



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 $< 1 \text{ pg m}^{-3}$ 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.

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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 perfluoroalkyl 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_3 FTOHs, Σ_2 FOSEs and Σ_2 FOSAs 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 $\sim 54\text{--}69^\circ\text{S}$ and $60\text{--}75^\circ\text{W}$, 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, $>0.7\text{-}\mu\text{m}$ 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*-Me₂FOSA, 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 $50\ \mu\text{L}$ of a $200\ \text{pg}\ \mu\text{L}^{-1}$ 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 $50\ \mu\text{L}$ of a $500\ \text{pg}\ \mu\text{L}^{-1}$ 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)

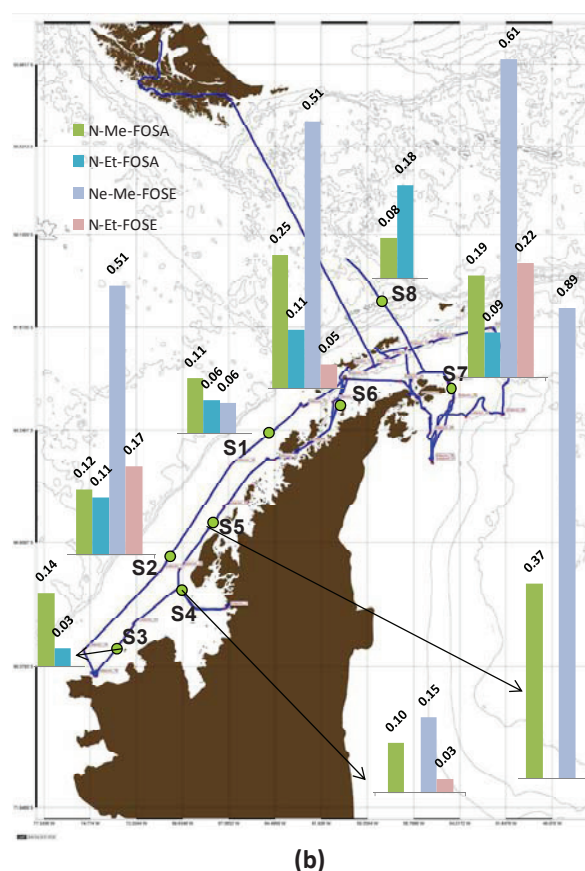
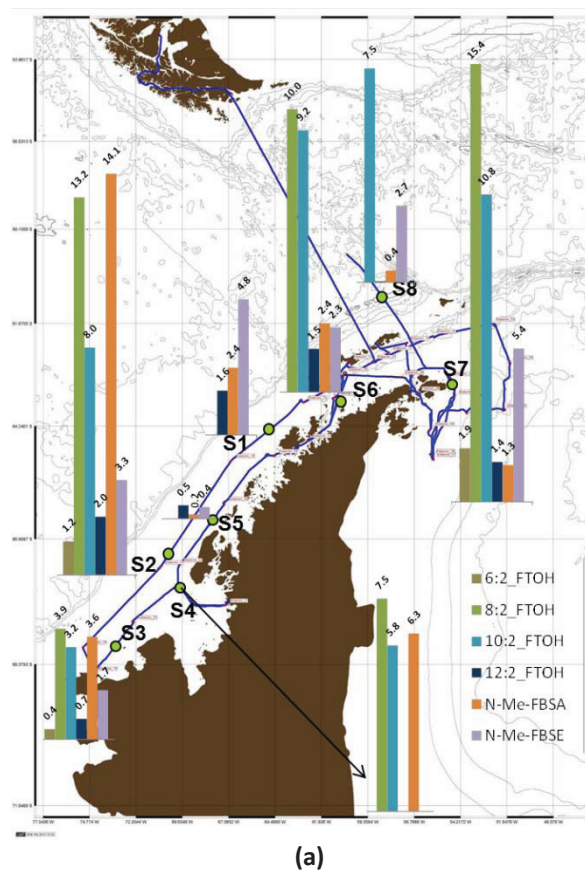


Figure 1. Gaseous concentrations ($\text{pg}\ \text{m}^{-3}$) of FTOHs, MeFBSA and MeFBSE (a); FOSAs and FOSEs (b), measured during February 2009.

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