



Temporal variations of perfluoroalkyl substances and polybrominated diphenyl ethers in alpine snow



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ABSTRACT

The occurrence and temporal variation of 18 perfluoroalkyl substances (PFASs) and 8 polybrominated diphenyl ethers (PBDEs) in the European Alps was investigated in a 10 m shallow firn core from Colle Gnifetti in the Monte Rosa Massif (4455 m above sea level). The firn core encompasses the years 1997–2007. Firn core sections were analyzed by liquid chromatography–tandem mass spectrometry (PFASs) and gas chromatography–mass spectrometry (PBDEs). We detected 12 PFASs and 8 PBDEs in the firn samples. Perfluorobutanoic acid (PFBA; 0.3–1.8 ng L⁻¹) and perfluorooctanoic acid (PFOA; 0.2–0.6 ng L⁻¹) were the major PFASs while BDE 99 (<MQL–4.5 ng L⁻¹) and BDE 47 (n.d.–2.6 ng L⁻¹) were the major PBDEs. This study demonstrates the occurrence of PFASs and PBDEs in the European Alps and provides the first evidence that PFASs compositions may be changing to PFBA-dominated compositions.

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1. Introduction

Industry has produced perfluoroalkyl substances (PFASs) and polybrominated diphenyl ethers (PBDEs) since the middle of the last century, but we are just beginning to understand their impacts on biotic and abiotic systems. An increasing number of scientific studies highlight the distribution, persistence, bioaccumulation potential and toxic properties of PFASs and PBDEs (Ahrens, 2011; Butt et al., 2010; Birnbaum and Staskal, 2003; De Wit, 2002; Dreyer et al., 2009a; Hites, 2004; Lau et al., 2007; Sturm and Ahrens, 2010). As a result of international environmental concerns culminating in the 2009 addition to the Stockholm Convention (Stockholm Convention 2009a,b), industry introduced voluntary phase-outs of these substances and governments launched restrictions for

the use and production of several PFASs (>C8) and PBDEs (3M, 2010; European Union, 2003, 2006).

Modeling studies predicted the long-range atmospheric transport of PBDEs to pristine ecosystems such as the Arctic (Breivik et al., 2006; Schenker et al., 2008b; Wania and Dugani, 2003). Observational studies confirm the model predictions and demonstrate that PBDEs can be atmospherically transported over long distances and to high mountain regions in the gaseous or particulate phase (Möller et al., 2011; Wang et al., 2009). The presence and phase of PBDEs in remote areas depends in part on environmental conditions. Temperature changes influence the partitioning of less-brominated PBDEs between gaseous and particulate phases (Harner and Shoeib, 2002). Photolysis causes the debromination of BDE 209 (Schenker et al., 2008b) and this reaction is an additional source of less-brominated PBDEs. In contrast, the completely-brominated BDE 209 is present only in the particulate phase (Gouin et al., 2006).

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The atmospheric long-range transport of PFASs to remote regions is slightly more complicated than for PBDEs (Dreyer et al., 2009a; Loewen et al., 2008). Neutral volatile PFASs such as fluorotelomer alcohols (FTOHs) and perfluoroalkane sulfonamide substances are transported mainly in the gaseous phase and may degrade to less volatile perfluoroalkyl acids (PFAAs) including perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) (Schenker et al., 2008a, Young and Mabury, 2010). These PFAAs can also be directly emitted to the atmosphere by manufacturing processes (Barton et al., 2006) where they are bound onto particles or dissolved in cloud, rain, or fog droplets (Arp and Goss, 2009).

Alpine ice and firn cores or snow pit samples provide records of classical organic pollutants such as pesticides, polycyclic aromatic hydrocarbons (PAHs) or polychlorinated biphenyl (PCBs) to estimate temporal or seasonal trends and/or reconstruct historical deposition (Gabrieli et al., 2010; Villa et al., 2006). To the best of our knowledge, researchers have only studied ice or snow cores as a natural archive for airborne PFASs or PBDEs in the Arctic (Hermanson et al., 2010; Meyer et al., 2012; Young et al., 2007). Other types of natural archives or sampling techniques that record temporal trends of PBDEs include long-term passive sampling (Schuster et al., 2010), vegetation and soil samples (Hassanin et al., 2005; Schuster et al., 2011), and lake sediment cores (Bogdal et al., 2008; Kohler et al., 2008). Peat bogs, human serum, sediment cores and associated biota record PFASs back to the 1950s (Ahrens et al., 2009; Dreyer et al., 2012; Sturm and Ahrens, 2010). However, sediment cores are influenced by their catchment areas and it is difficult to separate atmospheric and aquatic signals (Shotyky et al., 2004). Biota and human serum are influenced by different sources (diet, water, air) that complicate determining decadal trends. Short chain PFASs (<C8) are only negligibly bio-accumulative and therefore do not provide temporal trends in biological materials.

Accumulating persistent organic pollutants in the European Alps is a concern as glaciers preserve pollutants and can later release these pollutants into regional water resources (Bogdal et al., 2009). The Alps are the largest natural air barrier in central Europe and a potential trap for European anthropogenic atmospheric pollution (Eichler et al., 2004). Here, we use a 10 m firn core (Colle Gnifetti, Monte Rosa massif, Swiss/Italian Border, 4455 m above sea level; a.s.l.) to provide the first analysis of PFASs and PBDEs in the Alps. The objective of the study is to provide insight into airborne PFAS and PBDE concentrations between 1997 and 2007, thereby encompassing the time period of voluntary phase-outs and bans of the investigated chemicals. We examine if the changes in production and use of these chemicals resulted in decreased environmental concentrations.

2. Material and methods

2.1. Sampling and dating

In August 2008, a 10 m long, 6 cm diameter firn core (CG-08) was collected on Colle Gnifetti (45°55'51"N, 07°52'34"E, 4455 m a.s.l., Monte Rosa massif, near the Swiss/Italian border). Firn is compacted snow with a density of 400–830 kg m⁻³ that has not yet reached the >830 kg m⁻³ density of glacial ice (Cuffey and Paterson, 2010). The mean density of the firn core is 516 kg m⁻³ and the accumulation at this site is 0.44 m w.eq. yr⁻¹ (water equivalent) with a range of 0.3–0.6 m w.eq. yr⁻¹ during the studied period. This accumulation is within the reported accumulation range at this location between 0.1 and 1 m w.eq. yr⁻¹ (Suter and Hoelzle, 2002). Colle Gnifetti has a relatively low net accumulation compared to other Alpine summits. Accumulation primarily occurs during spring, while winter snow is mostly eroded by strong local winds. Melting is negligible as indicated by the visual observation of few melt features rarely exceeding 1 cm thickness. The CG-08 core was dated by annual layer counting using the seasonally-varying δ¹⁸O ratios and NH₄⁺ concentrations (Fig. 2) and by matching previously-detected Saharan dust horizons (A.D. 2000, 1999, 1996) with the CG-03 core (Jenk et al., 2009). All details dating and anion analyses details are included in Sigl (2009).

2.2. Sample preparation

Firn core sections with lengths from 33 to 74 cm were combined to obtain continuous samples with annual resolution. We analyzed a total of 13 samples including incomplete annual sections at the beginning and the end of the core (1996, 2008). Samples were melted at room temperature in a Class 1000 clean room. Solid phase extraction was performed with 1.5 g self-packed PAD-II glass columns connected to the top of OASIS WAX cartridges (6 cc, 150 mg, Waters, United States). Prior to extraction, melted water was spiked with 50 μL of a standard solution containing mass-labeled PFASs (¹⁸O₂-PFHxS, ¹³C₄-PFOS, ¹³C₄-PFBA, ¹³C₄-PFHxA, ¹³C₄-PFOA, ¹³C₄-PFNA, ¹³C₄-PFDA, ¹³C₄-PFUnDa, ¹³C₄-PFDoDa, ¹³C₈-FOSA; concentration of each mass-labeled standard = 20 pg μL⁻¹), and 50 μL of a PBDE standard solution (¹³C₁₂-BDE 77, ¹³C₁₂-BDE 138, ¹³C₁₂-BDE 209; concentration of each mass-labeled standard = 4 pg μL⁻¹). The PBDE fraction was eluted from the PAD-II glass columns with hexane and hexane:dichloromethane (1:1,v:v). The PFAS fraction was eluted with methanol and 0.1% ammonium hydroxide in methanol from the PAD-II glass columns and the OASIS Wax cartridges. The supporting information (SI) included full extraction method details and information about suppliers, purities and acronyms of chemicals, mass-labeled and native standards (Table SI 1).

2.3. Instrumental analyses

We determined 18 perfluoroalkyl substances (PFBS, PFHxS, PFHpS, PFOS, PFDS, PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFOcDA; full names in the SI) by high performance liquid chromatography (HP 1100, Agilent Technologies, Waldbronn, Germany) electrospray ionization (negative mode) tandem mass spectrometry (HPLC–ESI(–)–MS/MS; API 3000, AB Sciex, Darmstadt, Germany) using a Synergi Hydro RP 80A column (Phenomenex, USA; 150 × 2 mm, 4 micron). All details and specifications concerning the HPLC–MS/MS measurements are described by Kirchgeorg et al. (2010).

We analyzed 8 PBDEs (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183, BDE 209) by gas chromatography–mass spectrometry (GC–MS, 6890N – 5975 MSD System, Agilent Technologies) using negative chemical ionization (NCI). Analytes were separated on a HP-5MS column (Agilent Technologies, 30 m length, 250 μm diameter, 25 μm film thickness). Specifications and programmed temperatures were adapted from Weinberg et al. (2011a). Due to the low expected concentrations (<1 ng L⁻¹), PBDEs were detected on the mass to charge ratio 79/81, which is more sensitive compared to the more specific molecular masses. When concentrations were sufficiently high, molecular-specific mass to charge ratios were used (Weinberg et al., 2011a). Quantification was based on peak areas. Analyte concentrations were calculated with the internal standard method based on response factors using mass-labeled internal standards. Analyte concentrations were calculated with nine point calibrations. Method detection and quantification limits (MDL, MQL) for PFASs calculated on the basis of signal to noise ratios (S/N of 3 = MDL, S/N of 10 = MQL) in firn core samples ranged between 0.01 (PFPA) – 0.08 ng L⁻¹ (PFUnDA) and 0.03 (PFPA) – 0.25 ng L⁻¹ (PFBA), respectively. PBDE MDLs and MQLs were between 0.01 (BDE 47) – 0.33 ng L⁻¹ (BDE 209) and 0.04 (BDE 47) – 1.1 ng L⁻¹ (BDE 209), respectively. Detailed information about MDLs and MQLs is provided in the supporting information (Table SI 4).

2.4. Quality assurance/quality control

Sample preparation and extraction were conducted in clean labs. PFAS-containing materials were avoided during sampling, preparation, laboratory work and instrumental analysis. Glassware, non-glass items, tables, guides and the blade for cutting and handling the core were carefully cleaned with methanol and acetone before each use. Mass-labeled internal standards were used to correct losses occurring during laboratory work and instrumental analyses. Recovery rates (standard deviation in brackets) were determined in a preliminary extraction experiment (n = 5) using the extraction procedure described above and were between 79% (±8, PFHpA) and 114% (±3 PFBA) and 85% (±10, BDE 28) and 113% (±7, BDE 153). A set of 4 firn core samples and 1 laboratory blank of 1 L Millipore water were extracted simultaneously. Detected PFAS and PBDE concentrations were below the quantification limit in the blanks (Table SI 5). The combined uncertainty according to the Eurachem/CITAC guidelines (Ellison and Williams, 2000) calculated from mean concentration of the ice core samples ranged from 4% (PFUnDA) to 200% (PFPA) and from 10% (BDE 47) to 42% (BDE 209) for PFASs and PBDEs.

2.5. Statistical analyses and calculation of annual deposition

Statistical analyses were performed with Winstat (Version 2007, R. Fitch Software, Bad Krozingen, Germany) and Origin 8G (OriginLab Corporation, Northampton, USA). Normal distribution of analyte concentrations was determined using the Kolmogorov–Smirnov-Test. Compounds detected in less than 50% of the samples were excluded from the statistical analyses. Spearman rank correlations were applied to investigate relationships between analytes and firn core parameters. Regression analyses were used to evaluate any trends. 5 year moving averages of pollutant deposition were calculated on the basis of the measured concentrations in

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