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Short communication

Persistent organic pollutants in the atmosphere of the Antarctic Plateau

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HIGHLIGHTS

- The occurrence of POPs in the Antarctic Plateau is demonstrated for the first time.
- The mass per sample of PCBs, HCHs and HCB show a minimum at the South Pole.
- POPs reach the Antarctic Plateau by atmospheric transport from the free troposphere.

GRAPHICAL ABSTRACT

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ABSTRACT

Persistent organic pollutants (POPs) bioaccumulate in biota, have long residence times in the environment, and potential for long range atmospheric transport. Here, we show the first measurements of legacy POPs in the atmosphere of the Antarctic Plateau from 73° South to the South Pole. Samples were taken using passive samplers. The amount of polychlorinated biphenyls (as $\sum_{26}$PCBs) per sample ranged from 0.8 ng to 26 ng. The mass per sample of hexachlorobenzene (HCB) and γ-hexachlorocyclohexane (γ-HCH) in the gas-phase ranged from 0.67 ng to 2.7 ng and from non-detected to 2.6 ng, respectively. The lowest amounts of POPs were observed at the South Pole. This work shows that POPs have also reached the remotest region of Earth from primary sources. The assessment of the air mass back trajectories and current knowledge of atmospheric circulation over the Antarctic continent suggests that POPs reach the Antarctic Plateau by subduction of air masses from the free troposphere.

1. Introduction

Persistent organic pollutants (POPs) have the potential to bioaccumulate in organisms, to undergo long range transport reaching remote regions, and affect ecosystems (Lohmann et al., 2007; Nizzetto et al., 2010). The occurrence of POPs has previously been reported in the atmosphere, water and land for all Earth's regions except for most of the vast Antarctic Continent (Lohmann et al., 2007; Bengtson Nash, 2011; Galbán-Malagón et al., 2013a). Long range transport of semivolatile POPs occurs, generally, through successive volatilization and atmospheric deposition mediated by atmospheric transport, a process known as

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"grasshopping", with presumably oceanic transport being of minor importance (Wania and Mackay, 1996; Jurado and Dachs, 2008). The Antarctic continent is not only the remotest region from primary sources of POPs (Von Waldow et al., 2010), but it is also isolated from inputs of POPs from lower latitudes due to the dominant atmospheric and oceanic circulation patterns. Indeed, the Antarctic circumpolar current acts as a barrier limiting the oceanic transport of POPs to the Antarctic continent (Bengtson Nash et al., 2010). However, semivolatile POPs undergo long range atmospheric transport and can be deposited to remote regions, including locations south of the Antarctic circumpolar current (Risebrough et al., 1976; Galbán-Malagón et al., 2013a; 2013b; Bigot et al., 2016). Legacy and emerging POPs, such as polychlorinated biphenyls (PCBs), have been described in soils and vegetation (Borghini et al., 2005; Cabrerizo et al., 2012), the atmosphere (Baek et al., 2011; Kallenborn et al., 2013; Galbán-Malagón et al., 2013a; Gambaro et al., 2005), seawater (Galbán-Malagón et al., 2013b; Bigot et al., 2016), and biota (Risebrough et al., 1976; Miranda-Filho et al., 2007) from the maritime Antarctica. In the Southern Ocean, which is characterized by high primary productivity and phytoplankton biomass (Strutton et al., 2012), the biological pump effectively sequesters hydrophobic POPs from the atmosphere and surface waters by settling of organic matter bound-POPs to the deep ocean (Galbán-Malagón et al. 2012, 2013a). Therefore, even if POPs reach the Southern Ocean and its atmospheric boundary layer, their atmospheric and seawater concentrations will be reduced by oceanic sequestration (Galbán-Malagón et al., 2013a, 2013c).

The Antarctic continent is dominated by the katabatic winds (Bintanja et al., 2014) driven by the low temperatures found in the high elevation continental Antarctica. The average annual temperatures in the Antarctic Plateau are around − 50 °C (Jones and Lister, 2014). These air masses originate in the free troposphere and descend from the high elevation plateau to the Southern Ocean (Bintanja et al., 2014; Parish and Bromwich, 2007). The direction of the winds over the Antarctic continent is fairly constant, even during summer when the katabatic winds are weaker, due to the influence of the Antarctic orography (Parrish and Casano, 2003). Atmospheric circulation models show that transport of air masses from the coastal Antarctica boundary layer to the Antarctic plateau is unlikely as coastal air masses are too cold to rise to the Antarctic Plateau (Stohl and Sodemann, 2010). Therefore, subduction of air masses from the free trophosphere may transport POPs to the inner regions of the continent. However, the free troposphere has been largely unexplored in terms of POPs, except for measurements of POPs at mid-latitude mountains (Van Drooge et al., 2002; Lohmann et al., 2007; Wang et al., 2016), and few measurements from aircrafts (Knap and Binkley, 1991; Harner et al., 2005). Modelling exercises have shown that meridional transport and subduction of air masses from the free troposphere can contribute to the transport of POPs to the Arctic (Zhang et al., 2010), but the relevance of this process has not been previously assessed for Antarctica. The objective of this work is to report the first measurements of atmospheric POPs over the Antarctic Plateau.

2. Materials and methods

2.1. Sampling approach

Within the framework of the ACCIONA Wind Power expedition, a wind-driven sledge attached to a kite crossed the Antarctic Plateau (around 3000 m asl) in December 2011, covering 3100 km from Novolazarevskaya station (75 km from the coast) to Glaciar Union (Table S1 in supplementary material). During this transect, five atmospheric samples were taken for the analysis of POPs starting at 73°01' South, 05°24' East, until the South pole, and then finishing at 80°29' South, 79°55' West (Fig. 1, Table S1).

The sampling strategy was designed according to the limitations of performing sampling of atmospheric POPs from a wind powered sledge (Fig. S1), and by the likely low POP concentrations to be found in Antarctic air. High volume air samplers are the common approach used for sampling large volumes of air (Galbán-Malagón et al., 2013a), but this would have required electrical power which was not available during the expedition. The use of passive samplers is an alternative to overcome these constraints. Directional flow-through passive samplers (Xiao et al., 2007) allows for sampling large volumes of air within a time period of days with the high wind speeds found in Antarctica. We simplified the Xiao and coworkers' sampler design (Xiao et al., 2007) in order to gain in robustness. The sampler consisted in a horizontally aluminium tube of 60 cm length, 10 cm internal diameter, fixed onto one side of the wind powered sledge at approximately 1.5 m height (Fig. S1). The sampler contained a polyurethane foam (PUF), an anemometer and a temperature sensor connected to a data logger (Fig. S1). The PUFs diameter and length were of 10 cm. The PUF density was of 30 kg m^{-3}. This sampler allowed taking gas-phase samples of semivolatile organic compounds without the requirement of electrical power and with minimal work load for the expedition participants. Prior to the sampling campaign, all PUFs were precleaned with acetone-hexane 3:1 for 48 h, with the solvent exchanged every 24 h. Afterwards, PUFs were dried in a desiccator and stored in air-tight teflon bags. Before the shipping of the sampling equipment to the campaign, PUFs were fortified with PCB 65 and PCB 200 for their use as depuration compounds. Depuration compounds allow estimating the sampling rate (Pozo et al., 2004), and thus determining the effective air volumes provided these are depleted enough during the exposure time. In total, five samples (samples S1 to S5), covering the transect of 3500 km from Novolazarevskaya station (75 km from the coast) to Union Glacier, were taken and analysed (Fig. 1 and Table S1 show the location of

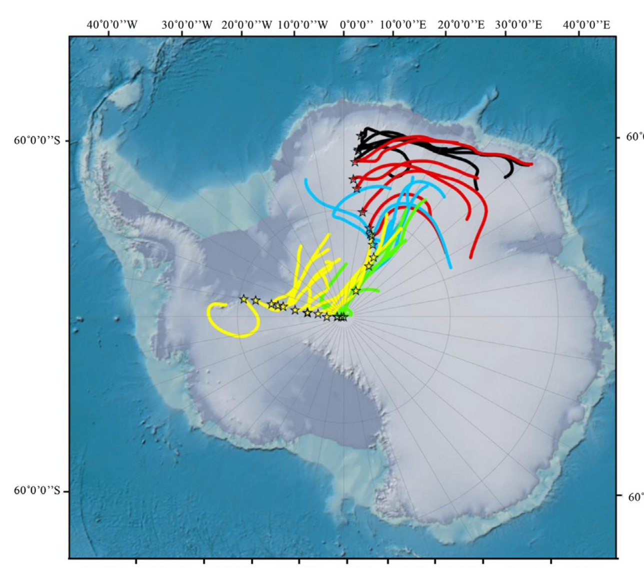

Fig. 1. Sampling transect in the Antarctic Plateau followed by the wind driven sledge from December 2011 until January 2012. One air mass back-trajectories (BT) is shown for every sampling day, the colour of the BT indicates to which one of the samples it contributed. Five samples were taken during transects as indicated in black (S1), red (S2), blue (S3), green (S4) and yellow (S5). The 48 h BT were estimated using the NOAAs Hysplit model at 25 m above ground level. Supplementary Material Fig. S2 shows the BT at 50 and 100 m above ground level. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)