



Seasonal accumulation of persistent organic pollutants on a high altitude glacier in the Eastern Alps[☆]



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ARTICLE INFO

Article history:

Received 29 March 2016

Received in revised form

2 August 2016

Accepted 3 August 2016

Available online 21 August 2016

Keywords:

PFAS

PBDE

PAH

Glacier

European Alps

ABSTRACT

The seasonal accumulations of perfluorinated substances (PFAS), polybrominated diphenyl ethers (PBDE) and polycyclic aromatic hydrocarbons (PAH) were measured in a 10 m shallow firn core from a high altitude glacier at Mt. Ortles (Italy, 3830 m above sea level) in South Tyrol in the Italian Eastern Alps. The most abundant persistent organic pollutants of each group were perfluorobutanoic acid (PFBA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) (for PFASs); BDE 47, BDE 99, BDE 209 (for PBDEs) and phenanthrene (PHE), fluoranthene (FLA) and pyrene (PYR) (for PAHs). All compounds show different extents of seasonality, with higher accumulation during summer time compared to winter. This seasonal difference mainly reflects meteorological conditions with a low and stable atmospheric boundary layer in winter and strong convective activity in summer, transformation processes during the transport of chemicals and/or post-depositional alterations. Change in the composition of the water-soluble PFCAs demonstrates the influence of meltwater percolation through the firn layers.

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1. Introduction

Perfluoralkyl substances (PFASs), polybrominated diphenyl ethers (PBDEs) and polycyclic aromatic hydrocarbons (PAHs) are ubiquitously distributed in the environment (Baek et al., 1991; de Wit, 2002; Prevedouros et al., 2006). Several of them are known as persistent organic pollutants, are considered to be toxic and have the ability to bioaccumulate (Conder et al., 2008; Schäfer et al., 2011; Tseng et al., 2008).

PFASs and PBDEs are man-made chemicals and have been produced and used since the middle of the last century. PFASs, including their major compounds perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), were used as water and oil repellents in several industrial applications (Buck et al., 2011; Kissa,

2001) and were analyzed in a wide range of consumer products (Fiedler et al., 2010; Fujii et al., 2013; Herzke et al., 2012; Schlummer et al., 2015). PBDEs, including the main technical mixtures pentaBDE, octaBDE and decaBDE, are additives that reduce the flammability of all various kinds of products (Prevedouros et al., 2004). PFASs and PBDEs can enter the environment during the entire product life cycle (Rauert and Harrad, 2015; Weinberg et al., 2011). Voluntary phase-outs, bans and regulations (including the addition to the Stockholm Convention in 2011 for PFOS and the pentaBDE and octaBDE mixtures) were recently introduced for several of these compounds. These regulations have already had an impact on the environmental burden of some of the corresponding compounds. For example, decreasing concentrations of PFOS in human serum were observed in recent years (Kato et al., 2011; Yeung et al., 2013). However, after the substitution of C8 PFCAs by short chain PFCAs by western companies, recent studies estimated a potential increase of the production of C8 PFCAs on the Asian market (Wang et al., 2014a, 2014b). PAHs mainly originate from the incomplete combustion processes of oil and wood; hence, in contrast to PFAS and PBDEs,

[☆] This paper has been recommended for acceptance by von Hippel Frank A.

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they have also natural sources and were only produced in small amounts for specific usages. Major PAH sources are linked to anthropogenic pollution, such as residential wood burning and the combustion of fossil fuels (Mastral and Callén, 2000). With benzo(a)pyrene (BaP) as reference compound, PAHs are included in several national and international monitoring programs.

Most of the PAHs and PBDEs have semi-volatile properties and can be transported through the atmosphere over long distances in the gaseous phase or attached to particles (Breivik et al., 2006; Lammel et al., 2009; Prevedouros et al., 2006; Wania and Dugani, 2003). Although recent studies detected perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) in the gaseous phase (Vierke et al., 2011), these acids are mainly transported attached to particles in the atmosphere. PFSAs and PFCAs in remote regions can also originate from the atmospheric degradation of volatile poly-fluorinated precursor substances (e.g., fluorotelomer alcohol, FTOH; Young and Mabury, 2010), which can undergo long-range atmospheric transport (Dreyer et al., 2009). Oceanic transport is an additional pathway for PFSAs and PFCAs to remote regions (Ahrens et al., 2010), as they can also be emitted by sea spray from the ocean surface (Reth et al., 2011). The transport and occurrence of these chemicals in remote regions was confirmed by several studies along transects and in remote regions, where PFASs, PBDEs and PAHs were detected in the atmosphere and snow (Butt et al., 2010; de Wit et al., 2010; Dreyer et al., 2009; Möller et al., 2011; Peters et al., 1995).

Worldwide glaciers have an important function as drinking water reservoirs, and suffer from the consequences of climate change (IPCC, 2007). Recent studies have discussed the potential future release of POPs such as DDT, pesticides and PCBs from glaciers long after the restriction of these substances. These chemicals are stored in the glaciers and hence might influence drinking water quality (Bogdal et al., 2009; Pavlova et al., 2015; Schmid et al., 2011). The fate and transport of POPs in the cryosphere and potential impact on drinking water safety and human health are an important topic of current organic pollution research (Grannas et al., 2013). Studies of the deposition and accumulation of PFASs and PBDEs in glaciers of the European Alps are rare (e.g., Arellano et al., 2014, 2013; Kirchgeorg et al., 2013). Most of these studies were conducted at lower altitudes compared to this study (3830 m above sea level (a.s.l.)). The aim of this study was to extend our knowledge about the occurrence of these compounds in the Eastern Alps and in particular in South Tyrol (Italy). To this aim, a 10-m firn core was drilled in June 2009 on Alto dell'Ortles (Italy, 3830 m a.s.l.) the highest glacier of the eastern European Alps (Fig. 1), in order to investigate the occurrence, seasonal accumulation and potential sources of PFASs, PBDEs and PAHs over 4 years.

2. Material and methods

2.1. Sampling location

The drilling site on the glacier Alto dell'Ortles (3830 m a.s.l.) is located near the summit of Mt. Ortles (46°30'32" N, 10°32'41" E, Italy, Fig. 1), the highest summit in the Eastern European Alps (3905 m. a.s.l.). Mt. Ortles is in turn located in the northern Ortles-Cevedale massif in the Southern Rhaetic Alps (South Tyrol, Italy). Due to the difficult access to this glacier, which also considerably limited the possibility of skiing and climbing activities, the first glaciological investigations were carried out only in 2007 (Gabrielli et al., 2010).

2.2. Sampling and dating

A 10-m shallow firn core (~10 cm of diameter) was drilled with a

lightweight hand auger in June 2009 at the glacier Alto dell'Ortles at an elevation of 3830 m a.s.l. Several studies on this firn core and snow packs were performed at this location, such as the seasonal variations of trace elements (Gabrielli et al., 2011). The core was cut into 10-cm sections. At the University of Venice, the outer layer of the core section was removed and aliquots were taken for ancillary analyses (Gabrielli et al., 2010). The remaining sample was sealed in clean bags and transported frozen to the Helmholtz-Zentrum Geesthacht, Germany, where they were kept frozen until they were melted at room temperature for the extraction and analyses of POPs. In order to achieve a sufficient sample volume, sections were combined to obtain a sample sufficient volume of about 0.5–1.5 L, which resulted in 21 samples. This separation followed the previously published study on the seasonality in this shallow core, based on stable isotopes, major ions, and trace elements (Gabrielli et al., 2010), and allowed the separation into cold (autumn–winter) and warm seasons (spring–summer). Seasonality was later corrected after pollen analyses (Festi et al., 2015), which provide seasonal information based on the detection of typical pollen for each season in the core sections. The later correction of the seasonality is the reason why some samples overlap between cold and warm seasons. The final dating of the core, based on stable-isotopic ratios, major ion concentrations and pollen analyses, spans from autumn 2005 to summer 2009. Details about sampling (Gabrielli et al., 2010) and pollen dating (Festi et al., 2015) are reported elsewhere.

2.3. Sampling preparation and instrumental analyses

The 21 frozen firn sections were melted at room temperature in a clean room. Details on the extraction and analyses of PFASs and PBDEs are described in Kirchgeorg et al. (2013). This procedure was only slightly modified for the additional analyses of PAHs. The samples were spiked with standards containing mass-labeled PFASs ($n = 9$), PBDEs ($n = 3$) and PAHs ($n = 7$) prior to the extraction. Extraction was performed by solid phase extraction (1.5 g self-packed PAD-II glass columns (PAH, PBDEs) and OASIS WAX cartridges (PFASs; 6 cc, 150 mg, Waters, United States) and separated in two fractions. One polar MeOH fraction, containing the PFASs and a second non-polar fraction of DCM:hexane (50:50; v:v) containing PBDEs and PAHs. 18 PAHs (NAP, APY, ACP, FLU, PHE, ANT, FLA, PYR, BaA, CHR, B(b+k)F, BeP, BaP, IND, DbA, BghiP, COR, full names in the SI) were separated and detected using gas chromatography-mass spectrometry (GC-MS, Agilent 6890 GC/5973 MSD) in electronic impact ionization mode. The 8 PBDEs (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183, BDE 209) were analyzed by GC-MS by negative chemical ionization. The 18 PFAS (PFBS, PFHxS, PFHpS, PFOS, PFDS, PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA; full names in the SI) were separated by high-performance liquid chromatography (HP 1100, Agilent Technologies, Waldbronn, Germany) and detected by electrospray ionization (negative mode) tandem mass spectrometry (API 3000, ABSciex). The internal standard method was used for quantification. Limits of detection (LOD) and limits of quantification (LOQ) were calculated on the basis of signal-to-noise ratios of 3 and 10, respectively; or, if blank values were detected: blank concentration + 3 (LOD) or 10 (LOQ) times the standard deviation (Table S2).

2.4. Quality assurance/quality control

Extraction and sample preparation were carried out in clean labs. Any piece of equipment that was in contact with the samples, such as glassware, tables and plastics, was cleaned with MilliQ water and solvents prior to usage. We monitored the absolute recovery of the mass-labeled standards during all the analyses in the

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