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Polycyclic aromatic hydrocarbon dynamics in soils along proglacial chronosequences in the Alps

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) were studied in the soils of three proglacial areas in France (Noir and Chardon Glaciers) and Italy (Miage Glacier). PAH contents, PAH stocks and PAH contents normalized to the total organic carbon contents (PAHs/TOC ratio) were investigated along proglacial soil chronosequences to infer their evolutions with soil age (from 3 to 4200 years), where the PAH contamination was only related to long-range atmospheric transport. Evolutions of PAH and TOC contents, PAHs/TOC ratio and PAH stock were fitted with exponential and logarithmic relations. For the three proglacial areas, PAH contents increased rapidly during the first 150 years of soil development, ranged from 4 to 152 $ng.g^{-1}$, and showed a strong relationship with total organic carbon (TOC) contents ($r=0.83$, $p < 0.05$). The joint increase of PAH and TOC contents suggested that PAH accumulation in soils were not only driven by PAH inputs but also by the capacity of soils to store these contaminants. PAH contents in the oldest soils (from 1200 BCE and 2200 BCE) were similar than for soils from 1850 CE. The period 1850-2019 CE corresponded to a decrease in the PAHs/TOC ratio suggesting both a faster accumulation of TOC than PAHs and a dilution effect of PAHs already present in soils. For the oldest soils, the PAHs/TOC ratio appeared similar to those for soils from 1850 CE, with values ranging from 0.48 to 2.06 $ng.mg^{-1}$, suggesting an equilibrium between both parameters for soils older than 170 years. Finally, PAH stocks ranged from 0.41 $mg.m^{-2}$ to 6.80 $mg.m^{-2}$ in the youngest and oldest soils, respectively. These results do not allow us to identify the same period of greatest emission as other studies (estimated ~1960), but they revealed changes in the capacity of soils to store these pollutants.

Keywords

PAHs • Soil formation • Glacier forelands • Soil organic matter • Mountain soils

1. Introduction

Since the beginning of Industrial Era, human activities have emitted large quantities of pollutants leading to large scale environmental contaminations. In alpine valleys in particular, mining, coal production, domestic heating, and road traffic had been significant sources of polycyclic aromatic hydrocarbons (PAHs). Due to the evolution of their sources, PAH emissions and their subsequent atmospheric fallout have varied over time. In Europe, they remained low until ~1850 CE (< 20 $\mu g.m^{-2}.yr^{-1}$) before increasing progressively and reaching peaks in flux (60-96 $\mu g.m^{-2}.yr^{-1}$;) and peaks in enrichment factor between 1930 and 1970 CE (Fernández et al., 2000; Gocht and Grathwohl, 2004).

Many PAHs are known to be carcinogenic and mutagenic (Srogi, 2007). They are therefore a public health and environmental threat, which led to numerous studies over the past decades (Bucheli et al., 2004; Cui et al., 2020; Froger et al., 2021; Gateuille et al., 2014; Hussain et al., 2019; Ukalska-Jaruga et al., 2019; Wilcke, 2000). Most of these studies quantified the sixteen priority PAHs from the list established by the US EPA (United States Environment Protection Agency). These compounds were chosen because of their abundance in the environment, their toxicity and their potential risk for humans (Demougeot-Renard, 2018).

PAHs are largely produced by incomplete combustion and pyrolysis of organic matter (Alegbeleye et al., 2017). They form a large family of several hundred compounds (Wilcke, 2000) that are ubiquitous and semi-volatile. Because of their hydrophobic and lipophilic nature, PAHs are considered as persistent organic pollutants (POPs) which remain in the environment for long time (Lundstedt, 2003): from several days in the atmosphere to years or decades in soils and sediments (Jones and de Voogt, 1999). However, it remains difficult to estimate their mean residence times in soils.

PAHs are subject to long-range atmospheric transport (Wania and Mackay, 1996). They can reach remote areas – such as high latitude and/or altitude regions (Daly and Wania, 2005; Hussain et al., 2019; Kallenborn, 2006; Quiroz et al., 2011) – where they are stored in soils for long time.

During their transport or after their deposition, PAHs undergo transformation or degradation processes such as photochemical reaction, sorption, biodegradation, volatilization or leaching (Tsibart and Gennadiev, 2013).

Soils have a major role in PAH dynamics as they represent both a receptacle and a sink for PAH atmospheric depositions: to date, it is estimated that two third of PAHs in the environment are stored in soils (Sehili and Lammel, 2007). In soils, PAH behaviour is mainly determined by the soil organic matter (SOM) content. Indeed, as PAHs tend to bind strongly to SOM, the latter gives soils a high storage capacity for these pollutants and an essential trapping role. This retention of PAHs in soils ultimately leads to the protection of downstream aquatic ecosystems.

Although the relationship between SOM and PAHs is well established (Tsibart and Gennadiev, 2013), their progressive accumulation in soil is still poorly understood. One way to work on this topic is to examine the formation of soils after a glacier retreat. In the Western Alps, the glacier retreat has been going on for several millennia but it is accelerating with climate change: the surface area covered by glaciers in the French Alps has decreased by 25% from the onset of the 1970s to the end of the 2000s (Gardent et al., 2014). This phenomenon has led to the exposure of new surfaces to weathering and the progressive formation of soils, resulting into a time sequence. The area located between the current front of the glacier and moraines formed by the glacier after his gradual retreat is called the proglacial area (Egli et al., 2006). These proglacial chronosequences therefore constitute key sites to investigate the dynamic of PAH accumulation and OM stocks from the earliest stages of soil formation to very evolved soils.

Several studies on proglacial areas have shown that SOM concentrations and stocks increased with soil age (Egli et al., 2012; Khedim et al., 2020). These stocks and concentrations generally increased rapidly in the early years before trending toward a plateau at different ages depending on the glacier (Egli et al., 2010; Schlesinger, 1990). Beyond accumulation, Khedim et al. (2020) also showed that the quality

of SOM evolves with soils age. To the best of our knowledge, no similar study on PAH accumulation has yet been conducted.

This study aimed at investigating the PAH accumulation during the first 150 years of soil formation and on two older soils (3200 and 4200 years old) in three proglacial areas. We hypothesized that soils accumulate both OM and PAHs over time, and that past deposition of atmospheric polycyclic aromatic hydrocarbons can be recorded in soils. To test these hypotheses, (i) we quantified PAH and TOC contents over time, (ii) we assessed variations in PAH contents considering variations in SOM contents and (iii) we calculated the PAH stocks variations over time in top soils in order to understand their temporal dynamics and estimate the period of greatest accumulation.

2. Materials and Methods

2.1 Study areas

Three proglacial areas were studied (Figure 1, Table 1). The Miage Glacier is located in the Italian Mont-Blanc massif, and Chardon and Noir Glaciers are located in the Ecrins massif (France). The altitudes of the Miage, Chardon and Noir Glacier fronts are respectively 1750 m a.s.l. (in 2022), 2341 m a.s.l. (in 2021) and 2246 m a.s.l. (in 2020).

Ages of moraines or glacier front positions were established with different methods depending on the age: the Miage oldest moraines (from 1200 BCE, 2200 BCE; Le Roy, 2012) by ^{10}Be exposure dating (for the method see Schaefer et al., 2022); the moraines and the glacier front position from the end of the Little Ice Age (LIA) to 2019 CE using historical pictures and studies (Kilian, 1902; Mougin, 1927), ancient maps (Etat-major maps, 1820-1866), dendrochronology, field observations, and aerial and satellite images (*Google Earth Pro, IGN Géoportail*).

All proglacial areas had moraines dating at least from the end of the Little Ice Age (~1850 CE) to current time (Table 1).

The glaciers are located in remote areas, far from any major sources of PAHs. As far as the Chardon and Noir Glaciers are concerned, the nearest large town is Briançon (44°54'04.2 "N, 6°38'28.6 "E; 11,400 inhabitants), located at 27 km and 20 km from the glaciers, respectively; the main roads are 18.5 km and 10.2 km away, respectively. Regarding the Miage Glacier, the nearest main town is Courmayeur (45°47'46.56"N, 6°58'8.02"E; 2700 inhabitants) at 8 km, and the nearest main road and the Mont Blanc tunnel are 7.8 km away.

2.2 Soil sampling

Top soil samples were collected (0-10 cm) during summer 2021. Soils were sampled by depth rather than by horizons because PAHs remain mainly at the surface of soils (Guggenberger et al., 1996;

Krauss et al., 2000). This type of sampling has been also often used in studies focusing on POPs (Bucheli et al., 2004; Froger et al., 2021; Gateuille et al., 2014) or on proglacial areas (Khedim et al., 2020; Schweizer et al., 2018).

For all moraines from each proglacial area, five soil samples were collected with an auger using nitrile gloves. In total, 64 samples were collected, transferred into calcined glass jars (2 hours at 525°C), transported in a cooler, and then stored at -18°C until analysis.

At each moraine, soil bulk density was estimated with a metal cylinder of 100 cm^3 in triplicates, except when the soils were too stony to collect 3 replicates. Known volumes of soil were dried for two days at 105°C, then coarse elements (> 2 mm) and fine earth (< 2 mm) were weighted. Percentages of coarse elements and fine earth in the samples are given in Table S1 (Supplementary Materials). The bulk densities (d_a) were calculated with fine earth (< 2 mm) as follow:

$$d_a = \frac{m_{fine\ earth}}{V_{metal\ cylinder}}$$

where $m_{fine\ earth}$ is the mass of fine earth (kg) weighed into the total volume of the metal cylinder ($V_{metal\ cylinder}$; m^3).

All soils dating from the LIA to 2019 CE were classified as Leptosols (IUSS Working Group WRB, 2015) and had mostly a sandy texture. For soils younger than 30 years, the 0-10 cm depth corresponded to *C* horizons (mineral horizon resulting from the alteration of the parent material). *A* horizons (organo-mineral horizon) only began to appear for soils from 1965 CE and older. No vegetation cover was observed for soils with an age from 1994 to 2019 CE. The vegetation appeared for soils from 1965 CE and older but remains sparse: only an herbaceous stratum for soils from 1950 and 1965 CE, and a mixture of an herbaceous and a shrub stratum for soil dating from the LIA.

The oldest soils in the Miage morainic amphitheatre (from 1200 BCE and 2200 BCE) corresponded to Podzols (IUSS Working Group WRB, 2015). These soils had an *O* horizon (entirely organic horizon) at their surface (with a thickness generally > 10 cm) and presented a developed vegetation cover. Soils

152 from 1200 BCE had forest stratum (mainly *larix decidua*) and a dense sub-shrub stratum dominated by
153 *Juniperus sp., Vaccinium myrtillus* and *Rhododendron sp*. Soils from 2200 BCE were dominated by an
154 herbaceous stratum of *Phleum sp., Bromopsis erecta, Arrhenatherum elatius*, *Carduus crispus*,
155 *Alchemilla sp.* and *Nardus stricta*, but also featured a shrub stratum mainly composed of *Juniperus sp.*
156 and *Vaccinium myrtillus*.

157

158 ## 2.3 PAH extraction protocol

159 Prior analyses, soil samples were freeze-dried during 48h (from 1 to 2 mbar, -58°C) in order to limit
160 loss or contamination by ambient air, then sieved at 2 mm. Analyses were only carried out on the fine
161 fraction of soils (i.e. < 2 mm).

162 The protocol was adapted from an Agilent Application Note (Volk and Gratzfeld-Huesgen, 2011).
163 Extractions were made by series of 12 to 24 soils, and blanks were made for each series. Soils aliquots
164 (5-20 g) and blanks were spiked with 250 µl of a solution containing 100 $ng.ml^{-1}$ acenaphthene-d10
165 (Ace-d10), anthracene-d10 (Ant-d10) and benzo[a]anthracene d-12 (Ant-d12) in order to calculate the
166 PAH extraction yields of each sample. The complete protocol was tested on certified material.

167 Fifteen ml of an acetone/dichloromethane mixture (20:80, v/v) were added. The soils were mixed for
168 10 seconds with a vortex agitator, and placed in an ultrasonic bath for 3 minutes at 50/60 Hz. Samples
169 were then centrifuged at 1800 rpm for 5 min to separate the solid phase from the solvent. These steps
170 were repeated three times. The 45 ml of supernatant were recovered and transferred to 200 ml
171 Zymark tubes and reconcentrated to 1 ml under nitrogen flow at 40°C in a *Turbovap* device. The walls
172 of the tubes were rinsed with heptane then reconcentrated extracts were recovered. Sodium sulphate
173 powder was added to remove potential residual water and the samples were filtered at 0.2 µm with a
174 glass syringe and PTFE filters. Then, 100 µl dimethylsulfoxide (DMSO) were added before a new
175 reconcentration to 100 µl under gentle nitrogen flow to prevent PAH volatilization. The remaining 100
176 µl were taken up with methanol (by 400, 500 or 1000 µl according to the samples). Finally, samples

177 were filtered again at 0.2 µm with a glass syringe and PTFE filters, to remove any solid phase that may
178 have re-precipitated during reconcentration. Samples were then transferred into HPLC vials and
179 stored in a freezer until analysis.

180

181 ## 2.4 HPLC-fluo

182 After extraction, 13 PAHs from the US EPA list have been measured: acenaphthene (Ace), fluorene
183 (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene
184 (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP),
185 benzo[ghi]perylene (BghiP), dibenzo[a,h]anthracene (DbahA) and indeno[1,2,3,-cd]pyrene (IP).

186 PAHs were analysed by high performance liquid chromatography (HPLC, Merck AS-2000A) coupled
187 with a fluorescence detector (Perkin Elmer Series 200a). Analyses were performed by injecting 20 µl of
188 the sample through a C18 column (EC 250/4.6 Nucléosil 100-5 C18 PAH, Macherey-Nagel), equipped
189 with a pre-column (EC 4/3 Nucléosil 100-5 C18 PAH, Macherey-Nagel). During the analysis, the column
190 and the pre-column were in an oven at a constant temperature of 25°C. A mixture of methanol
191 (Honeywell, for HPLC) and high-quality water (Maxima USF Elga, 18.2 MΩ) was used as carrier
192 solvents. The analysis of the samples was performed over 62 min with an elution gradient
193 programmed as follow: 2 min at 1 $ml.min^{-1}$ with 80 % CH_3OH and 20 % H_2O, 15 min at 1 $ml.min^{-1}$ with
194 83 % CH_3OH and 17 % H_2O, 5 min at 1 $ml.min^{-1}$ with 90 % CH_3OH and 10 % H_2O, 19 min at 1 $ml.min^{-1}$
195 with 100 % CH_3OH, 15 min at 1.4 $ml.min^{-1}$ with 100 % CH_3OH, and 5 min at 1 $ml.min^{-1}$ with 80 % CH_3OH
196 and 20 % H_2O.

197 For each set of analyses, a range of standards was analysed, from 1 $ng.ml^{-1}$ to 60 $ng.ml^{-1}$. Peak
198 identification of the samples was performed by comparison with the peaks of the internal standards of
199 the injection series.

200 ## 2.5 Quality controls

201 The protocol was tested on certified soils (CRM 170, Sigma-Aldrich). The yields calculated on these
202 standard samples ranged from 101 % to 175 % depending on the PAHs. Results presented below are
203 not corrected by these yields. The limits of detection (LOD) ranged from 0.02 to 1.00 $ng.g^{-1}$ and limits
204 of quantification (LOQ) ranged from 0.08 to 3.63 $ng.g^{-1}$ for all PAHs. Only the IP showed higher LOD
205 and LOQ values: 0.27 to 2.74 $ng.g^{-1}$ and 0.95 to 9.54 $ng.g^{-1}$, respectively. LOD and LOQ were
206 determined by the regression lines obtained from the external calibration data with the following
207 formulas:

208 $$LOD = \frac{\mathrm{b} + 3\ \mathrm{Sb}}{\mathrm{a}}$$

209 $$LOQ = \frac{\mathrm{b} + 10\ \mathrm{Sb}}{\mathrm{a}}$$

210 where *b* is the mean of the intercept, *Sb* is the standard deviation of the intercept and *a* is the slope of
211 the line. As PAH concentrations in recent moraines were very low, concentrations whose
212 measurements were below the LOQ were replaced by the LOQ/√(2) value (adapted from Croghan and
213 Egeghy, 2003).

214 Average blank levels were all lower than LOD, except for Flu, Fla and Pyr. These PAHs had mean blank
215 concentrations of 0.2 $ng.g^{-1}$, 0.5 $ng.g^{-1}$, and 1.2 $ng.g^{-1}$, respectively. Nevertheless, these values remain
216 well below the LOQ.

217 The deuterated PAHs Ace d-10, Ant d-10 and BaA d-12 were used as internal standards. The average
218 yield of Ace-d10, Ant-d10 and BaA-d12 was 41 ± 20 %, 37 ± 18 % and 63 ± 36 %, respectively. To
219 compensate PAH losses during the experiments, the measured PAH contents were corrected by the
220 yield of their respective deuterated analogues. Thus, Ace, Flu and Phe were corrected by the yields of
221 Ace-d10; Ant, Fla and Pyr were corrected by the yields of Ant-d10; and BaA, BbF, BkF, BaP, BghiP,
222 DbahA and IP were corrected by the yields of BaA-d12.

When data were not available (non-discernible peaks on chromatograms), missing values have been imputed: the average relative abundances of the missing PAHs were calculated from the remaining replicates. These relative abundances were then applied to the subject sample.

2.6 Stocks estimations

Based on the bulk densities of the fine earth (<2mm) estimated in the field, PAH stocks in soils were estimated for each age according to the following equation:

$$S_{PAHs} = C_{PAHs} \text{ x } e \text{ x } d_a$$

Where S_{PAHs} is the PAH stocks ($g.m^{-2}$), C_{PAHs} is the PAH contents ($g.kg^{-1}$), e (m) the depth of sampled soil and d_a the bulk density of the fine earth ($kg.m^{-3}$).

2.7 Carbon analysis

Analyses were carried out on the fine fraction of soil (< 2mm) with a Rock-Eval® 6 Turbo device. Prior total organic carbon (TOCre6) and mineral carbon (MinC) analyses, all soils were crushed with a disc mill during for 4 min at 750 rpm. TOCre6 and MinC concentrations were measured on 60 mg samples.

In this technique, TOCre6 is defined as the sum of organic carbon released during a pyrolysis phase (from 200°C to 650°C) and an oxidation phase (from 450 to 700°) in the form of HC, CO_2 and CO. MinC corresponds to the carbon released in the pyrolysis and oxidation phases in the form of CO and CO_2 above a certain temperature threshold (see Baudin et al. (2015) for details on the method). As explained by Delahaie et al. (2023), for carbonate-depleted soils (as in this study), the Rock-Eval® 6 Turbo method may underestimate the TOCre6 measurement, attributing a small portion of the TOCre6 to MinC. Therefore, to remedy this problem, the TOC values in the following of the results will correspond to the sum of TOCre6 and MinC.

2.8 Statistical analysis

All statistical analyses were performed using *Excel* (*Microsof Office Professionnal Plus 2019* version) and *R* software (3.6.3 version) for Windows. The data distributions were not normal therefore non-parametric tests were used. Spearman tests were used to study potential links between variables. Exponential and logarithmic relationships were used to study the evolution of the variables over the time (t), giving us access to the rate of accumulation over time of PAH and TOC contents and PAHs stocks. A LOESS model was used to compare results with exponential model.

3. Results

Due to the evolution of soils over time, the choice was made to present the results separately for soils formed from 1850 to 2019 CE and those from 2200 and 1200 BCE (in the proglacial areas of Miage). Because the development of soils since 1850 CE is still limited, we considered that all the 1850-2019 CE soils could be compared with each other in terms of concentrations and stock evolutions. However, because the oldest soils had O horizons, they were considered different and were therefore presented separately and excluded from the models. In the following, results are presented from the youngest soils to the oldest soils.

3.1 PAH and TOC contents as a function of time

During the first 150 years of soil formation and across all glaciers, both total PAH and TOC contents increased significantly with soil age (Figure 2.A and 2.B). A high intra-site variability was observed for all soils older than 50 years, both for TOC and PAH contents.

A strong correlation was found between PAH contents and soil age ($r= 0.82$; $p\text{-value} < 0.05$). Their relationship is described in Figure 2.A, showing a slow increase in PAH contents in the first years of soil formation followed by an acceleration of the accumulation for soils older than ~130 years. More

precisely, the exponential equation suggested that PAH concentrations increased with soil age by a factor of ~2 every 30 years.

The smallest PAH contents were found in the youngest soils (from 2019 CE), with a value of 3.65 ± 1,25 $ng.g^{-1}$. During the first 30 years, soils did not accumulate PAHs significantly. For soils older than 30 years and up to 72 years (*i.e.* soils from 1950 to 1990 CE), PAH contents increased slowly with a mean accumulation rate of 0.24 $ng.g^{-1}.yr^{-1}$. Then, contents increased rapidly with soil age, to reach a maximum accumulation rate of 2.25 $ng.g^{-1}.yr^{-1}$ between 1850 and 1870 CE. In 1850 CE, mean PAH contents was 148.32 ± 60.54 $ng.g^{-1}$.

The distribution pattern of PAHs - in terms of contents or relative abundances (Tables S2 and S3, Figures S1 to S6 – Supplementary Materials) - did not reveal any particular trend or signature according to the age of the soil or the glaciers. The distribution of PAHs also showed great variability within each soil. In order to study potential accumulation/preservation of certain PAHs in soils, the ratio between the sum of PAH contents with a Log Koc < 5.5 and the sum of PAH contents with a Log Koc > 5.5 was calculated (Figure S7), and showed no significant changes as a function of the age of the glacier soil, with an overall ratio of between 1 and 3.

As expected, a strong correlation between TOC contents and soil age was found ($r= 0.86$; *p-value* < 0.05). TOC contents followed a similar pattern than PAH contents, and increased significantly with soil age (Figure 2.B). The lowest concentration was obtained in the youngest soils (2019, Noir Glacier): 0.63 ± 0.09 $mg.g^{-1}$. However, as for PAHs, TOC accumulation was not significant during the first 30 years of soil formation. Accumulation then became significant and accelerated from 1950-1965 CE reaching an accumulation rate of 2.87 $mg.g^{-1}.yr^{-1}$ between 1850 and 1870 CE. According to the exponential equation, TOC contents increased with soil age by a factor of ~2 every 25 years. The average TOC contents measured in soils from 1850 CE was 124.62 ± 38.38 $mg.g^{-1}$ and 141.89 ± 36.62 $mg.g^{-1}$ for Chardon and Miage Glacier respectively.

The similarities of the evolution of PAH and TOC contents with the age of the soils was confirmed by a Spearman test between both variables, showing a correlation coefficient of 0.83 (*p-value < 0.05*). For soils from 1200 and 2200 BCE, both PAH and TOC contents showed a strong intra-site variability, with values ranging from 33 to 369 $ng.g^{-1}$ and from 29 to 235 $mg.g^{-1}$, respectively (Figure 2).

3.2 PAH contents normalized to TOC contents

Figure 3 shows the evolution of the ratio of total PAH contents normalized to TOC contents (PAHs/TOC) as a function of time. PAHs/TOC ratio was strongly correlated to the soils age (*r= -0.64; p-value <0.05*). Its relationship with soil age was described using a logarithmic equation (Figure 3). Since the high variability of TOC and PAH contents, and due to the strong correlation between these two variables, the PAHs/TOC ratio allows us to get rid of the TOC variability. This ratio highlighted noteworthy differences in the PAHs and TOC accumulation rates.

First, the results showed that the younger the soil, the higher the PAHs/TOC ratio. The ratio decreased rapidly during the first years of soil formation. For soils from 2007 to 2019 CE, the ratio ranged from 4.27 ± 4.94 to 9.92 ± 1.68 $ngPAHs.mgTOC^{-1}$. Then, between 1850 and 1965 CE, PAHs/TOC ratio still decreased but slower with mean values ranging from 0.88 ± 0.41 to 3.50 ± 2.29 $ngPAHs.mgTOC^{-1}$.

Finally, for soils from 1200 and 2200 BCE, the PAHs/TOC ratio remained in the same range of values than for soils from 1850 CE. Values ranged between 1.12 ± 0.54 $ngPAHs.mgOC^{-1}$ for soils from 1200 BCE and 1.15 ± 0.67 $ngPAHs.mgTOC^{-1}$ for soils from 2200 BCE.

3.3 PAH stocks

The evolution of PAH stocks over time at a depth of 0-10 cm is presented in Figure 4 and reflects the average balance between PAH inputs and losses as a function of soil age.

Results indicated that the lowest stocks were found in the most recent moraines (from 2003 to 2019 CE) with average stocks ranging from 0.36 ± 0.12 to 0.82 ± 0.63 $mg.m^{-2}$. As for contents, PAH stocks of soils from 1990 to 2019 CE did not increase significantly.

Then, PAH stocks increased with soil age: average stocks in 1990 CE for the Miage glacier were 0.65 ± 0.07 $mg.m^{-2}$, and reached mean values of 1.98 ± 1.04 and 2.10 ± 0.62 $mg.m^{-2}$ in 1850 CE (in Chardon and Miage soils, respectively).

Based on the exponential relationship obtained between PAH stocks and soil age (Figure 4), the accumulation rate between 2010 and 2019 CE was 4.4 $\mu g.m^{-2}.yr^{-1}$ and increased slowly with soil age. This exponential relationship implies that the period of greatest accumulation occurred between 1850 and 1870 CE with a rate of accumulation of 21 $\mu g.m^{-2}.yr^{-1}$. Finally, the exponential equation obtained (Figure 4) suggested that PAH stocks increased with soil age by a factor of about 2 every 75 years.

Regarding oldest soils from 1200 and 2200 BCE, PAH stocks were 6.80 ± 8.34 $mg.m^{-2}$ and 1.31 ± 0.79 $mg.m^{-2}$, respectively.

Although an exponential model seems to fit the data well, other models can be used. For instance, Figure S8 (Supplementary Material) shows results obtained with a LOESS model. According to this model, the period of greatest accumulation occurred between 1930 and 1950 CE with a rate of accumulation of 24 $\mu g.m^{-2}.yr^{-1}$. Then, stocks kept increasing with soil age but the rate of accumulation gradually slowed down reaching the highest PAH stock in 1875 CE (2.68 ± 0.30 $mg.m^{-2}$). From 1875 CE onwards, stocks started to decrease slowly, reaching 2.41 ± 0.37 $mg.m^{-2}$ in soils dating from 1850 CE.

4. Discussion

4.1 PAH contents

During the first 150 years of proglacial soil development, both PAH and TOC concentrations increased rapidly with soil age. For oldest soils – from 1200 to 2200 BCE – PAH concentrations agreed with those measured in other studies in mountain areas, and reflected the regional background. In the Swiss soil monitoring network (NABO), Bucheli et al. (2004) measured PAH contents ranging from 50 to 219 $ng.g^{-1}$ in grassland and forest soils, and Gubler et al. (2015) measured 19 $ng.g^{-1}$ in a remote mountain area in Switzerland. Other studies (Choi et al., 2009; Hussain et al., 2019) found levels ranging from tens of $ng.g^{-1}$ to 789 $ng.g^{-1}$ in remote sites of the Canadian Rocky Mountains. Our results were also consistent with those obtained by Nam et al. (2008) in remote soils from Norway (63-243 $ng.g^{-1}$), where the contamination reflected mainly the cumulative deposition after a long-range atmospheric transport, and represented thus the overall background of Western Europe.

Regarding the most recent soils formed from 1990 to 2019 CE, which showed very low PAH contents, the current literature does not yet allow us to compare our values to published data. Yet, PAHs were detected even in the youngest soils, suggesting that they had reached the soils shortly after the glacier retreat (years or decades).

A first explanation for the presence of PAHs in these recent soils could simply due to the arrival of PAHs by atmospheric depositions. The concentrations measured here would therefore be the result of the regional background combined with the capacity of soils to store PAHs.

At these altitudes (i.e. > 2200 m a.s.l.), deposition can be enhanced by snowfall because snow accounts for a significant proportion of annual precipitation, and it covers the ground for a large part of the year (Chardon, 1989). A few works have investigated PAH sorption by snowflakes during their atmospheric transport and deposition. Franz and Eisenreich (1998) suggested that snow would be more effective than rain in scavenging PAHs during their atmospheric transport and deposition, both for volatile PAHs and for those adsorbed on particles (Wania et al., 1999). Snow could thus play an important role in PAH dynamics and could bring more contaminants to the ground through the

snowpack. As the latter act as a temporary storage medium, the spring melt then results in a pulse of organic contaminants (Meyer and Wania, 2008), and some of which may be retained by the soils. Furthermore, through the sustained storage of various POPs from atmospheric deposition, several studies showed that glaciers are reservoirs of contaminants (Bogdal et al., 2009; Li et al., 2017; Schmid et al., 2011). However, due to climate change and the subsequent accelerated glacier shrinkage (Paul et al., 2020), glaciers are becoming secondary sources of pollutants to downstream ecosystems *via* meltwater (Saros et al., 2010). In particular, Bogdal et al. (2009) showed that the Oberaar Glacier (Switzerland) released large amounts of POPs, which had accumulated for decades in ice. In our study, the youngest soils (from 2003 to 2019 CE), located very close to the glacier front, were exposed to meltwater. Yet, given the concentrations measured, PAHs brought by the latter did not seem to be retained efficiently by proglacial soils. This point highlights the fact that, in their initial stage of formation, soils do not have a great capacity to retain these pollutants, mainly due to their low organic matter contents. Therefore, PAH contents in soils were not only driven by PAHs inputs, but also by the capacity of soils to adsorb these contaminants.

Regarding the PAH distribution in soils, it results of both PAH inputs and PAH preservation/transformation in soils. First, the lack of difference in the PAH signatures and in the Koc ratio can be explained by the fact that proglacial areas are located in remote areas, and thus only received PAHs from long-range atmospheric transport. These PAHs originate from a variety of remote sources and probably underwent dilution, mixing, dispersion and degradation processes prior to deposition. PAHs arriving at these sites cannot therefore reflect a particular source but represent a regional background.

Secondly, these findings can also translate the persistence of PAHs in soils. The lack of signature observed can indicate that soils did not preferentially accumulate or preserve specific PAH according to their age or the glaciers location. This may reflect low transformation or exportation of PAHs, due to little or no biodegradation, and minor leaching and erosion processes.

4.2 TOC contents

TOC contents increased significantly and non-linearly over the first 150 years of soil development. For soils dating from 1200 and 2200 BCE, TOC concentrations appeared in the same range of values than for soils from 1850 CE, but presented a high variability. These observations corroborate results obtained by Khedim et al. (2020) who showed that TOC levels increased significantly with soil age for 10 glaciers around the world, with values ranging from 0.5-4 $g.kg^{-1}$ for the youngest soils and up to 50-100 $g.kg^{-}$ in some older soils. Similar contents were also reported by Eckmeier et al. (2013) with very low TOC contents in the first 30 years of soil development (1.9-4.1 $g.kg^{-1}$), followed by an increase with soil age and a greater variability in oldest soils.

Beyond its amount, several studies observed changes in the nature of SOM with soil age. For instance, Khedim et al. (2020) observed more aliphatic and carbonyl/carboxyl functional groups in the most recent stages of soil formation, followed by an evolution towards a more aromatic composition for older soils. Egli et al. (2010) also showed that the hydrophobic character of SOM decreased with the age of the soil. Even if the relationships between PAH sorption and nature of SOM remains unclear, this parameter may play a role in the scavenging of PAHs in soils.

4.3 PAHs/TOC ratio evolution

Normalizing PAH concentrations by soil characteristics is a commonly used procedure for organic contaminants in soils and sediments (Kersten and Smedes, 2002; Maliszewska-Kordybach, 1996). The use of this ratio makes it possible to compensate for potentially heterogeneous soil characteristics, which may have an impact on the pollutant retention. In other words, normalization allows pollutants concentrations to be corrected for the influence of natural variability of soil properties (Kersten and Smedes, 2002). In our case in particular, OM contents evolved strongly with soil age. As this has been recognized as a major property in the sorption of PAHs in soils (Wilcke, 2000), normalization of PAH contents by TOC was justified.

Krauss and Wilcke (2005) compared the PAHs/TOC ratio between different types of land use in urban and peri-urban areas. They obtained a wide range of values, ranging from 12-17 $ng.mg^{-1}$ (in grassland, forest and agricultural soils) to 3890 $ng.mg^{-1}$ for roadsides soils. Contrastingly in rural soils, Choi (2014) calculated this ratio in order to study a time trend of PAH contamination in subsurface soils (from 1-2 to 5 cm deep) and litter after a forest fire in a rural area. For both, they obtained values similar to our study (from 0.5 to 2.9 $ng.mg^{-1}$ in soils, ~1 to ~14 $ng.mg^{-1}$ in litter). Consequently, our results from proglacial soils were as low as those found in rural and remote areas.

In our case, PAHs/TOC values along the chronosequences indicated that the amount of PAHs per amount of OM was higher in the most recent soils, suggesting that even these OM-depleted soils were able to retain PAHs. This observation then raises the question of the role of other soil components in PAH sorption for very recent soils. Especially, in young soils, the mineral fraction or atmospheric deposition of aerosols (such as black carbon (BC)) may have a more important sorbent role than in more developed soils.

Müller et al. (2007) studied the sorption of some PAHs onto different mineral surfaces and observed that the sorption of phenanthrene remained low or non-existent, but that pyrene and benzo(a)pyrene were able to sorb onto the different matrices. However, this study was carried out in laboratory on carbon-free mineral sorbents where no other component could compete with the mineral matrices. It is therefore difficult to estimate their role in soils, where other components are present and can provide sorption sites for PAHs. We suggest that sorption onto mineral matrices is probably not a dominant process in soils, even those with low OM contents. In particular, the mineral fraction of soils cannot compete with other compounds such as OM or BC particles from atmospheric deposits. These aerosols, which correspond to solid or dissolved particles (BC, OM, metals, *etc*.) in suspension in the atmosphere (Piot, 2011), can carry and bring PAHs to soils as they are deposited. Regarding BC, these compounds are usually co-emitted with pyrolytic PAHs and have very high sorption capacities. These compounds corresponds to soot, coals, cenospheres and other carbonaceous materials derived from

441 incomplete combustion of biomass and fossil fuels (Schmidt and Noack, 2000) and their sorption
442 capacities could dominate those of « amorphous » OM by 1 to 3 orders of magnitude in low PAHs
443 environments Cornelissen et al. (2005). The deposition and retention of such particles in soils may
444 therefore partly explain the subsistence of PAHs in the most recent soils.

445 Firstly, these particles can bring PAHs into the soil and are probably more easily retained than PAHs
446 arriving in gaseous form (more subject to volatilization and leaching, especially in soils where sorption
447 sites are almost non-existent). Secondly, once into the soil, these deposited aerosols can provide new
448 sorption sites for PAHs, and therefore improve the retention of PAHs arriving in gaseous form in soils
449 with low OM contents.

450 However, the youngest soils have no vegetation cover. They are therefore more sensitive to erosion
451 processes linked to run-off, melting snow cover, wind, *etc*. Thus, even if it is reasonable to think that
452 aerosol-type particles, and their adsorbed PAHs, are better retained by the soil than PAHs arriving in
453 gaseous form, they can also be exported from the soil through erosion. The retention capacity of soils
454 for these particles therefore appears to be a key element in the accumulation of PAHs in young soils.
455 But in view of the concentrations measured here in the youngest soils (from ~1990 to 2019 CE), these
456 particles are either few in number or poorly retained by the soils in the early stages of their formation.

457 Then, as the soil develops, the PAHs/TOC ratio decreased. Despite an increase in PAH emissions since
458 the industrial revolution (Elmquist et al., 2007; Fernández et al., 2000), the decreasing in the ratio
459 reflected both an accumulation of SOM faster than PAHs and a dilution of PAHs already present in
460 soils.

461 Then, for soils dating from 1850-1950 CE, the slow decrease of the ratio reflects the acceleration of
462 PAH accumulation. This accumulation is also the result of the accumulation of SOM, which favors the
463 storage capacity of soils and therefore a better sorption of PAHs.

464 Finally, the stability of the ratio for soils from 2200 BCE to 1850 CE may indicate that a thermodynamic
465 equilibrium between the PAH and TOC accumulation has been reached. This stability can lead to two

assumptions: (i) prior to the Industrial Era, PAH emissions were very low. As a result, PAH accumulations in soils may be difficult to discern (due to low inputs and spatial variations observed in soils). Thus, PAH accumulation in oldest soils may not be sufficiently important to cause a significant variation in the PAHs/TOC ratio. Or (ii) beyond 170 years, PAH inputs may be compensated by PAH losses. This may lead to a steady state where no significant increase or decrease in levels is observed. In this case, losses could be explained either by leaching and volatilization or by biodegradation processes involving various bacteria or fungi (Haritash and Kaushik, 2009; Roslund et al., 2018).

4.4 Evolution of PAHs stocks with time

In our study, PAH stocks in proglacial soils did not evolve significantly between 1990 and 2019 CE. These results are in accordance with a CITEPA (2022) report which indicates that PAH emissions in metropolitan France decreased between 1990 and 2018 CE (from > 150 tons.yr^{-1} to 60 tons.yr^{-1}). Our results also corroborate those of Arellano et al. (2018) in remote mountain areas of Europe, where measured deposition fluxes ranged from 0.80 to 2.1 µg.m^{-2}.month^{-1}. Regarding older periods, the historical record of atmospheric fallout in the sediments of Lake Noir sediments (Hautes-Alpes, France) showed that PAH fluxes in this region started to increase from 1900 CE (Fernández et al., 2000). According to this work, fluxes reached a first peak in ~1915 CE (~60 µg.m^{-2}.yr^{-1}) and a maximum in 1960 CE (~100 µg.m^{-2}.yr^{-1}), followed by a rapid decrease until today. These results are in line with those form a study in the Lake Stora Frillingen, which reflected the Nothern European background and showed an increase in PAH emission during the industrial revolution, reaching a maximum flux (> 300 µg.m^{-2}.yr^{-1}) during the period 1950-1960 CE (Elmquist et al., 2007). Thus, despite some local variations which could be explained by local influences (emissions, precipitations, wind patterns, *etc*.), all these studies indicated a maximum emission during the period 1920-1960 CE.

The exponential model used to describe the evolution of PAH stocks in the proglacial soils of our study does not allow us to identify this peak in PAH fluxes. This model fits the data for the first 150 years of

soil formation well. However, this model cannot be used over a long period because it tends towards infinity, which is unrealistic. In contrast, the LOESS model provides results which agree with these past studies, suggesting maximum accumulation rates between 1930 and 1950 CE. However, this model is more sensitive to natural variations in the data and suggests a decrease of stocks between 1850 and 1875 CE. Although this result could be explained by the natural dissipation of PAHs (leaching, volatilization), such a decrease is probably only the result of the higher values found for the 1895 CE soil (Glacier Noir), which have an impact on the model.

Beyond these results, the period of highest PAH emission identified by previous studies also coincides with a period of OM stocks increment for these soils. The storage capacities of the soils – mainly *via* SOM - increased thus during the periods of high PAH emissions, which probably also influenced PAH storage.

Through these results, our study also raises new questions and new perspectives of research. First of all, in this work the models were carried out by considering the whole of the proglacial areas, and not site by site, assuming that the overall PAH dynamics in soils from proglacial chronosequences were similar for all sites. However, whether each proglacial area had its own dynamics remains to be tested, especially if the rate of PAH accumulation was unique for each site. For future research, this question implies a larger number of samples per proglacial areas and over longer periods in order to improve PAH accumulation models.

Conclusion

During the first 150 years of soil development in the Miage, Noir and Chardon proglacial areas, PAH contents increase rapidly with soil age. This increase is strongly correlated with TOC contents, suggesting that SOM plays a major role in the scavenging of PAHs in soils. Regarding soils from 1200 and 2200 BCE, PAH contents reflect the regional background. In order to overcome the natural variations of OM content in soils, the PAHs/TOC ratio was used. It shows a decrease with soil age (until 1850 CE) but then similar values were found for soils from 1850 CE and 1200-2200 BCE. PAH stocks, reflecting the balance between PAH inputs and losses, do not allow us to identify the period of highest PAH emission estimated around 1960 CE by previous studies. All these observations are the result of PAH behavior in environment (gas/particle distribution, affinity for SOM, *etc*.) and related to many parameters (temperatures, precipitations, exportation processes, grain size, *etc*.). They highlight the capacity of soils to store present and past PAH emissions, mainly via SOM. In future research, different sampling methods could be applied (a larger number of samples, different sampling depths) to improve our understanding on the PAH dynamics and explore the impact of other parameters on their storage in proglacial soils.

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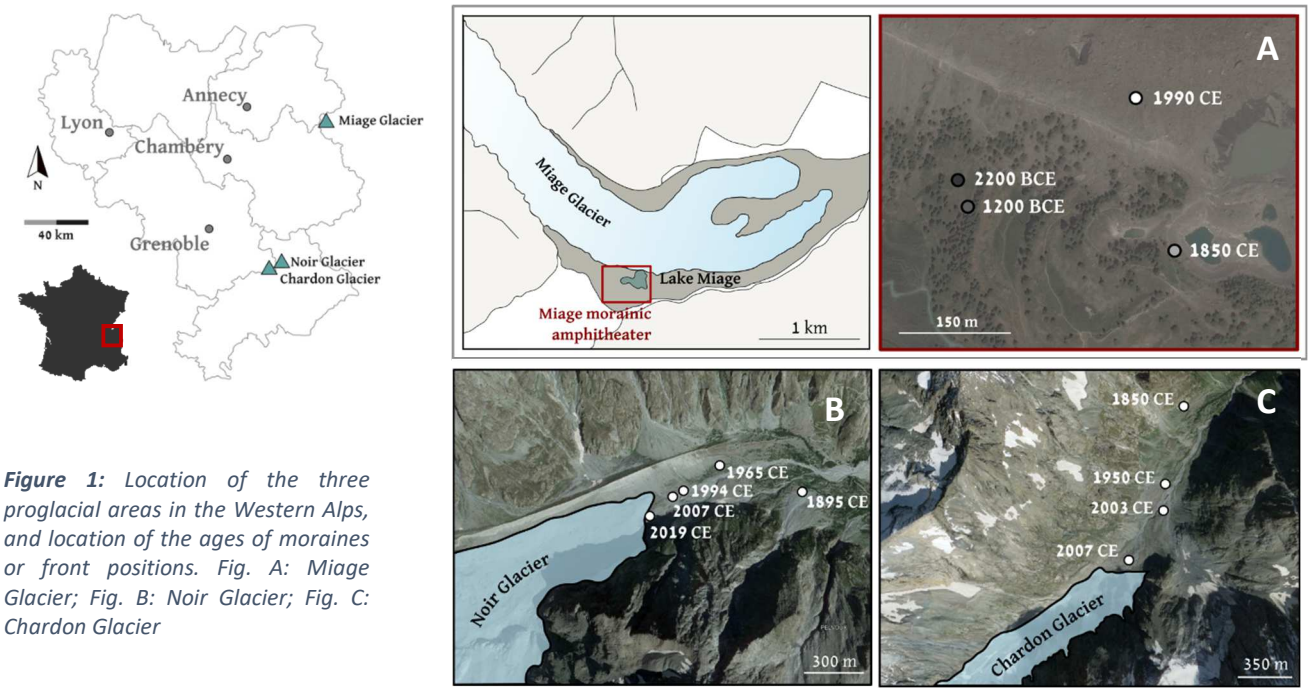


Figure 1: *Location of the three proglacial areas in the Western Alps, and location of the ages of moraines or front positions. Fig. A: Miage Glacier; Fig. B: Noir Glacier; Fig. C: Chardon Glacier*

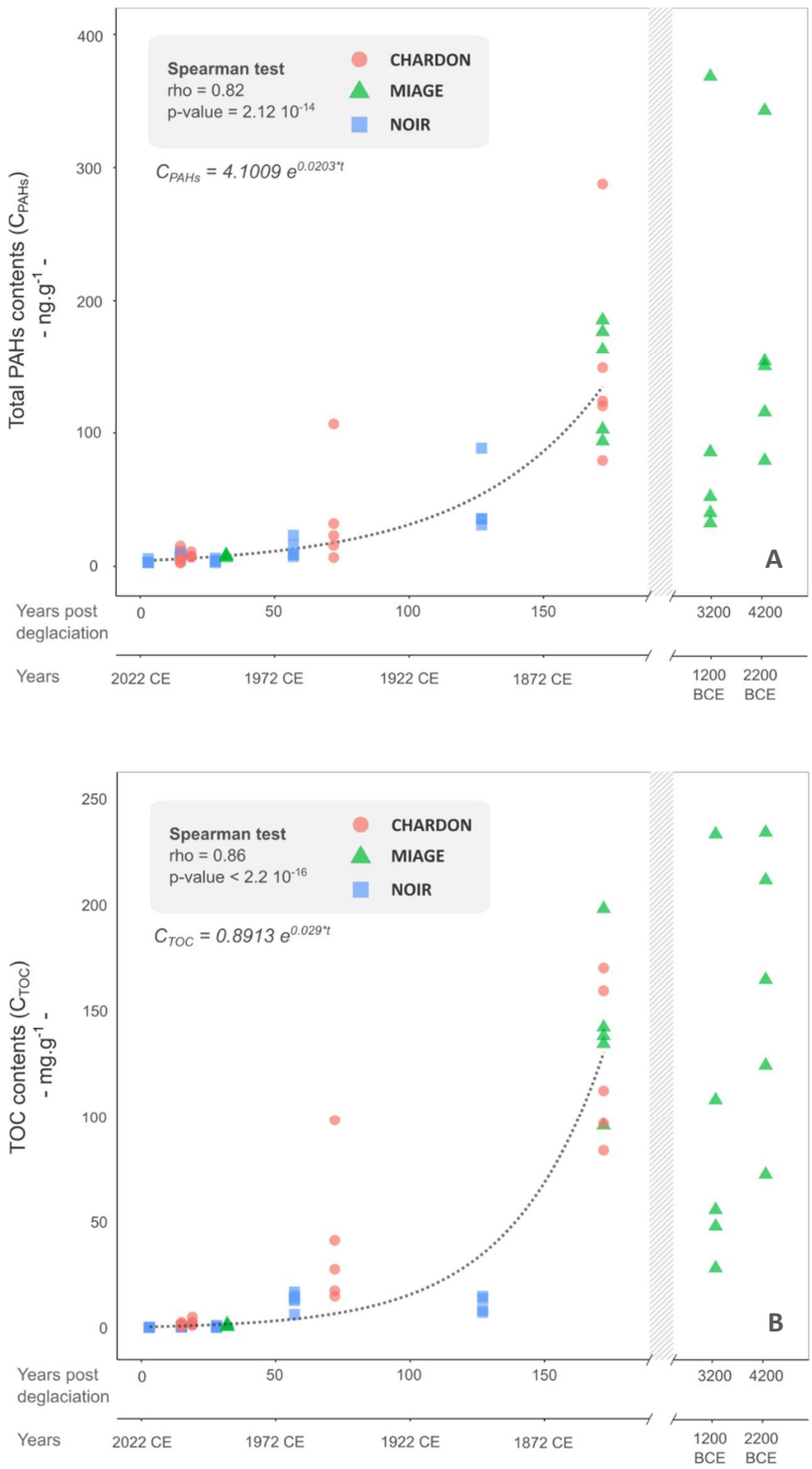


Figure 2: *(A) Total PAH contents (∑ 13 PAHs; ng.g^{-1}) in soils and (B) TOC contents (mg.g^{-1}) in soils of the three proglacial areas as a function of time, on the 172 first years after deglaciation, and for soils from 1200 and 2200 BCE.*

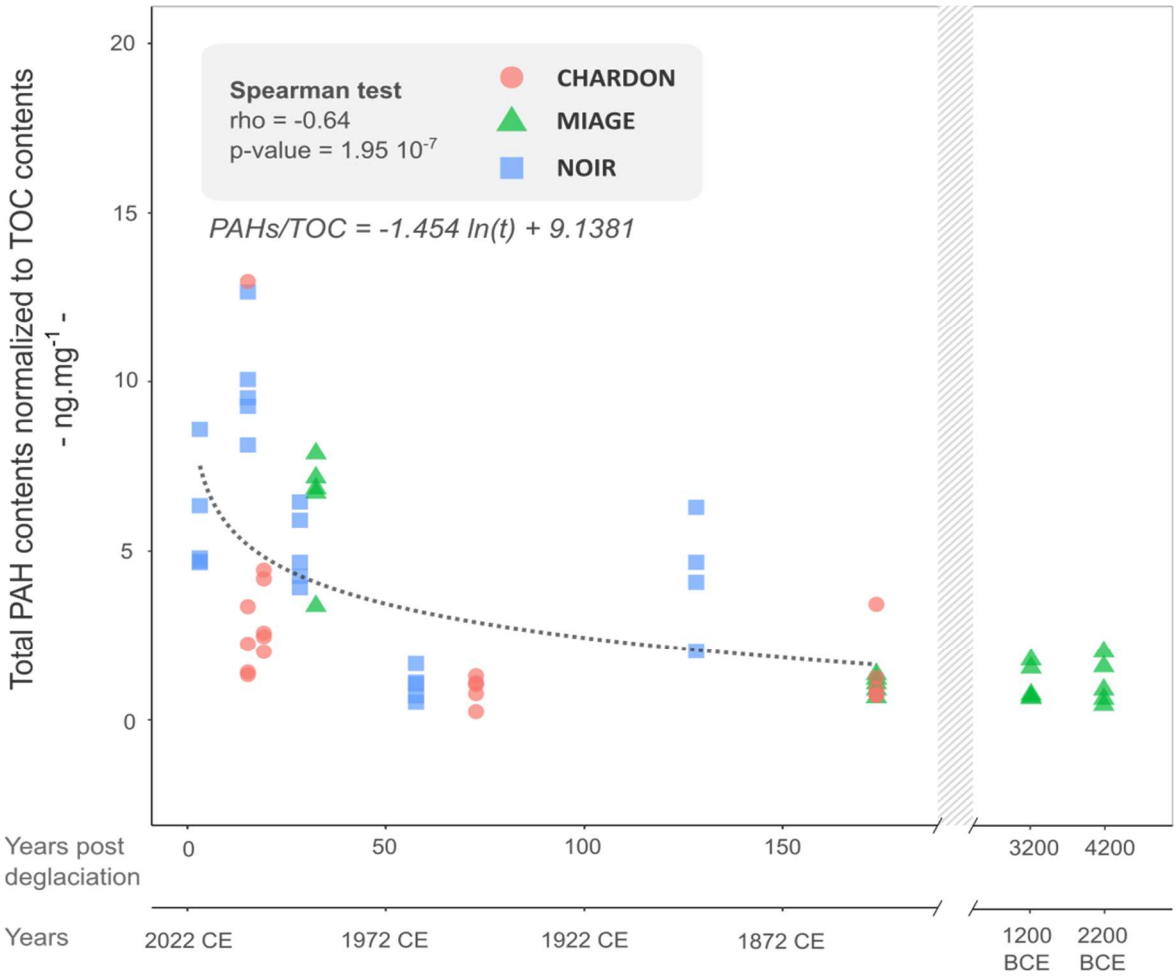


***Figure 3**: Total PAH contents (∑ 13 PAHs) normalized to the TOC contents in soils (ng.mg^{-1}) as a function of time for the three proglacial areas.*

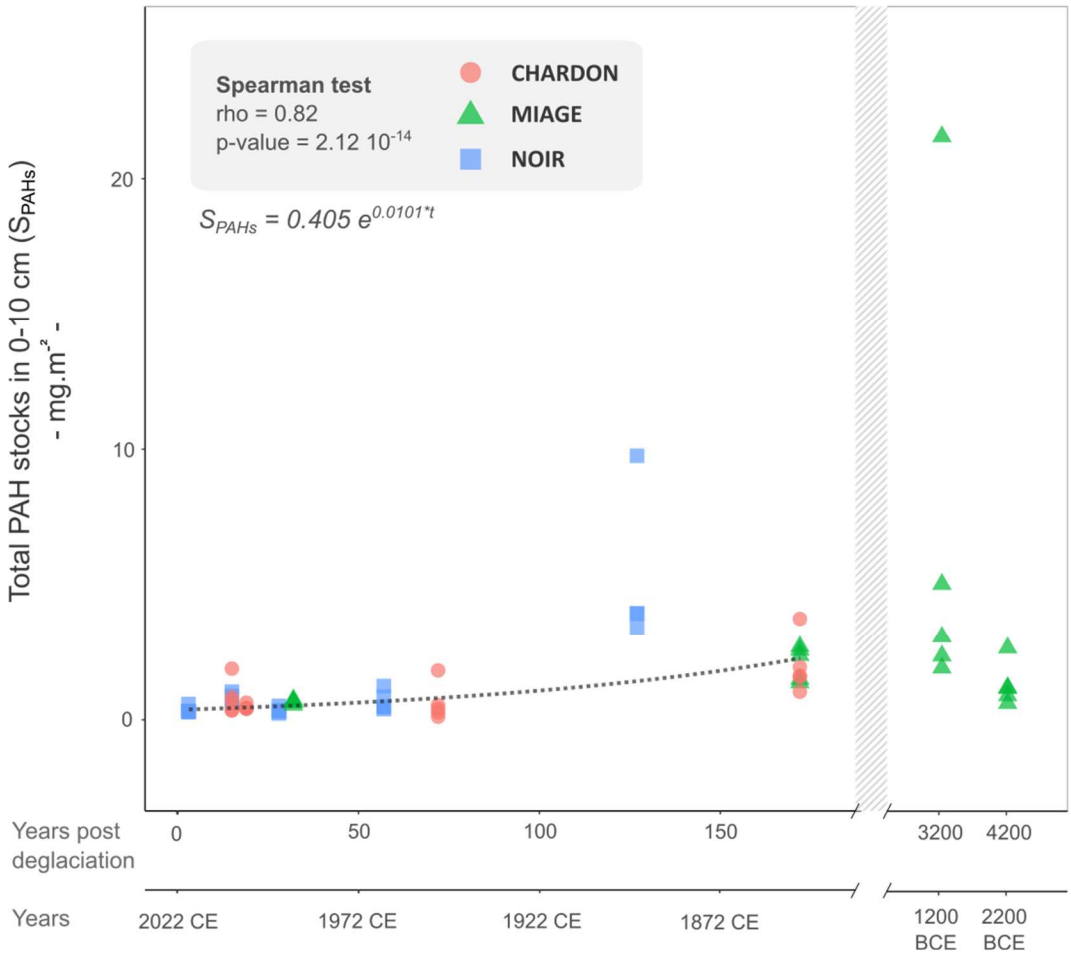
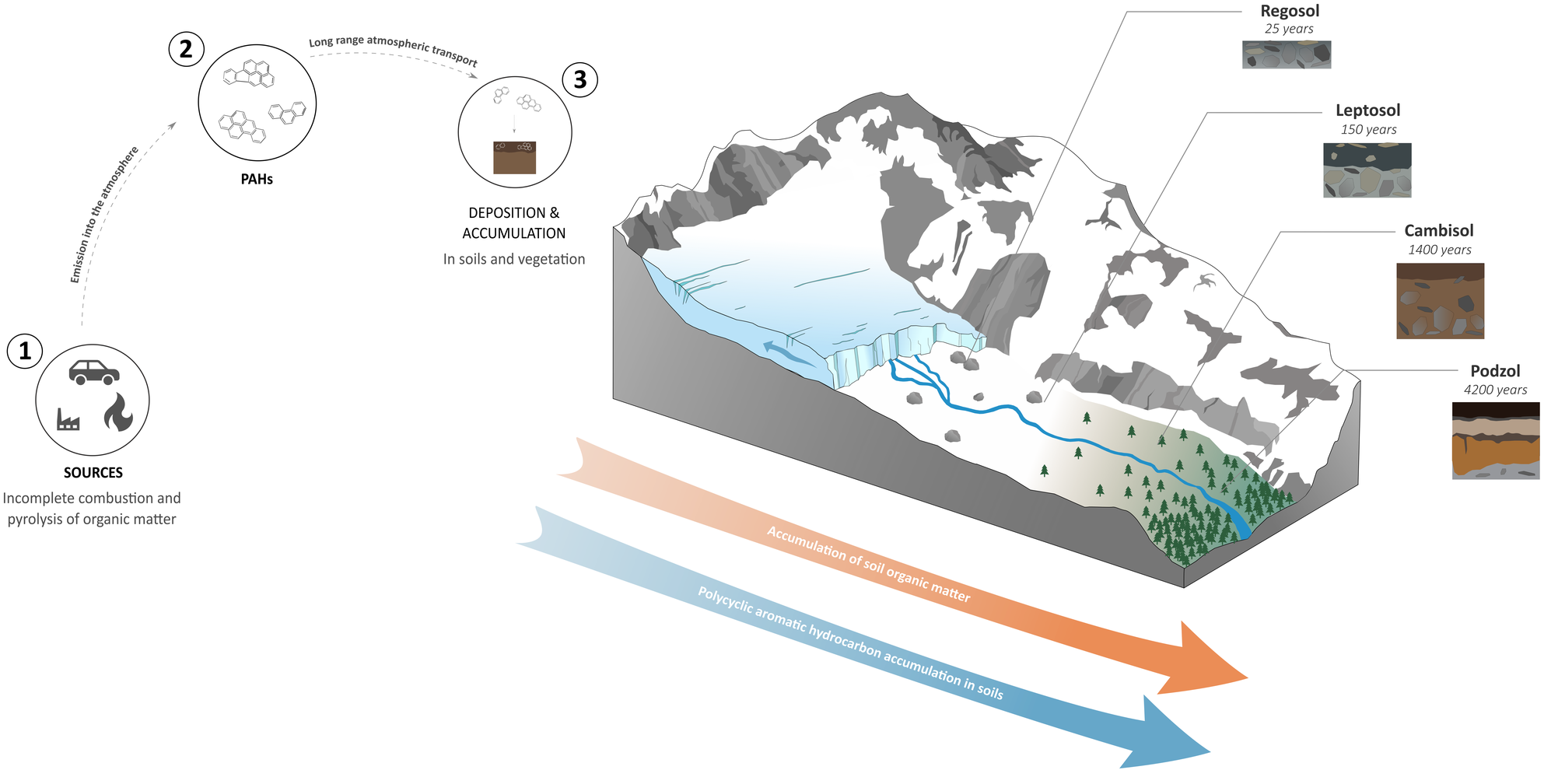


***Figure 4**: Total PAH stocks (∑ 13 PAHs; mg.m^{-2}) in the top 10 cm of soil as a function of time, for all proglacial areas.*

Table 1: *Characteristics of the studied proglacial areas*

Glacier name	Massif, Country	Coordinates	Lithology	Exposure	Ages of moraines or glacier front positions	Number of years since deglaciation
Miage	Mont Blanc,	45.785240 °N	Gneiss	South-east	2200 BCE	4200
	Italy	6,863955 °E	Micaschists		1200 BCE	3200
					1850 CE	172
					1990 CE	32
Chardon	Ecrins,	44.880734 °N	Migmatites	North-east	1850 CE	172
	France	6,286594 °E			1950 CE	72
					2003 CE	20
					2007 CE	15
Noir	Ecrins,	44.915464 °N	Granite	North-east	1895 CE	127
	France	6,385159 °E			1965 CE	57
					1994 CE	28
					2007 CE	15
					2019 CE	3


1
SOURCES
Incomplete combustion and pyrolysis of organic matter
Emission into the atmosphere
2
PAHs
Long range atmospheric transport
3
DEPOSITION & ACCUMULATION
In soils and vegetation
Regosol
25 years
Leptosol
150 years
Cambisol
1400 years
Podzol
4200 years
Accumulation of soil organic matter
Polycyclic aromatic hydrocarbon accumulation in soils