

1 **Paleo-environmental ice-core record of polycyclic aromatic hydrocarbons and**  
2 **polychlorobiphenyls at Northern Victoria Land, East Antarctica**

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12 **Keywords:** Antarctica, GV7, snow/firn core, PAHs, PCBs, one-century record

13  
14 **ABSTRACT**

15 In this paper we investigated the presence of Polycyclic Aromatic Hydrocarbons and Polychlorobiphenyls in  
16 a 50-m deep snow/firn core collected at the peripheral site GV7 in East Antarctica during the 2013-2014  
17 XXIX Italian expedition. The concentration depth profile was obtained on the basis of the total concentration  
18 of fourteen PAHs and seven PCBs individually determined by gas chromatography triple quadrupole mass  
19 spectrometry. Both classes of pollutants showed synchronized concentration vs time profile throughout the  
20 whole period of time covered by the snow/firn (1892-2012). A correlation between major explosive volcanic  
21 eruptions and the concentration maxima of the pollutants was found. PAH maximum was about 20 times  
22 higher than the background level (from 4.5 ng/L to 87 ng/L). PCBs showed a similar but more limited trend  
23 (from 0.10 ng/L to 0.65 ng/L). This concurrence highlights the contribution of the major explosive volcanic  
24 events to the global contamination level for PAHs, as expected, but also for PCBs whose industrial  
25 production and use began in 1930. Excluding the maximum values, PAHs and PCBs showed an increase in  
26 the period 1960-1990: PCBs from about 0.1 to 0.4 ng/l (400% increase), and PAHs from about 5.2 to 6.6 ng/l  
27 (25% increase). Finally, in the last decade (2000-2010) the trend of these pollutants was opposite: (i) PCBs  
28 constantly decrease (from 0.35 ng/L to 0.20 ng/L), thanks to the implemented restriction on their production

29 and on their use only in closed systems in many countries; (ii) PAHs slightly increases (from 5.2 ng/ to 6.5  
30 ng/L).

31

## 32 **1. INTRODUCTION**

33 Today, human activities have altered the chemical composition of the environment and different classes of  
34 pollutants are ubiquitous because they are present in all environmental components, including the human  
35 being [1]. A better understanding of changes in concentration of these substances in the environment on an  
36 appropriate time scale (paleo-environmental studies) plays an important role for the assessment of the  
37 possible sources of pollution [1, 2], and for the quantification of their contribution to the pollution level, i.e.  
38 source apportionment evaluation. The Antarctica is almost free of local sources of anthropogenic  
39 contamination [1,10,11] and is an ideal place to carry out paleo-environmental studies on global  
40 contamination and to possibly assess the contribution of human activities [2]. Moreover, the low  
41 temperatures during the whole year allow the wet deposition of chemical compounds that are present in the  
42 vapor phase as well as those that are associated to the atmospheric aerosol [4-7, 14,15]. In this way, snow  
43 stratification is obtained, whose chemical composition reflects that of the atmosphere at the time of  
44 deposition [1,3]. Many parameters can be used for dating an ice core [8] that can cover the chemical history  
45 by a few tens up to hundreds of thousands of years, depending on its length and the snow deposition rate in  
46 the sampling area [9]. These characteristics are valid only for some specific sites in Antarctica, where snow  
47 stratigraphy is undisturbed [2, 13].The reconstruction of past chemical composition of the atmosphere from  
48 ice stratigraphy is not an easy task. The annual snowfall are weak in Antarctica [12], thereby a 1-m long ice  
49 core may correspond to a time interval of many years [1,3-7,9]. The atmospheric transport mechanism of  
50 pollutants can be affected by the molecular weight (MW), volatility and tendency to adsorb on particulate  
51 matter [2, 4]. Chemicals with low MW, high volatility and low tendency to adsorb on particles can be more  
52 easily transported in the vapor/gas phase than those heavier, less volatile and highly adsorbed on particle.  
53 The former are deposited later and at higher distance from the source. As a result of these features, in large  
54 remote areas far from the urban/industrial sources, no significant spatial differences of the pollution level  
55 should be expected. On the contrary, heavier and less volatile pollutants which are largely adsorbed on  
56 particles, are generally deposited at a lower distance from the source and may present significant spatial

57 differences of the concentration. Moreover, the level of contamination is more tied to the position of the area  
58 of monitoring and, in the case of snowfall, also to the accumulation rate [6, 16]. Finally, degradation in the  
59 atmosphere during long-range transport and in the snow after deposition can take place [5, 17]. Such  
60 processes are obviously dependent on the chemical–physical properties of the compound considered [11].  
61 Therefore, the diffusion profile of the analytes and the eventual release back into the gas phases during the  
62 first years after the deposition can be different [2,15]. As a result, the concentration levels of each individual  
63 pollutant may change and it may appear a discrepancy between the observed pattern in cold remote areas [2,  
64 16]. A preliminary classification of the pollutants can be made on the basis of the process from which they  
65 are generated: (i) pollutant produced by chemical synthesis and used at the industrial level; (ii) the pollutant  
66 accidentally produced in nature or in anthropic activities. In the first case, once the overall level of  
67 contamination has been classified "dangerous to humans", the strategy regards the adoption of appropriate  
68 measures to restrict or even ban the industrial use of that compound. In the second case, the strategy to be  
69 effective requires a preliminary assessment of the relative contribution of the two possible sources (i.e.,  
70 natural events and human activities). POPs are a class of toxic organic compounds that is characterized by  
71 resistance to environmental degradation through biological, chemical and photolytic processes [10, 20, 21].  
72 Many of them are volatile or semi-volatile compounds, hence they can be carried through long distances in  
73 the atmosphere before deposition occurs [5, 21, 22]. In fact, these compounds are known to undergo global  
74 fractionation, accumulating toward the poles in a cold-trapping process.[9, 19] Two classes of the most  
75 studied organic pollutants are Polychlorobiphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs)  
76 [23]. PCBs were produced at an industrial level from 1930, and are exclusively considered a result of human  
77 activities [21, 24]. PAHs are mainly produced by combustion process of organic substances. Therefore, they  
78 can be produced by accidentally occurring natural events (volcanic eruptions or forest fires) or by  
79 combustion processes directly related to anthropic activities [25, 26]. Wang et al. reported a four-decade  
80 record of PAHs atmospheric deposition in one core collected in Mount Everest, highlighting an increasing  
81 concentration trend starting from the '90s [27]. This increase was reported also by Kawamura et al. for a  
82 sample gathered in Greenland [28]. In a previous work, we reported the profile of PAHs and PCBs in a four-  
83 centuries ice-core gathered at Talos Dome (Antartica). The anthropic contribution to global pollution of  
84 PCBs was confirmed, and was also clearly highlighted for the first time the contribution of volcanic

85 eruptions to the presence of PCBs in the environment [2]. Thereby the investigation of Antarctica ice core  
86 samples results an intriguing option to perform a baseline study on environmental contamination.  
87 Unfortunately, although these substances were detected in Antarctica decades ago, the knowledge of their  
88 basic patterns is still unfulfilled.[18, 19].

89 This work describes the most significant findings on the concentration profiles of PAHs and PCBs of an ice  
90 core collected at GV7 during the XXIX Italian expedition (PNRA project). The dating of the core showed  
91 that it covers more than one century (1892-2012). The contribution of both anthropic activities and accidental  
92 events occurring in nature are also discussed.

93

## 94 **2. MATERIALS AND METHODS**

### 95 **2.1 Reagents**

96 Pesticides Grade N-hexane Pestanal was purchased by Pestinorm (UK), Pesticides Grade Isooctane was  
97 supplied by Labscand (Ireland), and anhydrous Na<sub>2</sub>SO<sub>4</sub> by J. T. Baker (Netherlands). Standard solutions of  
98 native PCBs (ECP9605-PAR) and PAHs (L429-PAR) were purchased by Wellington Laboratories  
99 (CANADA). Standard working solutions were obtained by diluting the certified ones with Pesticide Grade  
100 Isooctane. <sup>13</sup>C-PCB used as injection standard were supplied by CIL (Cambridge Isotope Laboratories, UK),  
101 while <sup>13</sup>C-PCB (MBP-MXF and L429-IS, L429-AS, L429-RS) used as method standard and deuterated PAH  
102 solutions (L429-IS, L429-AS, L429-RS) were purchased by Wellington Laboratories (CANADA). All the  
103 solutions were stored in a refrigerator at 4°C. All reagents and chemicals were used without any further  
104 purification.

105

### 106 **2.2 Apparatus**

107 Analysis were carried out on an Agilent 7890B gas chromatograph, equipped with a PTV injector, an  
108 automatic liquid sampler Agilent 7693A, and an Agilent 7010 triple quadrupole mass spectrometer. The data  
109 system contains all of the software required for calibration, GC/MS-MS spectra collection and data  
110 processing for qualitative and quantitative analysis.

111

#### 112 **2.2.1 Optimization of GC-MS analysis**

113 To optimize MS/MS conditions, first chromatographic analysis of standard solutions in total ion current  
114 (TIC) mode was performed in order to attribute the peaks to each PCBs and PAHs on the basis of the  
115 characteristic mass spectra. Then, a Multiple Reaction Monitoring (MRM) mode was chosen, in order to  
116 have higher selectivity and to avoid matrix interferences. Fragmentation of each analyte was caused by  
117 collisions of selected precursor ions. Two transitions precursor ion/product ion were assigned to each  
118 compound. One transition (highest signal) was selected as quantifier ion, the other was selected as qualifier  
119 ion. The optimized parameters of the GC-MS/MS method are reported in the Supplementary Information  
120 (Table A). The injection volume was 50  $\mu$ L and the temperature profile of the injector was as follows: initial  
121 temperature 85  $^{\circ}$ C, isothermal for 0.5 min; 600  $^{\circ}$ C/min up to 300  $^{\circ}$ C and isothermal for 10 min, 100  $^{\circ}$ C/min  
122 up to 150  $^{\circ}$ C. The transfer line temperature was set at 320  $^{\circ}$ C. The chromatographic separation was  
123 performed on a fused silica capillary column MS-5 (Hewlett Packard, Italy) 95% dimethyl-5% phenyl  
124 polysiloxane chemically bonded stationary phase, 0.25 mm internal diameter, 0.25  $\mu$ m film thickness, 30 m  
125 length. The temperature profile of the chromatographic oven was as follows: initial temperature 70  $^{\circ}$ C,  
126 isothermal for 3 min; 50  $^{\circ}$ C/min up to 150  $^{\circ}$ C and isothermal for 2 min, 5  $^{\circ}$ C/min up to 320  $^{\circ}$ C and  
127 isothermal for 10 min. Helium 99.9995% purity (Rivoira, Italy) was used as a carrier gas at a constant flow  
128 of 1.2 mL/min. The pressure of the collision cell was fixed at 10 psi. 99.999% purity Nitrogen was used as  
129 collision gas with a flow of 1.5 mL/min and He was used as quench gas with a flow of 4.0 mL/min.

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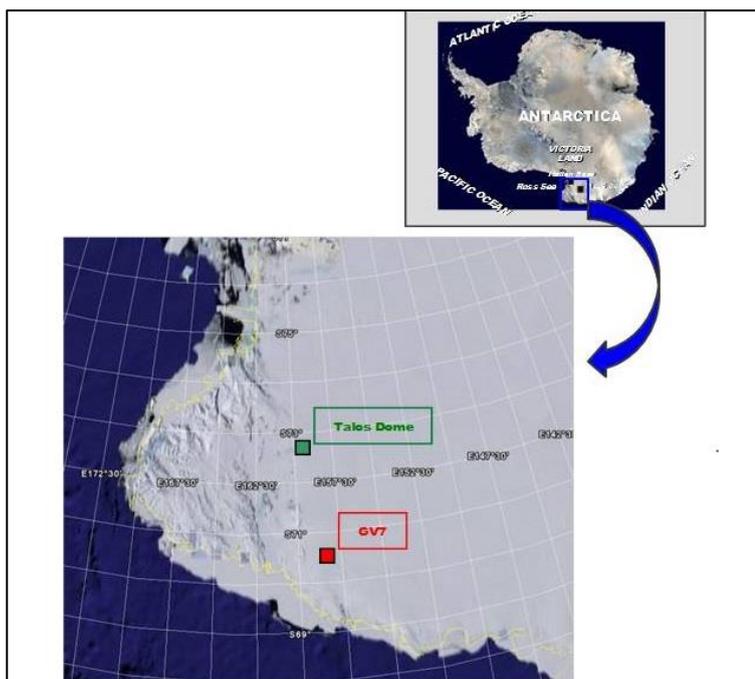
### 131 **2.3 Sampling site**

132 Sampling was performed during the XXIX Italian expedition (November 2013) at GV7 site in Antarctica  
133 (70 $^{\circ}$ 41'S, 158 $^{\circ}$ 52'E; 1950 m a.s.l.; average temperature -31,8 $^{\circ}$ C) and its location is shown in Fig. 1.

134 The site was selected after detailed geophysical and geological studies and is characterized by a high snow  
135 accumulation and an excellent stratigraphy (chemical and isotopic) [13, 30].

136 The ice core drilling was performed with a manual system (diameter 100 mm), and eighty four 60-cm long  
137 samples were obtained. The ice core was dated on the basis of data reported in literature for an ice core  
138 collected at the same site on 2007 [32], and taking into account the correction based on the depth water  
139 equivalent calculated for our samples.

140



141

142 *Fig. 1: Location of the drilling site at Talos Dome and GV7*

143

144 All samples were stored in pre-cleaned stainless steel containers at -20 °C until they underwent pre-treatment  
 145 and liquid–liquid extraction in the laboratory facility of the Italian base at Terra Nova Bay.

146

#### 147 **2.4 Sample preparation**

148 A core segment of three consecutive 60-cm long ice samples were allowed to melt together in a pre-cleaned  
 149 stainless steel container in the clean laboratory (class 100 laminar flow hood) of the Italian base in order to  
 150 obtain a sufficient amount of melt water for our analytical purposes. PAH and PCB concentrations and  
 151 dating were assigned at the middle point of each core-segment. Before extraction, a known amount of the  
 152 “method-standard” solution (see below) was added to the samples. The samples were immediately extracted  
 153 twice with 20 mL of n-hexane using a custom-made extraction system [35]. The two aliquots of organic  
 154 phase were recovered and combined, and the volume of the extracted melt water was measured accurately.  
 155 The organic phases were then stored in glass containers at -20 °C until their arrival in Italy. Once in the  
 156 analytical laboratory, the extracts were treated with anhydrous Na<sub>2</sub>SO<sub>4</sub> immediately before the analysis.  
 157 After recovering the solution, a solvent exchange was performed by adding 1 mL of isooctane and reducing  
 158 the volume of the sample to about 1 mL in a centrifuge vacuum evaporator. Finally, a known amount of the  
 159 “injection-standard” solution (see below) was added to the sample.

160 **2.5 Validation of the analytical procedure**

161 **2.5.1 Limit of detection and calibration curves**

162 Several field blank samples were prepared at the Antarctica laboratory with MilliQ-grade pre-extracted water  
163 and analyzed with the same MRM procedure used for the ice core samples. The limit of detection (LOD) and  
164 the limit of quantification (LOQ) were calculated for each compound as three times and ten times,  
165 respectively, the standard deviation of the blank (calculated on seven replicate blanks). The calibration  
166 curves of PAHs and PCBs were obtained by standard solutions in suitably selected concentration ranges on  
167 the basis of eight experimental points well distributed on the concentration axis. All measurements were  
168 performed in triplicate.

169

170 **2.5.2 Data normalization, recovery and precision**

171 The “injection-standard” and “method-standard” solutions consist in certified standard solutions of labeled  
172 <sup>13</sup>C-PCB and deuterated-PAH and were used in order to guarantee analytical data quality control and quality  
173 assurance. The concentrations were chosen in accordance with PAH and PCB levels reported in literature  
174 [2,10,18,33,34]. The “injection-standard” solution contained <sup>13</sup>C-PCB77, <sup>13</sup>C-PCB81, <sup>13</sup>C-PCB126 and <sup>13</sup>C-  
175 PCB169 at a level of 0.51 ng/L and was added to the final extract immediately before being injected into the  
176 GC-MS. The “method-standard” solution contained fourteen deuterated PAHs, namely <sup>8</sup>D-Acenaphthylene  
177 (<sup>8</sup>D-ACY), <sup>10</sup>D-Acenaphthene (<sup>10</sup>D-ACE, <sup>10</sup>D-Fluorene (<sup>10</sup>D-FLU), <sup>10</sup>D-Phenanthrene (<sup>10</sup>D-PHE), <sup>10</sup>D-  
178 Anthracene (<sup>10</sup>D-ANT), <sup>10</sup>D-Fluoranthene (<sup>10</sup>D-FLA), <sup>10</sup>D-Pyrene (<sup>10</sup>D-PYR), <sup>12</sup>D-Benzo[a]Anthracene, (<sup>12</sup>D-  
179 BaA), <sup>12</sup>D-Chrysene (<sup>12</sup>D-CRY), <sup>12</sup>D-Benzo[b]fluoranthene (<sup>12</sup>D-BbF), <sup>12</sup>D-Benzo[k]fluoranthene (<sup>12</sup>D-BkF),  
180 <sup>12</sup>D-Benzo[a]Pyrene (<sup>12</sup>D-BaP), <sup>12</sup>D-Indeno[1,2,3-c,d]Pyrene (<sup>12</sup>D-IPY) and <sup>12</sup>D-Benzo[g,h,i]Perylene (<sup>12</sup>D-  
181 BPE) at concentration levels ranging from 1.75 to 0.22 ng/L, and seven PCBs, namely <sup>13</sup>C-PCB28,  
182 <sup>13</sup>CPCB52, <sup>13</sup>C-PCB101, <sup>13</sup>C-PCB153, <sup>13</sup>C-PCB138, <sup>13</sup>C-PCB180 at 0.51 ng/L. The “method-standard” was  
183 added to the sample before the extraction in the laboratory facility at the Italian base in Antarctica, and  
184 enabled us to assess the overall recovery of the procedure, including any analyte concentration change that  
185 may occur during the transfer from Antarctica to Italy. The signal of an analyte was always normalized in  
186 respect to the nearest signal of the labeled compound in the injection-standard in order to minimize errors  
187 due to accidental and unpredictable changes in the injected volume or instrumental response. The values of

188 the concentration for each compound were then corrected by the recovery factor calculated for the  
189 corresponding labeled compound of the method-standard. The signal of PCB118 was corrected for the  
190 recovery factor of <sup>13</sup>C-PCB101. Stability of deuterated PAH and labeled PCB standard solutions was  
191 periodically checked over two months and was better than 10%. For every samples analyzed, the ratio  
192 between the retention time of an analyte and that of the corresponding labeled standard was within ±0.5% of  
193 the same ratio obtained for calibration solutions. Furthermore, the signal related to the chosen product ion for  
194 each analyte maximized at the same time within ±0.1 sec, and the relative abundance ratio was within ±10 %  
195 of the theoretical value obtained for calibration solutions.

196

## 197 **2.6 Data analysis**

198 The concentrations determined for each compound were used as variables in the multivariate principal  
199 component analysis using the PCA method by means of the XLSTAT 2015 software. The dataset of PAHs  
200 and PCBs were treated separately.

201

## 202 **3. RESULTS AND DISCUSSION**

### 203 **3.1 Validation of the analytical procedure**

#### 204 **3.1.1 Limit of detection and calibration curves**

205 The LOD and LOQ values for each analyte are reported in the Supplementary information (Table A). The  
206 range of LOD and LOQ resulted 0.0001-0.001 and 0.0004-0.006, and 0.0001-0.04 and 0.0003-0.1 ng/L for  
207 PCBs and PAHs, respectively. The analytes were grouped according to the expected concentration range and  
208 the corresponding calibration curves were obtained on the basis of the following eight concentration levels:

- 209 - ACY, ACE, FLU, PHE, ANT, FLA, and PYR at 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0 ng/L;
- 210 - BaA, CRY, BbF, BkF, BaP, IPY, and BPE at 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 ng/L;
- 211 - all PCBs at 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2 ng/L

212 All the calibration curves resulted linear in the observed concentration range, with a typically value of  $r^2$  of  
213 0.999, always better than 0.997.

214 Table 1 shows the overall recovery calculated for the labeled analytes present in the method-standard  
215 solution that was added to the sample before the extraction in Antarctica.

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Table 1: Recovery % and coefficient of variation (CV%, n=3) of the labeled PCBs and PAHs contained in the “method-standard” solution added to the melted sampled in Antarctica before the extraction.

Compound	Recovery %	CV %	Compound	Recovery %	CV %
<sup>8</sup> D-ACY	45	8	<sup>12</sup> D-BkF	64	10
<sup>10</sup> D-ACE	55	10	<sup>12</sup> D-BaP	62	8
<sup>10</sup> D-FLU	52	10	<sup>12</sup> D-IPY	67	8
<sup>10</sup> D-PHE	60	10	<sup>12</sup> D-BPE	60	7
<sup>10</sup> D-ANT	58	9	<sup>13</sup> C- PCB28	95	21
<sup>10</sup> D-FLA	64	11	<sup>13</sup> C- PCB52	106	16
<sup>10</sup> D-PYR	70	8	<sup>13</sup> C- PCB101	98	25
<sup>12</sup> D-BaA	65	10	<sup>13</sup> C- PCB153	103	20
<sup>12</sup> D-CRY	73	10	<sup>13</sup> C- PCB138	110	15
<sup>12</sup> D-BbF	61	10	<sup>13</sup> C- PCB180	113	15

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220

221 The recovery values and the corresponding CV% for PCBs and PAHs resulted significantly different. In  
222 particular, PCBs showed quantitative recoveries with a tendency to be overestimated, although this  
223 overestimation was always within the CV% (15-20%). On the other hand, the recovery of PAHs has never  
224 exceeded 73%, but with a CV% (8-10%), about half compared to that of PCBs.

225

### 226 3.2 Individual and total concentration of $\Sigma$ PAH<sub>14</sub> and $\Sigma$ PCB<sub>7</sub>

227 Fourteen PAHs and seven PCBs were determined in each sample (180-cm ice core segment) whose  
228 individual concentrations are reported in the Supplementary Information (Table B1 and Table B2, and Table  
229 C, respectively), along with the correspondent depth expressed both in meters and meters of water equivalent  
230 (m w.e.). The equivalent water was calculated as reported in ref. [36]. The dating of each ice-core segment is  
231 also reported. Table 2, and Fig.2 and Fig. 3 show the  $\Sigma$ PAH<sub>14</sub> and  $\Sigma$ PCB<sub>7</sub> total concentrations of each ice-  
232 core segment. Table 3 shows the most significant volcanic eruptions that occurred in southern hemisphere in  
233 the time span corresponding to our ice core that also are reported in Fig.2 and Fig. 3 for a better  
234 understanding of the trend in the ice-core.

235

236

237

238 Table 2:  $\Sigma\text{PAH}_{14}$  and  $\Sigma\text{PCB}_7$  total concentrations of each segment of the ice core gathered at GV7 during the XXIX  
 239 Italian expedition. Depth, both in meters and meter of water equivalent (m w.e.), and ice-core dating are also reported.  
 240 Standard deviations (n=3) are reported in brackets.

Depth, m	Depth, m w.e.	$\Sigma\text{PAH}_{14}$ , ng/L	$\Sigma\text{PCB}_7$ , ng/L	Year	Depth, m	Depth, m w.e.	$\Sigma\text{PAH}_{14}$ , ng/L	$\Sigma\text{PCB}_7$ , ng/L	Year
50.4	35.5	6.2 (0.5)	0.11 (0.01)	1893	25.2	15.4	5.2 (0.3)	0.06 (0.01)	1961
48.6	34.4	4.4 (0.3)	0.05 (0.01)	1898	23.4	14.1	7.0 (0.3)	0.10 (0.01)	1965
46.8	32.5	7.6 (0.1)	0.09 (0.02)	1903	21.6	12.8	4.3 (0.3)	0.06 (0.01)	1970
45	31.1	8.3 (0.2)	0.13 (0.01)	1908	19.8	11.6	4.8 (0.2)	0.09 (0.01)	1974
43.2	29.9	4.6 (0.3)	0.09 (0.01)	1913	18	10.3	6.4 (0.3)	0.17 (0.02)	1978
41.4	28.1	4.6 (0.2)	0.11 (0.01)	1918	16.2	8.9	5.6 (0.3)	0.16 (0.01)	1982
39.6	26.3	4.4 (0.2)	0.09 (0.01)	1923	14.4	7.8	7.8 (0.4)	0.21 (0.02)	1986
37.8	24.7	5.9 (0.3)	0.14 (0.02)	1928	12.6	6.6	9.1 (0.3)	0.18 (0.02)	1990
36	23.7	5.2 (0.3)	0.08 (0.01)	1933	10.8	5.5	6.3 (0.4)	0.15 (0.01)	1994
34.2	22.3	5.7 (0.3)	0.10 (0.01)	1938	9	4.4	7.2 (0.2)	0.15 (0.01)	1998
32.4	20.6	8.8 (0.4)	0.10 (0.01)	1942	7.2	3.2	6.6 (0.3)	0.17 (0.02)	2002
30.6	19.5	6.6 (0.5)	0.08 (0.01)	1946	5.4	2.2	6.0 (0.3)	0.15 (0.01)	2005
28.8	18.4	4.9 (0.2)	0.07 (0.01)	1952	3.6	1.2	6.0 (0.3)	0.13 (0.02)	2008
27	16.6	3.5 (0.2)	0.05 (0.01)	1956	1.8	0.5	6.4 (0.4)	0.11 (0.01)	2011

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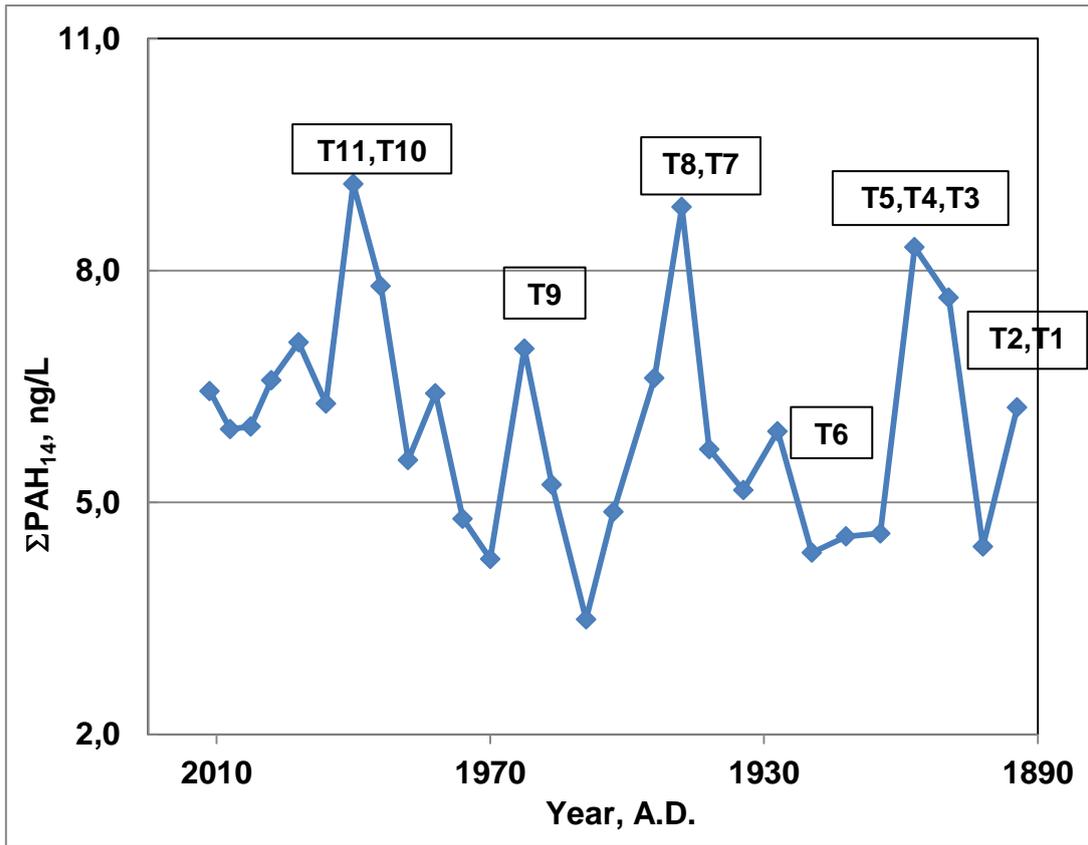
243 Table 3: Name, location and eruption year of the most important volcanic events whose non-sea-salt sulfate (nss-  
 244 SO<sub>4</sub>) signature was detected in the ice/snow core gathered at Talos Dome (Antarctica), (data from ref. 31).

Name	Location	Eruption Year	Explosivity Index
Krakatoa T1	Indonesia	1883	6
Mount Tarawera T2	New Zealand	1886	5
La Soufriere T3	W. Indie	1902	4
Mount Pelee T4	Martinique	1902	4
Santa Maria T5	Guatemala	1902	6
Kelut T6	Java	1919	4
Darney T7	Antarctica	1936	2
Rabaul T8	New Britain	1937	4
Mont Agung T9	Lesser Sunda	1963	4
Mount Pinatubo T10	Philippine	1991	6
Mount Hudson T11	Chile	1991	5

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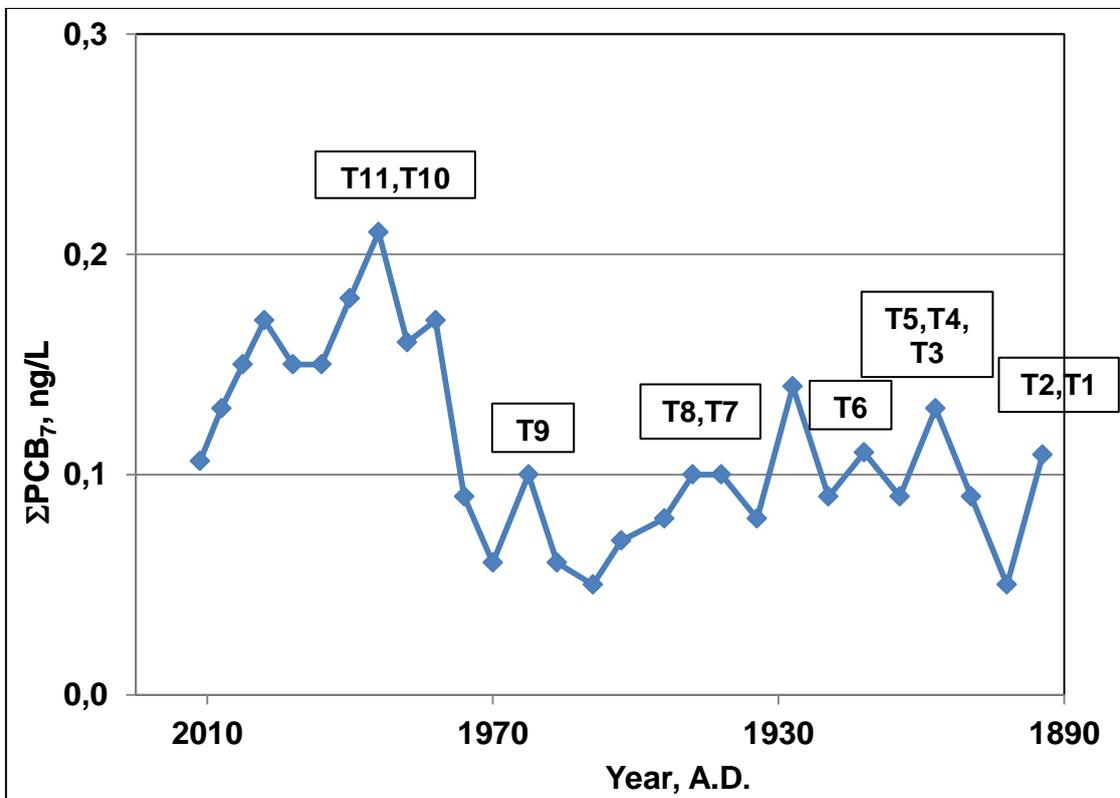
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Fig. 2: Trend of the  $\Sigma\text{PAH}_{14}$  total concentration during the last century as obtained from an ice-core gathered at GV7 (Antarctica). The temporal positioning of the eleven volcanic eruptions in Table 3 is also reported.



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Fig. 3: Trend of the  $\Sigma\text{PCB}_7$  total concentration during the last century as obtained from an ice-core gathered at GV7 (Antarctica). The temporal positioning of the eleven volcanic eruptions in Table 3 is also reported.

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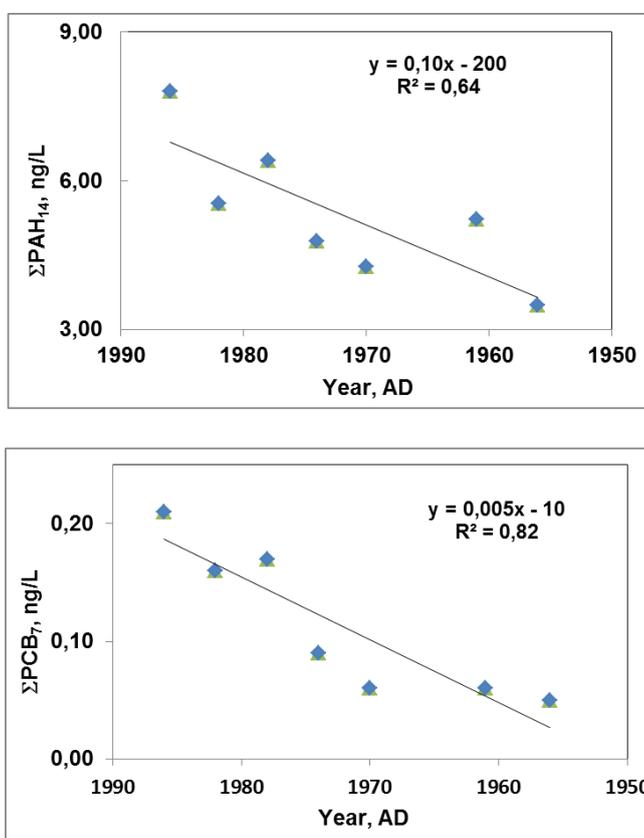
259 The levels of both classes of pollutants continuously and synchronously change within the observed time  
260 span.  $\Sigma\text{PAH}_{14}$  shows four absolute maxima that can be explained taking into account the well-known release  
261 of these compounds in the atmosphere during explosive volcanic eruptions [1,37]..[1, 2, 38]. These  
262 attributions are in very good agreement with the results reported in a previous study on an ice core gathered  
263 at Talos Dome [2]. The first maximum around 1905 can be related to the eruptions of T3, T4 and T5 that are  
264 reported for the same year (1902). Similarly, maxima centered around 1941, 1964 and 1990 can be  
265 associated to the eruptions of T7-T8 (1936-1037), T9 (1963), and T10-T11 (1991), respectively, as reported  
266 in Table 3. The discrepancies between concentration maxima and year of eruption can be easily explained by  
267 considering the time resolution of each ice-core segment. Since a segment was 180 cm long the time span  
268 covered is about 5 years for the deepest samples and about 3 year next to the surface. The most abundant  
269 non-alkylated PAHs are ACY, ACE, PHE, FLA and PYR, and the mean value of the sum of their  
270 concentration among all segments accounts for about 80 % of  $\Sigma\text{PAH}_{14}$  with a CV of 4%. This result is in  
271 good agreement with the data reported by previous studies for ice core matrices [2, 27, 28].

272 The trend of PCBs is quite similar to that of PAHs, although the volcanic maxima are less evident and almost  
273 confused with the “noisy background”. This result confirms the experimental evidence that PCBs also are  
274 produced during volcanic eruptions along with PAHs, as already observed for an ice-core gathered at Talos  
275 Dome [2]. In that case the very intense peak of the Tambora eruption in 1815 was included in the depth  
276 profile and caused the most intense PAH and PCB signature. The eruption of Tambora caused the highest  
277 peak concentration of non-sea-salt sulphates in the time span 1600-2000 observed in the ice-core gathered at  
278 Talos Dome. Thus, volcanic eruptions are responsible of PCB and PAH peak concentrations in the  
279 atmosphere, but very limited in time. In fact, according to our time resolution sampling (a 1.8 m long ice-core  
280 segment corresponds to 3-5 years) the maxima are generally represented with only a single experimental  
281 point. Before and after the maximum the concentration of PAHs drastically drop to the background level.  
282 This is true to a lesser extent also for PCBs for the reason mentioned previously. This default behavior  
283 presents two exceptions. The first relates to the period between 1940 and 1955. During this period the  
284 decrease of the pollutants is slower than usual both for PAHs and PCBs. In this respect, it is noteworthy  
285 considering the possible effects of the World War II on a temporary high level of the air pollution [39] as a

286 consequence of both an intense industrial production and an unusually great number of very intense and  
287 widespread fires on a large area caused by aerial bombardment.

288 The second exception emerges if the ice-core temporal profiles of PAHs and PCBs are examined excluding  
289 the limited period of time affected by the volcanic eruptions. In fact, the concentrations of PAHs and PCBs  
290 in the period 1956-1986 undergoes a progressive increase, as a signature of the anthropogenic activities,  
291 mainly industrial ones. In this period of time, the concentrations of both classes of pollutants increase almost  
292 linearly in the ice-core, with a slope of 0.1 ng/year ( $R^2=0,64$ ) and 0.005 ng/year ( $R^2=0,81$ ) for PAHs and  
293 PCBs, respectively (Fig. 4).

294



295  
296 Fig. 4. Total PAH and PCB concentration profiles observed in the  
297 ice-core gathered at GV7 for the period 1956-1986.  
298

299

300 In the period 1994-2011, PAHs and PCBs show a very different behavior to that observed in the previous  
301 period and also very different between them. In fact, during this period PAHs have a substantially constant  
302 concentration in the ice-core in the range 6-7 ng/L. PCBs instead show a clear and positive trend to the  
303 reduction, with a tendency curve (polynomial of the second degree,  $R^2 = 0.91$ ) which shows the maximum

304 around 1998-2000, and a virtually linear decrease in the period of 2002 -2011 ( $R^2 = 0.996$ ), with a negative  
305 slope of  $-0.007$  ng/year (Fig. 5).

306

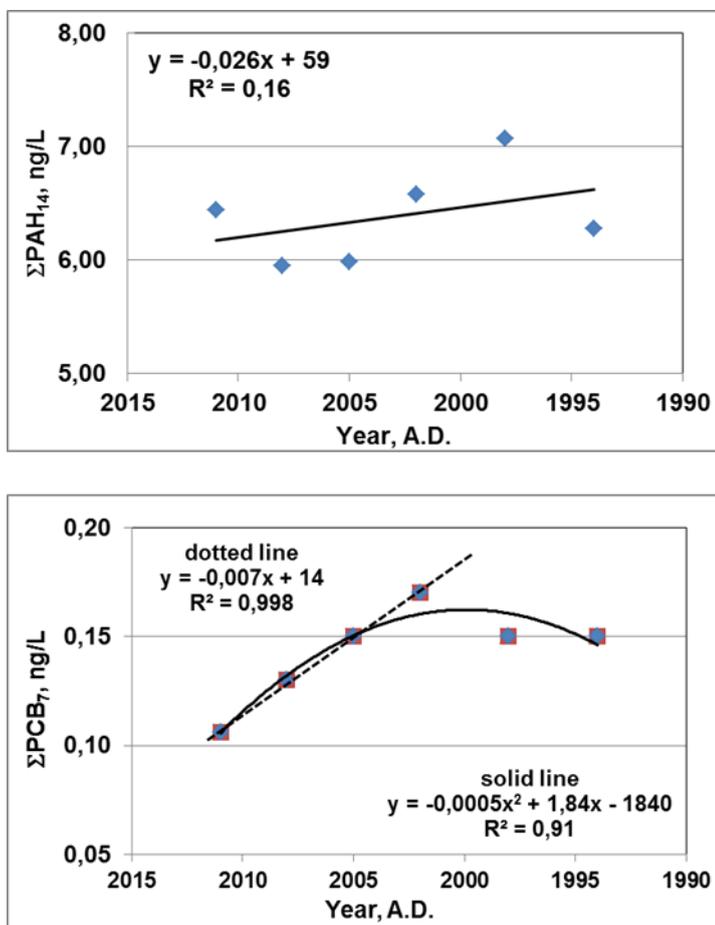


Fig. 5. Total PAH and PCB concentration profiles observed in the ice-core gathered at GV7 for the period 1994-2011.

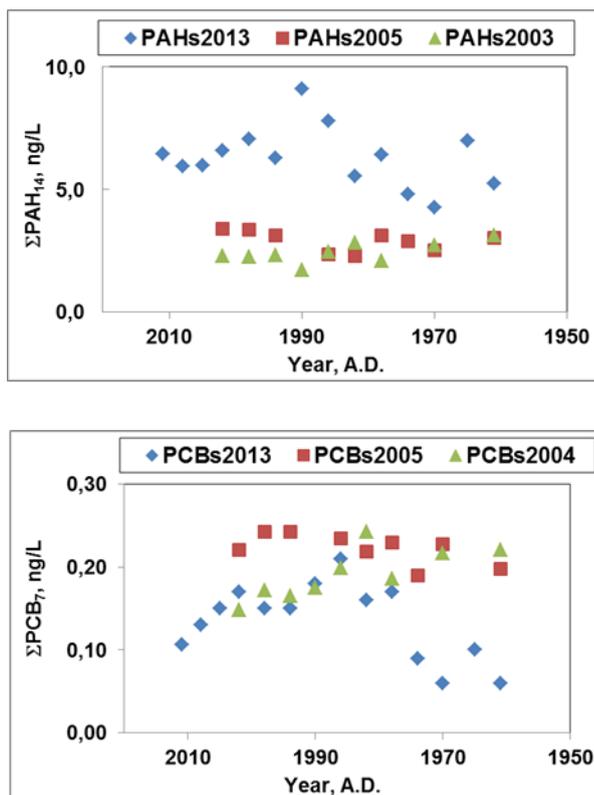
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312 The almost constancy of PAHs is in agreement with published studies of different ice-cores collected at Mt  
313 Everest [27], at Site-J in Greenland [28] and in Talos Dome.[2] It has to be taken into account that PAHs are  
314 unintentionally-produced as by-products of many industrial processes and anthropic activities [7]. The  
315 contribution of a wide range of sources is reflected in a major difficulty of controlling their trends and in a  
316 more difficult reduction of the anthropogenic provision.

317 As for PCBs, we should consider that industrial production of PCBs began in 1930 [21], and the maximum  
318 concentration is reached around 1990 as reported by Garmash et al. in an ice core collected on the  
319 Lomonosovfonna glacier, Svalbard.[21] After the '90s the production was definitely banned or restricted in  
320 many countries[21, 24], due to their known toxicity, and this is in accord with the decrease found in the more

321 superficial segments of the ice cores collected at GV7 and Talos Dome. The same decreasing trend was  
 322 observed also for an ice core collected at the Fiescherhorn glacier (Switzerland) from 1998 to 2009 [21].  
 323 The experimental evidences gathered from the ice-core of GV7 are very much in agreement with the data  
 324 obtained previously on two ice cores taken at Talos Dome. Fig. 6 shows the concentrations of PAHs and  
 325 PCBs measured in each of the three ice-core in the same period of time, i.e. 1960-2011.  
 326



327 Fig. 6. Total PAH and PCB concentration profiles observed in the ice-core of GV7 (2013)  
 328 and in the two ice-cores of Talos Dome (2005 and 2004) for the period 1960-2011.  
 329  
 330

331  
 332 The overall assessment of the data clearly confirms an almost constant level of PAHs in the last 10-15 years  
 333 and a clear trend of PCBs to decline. The main difference between the behavior of PAHs and PCBs regards  
 334 the absolute levels of concentration observed in GV7 and Talos Dome. The levels of PCBs measured in the  
 335 two sites are practically comparable, whereas the average level of PAHs at GV7 resulted twice that of Talos  
 336 Dome. In fact, Talos Dome is placed farther from the oceans compared to GV7, the latter being more  
 337 shielded from possible external atmospheric currents by the presence of the highlands [43], and less  
 338 subjected to katabatic winds [44]. Being the pollutants mainly transported by the aerosol that arrives from air  
 339 circulation coming through the ocean,[43] the increase detected is easily explicated.

340

#### 341 **4. CONCLUSIONS**

342 The analysis of the ice core collected in GV7 showed the presence of POPs in the atmosphere of the last  
343 century. The results confirm the diffusion of such pollutant also in a region that is considered one of the most  
344 uncontaminated in the world. Relevant concentration of PCBs were detected in the ice-core connected to the  
345 years of their industrial production (1930-1990), showing the effectiveness of the long distance transport  
346 processes of these compounds even to the most remote areas. Besides the anthropogenic contribution, a  
347 provision of pollutants (especially PAHs) is due to epochal natural events, i.e. explosive volcanic eruption.  
348 The high concentration of the analytes in conjunction with several volcanic eruptions are in agreement with  
349 the dating of the ice core. More in general, the totality of the data obtained has allowed us to hypothesize an  
350 evident contribution for both classes of compounds due to natural events (volcanic eruptions) and a  
351 significant anthropic contribution due to the long distance transport processes from the more industrialized  
352 areas. The decreasing trend noticed for PCBs is a considerable result, achieved through the implementation  
353 of very tight restriction rules in their use by national political bodies in many countries. In fact, even though  
354 PAHs levels are not decreasing, the major environmental concern is by far related to the higher toxic PCBs  
355 and to high molecular weight PAHs that are present only in low percentages in our samples.

356

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360

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515

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