et al., 2005; Salamova et al., 2014a) which were raising awareness on their environmental fate and adverse biological impacts.

PFASs are a series of synthetic organic chemicals with a wide range of industrial and consumer applications. High stability of the fluorine-carbon bond makes PFASs extremely persistent in the environment (Lindstrom et al., 2011). Among PFASs, perfluoroalkyl acids (PFAAs) have been produced and applied in high quantity and are ubiquitous in various environment matrices (Zhao et al., 2012). The long-chain PFAAs (with 7 or more perfluorinated carbon atoms), e.g. perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) have attracted great concerns owing to their toxicities and their persistent and bioaccumulation potentials (Nguyen et al., 2017). Consequently, the production and application of PFOA and PFOS and their related salts have been banned or regulated for certain application in many countries (Heydebreck et al., 2015). Although PFAAs are not susceptible to LRAT due to the low volatility and high water solubility of anionic form (Casal et al., 2017; Wild et al., 2015), they have been determined in open ocean and polar regions (Cai et al., 2012; Gonzalez-Gaya et al., 2019; Yeung et al., 2017). The different physiochemical properties, e.g. relatively low vapor pressure and high water solubility, make multimedia distribution and long-range transport processes of PFAAs different from those of other legacy persistent organic pollutants (POPs) (Casal et al., 2017; MacInnis et al., 2019; Prevedouros et al., 2006). It is believed that oceanic currents may play an important role for their transport at regional and global scale. Besides, the neutral and more volatile PFASs, such as fluorotelomeralcohols (FTOHs), perfluorooctane sulfonamidoethanols (FOSEs) and perfluorooctane sulfonamides (FOSAs), undergo LRAT to Polar Regions. Neutral PFASs can be degraded in the atmosphere to form PFAAs and deposit via wet and dry atmospheric deposition, which act as a secondary source of PFASs in the remote regions (Wang et al., 2015; Wong et al., 2018; Young et al., 2007).

Unlike PFAS and OPEs, PAHs are mainly released into the environment primarily through incomplete combustion of fossil fuels and biomass burning (Wang et al., 2010; Yu et al., 2019). They are of great concern owing to their toxicity, mutagenicity, persistent and long-range transport (Cabrerizo et al., 2014; Lammel et al., 2015; Lohmann et al., 2009; Muir et al., 1992; Szczybelski et al., 2019). PAHs are ubiquitous in the global environment, and have been determined in air, water, sediment, and biota in remote areas (Casal et al., 2018b; Ma et al., 2017a; Norregaard et al., 2015).

Polar regions are special eco-environmental systems and generally used as an important global background area. Previous results in polar regions have already provided key knowledge about global environmental behaviors, cycles and fates of POPs (Casal et al., 2018a; Casal et al., 2019; Li et al., 2017). LRAT and ocean current transport (OCT) are generally considered as the primary pathways of POPs into polar regions (Cheng et al., 2013; Li et al., 2017; MacInnis et al., 2019; Young et al., 2007). Compared with the Arctic, input loads of POPs via LRAT and OCT are believed to be weaker in the Antarctic due to the hindrance of the circumpolar current and polar vortex in the Southern Ocean (Bengtson Nash, 2011; Casal et al., 2019; Keyte et al., 2013). Furthermore, increasing human activities in the Antarctic may have notable impacts on local environments. Recently, influence of local sources (research stations and tourism) on the occurrence of legacy and emerging organic contaminants in snow, soil and air in the Antarctic have been reported most likely at coastal sites (Casal et al., 2017; Wild et al., 2015).

Pollution is relatively low in the Antarctic, and thus any influence of local sources may make obvious effects on environments (Wild et al., 2015). Considering the effectiveness of snow scavenging of air pollutants, snow acts as an important sink for the distribution of POPs among multimedia in polar regions known as "cold-trapping" (Casal et al., 2018a; Casal et al., 2019; Vecchiato et al., 2015). Especially, scavenging and remobilization of POPs by snow deposition and melting under the global climate change condition may enhance the pivotal impact on driving POPs exchange between environmental media.

In this study, occurrence and concentrations of typical legacy and emerging contaminants, OPEs, PFASs and PAHs were investigated in snow samples collected in summer 2016 at Concordia French-Italian research station at 3233 m above sea level at a location called Dome C on the Antarctic Plateau. The main objectives were (1) to provide, for the first time, the presence and concentrations of OPEs, PFASs and PAHs in snow at Dome C, one of the coldest places on the Earth; (2) to discuss their primary sources.

2. Materials and methods

2.1. Study site and sampling methodology

Dome C is one of the coldest places on the Antarctic plateau. Temperatures hardly rise above -25°C in summer and can fall below -80°C in winter. The annual average air temperature is -54.5°C (wikipedia.org/wiki/Dome_C). Eleven surface snow samples were collected at Concordia Research Station at Dome C in summer 2016. Briefly, the snow samples were collected with a 10-L stainless steel barrel, and sealed with a press tight deck. Collection was planned every two days from 28th of November to 18th of December 2016. Seven surface snow samples were collected in days characterized by diamond dust and snow precipitation (28/11, 30/11, 02/12, 06/12, 14/12, 16/12 and 18/12/2016), two sampling days with clear sky conditions (no fresh snow precipitation) (04/12 and 10/12/2016) and two with cirrus clouds and significant cloud cover, but no precipitation (08/12 and 12/12/2016). The sampling location is ca. 500 m away from the station to limit contamination as much as possible, in an area closed to ATMOS science shelter, specifically dedicated to atmospheric studies. Samples were stored at -20°C at the station and during transport.

2.2. Sample preparation and analysis

The detailed description of sample pretreatment and analysis has been presented elsewhere (Li et al., 2017). Briefly, snow samples melt at 20°C and then filtered with GF/F filters ($0.7\ \mu\text{m}$, 47 mm). 800 mL snow water was liquid-liquid extracted with 50 mL dichloromethane for the analysis of OPEs and PAHs. 1000 mL snow water was extracted with OASIS WAX cartridge (150 mg, 6 mL) for the determination of PFASs. Internal standards, e.g. d27-TnBP, d12-TCEP and d15-TPhP for

OPE, deuterated PAHs, and ^{13}C labeled PFAS were spiked prior to extraction. The extracts were concentrated to 150 μL for instrumental analysis as described in previous work (Li et al., 2017; Joeris et al., 2019; Ma et al., 2017a). The detail information of the analytes, analytical methods and quality assurance and quality control were summarized in the Supporting Information (SI).

2.3. Statistical analysis

Statistical analyses were performed with SPSS Statistics version 18 (IBM Corp.). Figures were plotted with Origin 2017G (OriginLab). GC-MS/MS data were analyzed using MassHunter B08 (Agilent), and LC-MS/MS data analysis was performed with Analyst 1.5 (Applied Biosystems), respectively.

3. Results and discussion

3.1. OPEs in snow

The concentrations of 9 OPE congeners in the 11 snow samples collected at Dome C are shown in Fig. 1 and summarized in Tables 1 and S8. The total concentrations of 9 OPEs (ΣOPEs) were from 7248 to 20,460 pg/L, with mean of $12,633 \pm 5037$ pg/L. To date, there have been few reports on OPEs in snow, or not measured the same set of compounds thus it is difficult to compare OPE levels in snow, especially in Polar Regions. OPE concentrations in snow at Dome C were higher than those observed in the Arctic snow (8 OPEs, mean: 7834 ± 2684 pg/L) (Li et al., 2017) and the East Antarctic ice sheet (TCEP, 50–2000 pg/L) (Cheng et al., 2013), while lower than those in northern Sweden (150000–26,000,000 pg/L) (Marklund et al., 2005) and central Germany (134000–570,000 pg/L) (Regnery and Puttmann, 2009).

Three chlorinated OPEs accounted for $72 \pm 17\%$ of ΣOPEs and $28 \pm 17\%$ for Six nonchlorinated OPEs, respectively. As the dominant compounds, TCPP, TCEP and TnBP accounted for 64.6%, 8.9% and 9.8% of ΣOPEs , respectively. TCPP was observed in most studies as the dominant compound in different environmental media far away from the sources (Li et al., 2017; Ma et al., 2017b; Zhong et al., 2017), which is consistent with the finding in the snow samples from the Dome C.

Significant positive correlations among OPEs would suggest a common source and/or similar environmental pathways (Shoeb et al., 2014). Table 2 summarizes the results of Pearson's correlation between individual OPE concentration in snow samples. Three chlorinated OPE

congeners were positively correlated with each other (Table 2), and significant positive correlation can be seen between TCEP and TDCP ($r = 0.733, p < .05$), which indicates they originate from similar predominant sources, have similar emission pathway and undergo similar long-range transport. Besides, TPhP showed significant correlations with TDCP ($r = 0.738, p < .05$), TPrP ($r = 0.660, p < .05$), TEHP ($r = 0.660, p < .05$), and TPeP ($r = 0.790, p < .01$). Indeed, the levels and profiles of OPEs in different media and regions depend on their sources, and further research is needed to clarify the profiles and apportion the local and remote sources.

As two dominant compounds of chlorinated and non-chlorinated OPEs, the variations of TnBP/TCPP ratios are determined by their physicochemical properties (vapor pressure) and half-life times. TnBP is with higher vapor pressure (0.465 Pa) and shorter atmospheric photodegradation half-life ($t_{1/2} < 1$ h) compared with TCPP (0.0014 Pa and $t_{1/2} = 8.6$ h) (Regnery and Puttmann, 2009). This makes TnBP more volatile in combination with a lower LRAT potential. While TCPP is more persistent and subject to LRAT potential. Thus, TnBP was often observed higher concentrations near the local sources, e.g. indoor and urban environment (Cui et al., 2017; Zhou et al., 2017), and lower level in remote areas (Li et al., 2017; Salamova et al., 2014b; Suhring et al., 2016).

As stated above, LRAT and/or OCT are primary pathways of POPs into polar regions. Cheng et al. (2013) regarded the ocean around the Antarctica as the main pathway of TCEP to snow in East Antarctica, and other OPEs may not possess the ability to transport sufficiently long from source regions to the Antarctica ice sheet (Cheng et al., 2013). Recent research indicated increasing human activities (research stations and tourism) posed considerable influence on local environment (Wild et al., 2015). It was found that the levels and profiles of PBDEs and PFASs in dust at Australian Antarctic research station (Casey Station) were consistent with those reported in home and offices from Australia (Wild et al., 2015). In the current study, the high ratios of TnBP/TCPP implied that OPEs in snow at Dome C were partially from local sources, e.g. emission from the building material at the research station, with dry deposition reinforces by diamond dust and snow precipitation scavenging occurring $>70\%$ of the collecting days. The 5-day and 10-day air mass back-trajectory analysis (Fig. S1) also showed that air mass near Dome C was controlled by atmospheric circulation on and around the Antarctic continent, and there was no obvious inter-continental transport during the sampling periods. The back-trajectory results in this study further confirmed that the influence of LRAT was weaker within the Antarctic continent due to the atmospheric dynamics of the region (polar vortex in the Southern Ocean) compared with the Arctic (Bengtson Nash, 2011; Casal et al., 2019; Keyte et al., 2013).

However, the high solubility of OPEs in water may allow that OPEs reach the southern Ocean by long-range transport via ocean current. Unfortunately, the data of OPEs in seawater of the Southern Ocean are rare. Gao et al. (2018) studied OPE in the lake water and seawater using an approach of aquatic time-integrated passive sampling on King George Island (Gao et al., 2018). TDCP, TEHP, TPhP and EHDPHP were detected in a few water samples with concentrations from 0.6 to 44.37 ng/L, suggesting OPEs can be discharged into the aquatic environment from the research stations via runoff and atmospheric deposition. Moreover, high concentrations of OPEs have been determined in seawater and lake water from high latitude, e.g. the North Pacific, North Atlantic and the Arctic (Li et al., 2017; Sun et al., 2020). Air-water-gas exchange fluxes of OPEs have been studied in the Arctic (Li et al., 2017). Gas-phase volatilization from seawater was found for TCEP, TCPP and TnBP. These results suggest that the water-air exchange processes are relevant to consider for the long-range transport of (OPEs). Interestingly, relatively high OPE concentrations have been measured in the air over the Southern Ocean (Castro-Jimenez et al., 2016; Moller et al., 2012), which might be caused by water to air volatilization and oceanic sea spray generated aerosols (Schiffer et al., 2018). Consequently, the exchange processes of air-water, air-snow, and air-ice

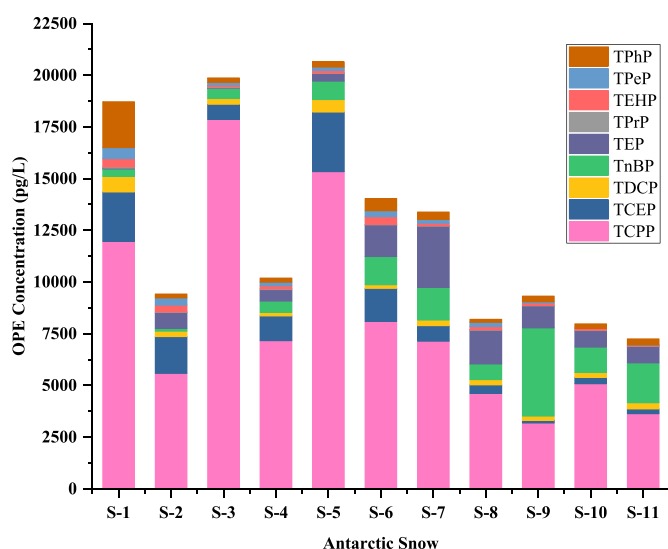


Fig. 1. Concentrations of 9 OPEs in snow samples from Dome C.

Table 1 Minimum, maximum, mean and standard deviation values of 16 PFASs, 17 PAHs and 9 OPEs concentrations (pg/L) in 11 snow samples collected at Concordia Research Station at Dome C in the Antarctic in summer 2016.

PFASs	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFHpS	PFOS	PFDS	HFPO-DA	Sum	
Min	73	92	94	273	38	22	5.6	2.3	0.5	0.9	17	1.3	0.6	36	0.1	6.3	702	
Max	446	373	266	539	95	41	11	6.3	3.6	4.3	35	12	4.4	62	0.8	13	1750	
Mean	175	222	183	358	73	30	8.0	3.9	2.1	2.3	24	6.0	1.5	46	0.3	9.2	1145	
Std	105	97	60	71	17	6.2	2.0	1.2	0.9	1.0	5.9	2.9	1.2	8.0	0.2	2.6	702	
PAHs	2-MP	1-MP	Ace	Acp	Fl	Phe	An	Flu	Pyr	Chr	BaA	BbF	BkF	BaP	InP	DbA	BghiP	Sum
Min	376	198	6.3	89	34	300	8.3	112	76	25	24	24	17	19	20	28	15	1597
Max	1167	733	30	165	74	778	1291	220	201	67	40	37	40	33	43	80	71	4363
Mean	758	442	19	126	50	512	220	149	142	38	28	31	28	27	31	47	55	2704
Std	269	164	8.3	29	13	128	426	36	37	12	4.5	4.1	7.5	4.8	7.6	13	15	741
OPEs	TCPP	TCEP	TDCP	TnBP	TEP	TPrP	TEHP	TPeP	TPhP	Sum								
Min	3190	141	174	139	22	11	46	8.6	138	7248								
Max	17,870	2883	752	4268	2970	59	400	535	2207	20,640								
Mean	8157	1128	319	1232	961	26	180	190	440	12,633								
Std	4860	928	185	1147	846	16	126	155	599	5037								

may drive the long-range transport and redistribution for OPEs from coast to inland.

3.2. PFASs in snow

The concentrations of 16 PFASs (Σ PFASs) in snow at Dome C ranged from 702 to 1750 pg/L with a mean of 1145 ± 283 pg/L (Tables 1 and S9). Perfluoroalkyl carboxylates (PFCAs) concentrations (1058 ± 281 pg/L) were 2 orders of magnitude higher than perfluoroalkanesulfonates (PFASs) concentrations (78 ± 11 pg/L). PFOA was the dominant PFCAs and PFOS was the dominant PFASs. The Σ PFASs was at similar level in comparison to those in Fildes Peninsula (1129–2491 pg/L) (Cai et al., 2012) and Livingston Island (760–3600 pg/L) (Casal et al., 2017) in the Antarctic, and two orders of magnitude higher than those in Canadian Arctic (22–80 pg/L) (Young et al., 2007), while lower than those in urban regions (910–23,900 pg/L) (Kim and Kannan, 2007).

The profiles of 16 PFASs did not show differences among sites ($p > .05$). In 16 PFASs, PFOA was the dominant compound (Fig. 2) with mean of 358 ± 71 pg/L, and following by PFHxA (mean: 222 ± 97 pg/L), PFHpA (mean: 183 ± 60 pg/L) and PFPeA (mean: 175 ± 105 pg/L). High levels of PFOA were also observed in snow, such as Livingston Island (29–1300 pg/L) (Casal et al., 2017), Fildes Peninsula (Cai et al., 2012), and glacial firn (200–600 pg/L) in the eastern Italian Alps (Kirchgeorg et al., 2013). Different profiles of PFASs were reported, for example, the dominant compounds were PFOA and PFNA in the Canadian Arctic, PFOA and PFDA in Greenland Arctic (Cai et al., 2012; Young et al., 2007). These implied that the profiles of PFAS in snow depended on their different sources or differing environmental processes along with the accumulation in snow (Codling et al., 2014).

Average PFCAs (except for PFOA) and PFASs (except for PFOS) concentrations were inversely correlated with their carbon number,

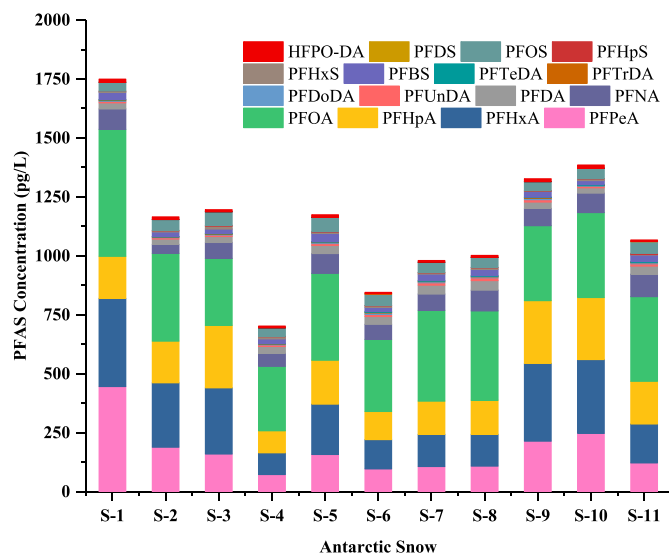


Fig. 2. Concentrations of 16 PFASs in snow samples from Dome C.

respectively ($r^2 = 0.86$ for PFCAs and $r^2 = 0.70$ for PFASs, $p < .01$), and long carbon chain PFCAs (C9–C14) presented low concentrations (<10% of Σ PFCAs), which may result from the LRAT potential and atmospheric oxidation ability of their volatile precursors. At present, C8 products are still widely used, at the same time, commercial products are shifting from long chain-length to shorter chain products (C4) and phasing out of commercial perfluorooctanesulfonyl fluoride (Ahrens et al., 2010; D'Eon et al., 2006; Möller et al., 2010). High levels of

Table 2 Pearson correlation coefficient matrix for 9 OPEs in snow.

	TCEP	TDCP	TnBP	TEP	TPrP	TEHP	TPeP	TPhP
TCPP	0.534	0.557	−0.441	−0.525	0.488	0.006	0.169	0.241
TCEP		0.733*	−0.490	−0.393	0.103	0.599	0.637*	0.469
TDCP			−0.323	−0.436	0.419	0.351	0.570	0.738*
TnBP				0.312	−0.132	−0.361	−0.469	−0.186
TEP					−0.664*	−0.131	−0.164	−0.283
TPrP						0.218	0.370	0.660*
TEHP							0.907**	0.660*
TPeP								0.790**

** Significant correlation at the level of .01 (bilateral).
* Significant correlation at the level of .05 (bilateral).

Table 3
Pearson correlation coefficient matrix for 16 PFASs.

	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTTrDA	PFTeDA	PFBS	PFHxS	PFHpS	PFOS	PFDS	HFPO-DA
PFPeA	0.863**	0.421	0.778**	0.260	-0.551	-0.418	-0.281	0.249	-0.278	0.196	-0.238	-0.256	-0.264	0.053	0.834**
PFHxA		0.783**	0.455	0.117	-0.742**	-0.416	-0.343	0.158	-0.266	0.001	-0.198	-0.101	-0.041	-0.222	0.909**
PFHpA			-0.025	0.231	-0.580	-0.128	-0.274	0.102	0.002	-0.142	-0.044	0.174	0.281	-0.498	0.636*
PFOA				0.399	-0.001	-0.071	-0.111	0.226	-0.196	0.567	-0.387	-0.292	-0.248	0.167	0.524
PFNA					0.380	0.455	0.180	0.499	0.310	0.552	-0.231	0.121	0.142	-0.144	0.098
PFDA						0.788**	0.526	0.319	0.318	0.545	-0.143	-0.005	0.118	0.063	-0.656*
PFUnDA							0.685*	0.504	0.528	0.361	-0.425	-0.049	-0.018	-0.013	-0.360
PFDoDA								0.568	0.658*	0.160	-0.525	0.026	-0.037	0.574	-0.394
PFTTrDA									0.133	0.491	-0.390	-0.391	-0.114	0.058	0.192
PFTeDA										-0.277	-0.056	0.228	0.161	0.482	-0.417
PFBS											-0.463	-0.020	0.167	-0.188	0.080
PFHxS												0.019	0.268	-0.246	-0.283
PFHpS													0.421	-0.052	-0.409
PFOS														-0.279	-0.173
PFDS															-0.260

** Significant correlation at the level of .01 (bilateral).

* Significant correlation at the level of .05 (bilateral).

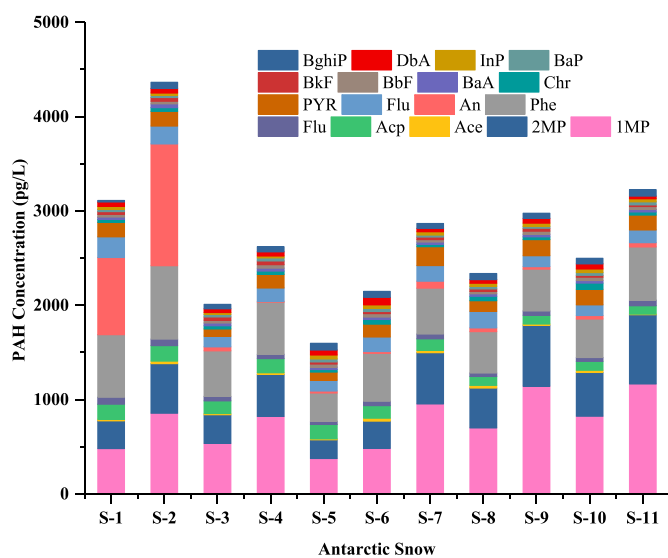


Fig. 3. Concentrations of 17 PAHs in snow samples from Dome C.

PFHpA, PFHxA and PFPeA observed in this study were the reflection of type changes of commercial products and increasing shorter chain products in remote pristine areas.

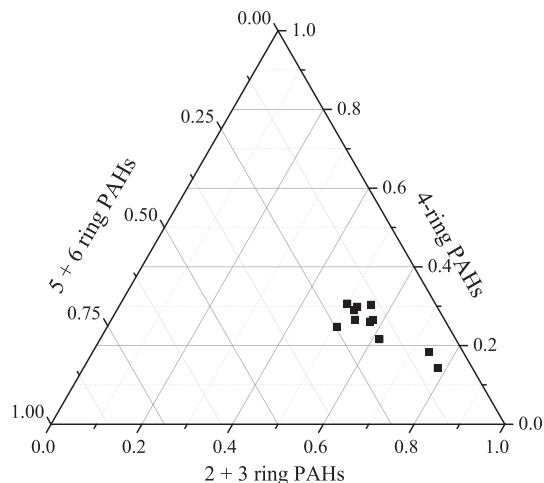


Fig. 4. Ternary diagram for different ring PAHs in snow samples collected Dome C.

It is worth noting that HFPO-DA was observed in snow at Dome C. To our knowledge, this is the first time of reporting on HFPO-DA in polar regions. HFPO-DA concentrations ranged from 4.7 to 13.0 pg/L, with mean of 8.8 ± 2.8 pg/L (Tables 1 and S9), which was at least 3 orders of magnitude lower than those in seawater of North and Baltic Seas (Joeris et al., 2019), rivers in Germany and China (Brandsma et al., 2019; Heydebreck et al., 2015).

HFPO-DA is the hydrolysis compound of perfluoro-2-propoxypropanoic acid (PFPrOPrA) and the ammonium salt of PFPrOPrA (GenX), which has been produced by DuPont since 2010 as a sustainable replacement of PFOA (Sun et al., 2016). The production volume and emission sources of HFPO-DA are limited. Recently Gaballah et al. have carried out evaluation of developmental toxicity, developmental neurotoxicity, and tissue dose in Zebrafish exposed to HFPO-DA and other PFAS, which showed negative results for HFPO-DA (Gaballah et al., 2020). More studies regarding its toxicity are warranted. Considering chemical stability and physicochemical properties, HFPO-DA is expected to pose similar ability as other PFASs to be transported to remote sites via LRAT of the precursors (Gomis et al., 2015; Heydebreck et al., 2015). The observation of HFPO-DA at Dome C provided the definitive evidence that this anthropogenic chemical can be transported to the Antarctic. Obviously, further studies are needed to fully understand transport pathways and behaviors of HFPO-DA in the Antarctic.

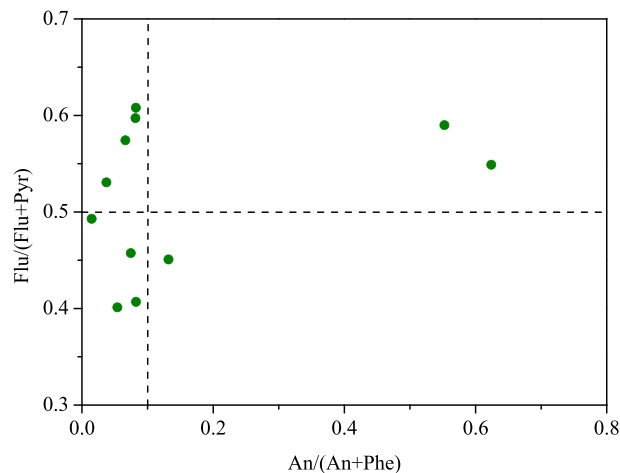


Fig. 5. Cross plot for the ratio of An/(An + Phe) versus Flu/(Flu + Pyr).

The results of Pearson's correlation between individual PFAS concentrations in snow samples are summarized in Table 3. Significantly positive correlation was observed between PFDA and PFUnDA ($r = 0.788, p < .01$), while only a moderate correlation ($r = 0.399, p < .05$) was noticed between PFOA and PFNA. As PFDA and PFUnDA are not primary substances in commercial products (Prevedouros et al., 2006; Young et al., 2007), their occurrence in Antarctic snow is believed to be the result of atmospheric oxidation of their precursors (Young et al., 2007). Based on Ellis et al., 8:2 FTOH can transform into PFOA and PFNA, and 10:2 FTOH into PFDA and PFUnA (Ellis et al., 2004). The concentrations of PFOA and PFNA were 1 order of magnitude higher than those of PFDA and PFUnA, while the ratios of PFDA/PFUnA (4.0 ± 0.6) and PFOA/PFNA (5.7 ± 2.5) were observed, indicating they were from atmospheric oxidation and/or LRAT of their precursors (8:2 FTOH and 10:2 FTOH). Among the short chain PFCAs, significant positive correlations were observed for PFHxA/PFPeA ($r = 0.863, p < .01$), PFHxA/PFHpA ($r = 0.783, p < .01$). Moreover, significantly positive correlations also presented among the long-chain PFCAs, e.g. PFUnDA/PFDoDA ($r = 0.685, p < .05$), PFDoDA/PFTeDA ($r = 0.658, p < .05$). Interestingly, HFPO-DA showed significantly positive correlations with three short chain PFCAs, e.g. HFPO-DA/PFPeA ($r = 0.834, p < .01$), HFPO-DA/PFHxA ($r = 0.909, p < .01$) and HFPO-DA/PFHpA ($r = 0.636, p < .05$). A moderate positive correlation was also observed between PFOA and the alternative HFPO-DA ($r = 0.524, p < .05$). The positive significantly correlations implied they have similar emission sources and environmental fate and long-range transport potential. Furthermore, these results suggest HFPO-DA have very similar environmental behavior like the current-used short chain PFCAs and PFOA. HFPO-DA will follow the footprint of PFOA and become a new concern for the polar environment.

3.3. PAHs in snow

Concentrations of 17 PAHs (Σ PAHs) (Fig. 3) were in the same order of magnitude with those detected in snow of the Northern Victoria Land, (Vecchiato et al., 2015) Livingston Island (Antarctica), (Casal et al., 2018a) and snow/firn cores at Talos Dome, (Fuoco et al., 2012) while lower than those in the Arctic (Keyte et al., 2013). 2-Methylnaphthalene, phenanthrene and 1-methylnaphthalene were the dominant compounds (Tables 1 and S10). The proportions of three groups (2 + 3 ring, 4 ring and 5 + 6 ring PAHs) to Σ PAHs are depicted by the ternary diagram (Fig. 4). For all snow samples, the proportions of 2 + 3 ring PAHs were >0.75 and the values of 5 + 6 ring species were <0.25 . Furthermore, most PAH species were not correlated significantly (Table S11), implying that PAHs in snow at Dome C were from LRAT, whereas there might be other sources.

High levels of 2-methylnaphthalene and 1-methylnaphthalene, as well as An/(An + Phe) and Flu/(Flu + Pyr) values (Fig. 5) indicated that PAHs were attributed mostly to combustion rather than petrogenic origin (Wang et al., 2007; Yunker et al., 2002). These results confirmed that regional sources (tourism, ships and research stations) dominated the PAHs on the Antarctic, which was consistent with the findings of contamination of Antarctic snow by PAHs from a coastal site in East Antarctica during 2002–2005 (Kukučka et al., 2010). Moreover, PAHs have been determined in air, water, ice and soil near the Antarctic coast (Cao et al., 2018; Pozo et al., 2017; Rodriguez et al., 2018; Szopinska et al., 2019). The exchange fluxes among different environmental matrices may significantly interfere the remobilization of PAHs on the Antarctic (Cabrerizo et al., 2014; Cao et al., 2018; Lammel et al., 2015).

4. Conclusions

By analyzing the levels and component characteristics of typical indicators of OPEs, PFASs and PAHs in snow at Dome C, a general finding

can be observed that these emerging organic contaminants can be transported to the inland of the Antarctic. Although the mechanism is not clear, both global distillation and cold trapping may play significant role to transport these chemicals from the Southern Ocean to the inland of Antarctic. Moreover, the human activities on research station have obvious impacts on local environments in the Antarctic with very low background POP concentrations. The results obtained in this study provide direct evidences of Antarctic research stations as potential primary sources of legacy and emerging contaminants. Immediate action to control the adverse impacts of expanding human activities (research, tourism and resource exploitation) on polar environments is needed as well the reduction and diversity of chemical applications.

CRediT authorship contribution statement

Zhiyong Xie: Writing - original draft, Methodology, Software, Formal analysis, Investigation, Data curation, Writing - review & editing, Visualization, Project administration, Funding acquisition. **Zhen Wang:** Writing - original draft, Methodology, Software, Formal analysis, Data curation, Writing - review & editing, Visualization. **Olivier Magand:** Writing - original draft, Resources, Methodology, Writing - review & editing, Project administration, Funding acquisition. **Alban Thollot:** Resources, Methodology. **Ralf Ebinghaus:** Writing - review & editing. **Wenyang Mi:** Methodology, Validation. **Aurelien Dommergue:** Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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