

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

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11
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 Na₂SO₄ 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. ¹³C-PCB used as injection standard were supplied by CIL (Cambridge Isotope Laboratories, UK),
101 while ¹³C-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 μ 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 μ 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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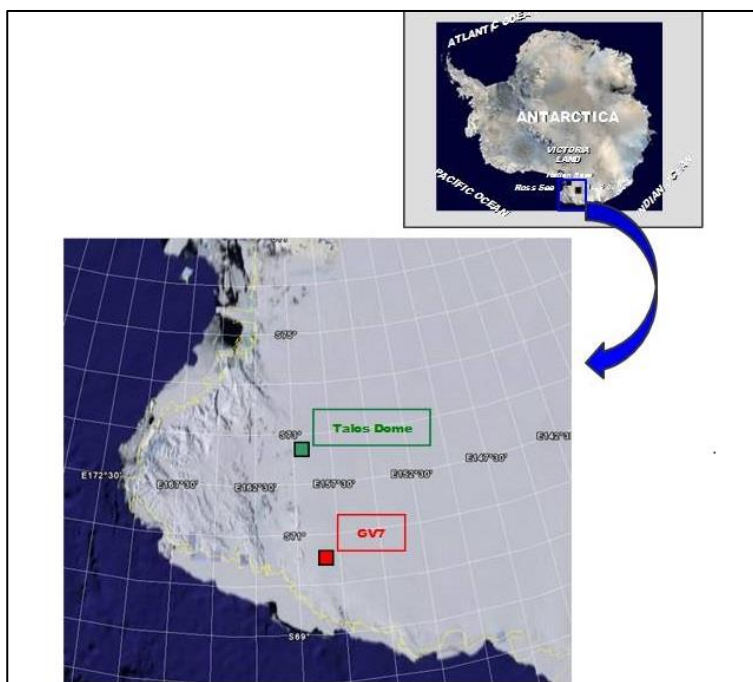
131 **2.3 Sampling site**

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.

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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 Na₂SO₄ 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 ¹³C-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 ¹³C-PCB77, ¹³C-PCB81, ¹³C-PCB126 and ¹³C-
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 ⁸D-Acenaphthylene
177 (⁸D-ACY), ¹⁰D-Acenaphthene (¹⁰D-ACE, ¹⁰D-Fluorene (¹⁰D-FLU), ¹⁰D-Phenanthrene (¹⁰D-PHE), ¹⁰D-
178 Anthracene (¹⁰D-ANT), ¹⁰D-Fluoranthene (¹⁰D-FLA), ¹⁰D-Pyrene (¹⁰D-PYR), ¹²D-Benzo[a]Anthracene, (¹²D-
179 BaA), ¹²D-Chrysene (¹²D-CRY), ¹²D-Benzo[b]fluoranthene (¹²D-BbF), ¹²D-Benzo[k]fluoranthene (¹²D-BkF),
180 ¹²D-Benzo[a]Pyrene (¹²D-BaP), ¹²D-Indeno[1,2,3-c,d]Pyrene (¹²D-IPY) and ¹²D-Benzo[g,h,i]Perylene (¹²D-
181 BPE) at concentration levels ranging from 1.75 to 0.22 ng/L, and seven PCBs, namely ¹³C-PCB28,
182 ¹³CPCB52, ¹³C-PCB101, ¹³C-PCB153, ¹³C-PCB138, ¹³C-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 ¹³C-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 %
⁸ D-ACY	45	8	¹² D-BkF	64	10
¹⁰ D-ACE	55	10	¹² D-BaP	62	8
¹⁰ D-FLU	52	10	¹² D-IPY	67	8
¹⁰ D-PHE	60	10	¹² D-BPE	60	7
¹⁰ D-ANT	58	9	¹³ C- PCB28	95	21
¹⁰ D-FLA	64	11	¹³ C- PCB52	106	16
¹⁰ D-PYR	70	8	¹³ C- PCB101	98	25
¹² D-BaA	65	10	¹³ C- PCB153	103	20
¹² D-CRY	73	10	¹³ C- PCB138	110	15
¹² D-BbF	61	10	¹³ C- PCB180	113	15

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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 Σ PAH₁₄ and Σ PCB₇

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 Σ PAH₁₄ and Σ PCB₇ 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.

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238 Table 2: Σ PAH₁₄ and Σ PCB₇ 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.	Σ PAH ₁₄ , ng/L	Σ PCB ₇ , ng/L	Year	Depth, m	Depth, m w.e.	Σ PAH ₁₄ , ng/L	Σ 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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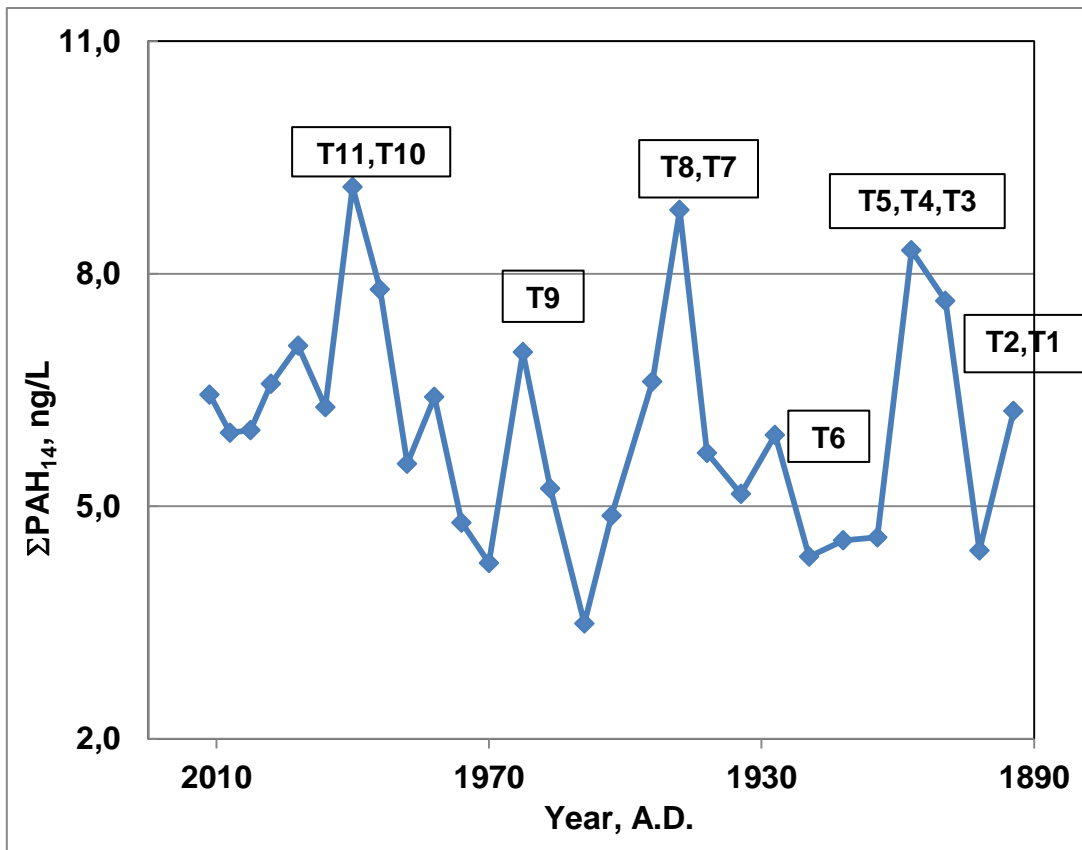
243 Table 3: Name, location and eruption year of the most important volcanic events whose non-sea-salt sulfate (nss-
 244 SO₄) signature was detected in the ice/snow core gathered at Talos Dome (Antarctica), (data from ref. 31).

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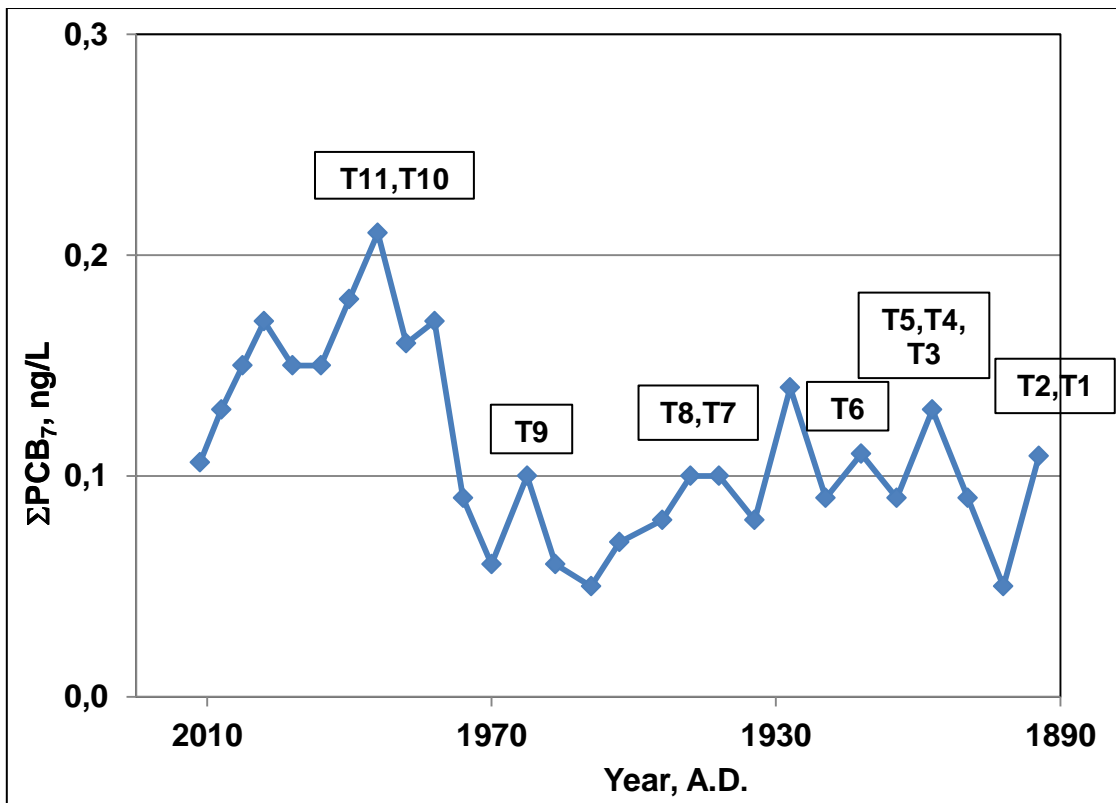
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Fig. 2: Trend of the ΣPAH_{14} total concentration during the last century as obtained from an ice-core gathered at GV7 (Antarctica). The temporal positioning of the eleven volcanic eruptions in Table 3 is also reported.



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Fig. 3: Trend of the ΣPCB_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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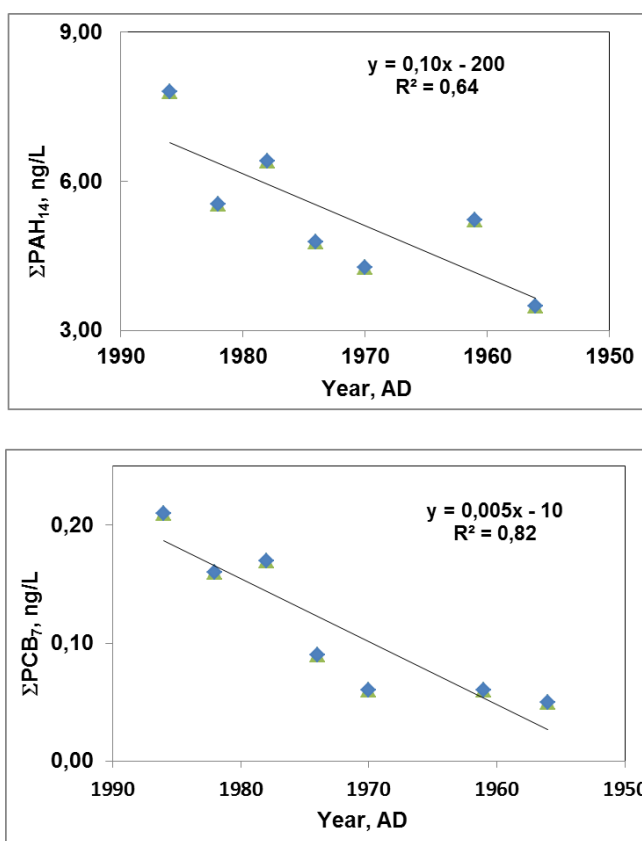
259 The levels of both classes of pollutants continuously and synchronously change within the observed time
260 span. ΣPAH_{14} shows four absolute maxima that can be explained taking into account the well-known release
261 of these compounds in the atmosphere during explosive volcanic eruptions [1,37]..[1, 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 ΣPAH_{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 (a1.8 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).

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

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).

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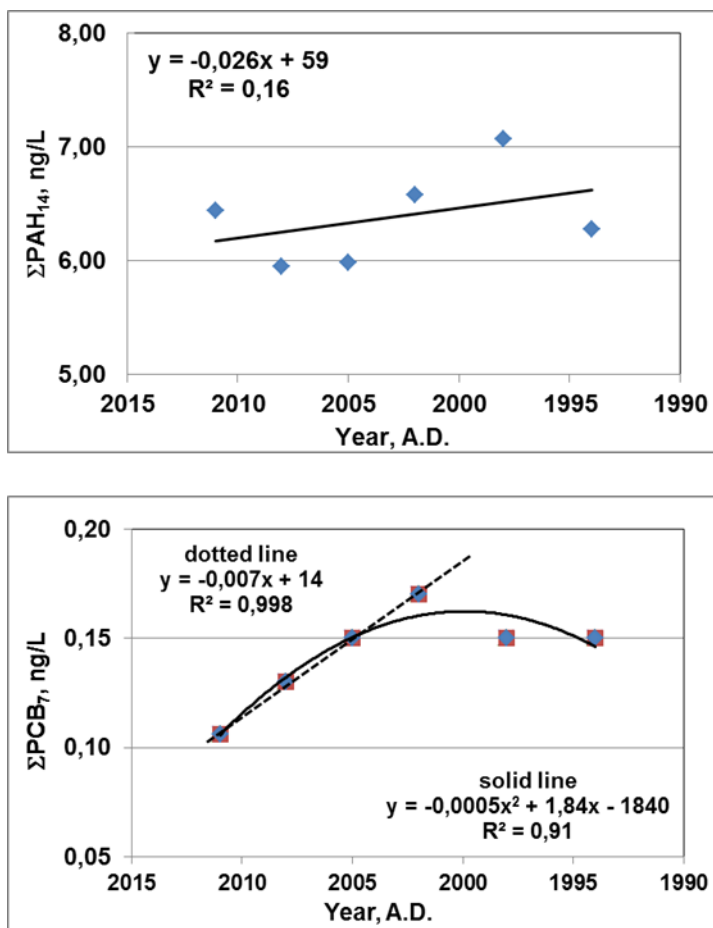


Fig. 5. Total PAH and PCB concentration profiles observed in the ice-core gathered at GV7 for the period 1994-2011.

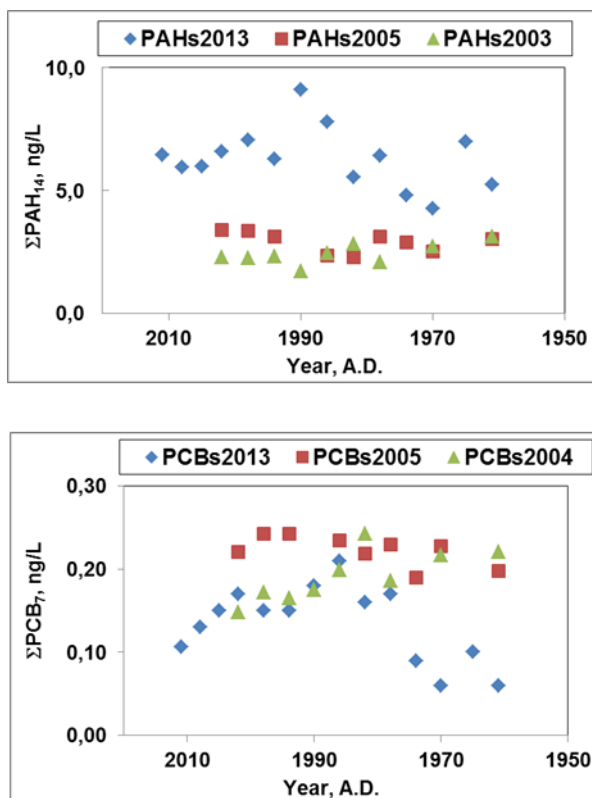
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312 The almost constancy of PAHs is in agreement with published studies of different ice-cores collected at Mt
313 Everest [27], at Site-J in Greenland [28] and in Talos Dome.[2] It has to be taken into account that PAHs are
314 unintentionally-produced 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.
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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.
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 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.

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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

357 **5. ACKNOWLEDGMENTS**

358 This work was financially supported by the Polar Chemistry project of the Italian Research Program
359 in Antarctica (PNRA).

360

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515

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