

## **Accumulation of perfluoroalkyl compounds in Tibetan mountain snow: temporal patterns from 1980 to 2010**

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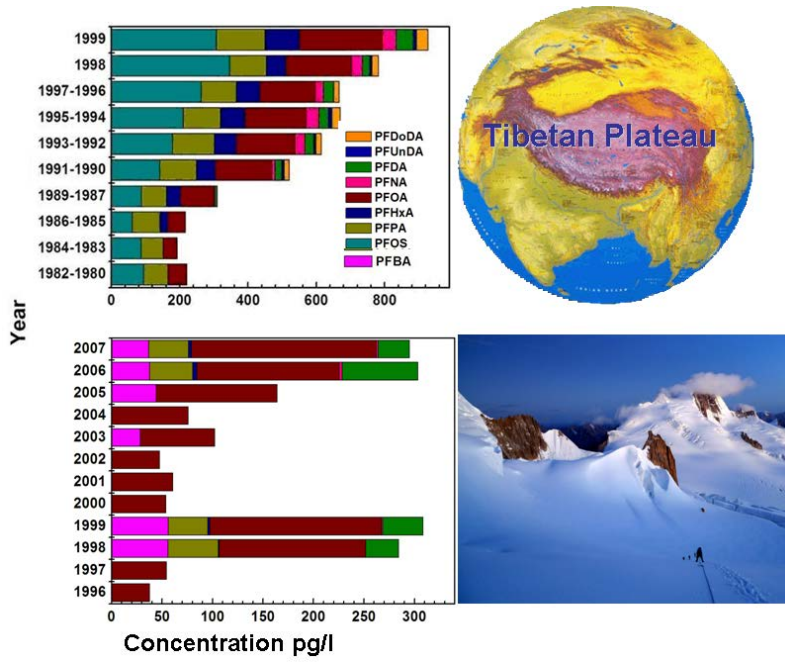
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9

10 Abstract

11 The use of snow and ice cores as recorders of environmental contamination is particularly  
12 relevant for **per- and polyfluoroalkyl substances (PFASs)** given their production history,  
13 differing source regions and varied mechanisms driving their global distribution. In a unique  
14 **study perfluoroalkyl acids (PFAAs)** were analysed in dated snow-cores obtained from high  
15 mountain glaciers on the Tibetan Plateau (TP). One snow core was obtained from the Mt  
16 Muztagata glacier (**accumulation periods of 1980-1999**), located in western Tibet and a  
17 second core from Mt. Zuoqiupo (**accumulation periods of 1996-2007**) located in south eastern  
18 Tibet, with fresh surface snow collected near Lake Namco in 2010 (southern Tibet). The  
19 higher concentrations of  $\Sigma$  PFAAs were observed in the older Mt Muztagata core and  
20 dominated by perfluorooctane sulfonate (PFOS) (61.4-346 pg/L) and **perfluorooctanoic acid**  
21 **(PFOA)** (40.8-243 pg/L), whereas in the Mt Zuoqiupu core the concentrations were lower  
22 (e.g. PFOA: 37.8-183 pg/L) with PFOS below detection limits. These differences in PFAA  
23 concentrations and composition profile likely reflect ~~the downwind-upwind~~ sources affecting  
24 the respective sites (e.g. European/central Asian sources for Mt Muztagata and India sources  
25 for Mt Zuoqiupo). **Perfluorobutanoic acid (PFBA)** dominated the recent surface snowpack of  
26 Lake Namco which is mainly associated with India sources where the shorter chain volatile  
27 PFASs precursors predominate. The use of snow cores in different parts of Tibet provides  
28 useful recorders to examine the influence of different PFASs source regions and reflect  
29 changing PFAS production/use in the Northern Hemisphere.

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32

### 33 Introduction

34 Per- and polyfluoroalkyl substances (PFASs) are widely distributed in the global  
35 environment<sup>1</sup> and are present in both humans<sup>2</sup> and a wide range of biota.<sup>3-5</sup> Due to its  
36 persistence, its ability to undergo long-range transport (LRT) and its bioaccumulative  
37 behaviour, perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonyl fluoride  
38 (POSF)-based chemicals which can degrade and form PFOS are now listed under Annex B of  
39 restricted substances of the UNEP Stockholm Convention on persistent organic pollutants  
40 (POPs).<sup>6</sup> In remote environments like the Arctic, perfluoroalkyl acids (PFAAs) arise  
41 through a combination of LRT processes, including advection with surface ocean currents as  
42 well as transport in the atmosphere.<sup>7-10</sup> In the atmosphere, PFAAs arise through the  
43 photochemical oxidation of volatile per- and polyfluoroalkyl precursors which are also  
44 subject to LRT.<sup>9,11-13</sup> PFAAs may also be transported by the creation of marine aerosol  
45 derived from ocean surfaces, complicating the pathways by which these chemicals enter  
46 remote environments.<sup>14, 15</sup> However, for the continental interiors such as the Tibetan Plateau  
47 (TP) the influence of oceanic sources will be greatly diminished and PFAAs deposited to  
48 surfaces will have arrived through photochemical oxidation of volatile precursors and/or  
49 particle-mediated transport from source areas.

50 Given the lack of long-term systematic observations of PFAAs in air monitoring programmes  
51 then their depositional/accumulation history preserved in snow-ice presents a useful way to  
52 assess the hemispheric or global use history and to observe changing sources or use practices.  
53 Young et al.<sup>10</sup> constructed an accumulation time series of C<sub>8</sub>-C<sub>12</sub> PFAAs for perennial  
54 snow/firn on the Devon Island icecap in the Canadian Arctic. They observed a decrease in  
55 PFOS concentrations from 1998 to 2006, indicating a fast response in environmental  
56 concentrations following the phase out of POSF-chemicals in the late 1990s/early 2000s.<sup>10</sup>  
57 The occurrence of perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA)  
58 in the Devon Island icecap indicate that atmospheric oxidation of volatile precursors is an  
59 important source of PFAAs to Arctic surfaces.<sup>10</sup> More recently, Kirchgeorg et al.<sup>16</sup>  
60 measured PFAAs accumulation in snow collected from Colle Gnifetti glacier in the  
61 Swiss/Italian Alps. They observed a significant increase in the proportion of the shorter chain  
62 (C<sub>4</sub>) perfluorobutanoic acid (PFBA) in the most recent years of the time-series and attributed  
63 this composition change to the increased release of PFBA (or precursors) by local sources.<sup>16</sup>

64 Snow and ice core records for chemical contaminants including POPs, have been obtained  
65 from temperate mountain environments.<sup>17-26</sup> The TP has the largest aggregate of glaciers  
66 outside the Polar Regions with many of the mountain glaciers located at high altitudes where  
67 summertime temperatures do not routinely exceed 0°C, thus reducing melt artefacts. TP is  
68 particularly interesting as this high altitude remote region allows an assessment of pollution  
69 impacts from Asia as well as the wider northern hemisphere and can make a useful  
70 comparison to deposition studies conducted in the European Alps<sup>16</sup> and Arctic.<sup>10</sup>

71 Recently, organochlorine pesticides have been reported in ice-cores from the TP and their  
72 temporal patterns related to chemical use practices and abatement strategies.<sup>24</sup> To date, the  
73 occurrence of the PFASs in lake fish of the Tibetan Plateau has been reported.<sup>27</sup> However,  
74 there is little or no information in the literature about levels of PFASs in mountain snow or  
75 ice of the Tibetan Plateau. In this study, snow cores and surface snow were sampled in the  
76 regions of Mt. Zuoqiupu (accumulation periods of 1996-2007), Muztagata glacier  
77 (accumulation periods of 1980-1999), and Namco (snow for 2010), respectively. The aim of  
78 this study was to determine the depositional history of PFASs over this time series and  
79 examine changes to chemical profiles given geographical differences among samples sites  
80 and the possible influence of difference PFAS-source regions.

## 81 2. Methods

82 **Location of sampling sites.** Three locations on the TP were chosen to investigate the  
83 temporal changes of PFASs (Figure 1). Snow cores were retrieved from the glaciers of Mt.  
84 Muztagata (75.10 °E, 38.28 °N, 6300 m, north-western TP) and Mt. Zuoqiupu (96.92 °E,  
85 29.21 °N, 5600 m, south-eastern TP), while surface snow was collected near Lake Namco  
86 (90.95 °E, 30.73°N, 4800m, southern TP). Details about the sampling locations are available  
87 as supporting information (SI, Figure SI-1). In general, snowfall on the northern and  
88 north-western parts of the Plateau is associated mainly with the westerly jet stream, which  
89 moves southward toward the Himalayas in winter (Figure 1).<sup>28</sup> Thus, glaciers on the southern  
90 plateau can receive precipitation through air masses from the south via the Indian monsoon  
91 during summer and from the west during winter (Figure 1).<sup>28</sup> As a result, due to the different  
92 upwind airsheds, these three snow sampling sites may differ with regards to their contaminant  
93 loading and profile due to the influence of different source regions.

94  
95 **Sampling methodology.** In September 1999, a 22.4 m snow core was retrieved at Mt.

96 Muztagata and a snow core of 30 m was collected in May of 2007 at Mt. Zuoqiupu. These  
97 scientific expeditions were organized by the Chinese Academy of Sciences (CAS). After the  
98 drilling, pre-combusted Al foil envelopes were employed for core handling in the field to  
99 minimize contamination. Snow core samples were packed in double-sealed polyethylene bags  
100 and transported frozen to the laboratory by refrigerated trucks. Preparation of snow core  
101 samples was carried out in a cold room (-20 °C). Snow cores (ID = 9cm) were mechanically  
102 peeled into three parts (the outer, middle materials and the inner core). The inner core was  
103 kept frozen in the dark in pre-cleaned glass jars until analysis. The outer and the middle parts  
104 of the snow core were cut into sections at 5 cm intervals for the measurements of  $\delta^{18}\text{O}$  for  
105 core-section dating. Based on the dating results (see below), the inner core was melted and  
106 extracted for PFASs. Details about the snow core is given in Table SI-1.

107

108 Snow samples were collected in December 2010. During November-December 2010, snow  
109 samples were collected during 3 snow events. Heavy snowfalls resulting in snow depth  
110 accumulations of ~31 cm and 40 cm occurred on 24 November and 10 December,  
111 respectively. Snow samples were collected vertically and obtained by excavating a snowpit  
112 down to the ground. The snowpit was dug to a depth of 86 cm. The pit wall was sub-sampled  
113 with a stainless-steel cube (volume: 1 L) at 10 cm intervals over the entire vertical profile.  
114 Approximately 4 L of snow were collected for each sample. The snow samples were  
115 transported to the laboratory in pre-rinsed stainless-steel containers and left to melt at room  
116 temperature. Snow depth (in water equivalents) and snow density were determined for each  
117 sample as described in Table SI-2. To avoid contamination, materials with fluoropolymer  
118 coatings and fluoropolymer products were strictly avoided at Namco.

119

120 **Snow Core Dating.** Snow core dating was achieved via the annual layer counting that is  
121 made from the continuous concentration profiles of seasonally varying  $\delta^{18}\text{O}$ . A preliminary  
122 time-depth profile of the ice core was achieved by assigning to the surface of the core a time  
123 point of 1999 and 2007 (the time of drilling) for the Mt. Muztagata glacier and Mt. Zuoqiupu  
124 glacier, respectively. The  $\delta^{18}\text{O}$ -depth profiles are shown in Figure SI-2. For the Mt.  
125 Muztagata glacier, the  $\delta^{18}\text{O}$  isotopic ratio displayed a seasonal trend, marked by higher  
126 values in summer precipitation and lower values in winter (Figure SI-2).<sup>29</sup> However in the Mt.  
127 Zuoqiupu core a more depleted  $\delta^{18}\text{O}$  isotopic ratio occurs during the summer periods with  
128 higher values during the winter, reflecting the influence of the summertime monsoon season,

129 <sup>30</sup> (for further details see Figure SI-2). The seasonality of  $\delta^{18}\text{O}$  details the approximate  
130 annual layers and provides a basis for dating. Using the seasonal fluctuations of  $\delta^{18}\text{O}$  along  
131 the profile, the 30-m snow core of Mt. Zuoqiupu was dated to 12 years (from 1996 to 2007,  
132 Figure SI-2) and the 22.4-m snow core of Mt. Muztagata was dated to 20 years (from 1980 to  
133 1999, Figure SI-2). The processes that may lead to dating uncertainties are provided in Text  
134 SI-1.

135 According to the dating results, the annual accumulation for these two snow cores  
136 differed from each other. Mt. Zuoqiupu snow core had the highest accumulation, with the  
137 highest SWE of  $11.9 \text{ kg m}^{-2} \text{ yr}^{-1}$  in 2004 (Table SI-1). However, the Mt. Muztagata snow core  
138 had a water equivalent accumulation of  $2.6\text{-}6.3 \text{ kg m}^{-2} \text{ yr}^{-1}$ , approximately a third to a half of  
139 that accumulated for Mt. Zuoqiupu (Table SI-1). Therefore, in order to achieve sufficient  
140 melt water (>2L) for PFC analysis, the Mt. Muztagata snow core sections representing 2 to  
141 3-years of accumulation were combined and melted (see Table SI-1 and Figure SI-2).  
142 Immediately after melting, the water sample was filtered through a quartz fibre filter (QFF)  
143 (previously baked at  $450^\circ\text{C}$ ). Filter samples were also extracted for PFASs and the amount of  
144 particulate matter for each sample was also measured and provided in Table SI-1.

145  
146 Three kinds of blanks were prepared in this study, namely deep snow/ice meltwater blank,  
147 ground-water blank and laboratory blanks. Deep snow/ice was taken from ~100 m depth and  
148 represented snow that was >100 and ~60 years old for Mts. Muztagata and Zuoqiupu glaciers,  
149 respectively. The ground water (~60m depth) was collected from the Lake Namco region,  
150 close to the surface snow sampling site of this study (Figure SI-1). In each case 2L of melted  
151 deep-snow water and ground water were used as blanks. Laboratory blanks were generated  
152 by spiking the PFASs recovery standard directly into SPE cartridges and following an  
153 extraction process identical to the real samples. In total, 6 melted deep snow water blanks, 3  
154 ground water blanks and 6 laboratory blanks were prepared to test for contamination artefacts  
155 and to generate limits of the detection (LOD).

156 **Sample Extraction.** Filtered metwater samples were subject to solid phase extraction (SPE)  
157 using Waters Oasis WAX cartridges ( $150 \text{ mg}$ ,  $6 \text{ cm}^3$ ,  $30 \text{ mm}$ ), akin to methods described  
158 elsewhere.<sup>31</sup> Prior to extraction, the samples were spiked with 400 pg absolute of a recovery  
159 standard (RS) mix (Table SI-3). After preconditioning with 5 mL MeOH and 5 mL distilled  
160 Millipore water, the SPE cartridge was loaded with the water sample (2-Liters) and eluted at  
161 ~1–2 drops per second, after which each cartridge was washed with 0.1% acetic acid and

162 dried for 20 minutes under vacuum. The cartridges and filters were then wrapped in Al-foil  
163 and sealed into air-tight containers with dry ice and transported to the Helmholtz-Zentrum  
164 Geesthacht, Germany. The cartridges and filters were stored at -20°C until extraction. Each  
165 cartridge was then air dried for 30 min under vacuum. For this operation an additional WAX  
166 cartridge was connected to the top of the sample cartridge to ensure that the air stream was  
167 free of PFASs.<sup>32</sup> Analytes were eluted from the WAX cartridges using 10 mL MeOH with  
168 0.1% ammonium hydroxide. The extracts were concentrated to 200 µL by nitrogen and  
169 spiked with 20 ng absolute of the injection standard <sup>2</sup>H-perfluoro-[1,2-<sup>13</sup>C<sub>2</sub>]-2-decenoic acid  
170 (8:2FTUCA) (50 µL of a 0.4 µg/mL solution, Table SI-3). The QFF were spiked with the  
171 same RS mix and sonicated with 20 mL of MeOH for 30 min. This extraction was performed  
172 three times and these 3 fractions were combined and reduced by rotary evaporation. Finally,  
173 the extract was reduced to 200 µL under a gentle stream of nitrogen and spiked with the  
174 injection standard mentioned above.

175

176 **Instrument analysis.** Details of the instrumental analytical method has been described in  
177 elsewhere.<sup>33</sup> Briefly, an HP 1100 HPLC-system (Agilent Technologies) was used with a  
178 Synergi Hydro RP C<sub>18</sub> 80A column (150 × 2 mm, 4 µm, by Phenomenex), combined with a  
179 suitable guard column (Synergi 2 µ Hydro RP Mercury, 20 × 2 mm, 2 µm). Modifications of  
180 the HPLC system were made by removing Teflon parts to eliminate instrumental blank  
181 contamination. The triple-quadrupole mass spectrometer [Applied Biosystems/MDS SCIEX  
182 (API 3000)] was operated in electrospray ionisation (ESI) in negative ionisation mode.  
183 Quantification was performed using response factors calculated and applied to an 8-point  
184 calibration curve ranging from 0 to 15 pg µL<sup>-1</sup> for individual analytes. Target analytes  
185 included the C<sub>4</sub>-C<sub>14</sub> perfluorocarboxylic acids (PFCAs) and C<sub>4</sub>-C<sub>10</sub> perfluorosulfonic acids  
186 (PFSAs). A full list of analytes is provided in Table SI-4.

187 **Quality controls and assurance.** Recovery of each spiked sample was provided in Table  
188 SI-5 and blank values are provided in Table SI-6. Compounds were classified as not detected  
189 (ND) when a signal to noise ratio (S/N) was <3. Only PFOA was detected in the laboratory  
190 blanks, while PFOS, PFBA, perfluoropentanoic acid (PFPA) and PFOA were detected in  
191 melted deep snow water (DSW) blanks. The limit of detection (LOD) was then quantified as  
192 the standard deviation of the average DSW blank. If chemicals were not detected in the DSW  
193 blanks, the LOD was calculated as a S/N ratio of 10. The LODs based on a 2 L water sample



194 were 25 pg/L for PFOS and PFPA, 15pg/L for PFBA, 5pg/l for PFUnDA, 10 pg/L for PFOA,  
195 PFNA and PFDoDA, and 20 pg/L for the other PFAAs. Table SI-7 provides the average  
196 blank concentrations and the corresponding LODs expressed as pg-/L. The LOD values  
197 reported here are similar to those reported by previous studies and the overall analytical  
198 quality has been assured through participation in inter-laboratory studies.<sup>10, 33-35</sup> The blank  
199 test indicated that field sampling did not result in contamination of the samples. No  
200 background contamination was detected in the filter blanks for the particulate phase. In the  
201 present study, a total of 6, 8 and 11 PFAAs of the 16 PFAAs in the standard were quantified  
202 in the Zuoqiupu glacier snow core, Muztagata snow core and fresh snow samples,  
203 respectively (all samples were blank corrected with ~~for~~ further details presented insee SI  
204 Tables SI 8-10). Recoveries ranged between 29-155% for recovery mix (see SI Table SI-5).  
205 All results were recovery corrected. Duplicate measurements were conducted on 15 paired  
206 samples (see Tables S-11 and S-12). The relative standard deviation between the duplicates  
207 was 5-40%, 4-48% for the Mt. Zuoqiupu ~~andsnow core~~, Mt. Muztagata snow core samples  
208 (Tables SI-13, SI-14), respectively, and 6-47% for triplicate fresh snow samples from Namco  
209 (see Table SI-10).

210

## 211 Results & Discussion

212 **Overview to the Tibetan Plateau and pollution sources.** Interpretation of the temporal  
213 changes of pollutants in a snow core depends on knowledge of the meteorology and major  
214 emission sources. The highest snowfall/precipitation on the Plateau coincides with the Indian  
215 monsoon, which reaches about 32 °N during summer (Figure 1).<sup>36</sup> However, snowfall on the  
216 northern and north-western parts of the plateau is associated mainly with the westerly air  
217 masses (Figure 1). Thus, wet deposition of airborne contaminants to Tibetan glaciers derives  
218 primarily from two directions: west and south. For example, Xu et al.<sup>30</sup> attributed decreased  
219 carbonaceous particle concentrations on the Muztagata glacier in the 1970s-1980s to  
220 diminished European sources following the rise in European environmental regulations<sup>30</sup>. In  
221 addition, Pb has been detected in an ice core from Mt. Muztagata. The temporal trends  
222 showed increasing Pb concentrations from 1955 to 1993, with a decrease after 1993.<sup>37</sup> This  
223 variation was closely associated with the anthropogenic emissions from countries in Central  
224 Asia.<sup>37</sup> On the other hand, pollutant source regions affecting the south-eastern Plateau have  
225 been largely assigned to south Asia.<sup>38</sup> For the Zuoqiupu glacier, the southern branch of the  
226 westerlies that sweep over the south side of the Himalaya-Hindu Kush range (Figure 1)

227 combined with the Indian monsoon make the Zuoqiupu site a receptor of south Asian  
228 sources.<sup>30</sup> This raises important questions with regards to PFAA contaminants. For example,  
229 can PFA profiles obtained from different snow cores across the TP reflect the influence of  
230 their corresponding source regions (Asian or European)? Recently, there is evidence that  
231 manufacturing of PFAAs has shifted from longer chain chemicals (C<sub>8</sub> and above) to shorter  
232 chain ones (C<sub>4</sub>)<sup>39,40</sup> and manufacturing output has increasingly centred on Asian countries.<sup>39,</sup>  
233 <sup>41-43</sup> Similarly, can the Tibetan snow record these shifts? Comparison of the PFAA  
234 concentrations, deposition fluxes and congener profiles of this study with other remote  
235 regions, such as the Arctic and European Alps, should provide a better understanding of the  
236 influence of different or changing sources across the Northern Hemisphere.

237

238 **PFA concentrations in snow.** The full dataset of the measured PFA concentrations in the  
239 Tibetan snow are available as Tables SI 8-10 (Supporting Information). Concentrations of the  
240  $\Sigma$  PFAAs in the Mt. Muztagata (western Tibet, accumulation periods of 1980-1999) snow  
241 ranged from 193 to 927 pg/L, while those in the Mt. Zuoqiupu glacier (south eastern Tibet,  
242 accumulation periods of 1996-2007) were markedly lower ranging from 37.8 to 370 pg/L.  
243 Relatively higher PFAA concentrations in the snow core of Mt. Muztagata may be due to the  
244 influence of the prevailing westerlies and the influence of upwind European sources during  
245 the earlier snow accumulation period.<sup>30</sup> The concentrations of PFAAs in the present study  
246 were compared with those observed in Polar and remote regions and provided in Table 1. The  
247 PFAA concentrations in the Mt. Zuoqiupu glacier are similar to the concentrations reported  
248 for the Devon Island icecap (Canadian Arctic, accumulation period of 1996-2006).<sup>10</sup>  
249 However, concentrations of  $\Sigma$  PFAAs in the Mt. Muztagata glacier are higher than those of  
250 the Devon Island study<sup>10</sup> but lower than those observed in a recent snow core from the Colle  
251 Gnifetti located in the Swiss/Italian Alps (accumulation range: 1996-2008).<sup>16</sup> PFAA  
252 emissions from European countries are likely to account for the higher levels of PFAAs  
253 observed in the Colle Gnifetti snow core<sup>16</sup> and support the assumption that higher levels  
254 observed in the older Mt Muztagata core are due to the influence of a European signal. Snow  
255 and rainfall are important wet depositional sources of PFAAs<sup>44</sup> and have been measured at  
256 several locations across the Northern Hemisphere.<sup>42</sup> Generally, high concentrations of  
257 PFAAs were found in urban areas with much lower concentrations reported for precipitation  
258 analysed from remote regions. The concentrations of  $\Sigma$  PFAAs measured in both Mt.  
259 Muztagata and Mt. Zuoqiupu glacier snow were lower than those observed in precipitation

260 (collected in 2002) from remote parts of Canada<sup>42</sup> as well as the lake water from a glacier-fed  
261 lake in the North American Rockies.<sup>45</sup> In this study, the surface fresh snow samples collected  
262 at Namco contained  $\Sigma$  PFAAs concentrations up to 4236 pg/L, which is similar to  
263 concentrations observed in surface snow from the Arctic<sup>46</sup> and Antarctic.<sup>47</sup> These  
264 comparisons indicate that concentrations of PFAAs in contemporary snow in the south  
265 eastern part of the TP are akin to those observed in the Polar Regions indicating the  
266 remoteness of this region.

267  
268 **Time-series and PFC depositional fluxes.** Depth concentrations of PFAAs measured on the  
269 Tibetan glaciers are shown in Figure 2 with data provided in Tables SI 8 and 9. For the Mt.  
270 Muztagata snow core, concentrations of  $\Sigma$  PFAAs increased continuously over the time  
271 period studied (see Figure 2a). Similar results were observed for individual PFAAs, such as  
272 PFOA and PFOS (Figure SI-3) and in broad agreement with the time series of global  
273 emissions for PFOA and PFOSF-based substances.<sup>48</sup> This finding generally supports the  
274 time-series of PFOS concentrations observed in selected Arctic biota, whereby PFOS levels  
275 have been observed to increase in Arctic ringed seals (*Phoca hispida*) up to the year 2000  
276 before levelling off or declining.<sup>49</sup> It must be noted however, that there are geographic  
277 disparities across the Arctic with regards to temporal trends of PFAAs in biota.<sup>49</sup> For Mt.  
278 Zuoqiupu, the time-series of  $\Sigma$  PFAAs concentrations in the snow core can be broadly  
279 broken down into three periods (Figure 2b). An increase was observed from 1996 to 1999,  
280 followed by a sharp decrease from 2000 to 2004 and then a marked increase from 2005  
281 onwards. The snow core of Mt. Zuoqiupu, (located in south-eastern TP) showed evidence of  
282 melting, with layers of ice marking freeze-thaw events in sections of the core (see description  
283 of the snow core, Table SI-1). Air temperatures during the summer regularly exceed 0°C  
284 resulting in seasonal snow melt. It is therefore plausible that some PFAAs may have migrated  
285 down the snow core thereby altering their vertical and hence temporal distribution. From  
286 Table SI-1, melting was clearly apparent within sections of the core dated as 1998 and 1999,  
287 i.e. ice layers of 87 and 80cm thick respectively were present in each of the core sections. The  
288 presence of ice layers will impede the percolation of meltwater from above, preventing  
289 further movement of soluble contaminants down the snow core and resulting in accumulation  
290 of PFAAs at these key layers.<sup>50</sup> This process may account for the elevated concentrations  
291 observed for the 1998/1999 layers and is supported to some extent by the PFAA profile in  
292 these layers which contain the more soluble, shorter chain compounds of PFBA (C<sub>4</sub>) and

293 PFPA (C<sub>5</sub>). These compounds are absent from the adjacent snow layers above (e.g. 2000 to  
294 2004). Nonetheless, higher concentrations of  $\Sigma$  PFAAs occur in the uppermost snow layers  
295 (e.g. 2005-2007), which are ~5-fold higher than concentrations in the middle layers  
296 (2000-2004), with PFOA concentrations increasing markedly from 2005 to 2007 (Figure 2b).  
297 This later increase in the uppermost snow layers may be due to the growing influence of  
298 atmospheric perfluoro-precursor sources in Asia,<sup>51</sup> which will particularly affect PFAA levels  
299 in the Mt Zuoqiupu area given its location in south-eastern Tibet.

300  
301 Annual deposition fluxes, calculated on the basis of measured concentrations of individual  
302 PFAAs and the annual water equivalent accumulation are shown in Table SI-15. The Mt.  
303 Muztagata snow core showed higher  $\Sigma$  PFAA deposition fluxes, with the maximum of 58755  
304  $\text{fg cm}^{-2} \text{yr}^{-1}$  (Table SI-15) whereas deposition fluxes of  $\Sigma$  PFAAs for the Mt. Zuoqiupu snow  
305 core ranged from 13575 to 41982  $\text{fg cm}^{-2} \text{yr}^{-1}$  (Table SI-15). The annual water equivalent  
306 accumulation for the Mt. Zuoqiupu snow core was 2~3 times higher than that of Mt.  
307 Muztagata (Table SI-1). However, due to the markedly lower PFAA concentrations in Mt.  
308 Zuoqiupu snow (Table SI-8 and 9) then the deposition fluxes were therefore lower and  
309 support the argument that different source regions influence the PFAA concentrations rather  
310 than simple differences in snow accumulation rates. The deposition fluxes of  $\Sigma$  PFAAs in  
311 these Tibetan glacier snow cores are similar to those reported for the Devon Island icecap,<sup>10</sup>  
312 but lower than Colle Gnifetti in the Italian Alps<sup>16</sup> and other depositional fluxes observed in  
313 temperate areas (Table SI-15).<sup>42,44</sup>

314 **PFAA composition in snow.** The dominant PFAAs in the Mt. Muztagata glacier snow core  
315 were PFOS followed by PFOA and PFPA, (Figure 2a), contributing 34% (27–45%), 26%  
316 (21-32%) and 22% (13-37%) to the  $\Sigma$  PFAAs, respectively. Short chain-PFAAs, such PFBA  
317 and PFBS were not detected in the Muztagata snow core, while the longer chain PFAAs  
318 ( $\Sigma$ (C<sub>10</sub>-PFDA, C<sub>11</sub>-PFUnDA and C<sub>12</sub>-PFDoDA), comprised <8% of the total PFAAs. In the  
319 Mt. Zuoqiupu glacier snow core, PFOA was the dominant species (Figure 2b), comprising 77%  
320 (38-100%) of the  $\Sigma$  PFAAs, followed by PFBA (average: 18%, range: 0-27%) and PFPA  
321 (average: 5%, range:0-16%). Interestingly PFOS was found at significant concentrations in  
322 the entire snow core for Mt Muztagata (61.4-347 pg/L) but was below detection limits for Mt  
323 Zuoqiupu. This reflects the older time-series at Muztagata (1980-1999 snow accumulation  
324 period) and the influence of upwind Eurasian source regions prior to the significant reduction

325 in POSF-based chemicals production in the early 2000s.<sup>32</sup> Low levels of PFOS (25–64 pg/L)  
326 were detected in the surface/fresh snow sampled at Lake Namco, located in the central region  
327 of the TP, and are broadly comparable to concentrations recently measured in Arctic snow  
328 (see Table 1). The PFAA profile in the surface snow of Lake Namco was dominated by the  
329 C<sub>4</sub>-C<sub>7</sub> PFCAs, particularly PFBA which displays the highest concentrations (913-2569 pg/L)  
330 for all the PFCs reported in this study (see Figure 3). The average proportion of PFA species  
331 in Namco surface snow was as follows: PFBA (61%), PFHpA (17%), PFPA (7%), PFHxA  
332 (4%), PFOA (5%), and PFNA (2%). Given snow samples were collected relatively recently  
333 (December 2010), then the dominance of the shorter chain compounds (e.g. PFBA) may be  
334 attributed to the shift in manufacturing towards shorter chain products such as the volatile  
335 fluorotelomer alcohol, 4:2FTOH, recently measured in ambient air in India.<sup>51, 53</sup>

336  
337 **Sources of PFAAs to the TP.** Unlike the marine environment of the Arctic where surface  
338 ocean currents play an important role in providing PFAAs to the Polar environment, the  
339 Tibetan Mountain glaciers will receive PFAA contaminants solely from the atmosphere. The  
340 Tibetan PFAAs could therefore arise from: i) the atmospheric oxidation of gas-phase volatile  
341 precursors,<sup>54</sup> followed by dry and wet deposition; the latter driven largely by snowfall; 2) the  
342 direct transport of gas-phase and/or aerosol-associated PFAAs.<sup>55</sup> In this study, particulate  
343 matter in the snow was subject to PFAA analysis. Particle concentrations in the Namco snow  
344 samples were relatively high with concentrations of ~100mg/L (see Table SI-2) while  
345 concentrations in the Mt. Zuoqiupu snow core (<10 mg/L) were lower than those of Mt.  
346 Muztagata (<50 mg/L). However, in all cases, PFAAs were not detectable in the filtered  
347 particles. This is akin to other studies that have reported negligible PFAA concentrations  
348 associated with atmospheric particulate matter collected in the remote ocean atmosphere.<sup>33, 56</sup>  
349 However, the low particle mass collected from the low-volume samples (2L) in this study  
350 could be responsible for the non-detects reported here. Nonetheless, the non-detects for  
351 particle-bound PFAAs indicate that the majority of PFAAs in the snow are present largely as  
352 a result of direct atmospheric transport in the gas-phase and/or atmospheric photooxidation of  
353 volatile precursors (i.e. FTOHs, fluorotelomer acrylates, olefins and iodides in the case of  
354 perfluorocarboxylic acids). As measurements of gas-phase PFAAs in remote air are rarely  
355 reported or are below the detection limit<sup>57,58</sup>, then the atmospheric photooxidation pathway  
356 of neutral precursors probably accounts for the majority of PFAAs measured in contemporary  
357 Tibetan snow. At present it is not clear whether this process occurs in the gas phase with

358 subsequent scavenging of the PFAAs by snowfall, or a heterogeneous reaction occurring on  
359 ice-crystal surfaces, or some combination of the two. Air masses over the TP are mainly  
360 dominated by continental air from central Asia/Europe (western Tibet) and maritime air from  
361 the Indian Ocean (southern Tibet).<sup>59</sup> The Mt. Muztagata snow core represents the earlier  
362 accumulation period from 1980 to 1999 and given its location in the western side of the TP  
363 this would account for the dominance of PFOS and PFOA – present in the environment  
364 through a wide variety of products and applications across Europe over this time period.<sup>52,60</sup>  
365 However, the Mt. Zuoqiupu snow core (1996 to 2007) is dominated by PFOA, with marked  
366 contributions of PFBA and PFPA in the 2005-07 layers. The lack of PFOS in this core likely  
367 indicates the decline in the presence of PFOS (or its precursors) in the atmosphere of the  
368 Northern Hemisphere in recent years, as well as the influence of different source regions  
369 affecting this part of the TP, e.g. sources in south Asia and India. Although PFOS was  
370 detected in snow core samples from Zuoqiupu the relatively high LOD for PFOS prevented  
371 its quantification and reporting. While the phase out of longer chain C<sub>8</sub>-based fluoro  
372 chemicals maybe gaining momentum globally, both 8:2 FTOH and 10:2 FTOH were still the  
373 dominant compounds in ambient air across Japan, China and India in 2009,<sup>51</sup> although,  
374 interestingly, 4:2 FTOH was the most abundant fluorotelomer alcohol measured at sites in  
375 India.<sup>51</sup> The dominance of PFBA in the fresh snow at Namco is likely to be attributed to the  
376 photooxidation of 4:2 FTOH with the incursion of air masses from the Indian sub-continent.  
377 This is most relevant during the Indian Monsoon period<sup>61</sup> which is a driving force for the  
378 atmospheric transport of pollutants from south Asia to the TP.<sup>38</sup> The lack of PFOS as well as  
379 the shorter chain PFSA in the Mt Zuoqiupu core, and the coincidently low levels of PFOS  
380 observed in the surface snow of Namco, may be due to the relatively lower amounts of  
381 fluorooctane sulfonamide (FOSA/E) and fluorobutane sulfonamide (FBSA/E) precursors in  
382 contemporary Indian air.<sup>51</sup> From the study of Li et al<sup>51</sup>, the air concentrations of these  
383 chemicals across India were low (aside from several point sources) and fall within the same  
384 ranges observed in contemporary European/North American studies,<sup>51</sup> which may account for  
385 the low levels of PFOS observed at Namco and Zuoqiupu.

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386  
387 As an indicator of related sources, a correlation matrix was undertaken for the PFAA data  
388 from the Mt Muztagata and Mt Zuoqiupu snow cores respectively (Table SI-16 and 17).  
389 Specifically, correlations were high ( $r > 0.80$ ,  $p < 0.01$ ) between PFOS and PFOA for Mt.  
390 Muztagata, moreover, PFBA showed higher correlations ( $r > 0.80$ ,  $p < 0.01$ ) with PFOA and  
391 PFHxA for Mt. Zuoqiupu. This implies that these chemicals arise from similar sources and/or

392 have experienced similar precursor oxidation and deposition processes.

393

394 PFAAs are present and have accumulated in mountain snow across Tibet over the last 30  
395 years, although there are clear regional differences across the Plateau in terms of the quantity  
396 of PFAAs deposited and their composition, and this is not solely due to differences in snow  
397 accumulation rates between the two study sites. The evidence here would suggest that  
398 different source regions affect different parts of the TP, with an earlier European signal in the  
399 west and an Indian/south Asian signal in the south and east. PFAA concentrations and  
400 accumulation fluxes have increased over the respective snowcore time series, with the highest  
401  $\Sigma$ PFAA concentrations in the surface snow (2010) from Namco. The PFA composition at this  
402 site, however, is dominated by the shorter chain PFBA, in marked contrast to the older  
403 accumulated snow at Mts. Muztagata and Zuoqiupu. This reflects the abundance of 4:2  
404 FTOH in air across India and a shift to shorter chain-length chemicals. The presence of PFBA  
405 in snow is in agreement with findings from a snow core study conducted recently in the  
406 European Alps.<sup>16</sup> Further monitoring at the Mt. Muztagata site would be useful in order to  
407 determine the contemporary European signal on western Tibet and to assess whether PFAAs  
408 in the snowpack show a shift towards the shorter chain length chemicals. PFASs  
409 accumulation in snow will provide a source of these chemicals to mountain lakes and  
410 catchment headwaters, and studies aimed at quantifying this transfer to freshwater habitats  
411 are now recommended.

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416 **Supporting Information.** The details about the sampling sites, snow cores and tables  
417 containing the chemical concentrations in blanks and snow cores, and the comparison of  
418 deposition fluxes are presented. This information is available free of charge via the Internet at  
419 <http://pubs.acs.org/>.

420

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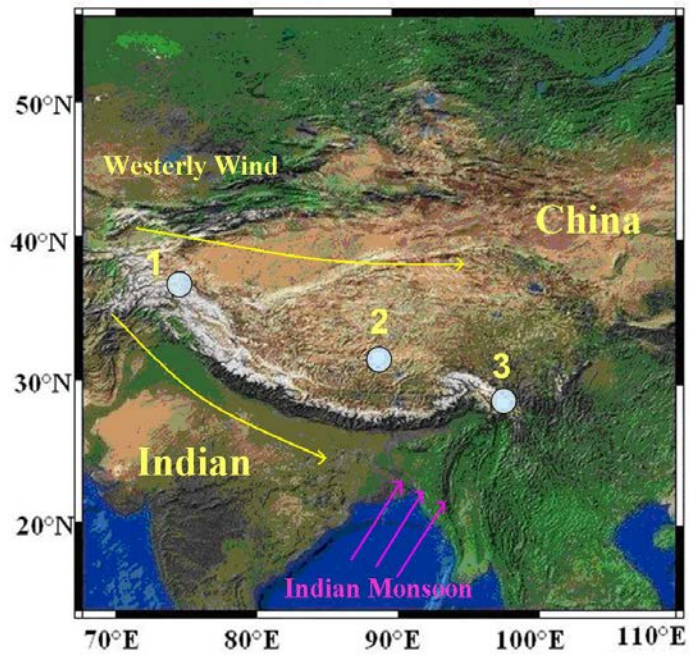
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**Figure 1 Schematic of air circulation systems and location of the sampling sites**

**1. Mt. Muztagata, 2. Namco Lake, 3. Mt. Zuoqiupu**

1

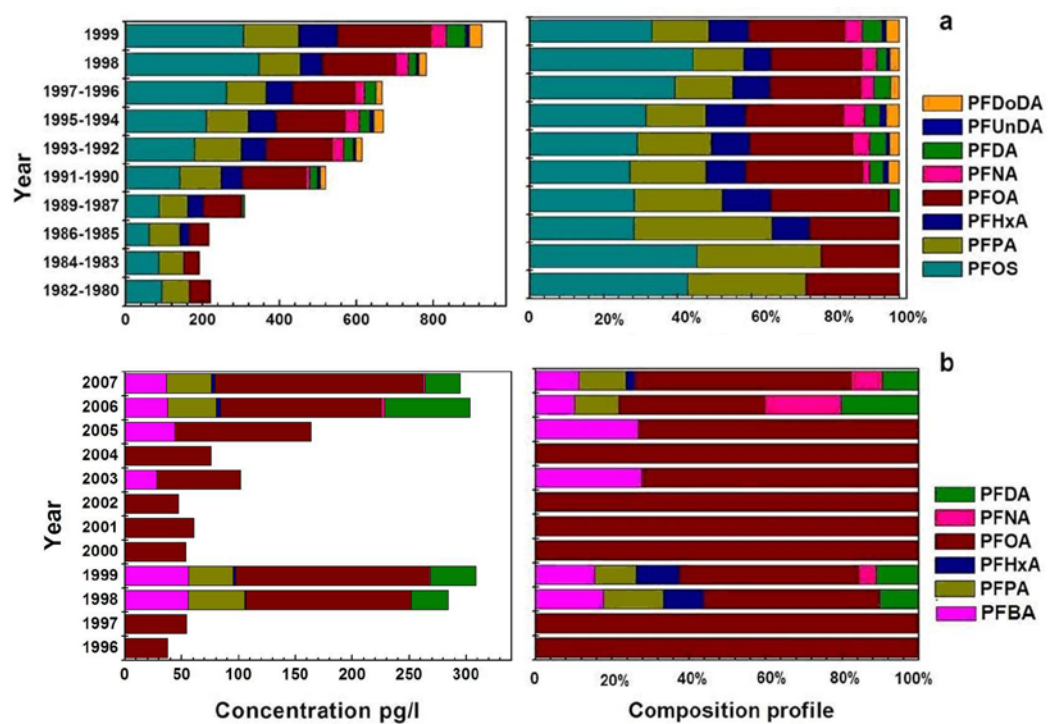
**Table 1 Comparison of the PFAAs concentrations (pg/L) obtained in this study with data from other remote regions**

time site	1980-1999 Mt. Muztagata snow core	1996-2007 Mt. Zuoqiupu snow core	2010 fresh snow from Namco	1996-2006 Devon Island icecap (Canadian Arctic)	1996-2008 Colle Gnifetti snow (Swiss/Italian Alps)	2006 Arctic snow/sea ice	Antarctic snow	2002 Precipitation of remote Canada	2004 Remote lake water, Canada
PFBS	ND	ND	BDL-5			BDL-1500	BDL-49.9		
PFHpS	ND	ND	ND				12.2-219		
PFOS	61.4-346	BDL	25-64.2	1.4-86		BDL-44	17.2-199		50-110
PFBA	BDL	BDL-56.2	913-2569		340-1870	BDL-1000	76.6-1112		
PFPA	64.5-142	BDL-49.8	94.5-3502		BDL-210	BDL-66	BDL-203		
PFHxA	22-100	BDL-40.5	63.5-140		60-340	BDL-66	142-678		
PFHPA	ND	ND	241-982		110-190	BDL-69			
PFOA	40.8-243	37.8-183	68-191	13.1-147	200-630	39-710	114-383	50-300	720-1000
PFNA	10.3-41.2	BDL-73.4	49.2-90.8	5.0-143	BDL-280	38-220	23.7-114	20-250	300-750
PFDA	7.9-50	1.2-75	9.2-35.8	BDL-21.8	BDL-240	BDL-280	BDL-111		100-250
PFUnDA	BDL-5.75	ND	BDL-18.1	BDL-27.3	ND-180	BDL-120	BDL-263		BDL-200
PFDoDA	BDL-24.1	ND	BDL-18.6		BDL-110	BDL-75	BDL-189		
PFTriDA	ND	ND	ND			BDL-500	BDL-485		
PFTeDA	ND	ND	ND			BDI-81	BDL-143		
FOSA	ND	ND	ND			BDL-26			
Sum	193-927	37.3-370	1875-4236	20.8-436	650-4060	220-8100	388-1309		
Reference		This study		(8)	(16)	(45)	(46)	(43)	(44)

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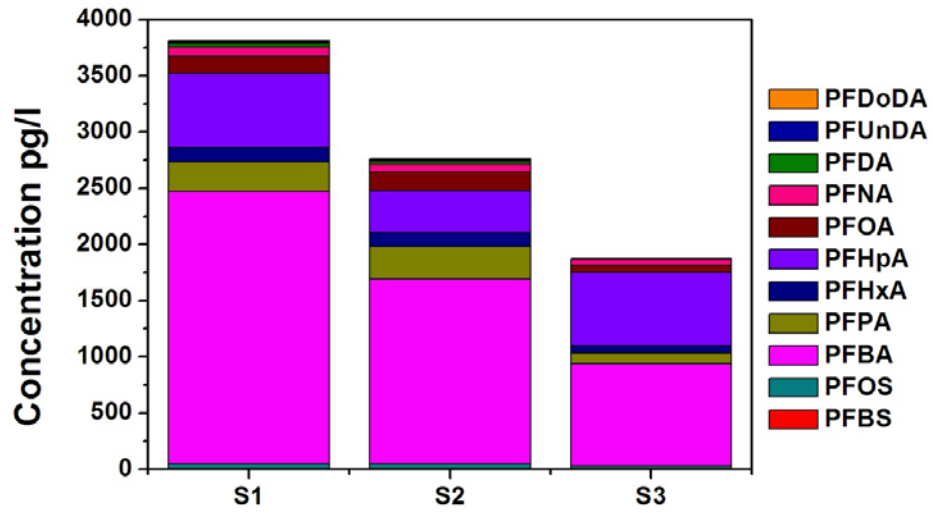


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6 **Figure 2** Time-series and composition profiles of individual PFAAs in Mt. Muztagata glacier (a) and Mt.Zuoqiupu glacier (b)



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Figure 3 PFAAs concentrations in fresh snow collected at Namco

