



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



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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,

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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 (Gabielli 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 (Gabielli 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 (Gabielli 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 (Gabielli 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 (Gabielli 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, PFTTrDA, 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

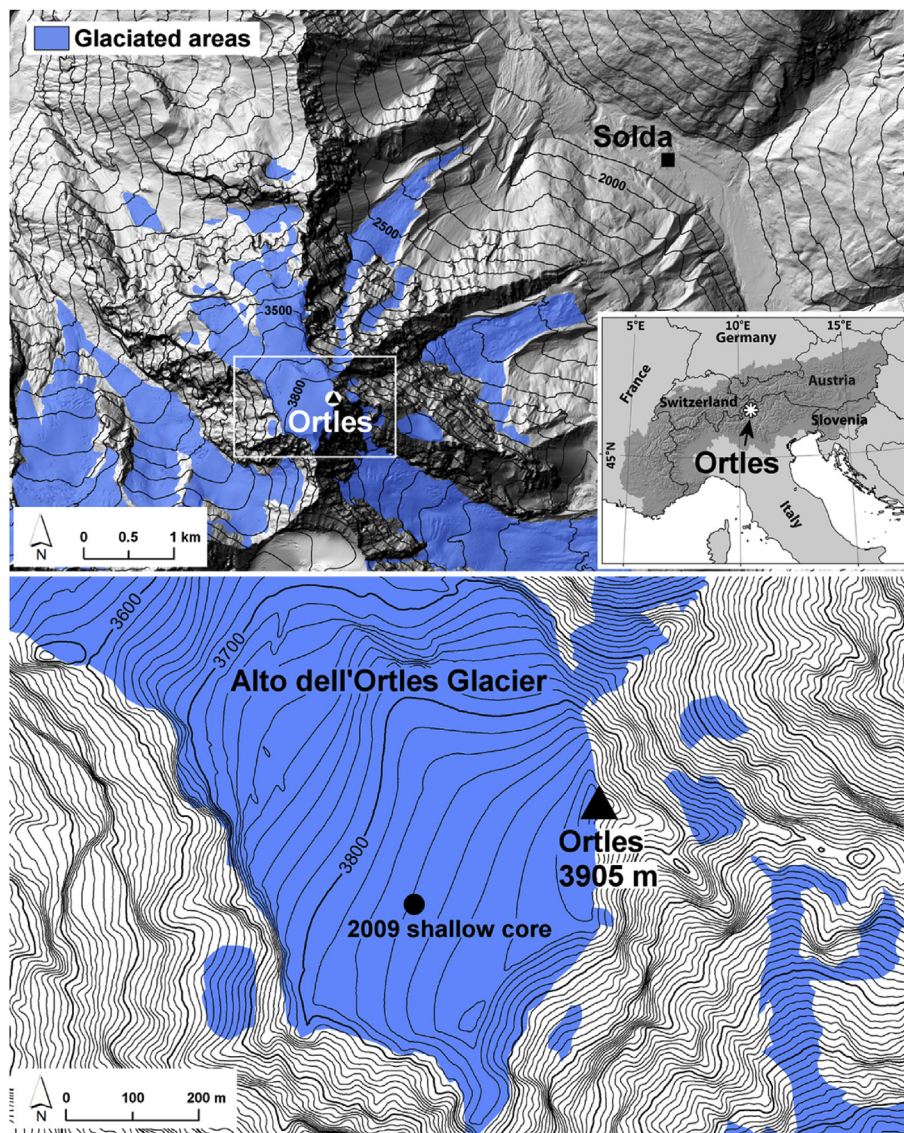


Fig. 1. Map of 2009 shallow core sampling location (Festi et al., 2015).

present study. The absolute recovery rates of the internal standards were between 59% ($\pm 24\%$; $^{13}\text{C}_5$ -PFNA) and 76% ($\pm 27\%$; $^{18}\text{O}_2$ -PFHxS) for PFASs. Average recovery rates of mass-labeled PBDEs were between 61% ($\pm 26\%$ $^{13}\text{C}_{12}$ -138) and 71% ($\pm 24\%$; $^{13}\text{C}_{12}$ -BDE 77). Six method blanks with 1 L of MilliQ water were extracted with each set of 4 samples. Concentrations of PFASs and PBDEs in blanks were below the LOQ. In some blank samples, PAHs (NAP, FLU, PHE, FLA, PYR, CHR) were observed in concentrations above the LOD. For these compounds, LOQs were calculated on the basis of the blank concentrations. NAP was excluded from further discussion, due to its high concentration in blanks (2.6 ng L^{-1}). In addition to the method/lab blanks, the sampling equipment was rinsed with MilliQ water to estimate blank concentrations from the hand auger and the bags. These blank levels were observed to be negligible. All the reported concentrations were calculated by the internal standard method and the final values were blank corrected (Table S3 – S5).

2.5. Calculation of the deposition rates

Statistical analyses were performed using the software Winstat

(Version, 2007; R. Fitch Software, Bad Krozingen, Germany) and Origin 8G (OriginLab Corporation, Northampton, USA). Seasonal accumulation of the analyzed species was computed on the basis of the measured concentrations in the firn core samples and the seasonal snow accumulation, and expressed for better comparison in $\text{ng}^{-1} \text{ m}^{-2} \text{ mo}^{-1}$ (concentration [ng kg^{-1}] \times seasonal accumulated snow [m] \times density [kg m^{-3}] \times 1/6 [mo]), assuming 6 months for each accumulation period. The seasonal snow accumulation was estimated from the thickness of each seasonal layer of the warm and cold seasons, based on the dating described above (Festi et al., 2015).

3. Results

3.1. Perfluoralkyl substances

12 of the 18 detected PFASs were: PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFOS (Fig. 2). The total PFAS concentrations ranged from 1 ng L^{-1} to 5.8 ng L^{-1} . The most abundant PFASs were PFBA, PFOA and PFNA with

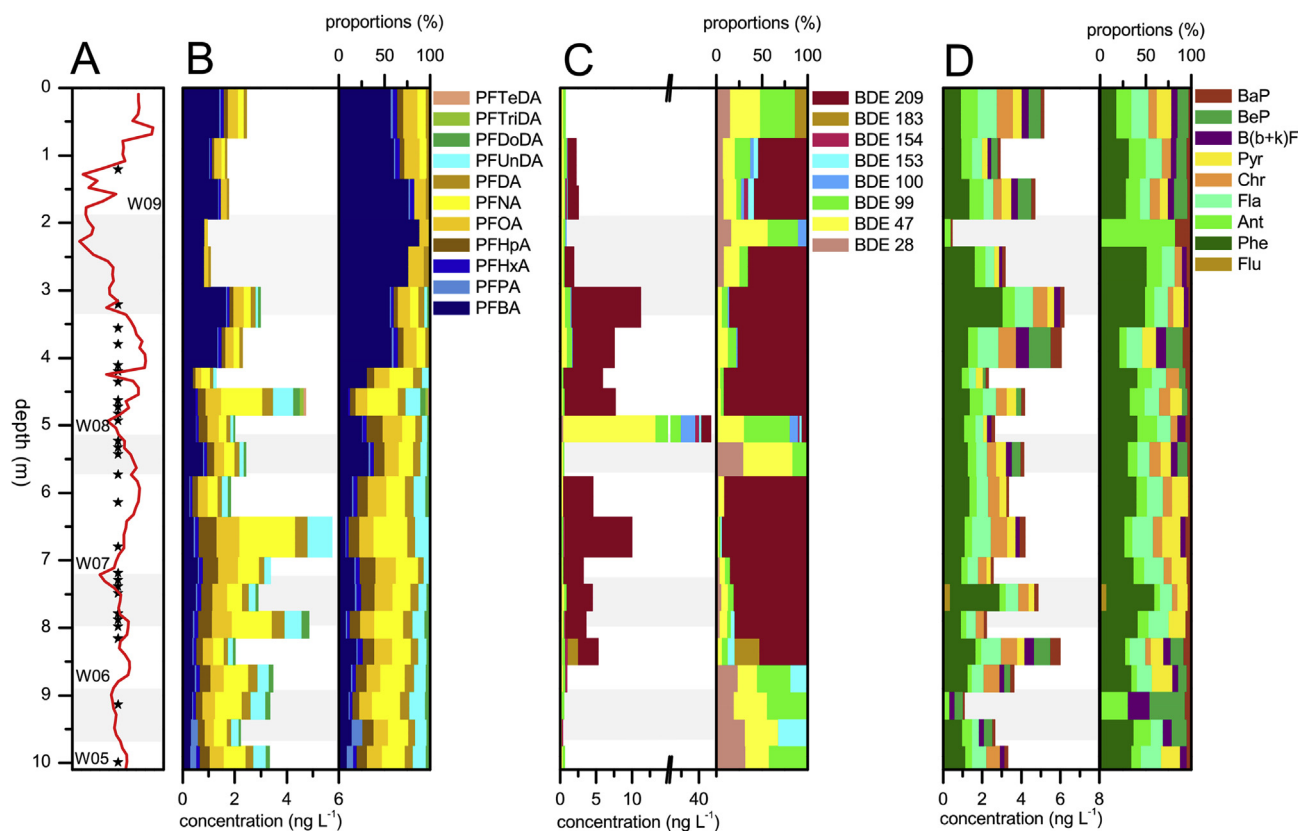


Fig. 2. Depth profile of the shallow firn core, with A: stratigraphy with marked cold seasons (gray) and $\delta^{18}\text{O}$ profile (red line), warm seasons (W05 – W09), and ice lenses (as indicator of melting and refreezing) observed in the core (asterisks); B: PFAS concentrations and relative proportions; C: PBDE concentrations and relative proportions; D: PAH concentrations and relative proportions. Note: compounds that were detected but not quantified were not included in the figure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentrations ranging from 0.3 to 1.7 ng L^{-1} , 0.1–0.9 ng L^{-1} and < LOQ – 2.1 ng L^{-1} , respectively. PFOS, PFTrDA and PFTeDA concentrations were always below the LOQ. All PFAS concentrations and their corresponding section depths are given in Table S3. In the upper 4 m of the core, PFBA dominates the PFAS composition profile with a contribution of more than 50% to the total PFAS concentrations. This rapidly changes below 4 m, where PFBA contributes less than 20% in most of the samples and the profile is dominated by PFOA and PFNA (Fig. 2B). Calculated monthly accumulation rates of PFBA were 9–147 $\text{ng m}^{-2} \text{ month}^{-1}$, PFOA 13–98 $\text{ng m}^{-2} \text{ mo}^{-1}$ and 4–158 $\text{ng m}^{-2} \text{ mo}^{-1}$. Mean values of the total PFAS accumulation rates were 313 $\text{ng m}^{-2} \text{ mo}^{-1}$ in the warm periods and 155 $\text{ng m}^{-2} \text{ mo}^{-1}$ in the cold periods.

3.2. Polybrominated diphenyl ethers

The total concentrations of the 8 detected PBDEs (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183, BDE 209) in the firn core ranged from 0.4 ng L^{-1} up to 43.5 ng L^{-1} . BDE 47, BDE 99 and BDE 209 were detected at the highest concentrations with values ranging from <LOQ – 8.1 ng L^{-1} , 0.1–21.7 ng L^{-1} and 0.1–12.9 ng L^{-1} (Fig. 2C). Elevated BDE 99 and BDE 47 concentrations were observed in only one sample (sample 10 at 5.1 m of depth). These concentrations suggest an external contamination or post-deposition concentration processes due to ice lenses (see below). Mean concentrations, excluding sample 10, were $0.32 \pm 0.16 \text{ ng L}^{-1}$ and $0.27 \pm 0.18 \text{ ng L}^{-1}$ for BDE 47 and BDE 99, respectively. BDE 209 was the dominating congener when detected above the LOQ, with an average contribution of 47% followed by

BDE 99 (27% on average) and BDE 47 (17% on average). Estimated monthly accumulation was between 5 and 316 $\text{ng m}^{-2} \text{ mo}^{-1}$, 8–527 $\text{ng m}^{-2} \text{ mo}^{-1}$, and < LOQ – 778 $\text{ng m}^{-2} \text{ mo}^{-1}$ for BDE 47, BDE 99 and BDE 209. Mean total PBDE accumulation rates were 503 $\text{ng m}^{-2} \text{ mo}^{-1}$ and 367 $\text{ng m}^{-2} \text{ mo}^{-1}$ in the cold and in the warm season, respectively. Excluding sample 10, monthly accumulation rates were between 5 and 41 $\text{ng m}^{-2} \text{ mo}^{-1}$ for BDE 47 and between 8 and 37 $\text{ng m}^{-2} \text{ mo}^{-1}$ for BDE 99.

3.3. Polycyclic aromatic hydrocarbons

FLU, PHE, ANT, FLA, CHR, PYR, B(b+k)F, BeP, BaP were the 9 quantified PAHs. Total PAH concentrations ranged from 0.5 ng L^{-1} to 6.2 ng L^{-1} . PHE (average concentration: 1.2 ng L^{-1}), FLA (0.6 ng L^{-1} on average) and PYR (0.4 ng L^{-1} on average) were the PAHs with the highest observed average concentrations (Fig. 2D). The PAH pattern was mainly dominated by PHE > FLA > ANT > PYR. An overview of all the concentrations and of the composition is provided in Table S5. Monthly accumulation rate ranged from 33 to 224 $\text{ng m}^{-2} \text{ mo}^{-1}$ (PHE), 13–109 $\text{ng m}^{-2} \text{ mo}^{-1}$ (FLA) and 3–97 $\text{ng m}^{-2} \text{ mo}^{-1}$ (PYR). The average total PAH accumulation was 439 $\text{ng m}^{-2} \text{ mo}^{-1}$ in warm periods and 199 $\text{ng m}^{-2} \text{ mo}^{-1}$ in cold periods.

4. Discussion

4.1. Concentration and composition

There are few reported data about PFAS in snow and ice, in

particular from European high alpine sites (Table S6). PFAS concentrations were reported in a shallow firn core sampled at Colle Gnifetti (4454 m a.s.l. in the Western Alps, Swiss-Italian border; Kirchgeorg et al., 2013). In these samples, PFBA concentrations ($0.3\text{--}1.8\text{ ng L}^{-1}$) were similar, and PFNA (n.d. - 0.31 ng L^{-1}) concentrations were up to one order of magnitude lower compared to this study. A study from different remote high mountain areas demonstrated similar PFBA concentrations in lake water from Lake Macun (0.8 ng L^{-1} ; Swiss Alps, 2600 m. a.s.l.; Greenpeace, 2015). PFOA snow concentrations (0.1 ng L^{-1} , Lake Macun; $0.1\text{--}0.3\text{ ng L}^{-1}$, 1720 m. a.s.l., High Tatra, Slovenia) were slightly lower, whereas PFNA snow concentrations ($0.3\text{--}0.5\text{ ng L}^{-1}$, Lake Macun; 0.7 ng L^{-1} , High Tatra) were within the concentration range of the present study (Greenpeace, 2015). In the same study PFOA and PFNA were not detected in the snow samples at the Norwegian sampling site (612 m a.s.l.; Troms fylke, Norway). PFOS was not detected or remained below the LOD of the present study in the Colle Gnifetti firn core samples and the snow samples from Lake Macun, the High Tatra or Troms fylke (Kirchgeorg et al., 2013; Greenpeace, 2015). Ortles firn core PFAS concentrations were in the same range as snow pack PFAS concentrations in a remote sampling site in Sweden (Codling et al., 2014). PFAS concentration reported in snow from ski tracks in Sweden were up to 1–4 order of magnitudes higher than in Ortles samples, probably due to the direct contamination resulting from intensive skiing activities (Plassmann and Berger, 2013). PFOA and PFNA concentrations in ice core samples from the European Arctic (Svalbard, Norway, Kwok et al., 2013) and snow pack samples from the Canadian Arctic (Young et al., 2007) were up to two orders of magnitude lower as in the present study, due to the distance to potential sources. PFAS concentrations in rain water sampled close to Hamburg (Germany) were up to one order of magnitude higher (Dreyer et al., 2010).

In the present study, PFBA was the most abundant PFAS in the upper 4 m of the core, which covers the middle of the warm season of 2008 and the warm season of 2009. Similar findings were observed in other studies from European regions (Codling et al., 2014; Dreyer et al., 2010; Kirchgeorg et al., 2013) or about freshly fallen snow from the Tibetan Plateau (Lake Namco, 4800 m a.s.l.; Wang et al., 2014a, 2014b). The dominance of PFBA may indicate the replacement of the C8-PFASs by short chain PFASs (Renner, 2006). In addition, modeling studies estimated an increase of 6:2 FTOH, a volatile precursor of PFBA (Wang et al., 2014a, 2014b). In the Ortles core, the PFAS composition changes below 4 m (middle of warm season 2008) (Fig. 2B), in particular due to the lower abundance of PFBA compared to the total PFCA concentration. This does not necessarily imply changes in the contamination itself; instead it might be a result of post-deposition-effects (Codling et al., 2014; Plassmann et al., 2011; Taniyasu et al., 2013). In fact, in contrast to the upper section, the lower core section is influenced by meltwater percolation (Gabrielli et al., 2010). These post-depositional processes become evident thanks to the presence of several ice lenses demonstrating refreezing processes in the deeper half of the core and smoothed concentrations observed for other water-soluble inorganic compounds and the δO^{18} signal (Gabrielli et al., 2011; Gabrielli et al., 2010). The water solubility of PFAS species differs depending on their chain length and pH. For instance, it has been shown that short-chain PFASs (e.g., PFBA) are removed faster by meltwater percolation (Plassmann et al., 2011). This suggests that the PFBA may be partly removed from the lower core section and relocated at depths below 10 m. This means that the change of the PFCA composition and PFBA concentrations below 4 m do not necessarily reflect the atmospheric composition at the time of the deposition.

As in the case of PFASs, PBDE data from European high-altitude regions is very limited. PBDE concentrations analyzed in the firn

core from Colle Gnifetti during the same period (2005–2009) (Kirchgeorg et al., 2013) are comparable to the concentrations presented in this study. Arellano et al. (2014) reported that the average total PBDE concentrations (BDE 47 + BDE 99 + BDE 100; $0.01\text{--}0.028\text{ ng L}^{-1}$) in a seasonal snow pack were one order of magnitude lower from an altitudinal gradient in the Tyrolean Alps (1100–2500 m. a.s.l.), but increasing concentrations with the altitude were observed for low-molecular-weight PBDEs (e.g., BDE 47), which might explain the higher concentrations at the more elevated sampling site of this study (Arellano et al., 2014). In surface snow from the Tatra Mountains (Slovakia; Arellano et al., 2011), BDE 47, BDE 99 were up to two orders of magnitude lower, compared to Mt. Ortles, with concentrations of $0.01\text{--}0.04\text{ ng L}^{-1}$, $0\text{--}0.06\text{ ng L}^{-1}$, respectively. The higher BDE concentrations of the present study might be related to the impact of the highly populated and industrialized Po region as discussed below. Meyer et al. (2012) reported concentration between $<0.02\text{--}0.55\text{ ng L}^{-1}$, $<0.03\text{--}1.2\text{ ng L}^{-1}$ and $0.68\text{--}100\text{ ng L}^{-1}$ in a Canadian Arctic snow pack for BDE 47, BDE 99 and BDE 209, respectively.

In contrast to water-soluble PFASs, PBDEs might be less influenced by meltwater percolation and might still reflect prior atmospheric deposited composition. Very strong melting and successive pre-concentration on an ice lens or a particular event (e.g., nearby fire) might be potential reasons for the high PBDE values at -5 m . However, we cannot exclude an external contamination of the sample, although we would also expect elevated values for the other measured compounds. In the present study, the observed composition is similar to the previously mentioned studies; BDE 209 is the dominating congener, followed by BDE 47 and BDE 99. This is also comparable to the atmospheric deposition congener profiles detected in different locations of the Alps (Offenthaler et al., 2009). BDE 209 is the main congener of the technical decaBDE mixture and BDE 47 and BDE 99 of the pentaBDE mixture.

PAHs were reported from different locations of the Alps. At Colle Gnifetti PAHs were determined in a deep ice core (Gabrieli et al., 2010b). The concentrations of the most recent sections of that core (2003) were slightly higher ($\Sigma\text{PAH}_8\ 12\text{ ng L}^{-1}$) than those measured in the Ortles firn core ($\Sigma\text{PAH}_8\ 6.2\text{ ng L}^{-1}$), and similar to the median PAH concentrations measured in snowpack at lower altitudes in the Tyrolean Alps ($\Sigma\text{PAH}_{24}\ 0.8\text{--}8.4\text{ ng L}^{-1}$) or the Dolomites ($\Sigma\text{PAH}_8\ 21\text{ ng L}^{-1}$) (Arellano et al., 2014; Gabrieli et al., 2010a). Gabrieli et al. (2010a) reported decreasing PAH concentrations in the Dolomites as the distance from potential sources increased. The PAH pattern at Mt. Ortles is dominated by PHE and FLA, which is similar to what was observed by Gabrieli et al. (2010a), whereas Arellano et al. (2014) reported a dominance of the PAH pattern by FLA followed by PYR, which might reflect differences sources. Van Drooge et al. (2010) compared PAH air concentrations at different high altitudes across Europe, demonstrated a quite homogenous pattern at all sites (PHE > FLU > FLA > PYR) and suggested this to be a result of homogenization during atmospheric long-range transport. Offenthaler et al. (2009) reported that FLA, PHE, PYR had the highest concentrations (excluding naphthalene) among the analyzed PAHs in high-altitude sites in Germany, Switzerland and Austria. The lower concentrations of PAHs detected in the shallow Ortles firn core compared to the previous studies performed in the Alps might be also due to the analytical limitations of the method (elevated blanks), but post-depositional effects cannot be excluded.

4.2. POPs accumulation and seasonality

Atmospheric deposition or accumulation data for PFASs from the European Alps are not available. Deposition rates from

precipitation in a semi-rural region in northern Germany were up to one order of magnitude higher ($60\text{--}2130\text{ ng m}^{-2}\text{ mo}^{-1}$; calculated from reported daily deposition values; Dreyer et al., 2009) compared to this study. PBDE seasonal accumulation rates of BDE 47 and BDE 99 (excluding the extreme high values of sample 10) were similar to atmospheric deposition measurements from Grossenköllsee (Tyrolean Alps, Austria, 2413 m a.s.l.) for these congeners, with $3\text{--}90\text{ ng m}^{-2}\text{ mo}^{-1}$ and $0\text{--}30\text{ ng m}^{-2}\text{ mo}^{-1}$, respectively (Arellano et al., 2013). In the same study BDE 209 ($0\text{--}247\text{ ng m}^{-2}\text{ mo}^{-1}$) deposition was up to 3 times lower compared to Mt. Ortles. Offenthaler et al. (2009) reported the deposition of BDE 47 ($4\text{--}25\text{ ng m}^{-2}\text{ mo}^{-1}$), BDE 99 ($2\text{--}9\text{ ng m}^{-2}\text{ mo}^{-1}$) and BDE 209 ($75\text{--}6960\text{ ng m}^{-2}\text{ mo}^{-1}$) from two high Alpine sites (Weissfluhjoch, Switzerland 2663 m a.s.l. and Zugspitze, Germany 2650 m a.s.l.), where BDE 209 deposition, in particular, was up to two orders of magnitude higher than the one reported for the Ortles firn core. Offenthaler et al. (2009) also reported PAH deposition rates from direct deposition measurements at the same sampling locations as mentioned for PBDEs. Deposition rates were between $30\text{ and }3500\text{ ng m}^{-2}\text{ mo}^{-1}$ for PHE, $30\text{--}5100\text{ ng m}^{-2}\text{ mo}^{-1}$ for FLA and $30\text{--}4200\text{ ng m}^{-2}\text{ mo}^{-1}$ for PYR.

Although to different extents, seasonal accumulation of all compounds in the Ortles core tends to be higher in warm periods (spring - summer) than in cold periods (autumn - winter) (Fig. 3). For PFCAs, this seasonal behavior was less pronounced in the deeper parts of the core, probably as a result of meltwater percolation and hence of the partial removal of water-soluble PFCAs, as discussed before. This potential influence of meltwater relocation

of PFCAs limits the discussion about seasonal accumulation. As PBDEs and PAHs are less water-soluble, these compounds might be less affected by meltwater.

Although PAHs emissions reach their highest levels in the winter due to residential heating, concentrations of frequently quantified PAHs also peaked in the spring - summer periods rather than in autumn - winter periods. This is probably due to the meteorological conditions that strongly influence the transport and deposition of contaminants and aerosols in high-altitude Alpine regions (Lugauer et al., 1998). It was suggested that the presence of a low and stable winter boundary layer plays a major role in blocking the upward transport of pollutants in winter. During the cold seasons, the Mt. Ortles glacier is mostly above the boundary layer and the Po basin is known for weather conditions with low and stable boundary layers during winter times (Gabrieli et al., 2011). Thus, during winter the deposition of contaminants and their concentrations measured in the snow might be rather influenced by long-range atmospheric transport than by uplifting from potential local and regional sources at lower elevation. The winter boundary layer also inhibits the transport of particles to higher altitudes, which might explain the strong seasonal accumulation of BDE 209 and of most of the other analyzed pollutants adsorbed to particles in the atmosphere (Lugauer et al., 1998). In spring and summer convective circulation induce the transport of pollutants from the lower regions to the eastern Alps including a highly populated and industrialized region such as the Po basin (Gabrieli et al., 2011).

For semi-volatile pollutants, emission, (repeated cycles of re-) volatilization at low altitudes, warm temperatures and condensation in cold environments may represent an alternative mechanism resulting in warm season concentration maximums and contaminant enrichment at higher-altitude glaciers (Daly and Wania, 2005). Increasing concentrations of lower brominated PBDEs and thus more volatile PFCAs with altitude were observed by Arellano et al., 2014 in the Alps. Loewen et al., 2008 demonstrated that concentrations of volatile PFCAs precursors, such as FTOH, were increasing with altitude ($800\text{--}2740\text{ m a.s.l.}$). However, an increasing trend was not observed for C8 - C11 PFCAs lake water concentrations at the same altitudinal gradient. It is unknown whether skiing activities or outdoor clothing can lead to seasonally different contamination signals in the Ortles firn. Finally, snow accumulation can change between warm and cold seasons. In the case of Ortles, the warm season snow layer is typically thicker at the beginning of the summer than the cold season snow layer, due to the high accumulation of snow in spring. This is also partially due to the removal of lighter winter snow by wind. This elevated snow accumulation during spring/summer may also explain the higher accumulation of persistent organic pollutants in the Ortles glacier during spring and summer.

4.3. Transport and source regions

Depending on the properties of the compounds, transport occurs in the vapor phase, particle phase or both. Although perfluorinated acids (PFAs), highly brominated PBDEs and high-molecular-weight PAHs (Dreyer et al., 2015; Lammel et al., 2009; Okonski et al., 2014) were reported to be transported by particles, a correlation of quantified PFCAs, BDE 209 and the investigated PAHs to particle concentrations ($0.20\text{--}0.68\text{ }\mu\text{m}$) measured in the glacier (Gabrieli et al., 2011) was not observed. PAH, PBDE and PFCAs concentration maxima were observed at particle sizes below the analyzed values (Dreyer et al., 2015 and references therein), which differ from those investigated in the Ortles. Thus, relevant particle sizes might not have biased the result of correlation analyses. Photochemical transformation of BDE 209 can be a source of lower

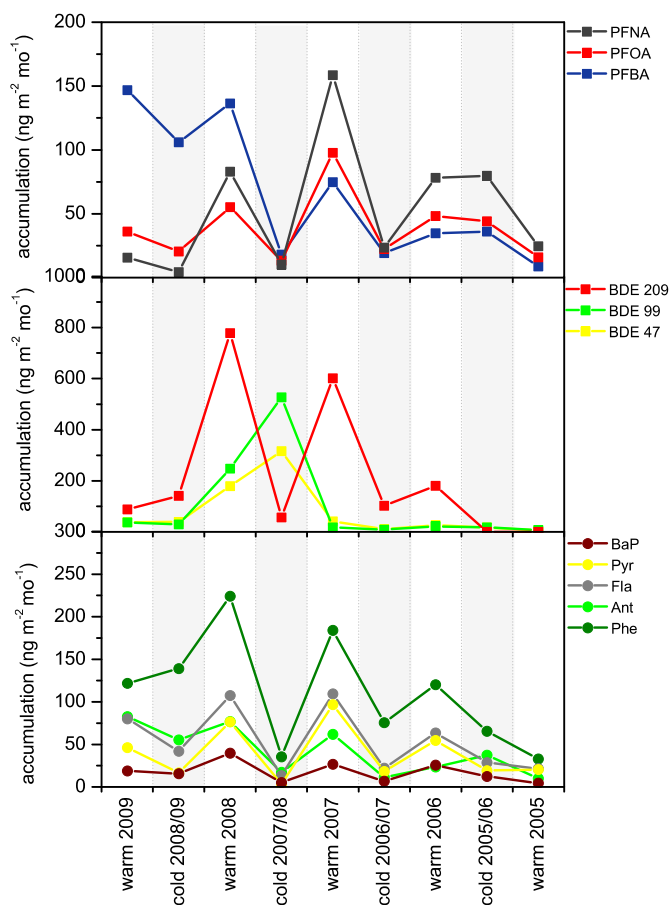


Fig. 3. Seasonal accumulation ($\text{ng m}^{-2}\text{ mo}^{-1}$) of selected PFASs (PFBA, PFNA, PFOA), PBDEs (BDE 47, BDE 99, BDE 209) and PAHs (PHE, PYR, FLA, ANT, PHE).

brominated PBDEs (Bezares-Cruz et al., 2004; Schenker et al., 2008) and transformation of PAHs initiated by OH radicals (Shiraiwa et al., 2009) may have also influenced PAH concentrations. Gas-phase transport was reported for low-brominated BDEs (Chen et al., 2006) and low-molecular-weight PAHs (Tsapakis and Stephanou, 2005) as well as for PFA precursors such as fluorotelomer compounds or perfluoroalkyl sulfonamides/amido ethanols (Young and Mabury, 2010). It was also suggested that small fractions of PFOA may exist as vapor (Vierke et al., 2011).

Pollutant contamination in the Ortles firn core may originate from several source regions. Upward transport of pollutants from nearby valleys may occur by upslope winds or by valley breezes on the basis of a daily cycle during periods of good weather. As temperatures at high altitudes are usually lower than in the surrounding valleys, particularly close to a glacier, semi-volatile pollutants may condense at higher altitudes (Wania and Westgate, 2008). In contrast, a low boundary layer and stable inversions during wintertime prevent upward transport of pollutants in the region investigated and may explain the described seasonal differences.

PAH concentration ratios of FLA/(FLA + PYR) of 0.54 ± 0.04 indicate wood pellet or natural wood heating (ratio of >0.5) as a source, which are quite popular in the Alpine regions (Gabrieli et al., 2010b). Note that PAH ratios determined in remote regions may have been altered by several processes during transport and after the deposition and might no longer represent a source-specific ratio.

The direct impact of the atmospheric emissions from the highly industrialized and populated Po valley (Italy) on the Alto dell'Ortles glacier was demonstrated by determining inorganic pollutants in a snow pit and back-trajectory analyses (Gabrieli et al., 2011). The Po valley is also known for high PFAS emissions to aqueous media (McLachlan et al., 2007; Pistocchi and Loos, 2009) and two chemical plants producing or applying PFAS were identified by Valsecchi et al. (2015). Although atmospheric emission data are not available, the presence of the chemical plants suggests the Po valley to be a potentially significant PFAS source region to Mt. Ortles.

As pentaBDE and octaBDE have been banned in Europe since 2003 and decaBDE since 2008 (RoHS Directive, 2003/11/EG), emissions from diffuse sources (product emissions during their life cycle) or emissions from waste-related facilities can be considered as the main sources for the time period covered by the firn core. Such sources are likely present in the Po valley, as corroborated from the occurrence of PBDEs in precipitation measurements in that region (Gambaro et al., 2009; Mariani et al., 2008). Furthermore, Belis et al. (2009) identified Austria and Italy as the most important emitters of PBDEs in Alpine regions, and the highest loads of PBDEs in soil and needles were reported in the Italian Alps in that study. Offenthaler et al. (2009) observed a predominance of BDE 183 of the congener pattern in forest humus from the north-eastern Alps. This suggests, that Ortles PBDE concentrations may originate mainly from the Mediterranean Site of the Alps, as BDE 183 is present in the core only at very low concentrations. The fact that BDE 47/BDE 99 ratios of 1.3 ± 0.8 differ from ratios observed in technical mixtures (PentaBDE) does not necessarily contradict this regional source as similar findings reported in snow of the Eastern Alps (Gossenköllesee, Arellano et al., 2013) were related to photochemical degradation of higher molecular PBDEs, resulting in lighter molecular PBDEs. Additionally other factors such as different scavenging efficiency of the congeners, enrichment of lighter BDE at higher altitudes due to a fractionating during condensation and re-volatilization cycles (Arellano et al., 2014, 2013), or removal of lighter PBDEs by strong winds (Bossi et al., 2008; Meyer et al., 2012) may have influenced the observed ratio. The low frequency of detection for octaBDEs (PBDE 153, PBDE 154,

PBDE 183) might be related to their more limited usage in Europe and corroborates the findings of other studies (Law et al., 2006).

Long-range atmospheric transport is an important transport mechanism of the investigated POPs to remote regions such as high-altitude alpine environments (Arellano et al., 2011; Bartrons et al., 2011; Wang et al., 2008). As described above, local or medium-range transport may account for the input of PBDEs, PAHs and PFASs to the Ortles, particularly in summer time. However, atmospheric long-range transport and degradation processes are assumed to be additional important contamination pathways to the Ortles, in particular in winter when the summit is above the boundary layer. In most cases, where the corresponding analytes could be reasonably quantified, concentrations of odd-chained PFCAs were higher or equal to those of even-chained PFCAs (e.g., PFUnDA > PFDA, PFNA > PFOA, PFHpA > PFHxA), indicating atmospheric transport and breakdown of PFCa precursors (such as FTOH) as important sources of the observed PFCAs (Scott et al., 2006; Taniyasu et al., 2008). Furthermore, in the Ortles firn core, PFOA:PFNA ratios are similar to those reported from the Arctic and from a shallow core in the Alps (Kirchgeorg et al., 2013; Young et al., 2007), where atmospheric degradation was assumed to be the dominant source, as these ratios differ from the estimated PFOA:PFNA (7:1 to 15:1) direct emission ratios from manufacturing processes in Europe/Russia and Asia (Armitage et al., 2009). This does not hold for PFBA, which appears to have other sources than precursor degradation. It may well be that vapor-phase PFBA is condensing at the glacier surface or that particles containing much more PFBA (than other PFCAs) deposited at the glacier. However, distinct PFBA sources to the atmosphere are unknown to the authors. Therefore, it can be anticipated that PFCAs > C4 detected here originated from the degradation of volatile precursors substances in the atmosphere or on the snow surface, as observed in aged snow (Taniyasu et al., 2013), rather than from the (mostly particle-related) direct emissions of the PFASs to the atmosphere itself. Volatile PFCa precursors, such as FTOH or FTA, are ubiquitously distributed (Dreyer et al., 2009) and FTOHs were reported in the air with increasing concentrations as the altitude increased (Loewen et al., 2008). Furthermore, the absence of PFSAs in the Ortles firn core and other European high-altitude studies (Kirchgeorg et al., 2013) might have been a result of the relatively low abundance of the volatile PFOS precursors in the atmosphere, supporting our assumption that indirect transport may be a major source of PFASs, as PFOS was detected in rain water from low-altitude sampling sites influenced by direct PFASs emissions and thus particulate transported PFSAs (Dreyer et al., 2010; Kwok et al., 2010).

5. Conclusions

This study demonstrates the occurrence of PFASs, PBDEs and PAHs in shallow firn core samples from the Alto dell'Ortles Glacier and thus reveals their transport to pristine regions such as high-altitude alpine environments. Source regions are probably located in northern Italy (Po river basin) or in a wider area (long-range atmospheric transport). For the investigated time period (2005–2009), different contaminants were observed during warm and cold periods for all the compounds analyzed. This seasonal difference reflects the influence of meteorology (low PBL in winter), transformation processes during the transport of the chemicals and/or post-depositional alterations. Post-deposition effects, such as meltwater percolation, particularly in the case of the more water-soluble compounds (PFCAs), limit the suitability of the lower part of this shallow firn core to determine the seasonal accumulation of these compounds. Other processes, such as chemical transformation, affect certain PAH and PBDE. Future investigations should focus on sampling sites with minimum or no snow melt

during the warm season and a minimum of wind erosion in winter. However, due to global warming, even Alto dell'Ortles, the most elevated glacier in the eastern Alps, is suffering from increasing temperatures making melt-free sites difficult to find.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.08.004>.

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