Atmospheric Pollution Research

Volatile per– and polyfluoroalkyl compounds in the remote atmosphere of the western Antarctic Peninsula: an indirect source of perfluoroalkyl acids to Antarctic waters?

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ABSTRACT

Volatile per– and polyfluoroalkyl compounds were measured in air in the vicinity of the Western Antarctic Peninsula during February 2009 (Austral summer). The 6:2, 8:2 and 10:2 fluorotelomer alcohols (FTOHs) were the most abundant compounds with 8:2 and 10:2 FTOH concentrations averaging 9.9 and 7.4 pg m^{-3} respectively, followed by the shorter chain (C_4) compounds of methyl perfluorobutane sulfonamide (MeFBSA) and sulfonamidoethanol (MeFBSE) with average concentrations of ~3 to 4 pg m^{-3}. Methyl/ethyl fluorooctane sulfonamides and sulfonamidoethanols (FOSA/Es) were <1 pg m^{-3} in all air samples (n = 8). The concentrations of FTOHs and FOSAs were in good agreement with a previous study (2007) that measured these chemicals in the background atmosphere of the Southern Ocean, although the levels of the MeFBSA/E were found to be ~10–fold higher and possibly indicative of the increased use of these chemicals. Air mass back trajectories revealed that air mass movement was from the Antarctic landmass or from the Southern Ocean, the latter in keeping with the prevailing direction of the Antarctic Circulation Current. Those samples corresponding to air passing over the Antarctic Peninsula did not show notable differences in chemical concentrations or profile indicating that the scientific bases located on or near the Peninsula did not appear to influence PFC levels in the regional atmosphere. Given the lack of air mass incursions from the north (i.e. from the South American continent) then the levels measured here are representative of background concentrations around Antarctica. However, the relatively high levels of MeFBSE were surprising given the reported reactivity of this chemical and short atmospheric residence time. It is likely that this compound, alongside MeFBSA, is providing a source of C_2–C_4 perfluoroalkyl acids (PFAs) to Antarctic surface waters. We recommend that long–term air monitoring be established in Antarctica for volatile PFCs and possibly accompanied by deposition monitoring for the PFAs.

1. Introduction

Per– and polyfluoroalkyl compounds (PFCs) including perfluoroalkyl acids (PFAs) like perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are widely distributed in the global environment (Ahrens, 2011) and are present in both humans (Olsen et al., 2012) and a wide range of biota (e.g. Giesy and Kannan, 2001). Biota studies from the Arctic show the accumulation of PFAs in organisms that occupy different trophic levels in both marine and terrestrial systems, with concentration time–series showing generally upward trends throughout the first half of the 2000s (reviewed by Butt et al., 2010). Due to its persistence, its ability to undergo long–range transport (LRT) and its bioaccumulative behavior, PFOS (its salts) and perfluorooctane sulfonyl fluoride (POSF)–based chemicals are now listed under Annex B of restricted substances of the UNEP Stockholm Convention on POPs. PFAs reach remote environments like the Arctic through a combination of LRT processes, including advection with surface ocean currents as well as transport in the atmosphere (Armitage et al., 2006; Wania, 2007; Ahrens, 2011). Indeed, PFAs in air might also arise through marine aerosol derived from ocean surfaces, complicating the pathways by which these chemicals enter remote environments (Webster and Ellis, 2010). Importantly, PFAs also arise through photochemical oxidation of volatile perfluroalkyl precursors which are also subject to LRT (e.g. Ellis et al., 2004; Wallington et al. 2006; Wania, 2007). These compounds

(or volatile PFCs) include the fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAs), perfluorooctane sulfonamides (FOSAs), and sulfonamidoethanols (FOSEs) and are released directly through fluoropolymer production processes and indirectly through use/disposal of fluoropolymer containing products (Dinglasan–Panlilio et al., 2006; Barber et al., 2007; Paul et al., 2009).

Measurements of volatile PFCs in remote atmospheres have been undertaken in the Canadian Arctic (Shoeib et al., 2006; Ahrens et al., 2011). In the later study of Ahrens et al. (2011) concentrations of gas–phase Σ_3FTOHs, Σ_2FOSEs and Σ_2FOSAs across the Canadian Archipelago ranged from 20–138 pg m^{-3}, 0.4–23 pg m^{-3} and 0.5–4.7 pg m^{-3}, respectively. At high latitudes in the Southern Hemisphere and around coastal Antarctica, measurements of PFCs, including PFAs, have been undertaken in both abiotic and biotic matrices (see Schiavone et al., 2009; Tao et al., 2006; Bengston Nash et al., 2010; Llorca et al., 2012), although measurements are not as extensive as those undertaken in the Arctic. There are now several studies which have examined levels of PFCs in seawater and air in marine locations extending to a latitude of 70 °S (Wei et al., 2007; Dreyer et al., 2009; Ahrens et al., 2010). Measured levels are at the lower range of concentrations reported in the Arctic, but indicate that long–range transport across the Southern Hemisphere is occurring and may account for the low levels of PFAs, specifically PFOS, present in marine surface

waters (Wei et al., 2007; Ahrens et al., 2010). Indeed, Ahrens et al. (2010) argue that the presence of PFOS in surface waters close to Antarctica – in the absence of more water soluble perfluorocarboxylic acids (PFCAs) – suggests an indirect source, probably through the photochemical oxidation of FOSA/E precursors present in the atmosphere. Bengtson Nash et al. (2010) demonstrated that the coastal waters of Antarctica are effectively decoupled from the waters of the South Atlantic; certainly on the time scale for the production and use of fluorinated polymers. This indicates that PFAs present in the marine environment close to Antarctica are unlikely to be attributed to recent oceanic transport from temperate regions to the north. Additional measurements of these chemicals are therefore needed as levels of these compounds may well be increasing or at least changing due to increased production and use of FTOHs since the recent phase out of POSF–based chemicals (Dupont, 2005, cited in Ahrens et al., 2011). In this study, we report the atmospheric concentrations of volatile PFCs from a scientific cruise that covered coastal areas of the Western Antarctic Peninsula. We therefore provide much needed data on atmospheric concentrations of these chemicals, allowing comparisons to be made with data collected further east near the Neumayer research station in Antarctica (Dreyer et al., 2009) and examine the possible influence of the South American continent on the atmospheric profile and levels of these chemicals.

2. Methods

Work was undertaken on the RV BIO–*Hesperides* a Spanish research vessel during austral summer 2009. Sampling of air and water (not reported here) was undertaken over the geographical region of ~54–69 °S and 60–75 °W, in places close to the Antarctica Peninsula (Figure 1).

2.1. High–volume air sampling

High volume air samples were collected onboard the R/V *Hesperides* along the Antarctic Peninsula during the austral summer in 2009. A Hi–Vol sampler was situated ~15 m above sea level towards the bow on the upper deck of the ship. Airborne PFCs were sampled using glass–fiber filters (GFFs, 460 × 570 mm, >0.7–µm particle retention, Whatman, UK) for the particle–phase followed by a polyurethane foam (PUF)/XAD–2 sandwich for the gas–phase, consisting of 25 g of XAD–2 resin (Supleco) between a PUF plug (76–mm diameter and 75 mm thick, Tisch Environmental, OH, USA) divided in half. Sampling times and air volumes averaged 48 h and 846 m^3, respectively.

2.2. Chemical analysis

The target analytes include 6:2 FTA, 6:2, 8:2, 10:2 FTOH, *N*–methyl perfluorobutane sulfonamide (MeFBSA) and sulfonamidoethanol (MeFBSE), methyl and ethyl FOSA and methyl and ethyl FOSE, plus ^{13}C mass–labelled recovery standards (RS) (see QA/QC section for a full list of compounds) and *N, N*–Me$_2$FOSA, 13:1 FTOH and ^{13}C–HCB (Hexachlorobenzene) as internal standards (IS). Extraction of the PUF/XAD–2 sandwiches was performed by sequential cold column extraction with ethyl acetate (Barber et al. 2007). Samples were spiked with 50 µL of a 200 pg µL^{-1} solution of a RS mixture containing mass–labeled FTOHs, FOSAs and FOSEs and were extracted by three separate immersions for 30 minutes in ethyl acetate. The three extracts were combined, reduced to around 1 mL by rotary evaporation and then cleaned–up by passing through 2 cm of Envi–Carb® columns. The extracts were concentrated by gentle nitrogen blow down to 0.5 mL, then 50 µL of a 500 pg µL^{-1} solution of IS were added and finally the extract was reduced to a volume of 0.1 mL prior to injection. The GFF samples were not extracted. Analysis was performed using gas chromatography (Thermo Trace GC Ultra, Thermo Scientific) – mass spectrometry (Thermo DSQ Quadrupole, Mass Spectrometer) (GC/MS) in selective ion monitoring (SIM)

(a)

(b)
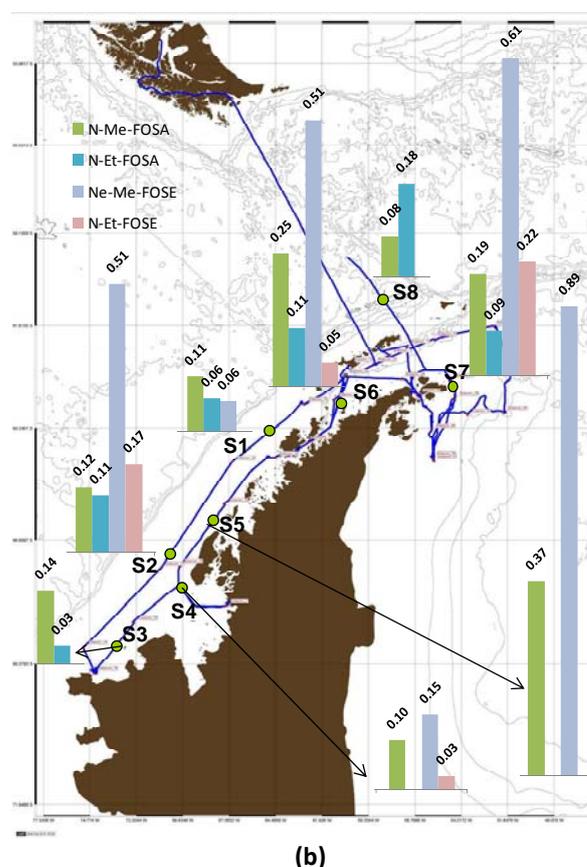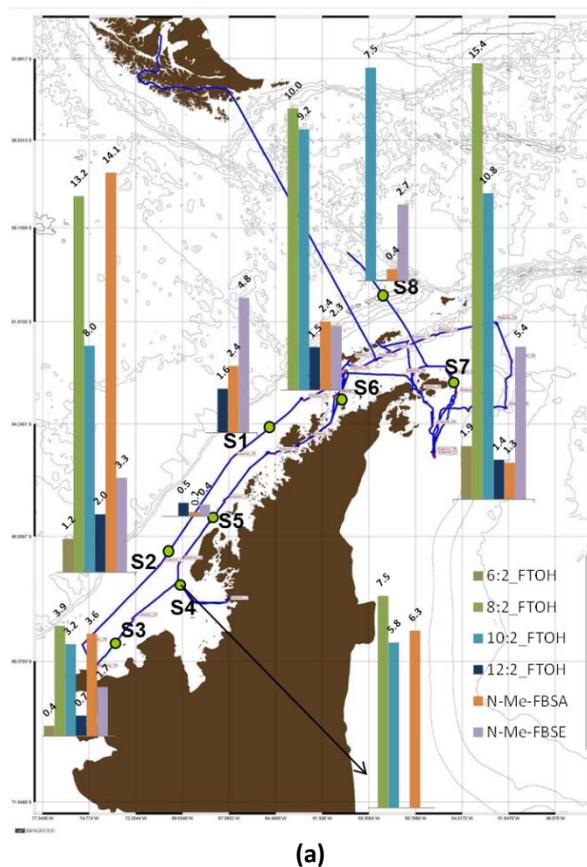
Figure 1. *Gaseous concentrations (pg m^{-3}) of FTOHs, MeFBSA and MeFBSE (a); FOSAs and FOSEs (b), measured during February 2009.*

mode using positive chemical ionization (PCI). Separation was performed using a CP–Wax 57 CB column and a FactorFour VF–200 ms trifluoropropyl methyl pre–column (15 m × 0.53 mm × 1.0 μm; Varian), fitted with a deactivated guard column (5 m × 0.53 mm; Agilent), using the following GC temperature program: 50°C (held 1 min), ramped at 3°C min^{-1} to 70°C, ramped at 10°C min^{-1} to 130°C, then ramped at 20°C min^{-1} to 225°C (held 12 min). A constant injection temperature of 200°C was used, with a 2 μL splitless injection. Focus–Liner injection liners (5 mm ID; Supelco) containing glass wool inserts were used for improved chromatography. Helium was employed as a carrier gas at a constant flow of 1 mL min^{-1}. The GC–MS transfer line temperature was set at 250°C.

2.3. QA/QC

A total of two field blanks comprising the PUF/XAD–2 matrix and two laboratory blanks were analyzed alongside the batch of collected air samples. Blank concentrations were < 3–18% of the 8:2 and 10:2 FTOH concentrations measured in the air samples; 10–58% of the FOSA/Es and 2–60% for FBSA/E. Recovery standards were added to each of the samples to monitor procedural performance. The average recoveries were: 59±23% for 5:1 FTOH, 48±11% for 7:1 FTOH, 45±23% for [M + 3] 6:2 FTOH, 74±13% for 9:1 FTOH, 113±50% for [M+5] 8:2 FTOH, 189±105% for 11:1 FTOH, 84±29% for [M+3] 10:2 FTOH, 109±30% for [M + 3]–NMeFOSA, 101±36% for [M+5] NEtFOSA, 367±114% for [M+7] NMeFOSE, and 308±113% for [M+9] NEtFOSE, respectively. High recoveries of 11:1 FTOH and the FOSEs were attributed to signal enhancement during GC/MS analysis and highlight the importance of the use of labeled compounds to correct for signal enhancement or suppression. All results were recovery and blank corrected; the later using the average blank value for each PFC analyte. Further details on the surrogates chosen for each native compound are provided in Shoeib et al. (2010).

3. Results and Discussion

3.1. Overview to PFC concentrations in air

Table 1 provides a summary of the PFCs detected and measured in this study while data for each air sample are provided in Table 1 of the Supporting Material (SM). The most abundant compounds were in the order 8:2 FTOH > 10:2 FTOH > MeFBSA ≈ MeFBSE. The FTOHs were the dominant compounds, with concentrations of 8:2 and 10:2 FTOHs averaging 9.9 and 7.4 pg m^{-3}, respectively. Levels of the shorter chain (C$_4$) MeFBSA and MeFBSE were lower, with mean concentrations of 3.8 and 2.9 pg m^{-3}, respectively. The concentrations of FOSAs and FOSEs were consistently <1 pg m^{-3} for all the samples. Aside from 6:2 FT–acrylate, which ranged from 0.37–1.75 pg m^{-3} (n = 3), the fluorinated olefins and acrylates were not detected. The concentrations measured in this study are markedly lower than those observed recently in the Canadian Arctic. For example, the average gas–phase concentrations of Σ$_3$FTOH (Σ$_3$ = 6:2, 8:2 and 10:2 FTOHs) ranged from 37–75 pg m^{-3} for a ship–based cruise conducted in 2007–2008 across different regions of the Canadian Arctic Archipelago (Ahrens et al., 2011). Similarly, average concentrations of Σ$_2$ FOSAs and Σ$_2$FOSEs ranged from 1.1–3.3 and 1.4–13 pg m^{-3} respectively, compared to averages of 0.24 (Σ$_2$FOSAs) and 0.53 (Σ$_2$FOSEs) pg m^{-3} measured in this study.

The concentrations of PFCs reported in Table 1 are in agreement with concentrations observed in the marine atmosphere of the Southern Hemisphere on a cruise conducted in 2007 by Dreyer et al. (2009) (also summarized in Table 1). In this case, marine air samples were taken across the Southern Ocean between South Africa and Antarctica (Neumayer Station) and were considered as "background" in that they were not influenced by land–derived air masses from southern Africa. The average gas–phase concentrations of 8:2, 10:2 and 12:2 FTOHs in Dreyer et al.

(2009) were 6.0, 2.7 and 1.0 pg m^{-3}, respectively, compared to the means reported in Table 1 of this study of 9.9, 7.4, 1.1 pg m^{-3}. For the FOSAs and FOSEs then the average concentrations were similar or lower compared to Dreyer et al. (2009). For example, Me–FOSE and Et–FOSE had average concentrations of 0.5 and 0.1 pg m^{-3} in this study compared to averages of 1.6 and 0.5 pg m^{-3} measured by Dreyer et al. (2009). To our knowledge, the measurements by Dreyer et al. (2009) provide the only other reported measurements of volatile PFCs in the atmosphere of the Southern Ocean and the Antarctic region. The notable difference between the two studies is for the shorter chain compounds of MeFBSA and MeFBSE. Dreyer et al. (2009) reported averages of 0.2 and 0.3 pg m^{-3} respectively, for the "background" Southern Ocean, whereas the higher values reported in this study (~3 to 4 pg m^{-3}) are more akin to concentrations observed by Dreyer et al. (2009) in the marine environment of the Northern Hemisphere. It is plausible that analytical differences may account for some of this discrepancy, although inter–laboratory studies between our laboratory and Environment Canada, NILU, Norway and HZG, Germany (Barber et al., 2007; Dreyer et al., 2010; Ahrens et al., 2011), show close agreement for measurements of FTOHs and FOSA/Es. The ~10–fold increase in concentrations of MeFBSA and MeFBSE between this study (February 2009) and that of Dreyer et al. (2009) could reflect increasing concentrations of these chemicals in the remote atmosphere. This is due to increased production/use and subsequent long–range transport of the shorter chain perfluoro–class of chemicals in recent years following the phase out of perfluorooctane sulfonyl fluoride (POSF) and related compounds under the UNEP Stockholm Convention on POPs (D'eon et al., 2006; Ahrens, 2011). Interestingly, since 2003, perfluorobutane sulfonyl compounds have been increasingly used in new surface–treatment products (see Ritter, 2010).

Table 1. *Gas-phase concentrations (pg m^{-3}) of neutral PFCs measured in the marine atmosphere of the Western Antarctic Peninsula (this study) and mean concentrations measured in the 'background' atmosphere of the Southern Ocean and coastal Antarctica (Southern Hemisphere – SH) by Dreyer et al. (2009). Note that concentrations for each of the 8 air samples are provided in Table S1 of the Supporting Material*

	This study (n = 8)			Dreyer et al. (2009)
	min	max	mean	mean (background-SH)
6:2 FTA	0.4	1.8	0.9	1.0
6:2 FTOH	0.4	1.9	1.1	1.2
8:2 FTOH	3.9	15.4	9.9	6.0
10:2 FTOH	3.3	10.8	7.4	2.7
12:2 FTOH	0.03	2.1	1.1	1.0
Σ$_5$ FTOHs	7.6	30.2	19.5	11
N-Me-FBSA	0.2	14.1	3.8	0.2
N-Me-FOSA	0.1	0.4	0.2	0.6
N-Et-FOSA	0.03	0.2	0.1	0.3
Σ$_3$ FASAs	0.3	14.7	4.1	1.1
N-Me-FBSE	0.4	5.4	2.9	0.3
Ne-Me-FOSE	0.06	0.9	0.5	1.6
N-Et-FOSE	0.03	0.2	0.1	0.5
Σ$_3$ FASEs	0.5	6.5	3.5	2.2

3.2. Air concentrations around the Western Antarctic Peninsula

Figure 1 illustrates the concentrations of FTOHs, MeFBSA/E (a) and FOSA/Es (b) along the cruise track in the vicinity of the coastline of the western Antarctic Peninsula. The air samples were taken along a transect from ~59 to 69 °S, that followed the western edge of the Peninsula. Air mass back trajectories (48 h) for the campaign period (12–30 February), were calculated using the HYSPLIT model (Draxler and Rolf, 2012). Figure 2 illustrates air mass trajectories calculated for S2 and S7, respectively, that depict the prevailing air mass movements over the campaign. For the first

part of the campaign (12–20 February; samples, S1 to S4) air mass movement originated or passed over the Peninsula with slow moving air tracking from east to west or south to north (e.g. Figure 2a). For the latter part of the campaign (20–30 February, corresponding to samples S5 to S8) air mass trajectories tracked west to east reflecting the prevailing wind direction associated with the Antarctic Circumpolar Current (ACC) (Figure 2b) (all the air mass trajectories corresponding to each sample are provided in Figure S1 (see the SM). Although the campaign could be broadly divided into the "land–derived" and "ACC derived" air sheds, the PFC concentrations and chemical profiles did not display marked differences between these prevailing air mass directions, although the low number of samples precluded a thorough statistical assessment of the PFC data. This would suggest that the Antarctic land mass is not a regional source of volatile PFCs given the relatively large number of scientific bases located on the Peninsula and adjacent islands compared to the rest of Antarctica (Bengtson Nash et al., 2010). Possible sources might include evaporative emissions of volatile PFCs from various fluorinated materials/coatings used in furnishings and consumer items present on these bases. Furthermore, the lack of direct north to south incursions of air masses during the campaign excludes the possibility of relatively contaminated air masses arriving from the South American continent, indicating that the levels reported here represent true background concentrations in the air of the Southern Ocean/western Antarctica. To explore this further, the ratios of 6:2 to 8:2 to 10:2 FTOH were examined as they indicate the degree of weathering as the FTOHs have different rates of photochemical reactivity with the 8:2 and 10:2 possessing longer lifetimes in the atmosphere of ~80 and 70 days, respectively, compared to ~50 days for the 6:2 FTOH (Piekarz et al., 2007). Higher ratios therefore indicate the degree to which 6:2 FTOH has been removed from the atmosphere and the aged nature of the air mass relative to source regions. Based on the average concentrations measured in this study, the 6:2/8:2/10:2 FTOH ratio was 1.0/8.8/6.5. In the Arctic atmosphere, Ahrens et al. (2011) reported the FTOH ratio as 1.0/6.4/2.1, compared to a ratio observed in the air of Toronto, Canada, as 1.0/2.3/1.2 (Shoeib et al., 2006). For the other Antarctic study of Dreyer et al. (2009), only those samples taken close to Antarctica were used (specifically sample numbers 40 and 43, where 6:2 FTOH was reported), resulting in ratios of 1.0/9–13/4.4–6, which are in broad agreement to the ratios observed in this study and higher than those reported for the Arctic, indicating the aged nature of the FTOH composition in coastal Antarctic air masses.

3.3. The fate of volatile PFCs

In comparison to persistent organic pollutants such as the relatively volatile hexachlorobenzene (HCB), the volatile PFCs are considered to have much shorter atmospheric lifetimes. Both smog–chamber studies and predicted lifetimes (based on the Junge lifetime–variability relationship) estimate that FTOHs have lifetimes in the atmosphere of ~10–80 days (Ellis et al., 2003; Piekarz et al., 2007; Dreyer et al., 2009) and for gas–phase alkyl–FBSA/Es, ~2–50 days (D'eon et al., 2006; Martin et al., 2006). While these lifetimes would allow atmospheric transport over considerable distances, they imply that there is a constant "re–supply" of these chemicals to the remote oceanic atmosphere of the Southern Hemisphere, particularly if the observed concentrations close to Antarctica do not relate to direct incursions of air masses from the major continents to the north i.e. South America in the case of this study. According to Bengtson Nash et al. (2010) the only company in South America with a history of ionic PFA manufacture and supply, and hence a possible major point source, is an agrochemical company (Milenia Agrociencias S.A.) based in Londrina, Brazil; ~4 700 km from the Antarctic Peninsula. Therefore, diffusive emissions (rather than point source industrial releases) through the use, degradation and disposal of fluoropolymer materials in populated areas are more likely to serve as the major source of volatile PFCs to the atmosphere

across the Southern Hemisphere. To support this, Dreyer et al. (2009) reported relatively elevated concentrations of FTOHs off the coast of Brazil, in the vicinity of Recife, and higher proportions of MeFOSA close to Cape Town, South Africa, although, in general, concentrations in the background marine atmosphere of the Southern Hemisphere (Σ_5FTOH, 11 pg m^{-3}, $n = 16$) were lower than concentrations measured in the background atmosphere of the Northern Hemisphere (Σ_5FTOH, 19 pg m^{-3}, $n = 28$).
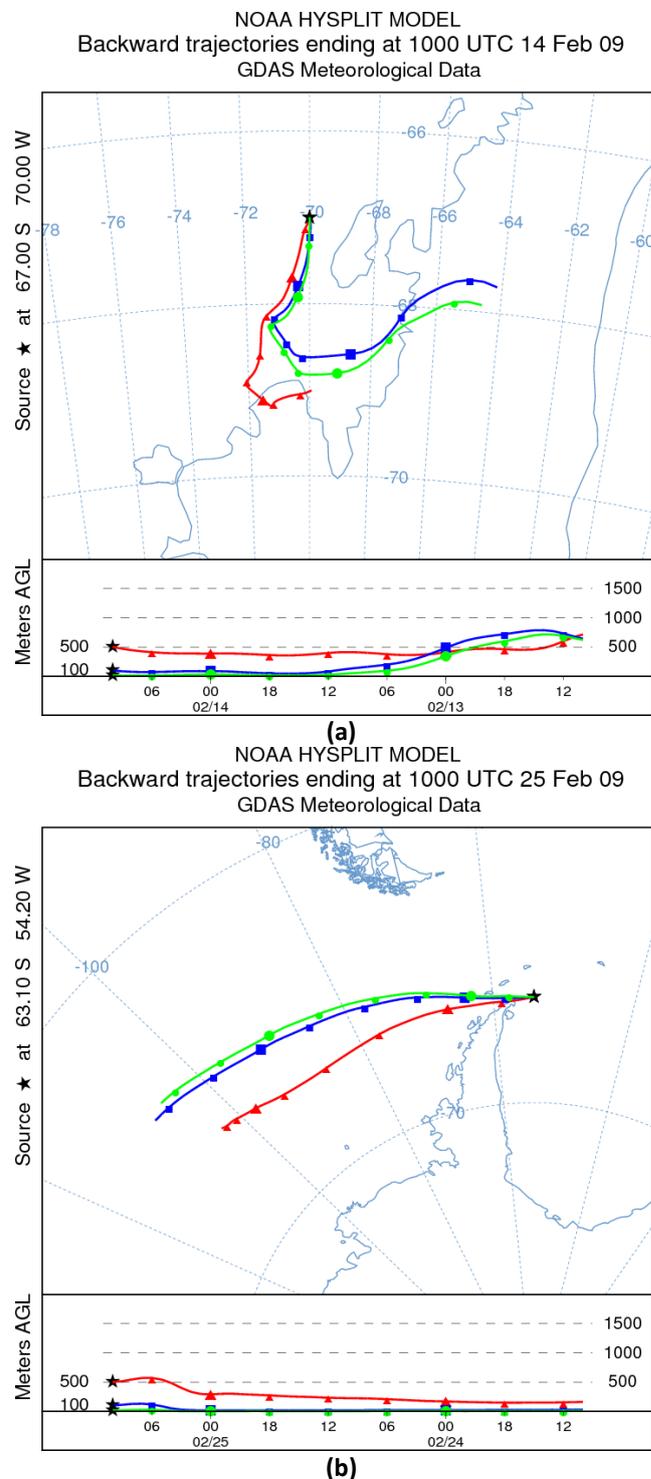
Figure 2. Representative 48 h air mass back trajectories for samples S2 *(a)* and S7 *(b)*. These two samples represent air mass movement from the Antarctic land mass and the west-to-east air movement associated with the Antarctic Circulation Current, respectively. Air mass trajectories corresponding to all the sample periods (S1 to S8) are provided in Figure S1 of the Supporting Material.

The fate of volatile PFCs in remote atmospheres like the Southern Ocean is influenced by a number of processes including photochemical degradation (during the sunlit austral summer), and to a much lesser extent by dry and wet depositional processes (Martin et al., 2006). Particle–bound fractions however will undergo deposition, particularly for the FOSA/Es. Ahrens et al. (2011) reported 9–25% of FOSAs and FOSEs as particle associated in the Arctic atmosphere. This is likely to be the case in the Antarctic atmosphere as ambient air temperatures ranged from –5 to 5 °C during this campaign, although the particle–bound concentrations were not measured. As a consequence the FOSA/E data reported here are likely to be an underestimation of the actual concentrations by as much as ~25%. Atmospheric photochemical transformation of volatile PFCs to perfluorocarboxylic and sulfonic acids is a plausible pathway and a possible source of these compounds to marine surface waters. However, to date those studies that report PFA measurements for seawater samples taken close to Antarctica, generally find the perfluorocarboxylic acids such as PFOA and perfluorononanoic acid (PFNA) below the limit of quantification (see Wei et al., 2007; Ahrens et al., 2010) reflecting both the low concentrations of FTOH precursors in the Antarctic atmosphere and the relatively low yield of PFOA formation (<10%) through photochemical oxidation (via ·OH radicals) of 8:2 FTOH (Wallington et al., 2006; Wania, 2007). Interestingly, Wania (2007) modeled the sources of PFOA to the Arctic Ocean, and noted that by "switching off" the oceanic transport pathway resulted in the atmospheric source being insufficient to account for the concentrations observed in Arctic seawater (i.e. the modeled concentrations in seawater were two orders of magnitude less than measured values). For Antarctic surface waters, then assuming the lack of PFA input through surface ocean currents (see Bengtson Nash et al., 2010), then the atmospheric FTOH transformation pathway would yield PFOA at insufficient quantities to allow detectable levels using current sampling procedures (e.g. 2–3 L of seawater). This is in agreement with the few studies that have examined PFAs in the vicinity of Antarctica. PFOS, however, has been detected and measured with concentrations ranging from ~5–60 pg L^{-1} (Ahrens et al., 2010). In addition, PFOS and perfluorohexanoic acid (PFHxA) have also been measured in soil collected in the Western Antarctic Peninsula at concentrations <1 ng g^{-1} (Llorca et al., 2012), implying an atmospheric pathway. The kinetics of photochemical degradation of the perfluorosulfonyl compounds, specifically the shorter chain MeFBSE and MeFBSA have been investigated, and the reaction rates with the ·OH radical (k_{OH}) determined experimentally (D'eon et al., 2006; Martin et al., 2006). For example, k_{OH} for MeFBSE was measured as 5.8±0.8 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, notably faster than k_{OH} for EtFBSA at 3.74±0.77 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. By analogy, the longer chain alkyl–FOSEs will have higher k_{OH} values than the corresponding alkyl–FOSAs (Martin et al., 2006). The significance of this, is that the reaction of the sulfonamidoethanols with ·OH is faster by ~5–fold than for 8:2 FTOH [k_{OH} is 1.07±0.22 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Ellis et al. 2003)]. This implies that their atmospheric transformation, which ultimately yields PFOS (from FOSE) or shorter chain sulfonic acids (e.g. from FBSE), may occur more efficiently. This process is likely to account for PFOS in Antarctic surface waters, particularly as atmospheric concentrations of FOSA/Es may well have been higher in the past prior to their phase out in the 2000s. There are caveats with this argument though, because: (i) ambient temperatures in the Antarctic atmosphere are low and hence reaction rates will differ relative to temperate regions (the k_{OH} values above are not temperature adjusted); (ii) concentrations of ·OH radicals vary markedly with season and latitude; and (iii), the initial reaction of gas phase volatile PFCs with ·OH initiates a chain of reactions, each with their own rate constants and hence rate limiting steps, that may ultimately lead to PFA formation with varying yields (D'eon et al., 2006; Wallington et al., 2006). However, the interesting observation of relatively high concentrations of MeFBSE in this study implies rapid atmospheric transport. D'eon et al. (2006) calculated that the atmospheric residence time of MeFBSE would

be ~2 days given its reactivity with ·OH, although the residence time for MeFBSA is considered to be much longer at ~20 days. Therefore, it is likely that the presence of this MeFBSE in the Antarctic atmosphere, coupled to its relatively high reactivity, would provide a source of short chain (C_2–C_4) PFAs to marine waters (D'eon et al., 2006; Martin et al., 2006). To date, perfluorobutane sulfonic acid (PFBS) has been reported in Antarctic seawater (2.9 pg L^{-1}) at one of the sampling sites in the marine study by Wei et al. (2007), providing limited evidence that volatile PFCs are undergoing oxidative transformation in the Antarctic atmosphere with subsequent deposition.

4. Conclusions

Low concentrations of volatile PFCs were present in the remote atmosphere of the western Antarctic Peninsula and local sources associated with the numerous scientific bases do not appear to be influencing levels on a regional basis. The ratio of the three dominant FTOHs reflect an aged chemical profile indicative of long range environmental transport of these chemicals to high latitudes in the Southern Hemisphere. There is some evidence that concentrations of the shorter chain (C_4) FBSA/Es have increased in recent years, possibly associated with the increased production/ use of these chemicals, although systematic atmospheric monitoring at a land–based station in Antarctica is required to confirm this. Given the atmospheric reactivity of MeFBSE, with an estimated residence time of ~2 days, it is surprising that this compound is present at the relatively high concentrations observed here and further work is needed to investigate the sources and fate of this chemical during atmospheric transport to remote environments. It is plausible that given the relative reactivity with ·OH radicals, then the longer chain FOSE/As serve as a source of PFOS to marine waters in this region and likewise the FBSE/As will provide an atmospheric source of shorter chain sulfonic and carboxylic acids. FTOHs remain the dominant group of volatile fluorinated chemicals in the atmosphere of Antarctica and are likely to remain so given their ongoing production and use in temperate regions. Their continued presence in remote atmospheres and subsequent transformation to bioaccumulative and/or toxic PFAs raises policy issues concerning their use and release.

Supporting Material Available

A table providing the concentrations of PFCs in each of the air samples is provided (Table S1) as well as the air mass trajectories for each of the sample periods (S1 to S8) (Figure S1). This information is available free of charge via the Internet at http://www.atmospolres.com.

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