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# 1 Temporal Variations of Perfluoroalkyl Substances and 2 Polybrominated Diphenyl Ethers in Alpine Snow

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28

29 **Abstract**

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

40

41 **Capsule**

42 PFAS and PBDE concentrations in European Alpine snow provide information about the  
43 occurrence, accumulation and recent changes of these persistent organic pollutants in Alpine  
44 regions.

45

46 **Keywords**

47 PFAS; PBDE; European Alps; Deposition; Temporal Trend

48

## 49 **Introduction**

50 Industry has produced perfluoroalkyl substances (PFASs) and polybrominated diphenyl ethers  
51 (PBDEs) since the middle of the last century, but we are just beginning to understand their impacts  
52 on biotic and abiotic systems. An increasing number of scientific studies highlight the distribution,  
53 persistence, bioaccumulation potential and toxic properties of PFASs and PBDEs (Ahrens, 2011;  
54 Butt et al., 2010; Birnbaum and Staskal, 2003; De Wit, 2002; Dreyer et al., 2009; Hites, 2004; Lau et  
55 al., 2007; Sturm and Ahrens, 2010) As a result of international environmental concerns culminating  
56 in the 2009 addition to the Stockholm Convention (Stockholm Convention 2009a, 2009b), industry  
57 introduced voluntary phase-outs of these substances and governments launched restrictions for the  
58 use and production of several PFASs (> C8) and PBDEs (3M, 2010; European Union, 2003, 2006).  
59 Modeling studies predicted the long-range atmospheric transport of PBDEs to pristine ecosystems  
60 such as the Arctic (Breivik et al., 2006; Schenker et al., 2008b; Wania and Dugani, 2003).  
61 Observational studies confirm the model predictions and demonstrate that PBDEs can be  
62 atmospherically transported over long distances and to high mountain regions in the gaseous or  
63 particulate phase (Möller et al., 2011; Wang et al., 2009). The presence and phase of PBDEs in  
64 remote areas depends in part on environmental conditions. Temperature changes influence the  
65 partitioning of less-brominated PBDEs between gaseous and particulate phases (Harner and Shoeib,  
66 2002). Photolysis causes the debromination of BDE 209 (Schenker et al., 2008b) and this reaction is  
67 an additional source of less-brominated PBDEs. In contrast, the completely-brominated BDE 209 is  
68 present only in the particulate phase (Gouin et al., 2006).

69  
70 The atmospheric long-range transport of PFASs to remote regions is slightly more complicated than  
71 for PBDEs (Dreyer et al., 2009; Loewen et al., 2008). Neutral volatile PFASs such as fluorotelomer  
72 alcohols (FTOHs) and perfluoroalkane sulfonamide substances are transported mainly in the gaseous  
73 phase and may degrade to less volatile perfluoroalkyl acids (PFAAs) including perfluoroalkyl  
74 carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) (Schenker et al. 2008a, Young  
75 and Mabury, 2010). These PFAAs can also be directly emitted to the atmosphere by manufacturing

76 processes (Barton et al., 2006) where they are bound onto particles or dissolved in cloud, rain, or fog  
77 droplets (Arp and Goss, 2009).

78

79 Alpine ice and firn cores or snow pit samples provide records of classical organic pollutants such as  
80 pesticides, polycyclic aromatic hydrocarbons (PAHs) or polychlorinated biphenyl (PCBs) to  
81 estimate temporal or seasonal trends and/or reconstruct historical deposition (Gabrieli et al., 2010;  
82 Villa et al., 2006). To the best of our knowledge, researchers have only studied ice or snow cores as  
83 a natural archive for airborne PFASs or PBDEs in the Arctic (Hermanson et al., 2010; Meyer et al.,  
84 2012; Young et al., 2007). Other types of natural archives or sampling techniques that record  
85 temporal trends of PBDEs include long-term passive sampling (Schuster et al., 2010), vegetation and  
86 soil samples (Hassanin et al., 2005; Schuster et al., 2011), and lake sediment cores (Bogdal et al.,  
87 2008; Kohler et al., 2008). Peat bogs, human serum, sediment cores and associated biota record  
88 PFASs back to the 1950s (Ahrens et al., 2009; Dreyer et al., 2012; Sturm and Ahrens, 2010).  
89 However, sediment cores are influenced by their catchment areas and it is difficult to separate  
90 atmospheric and aquatic signals (Shotyk et al., 2004). Biota and human serum are influenced by  
91 different sources (diet, water, air) that complicate determining decadal trends. Short chain PFASs (<  
92 C8) are only negligibly bio-accumulative and therefore do not provide temporal trends in biological  
93 materials.

94

95 Accumulating persistent organic pollutants in the European Alps is a concern as glaciers preserve  
96 pollutants and can later release these pollutants into regional water resources (Bogdal et al., 2009).  
97 The Alps are the largest natural air barrier in central Europe and a potential trap for European  
98 anthropogenic atmospheric pollution (Eichler et al., 2004). Here, we use a 10 m firn core (Colle  
99 Gnifetti, Monte Rosa massif, Swiss/Italian Border, 4455 m above sea level; a.s.l.) to provide the first  
100 analysis of PFASs and PBDEs in the Alps. The objective of the study is to provide insight into  
101 airborne PFASs and PBDEs concentrations between 1997 to 2007, thereby encompassing the time

102 period of voluntary phase-outs and bans of the investigated chemicals. We examine if the changes in  
103 production and use of these chemicals resulted in decreased environmental concentrations.

104

## 105 **Material and Methods**

### 106 **Sampling and Dating**

107 In August 2008, a 10 m long, 6 cm diameter firn core (CG-08) was collected on Colle Gnifetti  
108 (45°55'51''N, 07°52'34''E, 4455 m a.s.l., Monte Rosa massif, near the Swiss/Italian border). Firn is  
109 compacted snow with a density of 400 – 830 kg m<sup>-3</sup> that has not yet reached the > 830 kg m<sup>-3</sup> density  
110 of glacial ice (Cuffey and Paterson, 2010). The mean density of the firn core is 516 kg m<sup>-3</sup> and the  
111 accumulation at this site is 0.44 m w.eq. yr<sup>-1</sup> (water equivalent) with a range of 0.3 to 0.6 m w.eq. yr<sup>-1</sup>  
112 during the studied period. This accumulation is within the reported accumulation range at this  
113 location between 0.1 and 1 m w. eq. yr<sup>-1</sup> (Suter and Hoelzle, 2002). Colle Gnifetti has a relatively  
114 low net accumulation compared to other Alpine summits. Accumulation primarily occurs during  
115 spring, while winter snow is mostly eroded by strong local winds. Melting is negligible as indicated  
116 by the visual observation of few melt features rarely exceeding 1 cm thickness. The CG-08 core was  
117 dated by annual layer counting using the seasonally-varying  $\delta^{18}\text{O}$  ratios and  $\text{NH}_4^+$  concentrations  
118 (Fig. 2) and by matching previously-detected Saharan dust horizons (A.D. 2000, 1999, 1996) with  
119 the CG-03 core (Jenk et al., 2009). All details dating and anion analyses details are included in Sigl  
120 (2009).

121

### 122 **Sample Preparation**

123 Firn core sections with lengths from 33 to 74 cm were combined to obtain continuous samples with  
124 annual resolution. We analyzed a total of 13 samples including incomplete annual sections at the  
125 beginning and the end of the core (1996, 2008). Samples were melted at room temperature in a Class  
126 1000 clean room. Solid phase extraction was performed with 1.5 g self-packed PAD-II glass  
127 columns connected to the top of OASIS WAX cartridges (6cc, 150 mg, Waters, United States). Prior  
128 to extraction, melted water was spiked with 50  $\mu\text{L}$  of a standard solution containing mass-labeled

129 PFASs ( $^{18}\text{O}_2$ -PFHxS,  $^{13}\text{C}_4$ -PFOS,  $^{13}\text{C}_4$ -PFBA,  $^{13}\text{C}_4$ -PFHxA,  $^{13}\text{C}_4$ -PFOA,  $^{13}\text{C}_4$ -PFNA,  $^{13}\text{C}_4$ -PFDA,  
130  $^{13}\text{C}_4$ -PFUnDa,  $^{13}\text{C}_4$ -PFDODA,  $^{13}\text{C}_8$ -FOSA; concentration of each mass-labeled standard =  $20\text{ pg }\mu\text{L}^{-1}$   
131  $^1$ ), and  $50\text{ }\mu\text{L}$  of a PBDE standard solution ( $^{13}\text{C}_{12}$ -BDE 77,  $^{13}\text{C}_{12}$ -BDE 138,  $^{13}\text{C}_{12}$ -BDE 209;  
132 concentration of each mass-labeled standard =  $4\text{ pg }\mu\text{L}^{-1}$ ). The PBDE fraction was eluted from the  
133 PAD-II glass columns with hexane and hexane:dichloromethane (1:1,v:v). The PFAS fraction was  
134 eluted with methanol and 0.1% ammonium hydroxide in methanol from the PAD-II glass columns  
135 and the OASIS Wax cartridges. The supporting information (SI) included full extraction method  
136 details and information about suppliers, purities and acronyms of chemicals, mass-labeled and native  
137 standards (Table SI 1).

138

### 139 **Instrumental Analyses**

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

147

148 We analyzed 8 PBDEs (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183,  
149 BDE 209) by gas chromatography – mass spectrometry (GC-MS, 6890N – 5975 MSD System,  
150 Agilent Technologies) using negative chemical ionization (NCI). Analytes were separated on a HP-  
151 5MS column (Agilent Technologies, 30 m length,  $250\text{ }\mu\text{m}$  diameter,  $25\text{ }\mu\text{m}$  film thickness).  
152 Specifications and programmed temperatures were adapted from Weinberg et al. (2011a). Due to the  
153 low expected concentrations ( $< 1\text{ ng L}^{-1}$ ), PBDEs were detected on the mass to charge ratio 79/81,  
154 which is more sensitive compared to the more specific molecular masses. When concentrations were  
155 sufficiently high, molecular-specific mass to charge ratios were used (Weinberg et al., 2011a).

156 Quantification was based on peak areas. Analyte concentrations were calculated with the internal  
157 standard method based on response factors using mass-labeled internal standards. Analyte  
158 concentrations were calculated with nine point calibrations. Method detection and quantification  
159 limits (MDL, MQL) for PFASs calculated on the basis of signal to noise ratios (S/N of 3 = MDL,  
160 S/N of 10 = MQL) in firn core samples ranged between 0.01 (PFPA) - 0.08 ng L<sup>-1</sup> (PFUnDA) and  
161 0.03 (PFPA) - 0.25 ng L<sup>-1</sup> (PFBA), respectively. PBDE MDLs and MQLs were between 0.01  
162 (BDE 47) - 0.33 ng L<sup>-1</sup> (BDE 209) and 0.04 (BDE 47) - 1.1 ng L<sup>-1</sup> (BDE 209), respectively. Detailed  
163 information about MDLs and MQLs is provided in the supporting information (Table SI 4).

164

### 165 **Quality Assurance/Quality Control**

166 Sample preparation and extraction were conducted in clean labs. PFAS-containing materials were  
167 avoided during sampling, preparation, laboratory work and instrumental analysis. Glassware, non-  
168 glass items, tables, guides and the blade for cutting and handling the core were carefully cleaned  
169 with methanol and acetone before each use. Mass-labeled internal standards were used to correct  
170 losses occurring during laboratory work and instrumental analyses. Recovery rates (standard  
171 deviation in brackets) were determined in a preliminary extraction experiment (n=5) using the  
172 extraction procedure described above and were between 79% (±8, PFHpA) and 114% (±3 PFBA)  
173 and 85% (±10, BDE 28) and 113% (±7, BDE 153). A set of 4 firn core samples and 1 laboratory  
174 blank of 1 L Millipore water were extracted simultaneously. Detected PFASs and PBDEs  
175 concentrations were below the quantification limit in the blanks (Table SI 5). The combined  
176 uncertainty according to the Eurachem/CITAC guidelines (Ellision and Williams, 2000) calculated  
177 from mean concentration of the ice core samples ranged from 4% (PFUnDA) to 201% (PFPA) and  
178 from 10% (BDE 47) to 42% (BDE 209) for PFASs and PBDEs.

179

### 180 **Statistical analyses and calculation of annual deposition**

181 Statistical analyses were performed with Winstat (Version 2007, R. Fitch Software, Bad Krozingen,  
182 Germany) and Origin 8G (OriginLaB Corporation, Northampton, USA). Normal distribution of



183 analyte concentrations was determined using the Kolmogorov-Smirnov-Test. Compounds detected  
184 in less than 50% of the samples were excluded from the statistical analyses. Spearman rank  
185 correlations were applied to investigate relationships between analytes and firn core parameters.  
186 Regression analyses were used to evaluate any trends. 5 year moving averages of pollutant  
187 deposition were calculated on the basis of the measured concentrations in the melted ice core  
188 samples and the accumulated snow (concentration x snow depth x density).

189

## 190 **Results and Discussion**

### 191 **Concentrations and variations**

#### 192 *Perfluoroalkyl substances*

193 PFASs concentrations in all firn core sections between 1996 and 2008 were in the low  $\text{ng L}^{-1}$  range.  
194 Of the determined PFASs, 12 of 18 examined PFASs (PFOS, PFBA, PFPA, PFHxA, PFHpA,  
195 PFOA, PFNA, PFDA, PFUnDA, PFDODA, PFTrDA, PFTeDA) were above the MDL (Table SI 6).  
196 The majority of the PFCAs were the following compounds, where their proportion of the total  
197 PFASs concentrations are included in parentheses: PFBA 0.34 – 1.83  $\text{ng L}^{-1}$  (26 – 63%); PFOA 0.20  
198 – 0.63  $\text{ng L}^{-1}$  (11 – 33%); PFNA < MQL – 0.31  $\text{ng L}^{-1}$  (0 – 15%); PFDA < MQL – 0.31  $\text{ng L}^{-1}$  (0 –  
199 15%). PFOS was detected but concentration levels were below the MQL. Total PFAS concentrations  
200 by depth and the relative proportions of individual PFASs are illustrated in Figure 1.

201

202 PFCAs concentrations in the Colle Gnifetti firn core are up to one order of magnitude higher than  
203 concentrations reported in ice core samples across the Canadian Arctic (Young et al., 2007). PFAS  
204 concentrations in precipitation from rural or urban regions in Europe and North America were up to  
205 two orders of magnitude higher than those at Colle Gniffetti (Dreyer et al., 2010; Kwok et al., 2010;  
206 Scott et al., 2006). As expected, firn core concentrations at high altitudes were lower than reported  
207 concentrations close to urban regions.

208

209

## 210 *Polybrominated diphenyl ethers*

211 All of the investigated eight PBDEs were observed in the 10 m firn core from Colle Gnifetti, where  
212 their concentrations and proportions of the total PBDE concentration vary with depth (Figure 2,  
213 Table SI 7). BDE 47 (concentration: n.d. – 2.61 ng L<sup>-1</sup>, proportions: 0 – 100%), BDE 99 (< MQL –  
214 4.54 ng L<sup>-1</sup>, 0 - 100%) and BDE 100 (n.d. – 0.74 ng L<sup>-1</sup>, 0 – 17%) were detected most frequently and  
215 with the highest concentrations of the group. The higher-brominated BDE 153 (n.d. - 0.46 ng L<sup>-1</sup>; 0 –  
216 6%), BDE 154 (n.d. – 0.32 ng L<sup>-1</sup>, 0 – 4%), and BDE 183 (n.d. - < MQL; 0%) were only detected in  
217 a few samples. BDE 209 (n.d. – 2.85 ng L<sup>-1</sup>, 0 – 97%) was detected above the MQL in three  
218 samples, in four samples it was above the MDL (> 0.33 ng L<sup>-1</sup>) but below the MQL (< 1.1 ng L<sup>-1</sup>).

219

220 The predominance of BDE 99 and BDE 47 is similar to other studies of European Alpine snowpack.  
221 BDE 47 tends to predominate in air samples while precipitation is partly characterized by higher  
222 BDE 99 concentrations (Arellano et al., 2011; Möller et al., 2011; Ter Schure and Larsson, 2002).  
223 The elevated firn core concentrations for 1997, 1998 and 2002 were up to two orders of magnitude  
224 higher than those reported in snowpack from the Tatra Mountains, Slovakia (1683 m a.s.l. –  
225 2634 m a.s.l.; Arellano et al., 2011), rainwater at Lake Maggiore, Italy (Mariani et al., 2008) or  
226 rainwater in Sweden (Ter Schure and Larsson, 2002). After excluding these few high peaks, the  
227 concentrations of the remaining years are comparable to reported European PBDE concentrations.  
228 Several previous studies observed high BDE 209 concentrations in precipitation (Mariani et al.,  
229 2008; Offenthaler et al., 2009), but due to high MQL for BDE 209 in this study we do not have  
230 enough data for a comparison.

231

## 232 **Atmospheric deposition rates**

233 In order to obtain an approximation of the actual atmospheric deposition to the Alpine region, we  
234 calculated average contaminant deposition as described the method section. However,  
235 concentrations of persistent organic pollutants are influenced by several post-depositional effects  
236 such as volatilization and degradation of compounds, dissolution of substances in meltwater or wind

237 scour of deposited snow (Daly and Wania, 2004; Wania, 1997). Colle Gnifetti air temperatures  
238 during the investigated period were almost always below 0 °C and the borehole temperatures ranged  
239 from -12.5°C to -13.5°C, minimizing the risk of snow melt and meltwater percolation. The well-  
240 preserved chemical and isotopic profiles and the presence of few visible ice lenses in the core  
241 confirm the lack of melt. Conditions with mean annual temperatures below 0°C reduce the  
242 degradation of persistent organic compounds and affect the re-volatilization of PBDEs and PFASs.  
243 However, temperature affects re-volatilization even at low temperatures and may influence BDE 47,  
244 BDE 99 and BDE 100 concentrations (Bossi et al., 2008). Colle Gnifetti is also susceptible to wind  
245 erosion, which may enhance the re-volatilization of lighter PBDEs and PFASs (Meyer et al., 2012).  
246 Wind erosion predominantly removes the winter snow leading to a low annual net accumulation rate  
247 preserving only 7 to 41 % of the originally deposited snow on the mountain (Schwikowski et al.,  
248 2004). The pollution signal trapped in the net Colle Gnifetti accumulation represents non-winter  
249 deposition. The enhanced atmospheric mixing during the summer results in increased trace species  
250 deposition (Eichler et al., 2004), and we assume that this relationship applied to PFASs and PBDEs  
251 deposition. Thus the derived deposition is assumed to reflect annual deposition. However, all of  
252 these aspects enhance the uncertainty of atmospheric deposition estimates (Table SI 8). To overcome  
253 the varying accumulation rates we calculated 5-year averages that resulted in a total PFAS  
254 deposition of 756 ng m<sup>-2</sup> yr<sup>-1</sup> (1997 - 2002) and 1091 ng m<sup>-2</sup> yr<sup>-1</sup> (2003 - 2007) with a total PBDE  
255 deposition of 1324 (1997 – 2002) and 325 ng m<sup>-2</sup> yr<sup>-1</sup> (2003 - 2007) (SI Table 8).

256

257 Reported PFAS and PBDE deposition rates (Table 1) provide a limited comparison because  
258 precipitation data at the recording sites are influenced by effects other than those influencing the  
259 high alpine ice core locations. European ice core data for these compounds is very limited, thus this  
260 comparison helps provide a rough contamination level. Average PFAS deposition rates at Colle  
261 Gnifetti were up to 4 times higher than in the Canadian Arctic (Young et al., 2007). Deposition rates  
262 at Colle Gnifetti were in the same range as those reported from precipitation in remote regions in  
263 Canada (Northern Ontario and Nova Scotia) (Table 1). In Europe, Dreyer et al. (2010) determined

264 significantly higher PFAS deposition in precipitation close to Hamburg (Germany) compared to the  
265 estimated deposition in the present study. Kwok et al. (2010) reported higher fluxes from residential,  
266 business and industrial areas in Japan and the US and Scott et al. (2006) also describe increased  
267 PFAS concentrations from near-urban and rural places in the US.

268

269 In comparison to previous PBDE studies from the European Alps, deposition rates were determined  
270 in fresh fallen snow collected with a deposition sampler at three Alpine summits (Weissfluhjoch,  
271 Switzerland, 2663 m a.s.l., Zugspitze, Germany, 2650 m. a.s.l. and Sonnblick, Austria, 3100 m a.s.l.)  
272 by Offenthaler et al. (2009). Excluding the summit (Sonnblick) where the authors suggested a local  
273 source contamination, the deposition of BDE 209 at two summits (Weissfluhjoch and Zugspitze)  
274 was up to 2 orders of magnitude higher than values at Colle Gnifetti. The lower altitude of these  
275 summits compared to Colle Gnifetti may be a reason for their higher concentrations. In contrast, the  
276 remaining lower-brominated PBDEs were up to one order of magnitude higher at Colle Gnifetti. The  
277 possibility of different source regions and transport behavior as a reason for these differing  
278 concentrations is discussed in detail in the following sections.

279

280

281

282

Table 1: Comparison of PFAS and PBDE deposition fluxes (ng m<sup>-2</sup> yr<sup>-1</sup>)

site	time	category	matrix	PFBA	PFOA	PFNA	PFUnDA	PBDEs	BDE 209
Colle Gnifetti, Swiss/Italian Border <sup>(this study)</sup>	1996 - 2008	remote	firm core	242 - 545	165 - 207	86 - 113	0 - 53	325 - 1482	181 - 354
Devon Ice Cap, High Arctic Canada <sup>(Young et al., 2007)</sup>	1996 - 2006	remote	snow / firm	n.r.	0 - 81	0 - 103	0 - 13	-	-
Barsbüttel, Germany <sup>(Dreyer et al., 2010)</sup>	2007	near urban	precipitation	2136	1050	450	70	-	-
Remote Canada (ON, NS) <sup>(Scott et al., 2006)</sup>	2002	remote	precipitation	n.r.	50 - 300	20 - 250	n.r.	-	-
Eastern US <sup>(Scott et al., 2006)</sup>	1998 - 1999	near urban	precipitation	n.r.	3200 - 11400	1600 - 12600	n.r.	-	-
Continental US <sup>(Scott et al., 2006)</sup>	1998 - 1999	rural	precipitation	n.r.	2300 - 4200	600 - 1700	n.r.	-	-
Tsukuba, Japan <sup>(Kwok et al., 2010)</sup>	2007 - 2008	residential	precipitation	1280 - 2030	1290 - 2620	2060 - 2180	552 - 465	-	-
Kawaguchi, Japan <sup>(Kwok et al., 2010)</sup>	2007 - 2008	industrial	precipitation	1420 - 1660	2040 - 2910	1380 - 3160	328 - 741	-	-
Slingerlands, NY, US <sup>(Kwok et al., 2010)</sup>	2007 - 2008	residential	precipitation	< MQL	2050	2070	456	-	-
Downtown Albany, NY, US <sup>(Kwok et al., 2010)</sup>	2007 - 2008	business	precipitation	< MQL	2090	2320	794	-	-
Svalbard, Norway <sup>(Hemanson et al., 2010)</sup>	1995 - 2005	remote	ice core	-	-	-	-	420 <sup>d</sup>	3220
Tatra Mountains, Slovakia <sup>(Arellano et al., 2011)</sup>	2005	remote	snow pack	-	-	-	-	90 - 240 <sup>e</sup>	1200 - 3700
Devon Ice Cap, High Arctic Canada <sup>(Meyer et al., 2012)</sup>	1993 - 2008	remote	snow core	-	-	-	-	40 - 350 <sup>f</sup>	900 - 20000
Weissfluhjoch, Austria <sup>(Offenthaler et al., 2009)</sup>	2005 - 2007	remote	snow	-	-	-	-	214 <sup>g</sup>	32785
Zugspitze, Germany <sup>(Offenthaler et al., 2009)</sup>	2005 - 2007	remote	snow	-	-	-	-	125 <sup>g</sup>	8614
Lake Maggiore, Italy <sup>(Mariani et al., 2008)</sup>	2005	rural	bulk deposition	-	-	-	-	3325 <sup>g</sup>	3103
Lake Thun, Switzerland <sup>(Bogdal et al., 2007)</sup>	2006	Rural	bulk deposition	-	-	-	-	1387 <sup>g</sup>	1825
Southern Sweden <sup>(Ter Schure et al., 2004)</sup>	2002	SWTTP <sup>e</sup>	bulk deposition	-	-	-	-	6424 <sup>h</sup>	23290
Southern Sweden <sup>(Ter Schure et al., 2004)</sup>	2002	urban	bulk deposition	-	-	-	-	2519 <sup>h</sup>	5366
Southern Sweden <sup>(Ter Schure et al., 2004)</sup>	2002	rural	bulk deposition	-	-	-	-	584 <sup>h</sup>	1570

<sup>a</sup>data from continuous measurements <sup>b</sup>extrapolated <sup>c</sup>solid waste treatment plant <sup>d</sup>BDE 49 <sup>e</sup>BDE 47+99+100+183 <sup>f</sup>pentaBDE + octaPBDE <sup>g</sup>BDE 28+47+99+100+153+183 <sup>h</sup>BDE 28+47+66+99+100+153+154+183; n.r.: not reported

284

285

286

## 287 **Sources of PFASs**

288 The measured PFAS composition compared to the composition of snow from skiing regions  
289 subjected to ski waxes (Freberg et al., 2010) suggests that direct contamination from human  
290 activities (skiing, sampling campaigns) is negligible for the sampling location. We therefore assume  
291 that PFAS contamination has completely resulted from atmospheric wet and dry deposition. In  
292 general, Colle Gnifetti is influenced by the westerly wind systems (Eichler et al., 2004). During  
293 summer months the majority of precipitation arrives by convective activity. In summer the planetary  
294 boundary layer is located at higher altitudes and air masses from local sources may be able to reach  
295 this altitude (> 4000 m. a.s.l.)(Lugauer et al., 1998).

296

297 Primary emission sources of particle-bound and gaseous PFASs include manufacturing processes,  
298 waste-related facilities and waste water treatment plants. PFASs can be released and volatilized as a  
299 result using products containing PFASs (e.g. lubricants) (Fiedler et al., 2010). Secondary emission  
300 sources to the atmosphere include sea spray generation and the degradation of volatile precursor  
301 substances (Webster and Ellis, 2010; Young and Mabury, 2010). PFASs originating from sea spray  
302 may be a source of PFASs (Reth et al., 2011), but we only observed low sea salt tracer  
303 concentrations in the firn core, indicating a low influence of marine air masses. In addition, PFAS  
304 concentrations did not correlate with sodium and chloride ( $p > 0.1$ ), suggesting that marine sea spray  
305 formation may be negligible for Colle Gnifetti PFAS contamination.

306

307 Armitage et al. (2009) estimated PFOA:PFNA ratios for direct emissions from manufacturing  
308 processes of 7:1 - 15:1 for Europe/Russia and Asia. In the present study PFOA:PFNA ratios were  
309 between 0.7:1 and 3.3:1 suggesting a influence of secondary sources such as the degradation of  
310 volatile precursor substances. The PFOA:PFNA ratio at Colle Gnifetti is close to the ratio of 1.8  
311  $\pm 0.8$  reported from the Canadian Arctic (Young et al., 2007) corroborating the hypothesis of an  
312 indirect contamination origin for these PFCAs. Previous studies assumed that the occurrence of  
313 longer chain PFASs (> C 10) is an indicator of atmospheric degradation of volatile precursors, as

314 significant commercial sources are not known (Prevedouros et al., 2006). In addition none of these >  
315 C8 PFCAs correlate with sulfate in the firn core, where sulfate was used for to identify the influence  
316 of local aerosol rich air masses. This suggests that the major source of > C8 PFCAs might be the  
317 degradation of volatile precursors which can be transported over long distances and do not have to  
318 originate from local sources.

319

320 In contrast to longer-chain PFCAs (> C8), elevated PFBA concentrations at Colle Gnifetti cannot be  
321 explained by the atmospheric degradation of volatile precursors, as studies only report very low  
322 concentrations of 4:2 FTOH in central European ambient air (Dreyer et al., 2009). Although PFBA  
323 can be atmospherically formed by several volatile precursors with a chain length > C4, the  
324 degradation of long-chain precursors (e.g. 8:2 FTOH) would primarily result in the formation of  
325 PFOA and PFNA. This lack of degradation suggests that PFBA originated from direct emissions. As  
326 PFBA vapor pressure is higher than that of PFOA or other long-chain PFAAs, the atmospheric  
327 transport efficiency in the gas-phase to higher altitudes may be enhanced (Kaiser et al., 2005; Steele  
328 et al., 2002). If PFBA only originates from direct local emissions, we would expect a correlation  
329 with sulfate or ammonia, a tracer for aerosol-rich air masses. However, PFBA does not correlate  
330 with sulfate or ammonia, suggesting that it is not only influenced by local sources.

331

332 The voluntary phase-out and replacement of PFOS may explain the low concentrations (< MQL)  
333 observed in Colle Gnifetti firn. Ahrens et al. (2010) suggested that in contrast to PFCAs, PFOS  
334 deposition in high altitude European Alpine lakes (1649 – 2448 m a.s.l.) is mainly related to the  
335 atmospheric degradation of low concentration volatile precursors and not from direct emissions of  
336 PFOS to the atmosphere. Low PFOS concentrations on Colle Gnifetti may also result from the  
337 different atmospheric transport behavior of directly-emitted PFSAs compared to PFCAs, due to their  
338 different gas-particle partitioning and particle size-distribution. PFSAs were reported to be almost  
339 100 % absorbed to particles whereas PFCAs showed different partitioning behavior regarding their  
340 chain-length (Vierke et al., 2011). Furthermore, PFSAs tend to absorb to larger particle than PFCAs

341 (Dreyer et al., 2011). Wet or dry deposition may effectively remove particles before they reach  
342 altitudes above 4000 m.

343

#### 344 **Sources of PBDEs**

345 The analyzed PBDEs may have originated from primary sources such as emissions from  
346 manufacturing processes, waste-related facilities, or from the release of PBDE-containing products  
347 to the atmosphere (Watanabe, 2003; Weinberg et al., 2011a, 2011b). In 2003, Directive 2003/11/EC  
348 (European Union, 2003) banned using or producing pentaBDE and octaBDE mixtures in Europe.  
349 The ban included BDE 209 in 2008, which is outside the investigated period. The predominance of  
350 BDE 47 and BDE 99 is typical for technical pentaBDE mixtures. However, these compounds can  
351 also originate from secondary sources such as the debromination of BDE 209 (Schenker et al.,  
352 2008b) and/or condensation and re-volatilization processes at lower altitudes. BDE 209 is strongly  
353 influenced by direct sources, while lower brominated BDEs are influenced by a combination of  
354 primary and secondary sources (Gouin et al., 2006).

355

356 We used sulfate and ammonium as tracers for aerosol-rich air masses influenced by anthropogenic  
357 activities to obtain a rough estimate of the potential origin of PBDEs. We did not observe any  
358 correlations between BDE 99 and BDE 47 with sulfate and ammonium ( $p > 0.1$ ). This lack of  
359 correlation suggests that PBDEs do not primarily originate from aerosol-rich air masses from source  
360 regions. Due to the limited dataset, we did not perform correlation analyses for the remaining  
361 PBDEs. Belis et al. (2009) reported PBDE concentrations in humus, soil and spruce needles from  
362 different locations and altitudes in the European Alps. The highest PBDE loads were observed in  
363 Italy. During the summer, re-volatilization from humus and soil in lower altitudes and cold  
364 condensation in higher altitudes may be other PBDEs sources in high alpine regions and may explain  
365 the observed elevated concentrations of BDE 47 and BDE 99 in the present study (Gouin et al.,  
366 2006; Wania and Westgate, 2008). Increasing concentrations with altitude were recently observed



367 for all PBDEs except for BDE 209 in the Tatra Mountains, Slovakia (1683 m a.s.l. – 2634 m  
368 a.s.l.)(Arellano et al., 2011).

369

### 370 **Temporal Variations**

371 Despite recent efforts to reduce PFASs in the environment, we only observe a slight decrease in  
372 PFOA concentrations in the firm. We detected PFUnDA in samples after 2002. PFBA, one substitute  
373 for longer chain PFCAs, increased during this same time period. PFCA concentrations in the snow  
374 are strongly influenced by changing weather conditions and the snow accumulation. However, we  
375 observed a significant change in PFAS proportions (Figure SI 1) over the studied time period. PFBA  
376 proportions (Figure 3) increased significantly ( $p < 0.01$ ) in the most recent years and are responsible  
377 for the overall increase in the total estimate of the 5-year depositional averages. This corroborates  
378 recent atmospheric measurements where PFBA was the most abundant PFCA (Ahrens et al., 2012).  
379 PFHpA ( $p < 0.01$ ), and PFOA proportions decreased ( $p < 0.001$ ) during this period probably as  
380 result of recent replacements of C8-PFASs by their short-chain analogues (Renner, 2006). Long-  
381 term atmospheric deposition data is limited, and recent European temporal trend studies for  $> C8$   
382 PFCAs from biota samples reported different trends for the period after 2000 (Ahrens et al., 2011;  
383 Kratzer et al., 2011). Short chain PFASs are less bioaccumulative, thus the shift to shorter chain  
384 PFASs cannot be observed in temporal trend studies conducted in biota. Therefore data regarding  
385 temporal trends of  $< C8$  PFCAs are limited.

386

387 The PBDE concentrations and proportions did not indicate any significant trend due to both elevated  
388 concentrations in three samples and missing data from concentrations below the quantification limit  
389 (Table SI 4). Due to this data variability, we cannot confirm a decline in PBDE concentrations after  
390 their regulation. Recent studies of temporal trends of PBDEs in different matrixes also show no clear  
391 trends (Bogdal et al., 2008; Hermanson et al., 2010; Kohler et al., 2008; Meyer et al., 2012; Schuster  
392 et al., 2010, 2011). These various archives and long-term measurements were influenced by factors  
393 such as diverse sources or post-depositional effects that may explain some of the differences  
394 observed between the results.

395 **Conclusions**

396 The results of this first study of PFASs and PBDEs in a firn core from the European Alps  
397 demonstrate the occurrence, accumulation and recent changes of these persistent organic pollutants  
398 in Alpine regions. We did not observe trends in PBDEs, but PFAS changed from PFOA to a PFBA  
399 dominated composition. The persistence of PFASs and PBDEs has implications for water resources;  
400 as they are likely to be remobilized in glacial meltwater and eventually reach drinking water  
401 supplies. Future analyses of natural archives and long-term monitoring programs will demonstrate if  
402 governmental regulations and voluntary activities by industry will lead to a reduction of persistent  
403 organic pollutants in the alpine environment.

404

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407 isotopes, and dating the firn core.

408

409 **Supporting Information**

410 Additional details on extraction procedures, PFC and PBDE concentrations and QA/QC data are  
411 provided in the supporting information.

412

413

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415

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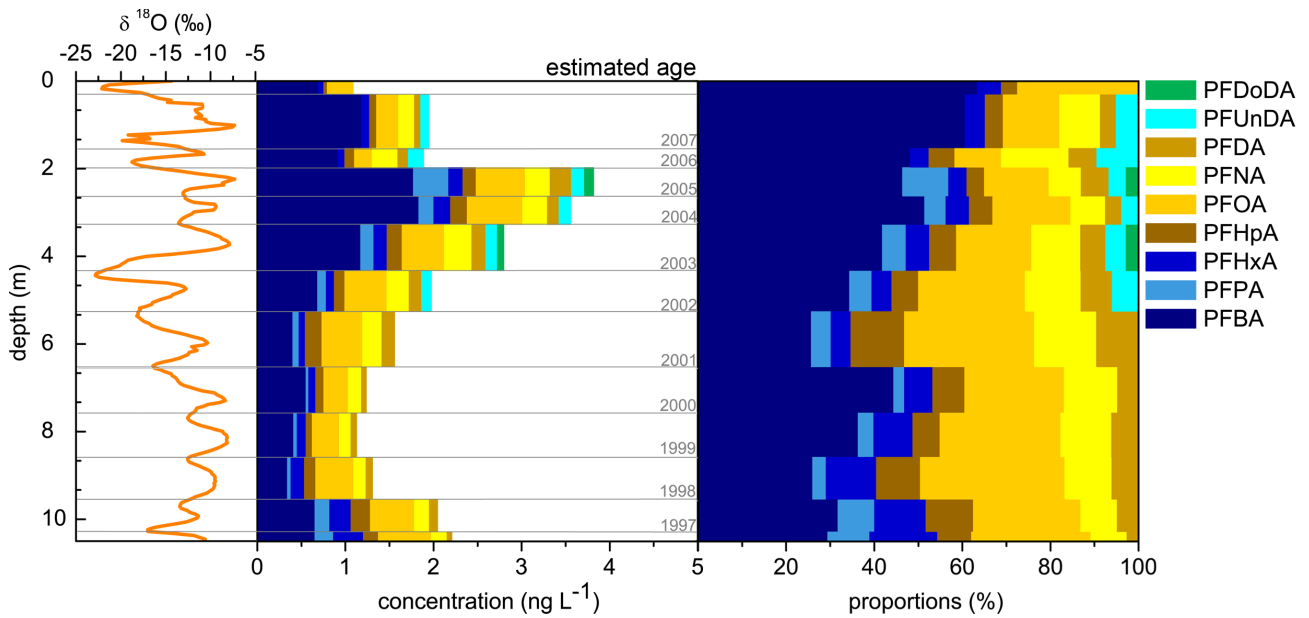
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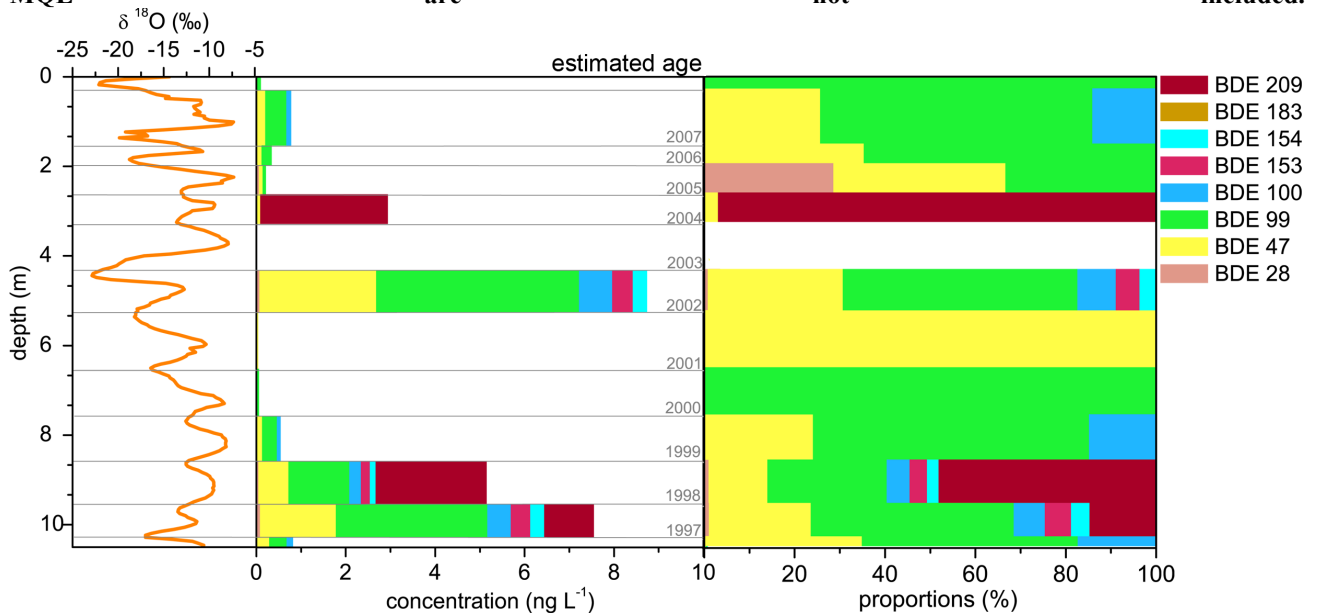
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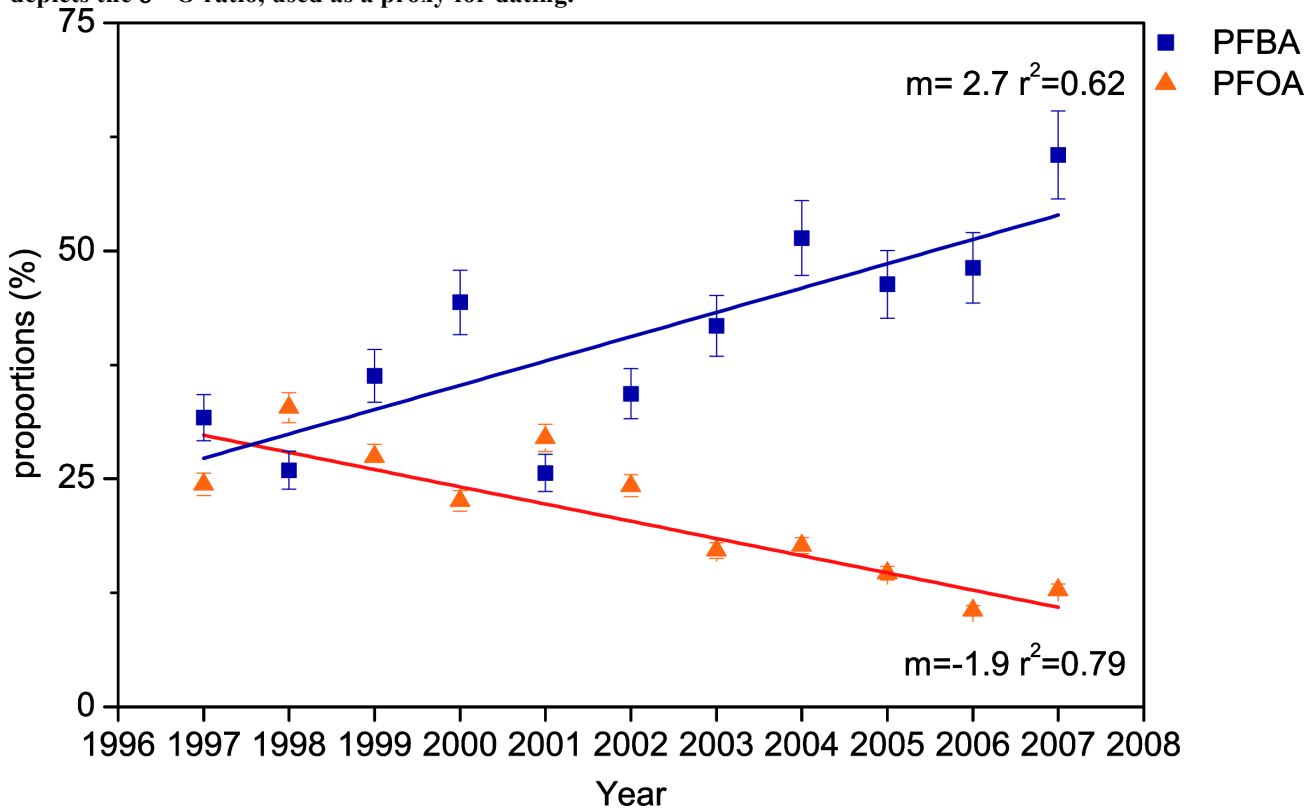
**Figure 1. Depth profiles of concentrations ( $\text{ng L}^{-1}$ ) and proportions (%) of the most frequently detected PFASs. The orange line depicts the  $\delta^{18}\text{O}$  ratio, used as a proxy for dating. PFASs (PFOS, PFTTrDA, PFTeDA) below the MQL are not included.**



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Figure 2. Depth profiles of concentrations ( $\text{ng L}^{-1}$ ) and proportions (%) of detected PBDEs. The orange line depicts the  $\delta^{18}\text{O}$  ratio, used as a proxy for dating.



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Figure 3. Annual proportion (%) changes of PFBA and PFOA from 1997 – 2007. Trend line: linear regression. Error bars: combined method uncertainty.

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