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Original

A sensitive microextraction by packed sorbent-gas chromatography-mass spectrometry method for the assessment of polycyclic aromatic hydrocarbons contamination in Antarctic surface snow / Arcoleo, Angela; Bianchi, Federica; Careri, Maria. - In: CHEMOSPHERE. - ISSN 0045-6535. - 282:(2021). [10.1016/j.chemosphere.2021.131082]

Availability:

This version is available at: 11381/2893943 since: 2024-04-28T09:29:27Z

Publisher:

Elsevier

Published

DOI:10.1016/j.chemosphere.2021.131082

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(Article begins on next page)

1 **A sensitive microextraction by packed sorbent-gas chromatography-mass**
2 **spectrometry method for the assessment of polycyclic aromatic hydrocarbons**
3 **contamination in Antarctic surface snow**

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27 ABSTRACT

28 For the first time an eco-friendly method involving microextraction by packed sorbent (MEPS)
29 coupled to gas chromatography-mass spectrometry (GC-MS) was developed for the determination of
30 the 16 US-EPA priority pollutant polycyclic aromatic hydrocarbons (PAHs) as indicators of
31 anthropogenic contamination in snow samples collected in polar regions. MEPS was carried out by
32 using C8 sorbent material packed in a barrel insert and needle (BIN) and integrated in the eVol[®] semi-
33 automatic device. For optimization purposes a Face Centred Design and the multicriteria method of
34 the desirability functions were performed to investigate the effect of some parameters affecting the
35 MEPS extraction efficiency, i.e. the number of loading cycles and the number of elution cycles. The
36 developed MEPS-GC-MS method proved to be suitable for PAHs analysis at ultra-trace level by
37 extracting small sample volumes achieving detection limits for 16 PAHs in the 0.3 – 5 ng L⁻¹ range,
38 repeatability and intermediate precision below 11% and 15%, respectively, and good recovery rates
39 in the 77.6 (± 0.1)–120. 8 (± 0.1)% range for spiked blank snow samples. Enrichment factors in the
40 64 (± 7)–129 (± 18) range were calculated. Finally, the proposed method was successfully applied to
41 the determination of PAHs in surface snow samples collected in 2020 – 2021 from four locations of
42 Northern Victoria Land, Antarctica. Local emission sources such as ships and research stations were
43 found to influence PAHs concentrations in the surface snow.

44 *Keywords:*

45 Microextraction by packed sorbents

46 Gas chromatography–mass spectrometry

47 Polycyclic aromatic hydrocarbons

48 Antarctica

49 Snow

50 1. Introduction

51 Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that consist of two or
52 more aromatic rings and have both natural and anthropogenic sources (Srogi, 2007). PAHs include
53 16 priority pollutants regulated by the U.S. Environmental Protection Agency (US-EPA) due to their
54 potential toxicity in humans and other organisms as well as their occurrence and ubiquity in the
55 environment (Hussar et al., 2012; U.S. Environmental Protection Agency, 2014). As PAHs are semi-
56 volatile compounds, they are subject to long-range transport from emission sources to remote areas
57 (Wang et al., 2009; Korosi et al., 2015), i.e. places with a minimum contribution of anthropogenic
58 emissions such as Arctic and Antarctica (Baltensperger and Furger, 2008) or high altitude
59 environments like Alps and Caucasus (Gabrieli et al. 2010a; Vecchiato et al., 2020). In these regions,
60 low temperatures cause the deposition of organic compounds and their accumulation in the polar
61 environment (Cao et al., 2018), producing a snow stratification which reveals the chemical
62 composition of the atmosphere at the time of the deposition (Legrand and Mayewski, 1997).
63 Therefore, PAHs play an important role in paleoenvironmental studies being considered tracers of
64 both anthropogenic fossil fuel combustion and global natural events (Giannarelli et al., 2017; Giorio
65 et al., 2018). Several investigations have been focused on their distribution patterns, seasonal
66 depositions and accumulation trends in order to obtain chemical records and the assessment of
67 contamination sources (Jaffrezo et al., 1994; Wang et al., 2009; Kukučka et al., 2010; Giannarelli et
68 al., 2017; Cao et al., 2018; Vecchiato et al., 2018). However, it should be noted that the analysis of
69 PAHs in ice and snow samples requires high sensitivity and selectivity due to the presence of these
70 compounds at ultra-trace levels. In addition, sample volume is a critical issue because low sample
71 volume is fundamental to obtain an adequate temporal resolution of the glacial stratification (Barbante
72 et al., 2017), thus challenging the applicability of sample preparation methods to paleoclimatic
73 investigation of organic compounds (Gabrielli and Vallelonga, 2015).

74 Liquid-liquid extraction (LLE) (Brum et al., 2008; Dasgupta et al., 2011) and solid-phase extraction
75 (SPE) (Ma et al., 2010; Okoli et al., 2016) are the most commonly used to extract and preconcentrate
76 PAHs from water samples. Nevertheless, these methods are time-consuming and require large sample
77 volumes, so they are difficult to apply to obtain a proper temporal resolution in the analysis of snow
78 samples. These drawbacks are overcome by the development of cost-effective and environmental
79 friendly analytical methods based on miniaturized techniques to improve the classical procedures
80 used for sample treatment in environmental analysis. Miniaturization of the sample treatment
81 technique allows the use of small sample volumes and its feasible manipulation in a miniaturized
82 environment, the reduction of the number of steps required for sample preparation and the
83 consumption of a low amount of organic solvents, providing a greener approach for analytical
84 procedures (Ramos et al., 2005; Płotka-Wasyłka et al., 2015).

85 Microextraction by packed sorbent (MEPS) was first developed by Abdel-Rehim as a miniaturization
86 of conventional SPE technique (Abdel-Rehim, 2004), allowing the integration of sampling, clean-up
87 and pre-concentration of the analytes into a single device (Moein et al., 2015). In MEPS, 1 – 4 mg of
88 the sorbent material is packed inside a syringe as a plug or in the barrel insert and needle called BIN,
89 enabling for a semi or fully automated system (Abdel-Rehim, 2011; Moein et al., 2015). The small
90 amount of sorbent used in MEPS can easily be washed and reused more than 300 times for water
91 sample analysis (Moein et al., 2015). A key-point of this miniaturized technique is the possibility to
92 handle very low sample volume, i.e., a few microliters. Thus, at first MEPS was attractive for
93 bioanalysis application, since the sample volume available for testing body fluids is limited (Pereira
94 et al., 2014; Woźniakiewicz et al., 2014; Saracino et al., 2015; Fernández et al., 2017; Bianchi et al.,
95 2019). Nevertheless, MEPS has also been applied to environmental analysis in order to reduce the
96 extraction time and to enhance the degree of automation and sensitivity (Moeder et al., 2010; Prieto
97 et al., 2011). Although different studies described MEPS procedures for the determination of PAHs
98 in water samples (El-Beqqali et al., 2006; Prieto et al., 2010; Fu et al., 2012; Quinto et al., 2012, 2014;

99 Yang et al., 2017), up to date, the application of this technique has not been reported for paleoclimatic
100 purposes, despite the acknowledged advantages.

101 The present study is part of a research project that aimed to develop innovative analytical methods
102 and miniaturized procedures for sample preparation, investigate new chemical proxies and, lastly,
103 characterize the chemical load present in ice cores (Arcoleo et al., 2020). Thereby, the aim of the
104 herein described work was the development and optimization of a semi-automatic MEPS-GC-MS
105 method to determine the 16 priority PAHs in Antarctic water samples as paleoenvironmental proxies.
106 To best of our knowledge, the use of miniaturized techniques for pre-treatment of polar water samples
107 is scarce, particularly for the determination of PAHs present in ice cores and snow samples. In this
108 study, a fast and ultra-sensitive MEPS–GC–MS analytical method was established and successfully
109 applied to the analysis of five surface snow samples from Antarctica.

110 2. Material and methods

111 2.1. Chemicals and reagents

112 The standard mixture of 16 PAHs including naphthalene (Nap), acenaphthene (Ace), fluoranthene
113 (Flt), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), pyrene (Py),
114 benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene
115 (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (InPy), dibenzo[a,h]anthracene (DiahA) and
116 benzo[g,h,i]perylene (BghiP) (each component at a concentration of 100 $\mu\text{g mL}^{-1}$ in acetonitrile), and
117 deuterated PAHs internal standard (IS) containing naphthalene-d8 (Nap-d8), acenaphthene-d10 (Ace-
118 d10), phenanthrene-d10 (Phe-d10), anthracene-d10 (Ant-d10), benzo[a]anthracene-d12 (BaA-d12),
119 chrysene-d12 (Chr-d12) benzo[g,h,i]perylene-d12 (BghiP-d12), dibenzo[a,h]anthracene-d14
120 (DiahA-d14), acenaphthylene-d8 (Acy-d8), fluorene-d10 (Flu-d10), fluoranthene-d10 (Flt-d10),
121 pyrene-d10 (Py-d10), benzo[a]pyrene-d12 (BaP-d12), benzo[b]fluoranthene-d12 (BbF-d12),
122 benzo[k]fluoranthene-d12 (BkF-d12) and indeno[1,2,3-c,d]pyrene-d12 (InPy-12) (each component at

123 a concentration of $10 \mu\text{g mL}^{-1}$ in acetonitrile) were purchased from Neochema (Bodenheim,
124 Germany) and were stored in the absence of light at $4 \text{ }^{\circ}\text{C}$.

125 Hexane (puriss. p.a., ACS reagent, $\geq 99.0\%$ GC), ethyl acetate (EtAc) (puriss. p.a. ACS, Reag. Ph.
126 Eur., Reag. ISO) and dichloromethane (DCM) (puriss., meets analytical specification of Ph. Eur., NF,
127 $\geq 99\%$ GC) were supplied by Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Methanol
128 (MeOH) ($\geq 99.7\%$ purity) was purchased by Honeywell Riedel-de Haën (Seelze, Germany). Ultrapure
129 water from a Millipore Milli-Q Element A10 Water Purification System (Merck-Millipore, Milan,
130 Italy) was used during the experimental procedure.

131 Intermediate stock solutions of native and deuterated PAHs, each at 1 mg L^{-1} , were prepared in
132 methanol. Daily, standard native and deuterated PAHs working solutions were prepared by proper
133 dilution of the stock solutions before use.

134 2.2. *Environmental snow sample collection*

135 Surface snow samples collected on the coastal area of Victoria Land (Antarctica) during the 2020 –
136 2021 austral summer were kindly provided by the National Antarctic Research Program (PNRA).
137 Samples were maintained at -20°C until analysis, then they were thawed in the laboratory at room
138 temperature preventing exposure to solar irradiation and subjected to MEPS procedure.

139 2.3. *Semi-automated MEPS procedure*

140 The hand-held digital device eVol[®] Sample Dispensing System, the XCHANGE[®] enabled analytical
141 syringe ($50 \mu\text{L}$), the Barrel Insert and Needle assemblies (BIN) packed with 4 mg of three different
142 silica-based sorbents (C2, C8 and C18), respectively were from SGE Analytical Science (SGE
143 Analytical Science Pty Ltd., Victoria, Australia).

144 Prior to first use, each BIN was activated three times with $50 \mu\text{L}$ of methanol followed by the same
145 volume of ultrapure water at a speed of $10 \mu\text{L s}^{-1}$.

146 Before the microextraction procedure, all glassware was rinsed three times with ultrapure hexane in
147 order to avoid residues of organic contaminants (Arcolego et al., 2020), as recommended when
148 determining hydrophobic compounds (Giorio et al., 2018).

149 The sample (4 mL) was extracted from a 10 mL glass vial by 80 loading steps of 50 μL each at a
150 speed of $12.50 \mu\text{L s}^{-1}$ and all portions were discarded into the waste. Then the sorbent was dried by
151 10 cycles of pulling and pushing air at a flow rate of $25.00 \mu\text{L s}^{-1}$.

152 Considering that small aliquots commonly elute analytes of interest more efficiently than one large
153 aliquot (Beyer and Biziuk, 2010), the adsorbed PAHs were collected in three fractions (10 μL each)
154 eluting with ethyl acetate at the speed of $1.67 \mu\text{L s}^{-1}$. The eluate was spiked with IS at the
155 concentration of $10 \mu\text{g L}^{-1}$ and 1 μL of the solution was injected in the GC-MS. After the elution step
156 the sorbent was washed with ethyl acetate, methanol and ultrapure water (50 μL each) to avoid any
157 carry-over and to condition the solid phase before the next extraction.

158 2.4. GC-MS analysis

159 The analysis of the 16 PAHs was performed using a HP 6890 Series Plus gas chromatograph (Agilent
160 Technologies, Milan, Italy) equipped with a PAL Combi-xt autosampler (CTC Analytics AG,
161 Switzerland) and coupled to a MSD 5973 mass spectrometer (Agilent Technologies). The S/SL
162 (Agilent Technologies) injection port temperature was set at $300 \text{ }^\circ\text{C}$ and the gas chromatograph was
163 operated in the splitless injection mode. Separation was achieved on a Rxi-5Sil MS capillary column
164 (30 m x 0.25 mm i.d, 0.25 μm film thickness) (Restek, Bellefonte, PA, USA). Helium was used as
165 carrier gas at a constant flow rate of 1.0 mL min^{-1} . The GC oven temperature program was set as
166 follows: $70 \text{ }^\circ\text{C}$; $15 \text{ }^\circ\text{C min}^{-1}$ to $290 \text{ }^\circ\text{C}$ (held for 4 min) for a total run time of 19.17 min. The mass
167 spectrometer was operated with an electron ionization (EI) ion source using an electron energy of 70
168 eV. A solvent delay time of 3.90 min was applied. The transfer line was maintained at $280 \text{ }^\circ\text{C}$ and the
169 ion source at $150 \text{ }^\circ\text{C}$.

170 Preliminarily, the full scan mass spectral data were recorded in the 40–400 amu range (scan time: 2
 171 scan s⁻¹) to select a list of both qualifier and quantifier ions per target analyte prior to analysis by GC-
 172 MS under selected ion monitoring (SIM) conditions. The SIM mode was used for quantitative
 173 measurements with a dwell time of 30 ms for each ion. The selected ions are listed in Table 1. The
 174 ChemStation (Agilent Technologies) was used for signal acquisition and data processing.

Table 1

Retention times and ions monitored for target PAHs (quantifier ions are underlined) in SIM mode.

PAHs	Retention time (min)	Qualifier and quantifier ions (<i>m/z</i>)
Nap-d8	4.40	<u>136</u> , 137, 108
Nap	4.43	<u>128</u> , 127, 102
Acy-d8	6.80	<u>160</u> , 158, 161
Acy	6.82	<u>152</u> , 151, 76
Ace-d10	7.04	<u>162</u> , 164, 160
Ace	7.09	<u>153</u> , 154, 76
Flu-d10	7.89	<u>176</u> , 174, 175
Flu	7.91	<u>166</u> , 165, 139
Phe-d10	9.41	<u>188</u> , 189, 184
Phe	9.45	<u>178</u> , 176, 152
Ant-d10	9.49	<u>188</u> , 189, 184
Ant	9.51	<u>178</u> , 176, 152
Flt-d10	11.27	<u>212</u> , 208, 213
Flt	11.30	<u>202</u> , 200, 101
Py-d10	11.61	<u>212</u> , 211, 208
Py	11.64	<u>202</u> , 200, 101
BaA-d12	13.54	<u>240</u> , 236, 241
BaA	13.57	<u>228</u> , 226, 113
Chr-d12	13.59	<u>240</u> , 236, 241
Chr	13.62	<u>228</u> , 226, 113
BbF-d12	15.14	<u>264</u> , 265, 260
BbF	15.17	<u>252</u> , 253, 126
BkF-d12	15.18	<u>264</u> , 265, 263
BkF	15.21	<u>252</u> , 253, 126
BaP-d12	15.60	<u>264</u> , 265, 260
BaP	15.64	<u>252</u> , 253, 126
InPy-d12	17.59	<u>288</u> , 289, 144
DiahA-d14	17.65	<u>292</u> , 288, 293
InPy	17.64	<u>276</u> , 279, 278, 277, 139
DiahA	17.72	<u>278</u> , 279, 277, 276, 139
BghiP-d12	18.13	<u>288</u> , 287, 289
BghiP	18.19	<u>276</u> , 279, 278, 277, 139

175 2.5. Sorbent and elution solvent selection

176 The method was developed using uncontaminated snow from Antarctic Plateau as blank matrix after
177 verifying in the chromatogram the absence of detectable signals attributable to the analytes (Fig. S1).
178 Three reversed-phase sorbent materials (silica-C2, silica-C8 and silica-C18) were evaluated and
179 compared for the enrichment of the target PAHs from water samples. For each sorbent the extraction
180 of three independent replicate sample solutions spiked with PAHs at 500 ng L⁻¹ was performed.
181 After the optimization of best sorbent material, the effect of three different elution solvents
182 (dichloromethane, ethyl acetate and methanol) on PAHs desorption was investigated performing
183 extraction of three independent sample solutions spiked with PAHs at 250 ng L⁻¹ for each solvent.
184 The performance of the sorbents and the elution solvents was expressed in terms of the relative
185 chromatographic peak areas using the formula:

$$186 \text{ Area ratio} = A(\text{spike, net})/A(\text{internal standard})$$

187 where: A(spike, net) is the net chromatographic peak area of the compound in a spiked “blank”
188 sample which was subjected to MEPS; A(internal standard) is the chromatographic peak area of the
189 internal standard added after sample extraction.

190 2.6. *Optimization of the MEPS procedure by experimental design*

191 For optimization of experimental parameters, measurements were carried out on blank water derived
192 from uncontaminated snow spiked with PAHs mixture at 250 ng L⁻¹. The influence of two factors on
193 MEPS performance was studied using a face centred design (FCD). The investigated factors were the
194 following: the number of loading cycles (x_1) and the number of eluting cycles (x_2). Low and high
195 levels were: $x_1=40-80$, $x_2=3-10$.

196 This experimental plan allows the simultaneous investigation of the effects of the selected variables
197 and of their interactions (Bianchi and Careri, 2008). Four replicates at the centre point were
198 considered in the model to estimate the experimental variability. The FCD was used to calculate the
199 final regression models which were used to identify the optimal conditions by means of the

200 multicriteria method of the desirability functions (Vera Candiotti et al., 2014). The software package
201 SPSS Statistics 23.0 (IBM, Milano, Italy) was used for statistical calculations.

202 2.7. *Analytical validation*

203 Method validation was performed under the optimized conditions according to EURACHEM
204 guidelines (Magnusson and Örnemark, 2014). Uncontaminated snow from Antarctic Plateau was
205 used as blank samples. Limits of detection (y_D) and of quantification (y_Q) were estimated as signals
206 by using the standard deviation (s_b) and the mean (x_b) calculated from 10 blank replicate
207 measurements as follows: $y_D = x_b + 3 s_b$ and $y_Q = x_b + 10 s_b$. The concentration values of the limit of
208 detection (LOD) and the limit of quantification (LOQ) were obtained by projecting the corresponding
209 responses y_D and y_Q against the concentration axis through a calibration plot $y = f(x)$. Calibration
210 curves were constructed on six concentration levels in the LOQ–150 ng L⁻¹ range performing three
211 replicated measurements for each level. Mandel's fitting test was applied to assess the linearity and a
212 Student's *t*-test was used to establish the significance of the intercept (significance level 5%).
213 Repeatability and intermediate precision over three days were calculated in terms of RSD%
214 performing six measurements on three concentration levels (15, 50 and 150 ng L⁻¹), respectively.
215 Trueness in terms of recovery rate (RR%) was evaluated carrying out ten replicated measurements at
216 20, 70 and 130 ng L⁻¹, respectively, and calculated as follows:

$$217 \quad RR\% = \frac{c_1}{c_2} \times 100$$

218 where c_1 is the measured concentration and c_2 is the concentration determined from the amount spiked
219 in the sample.

220 Before each injection, IS was added at 10 µg L⁻¹ to the PAH standard solutions and to samples after
221 extraction.

222 2.8. *Enrichment factors*

223 The enrichment capabilities of semi-automated MEPS-C8 were evaluated in terms of enrichment
224 factors (EFs). Under the optimized conditions, EFs were calculated as the ratio of the concentration
225 of the analytes at 20 and 50 ng L⁻¹ extracted by MEPS to that obtained by the direct injection of 1 µL
226 of standard solution of PAHs at 10 µg L⁻¹. Experimentally, the ratio of the chromatographic peak area
227 for each analyte after MEPS was compared to that obtained by direct injection and corrected by using
228 the proper response factor (Riboni et al., 2016). Three replicate measurements were carried out.

229 3. Results and discussion

230 3.1. *Development of MEPS procedure*

231 In the present study, MEPS was carried out using the “extract-discard” procedure, which consists in
232 discarding each sample portion into the waste after the aspiration step. Differently, in the “draw-eject”
233 mode the sample is aspirated and dispensed in the same vial several times. According to previous
234 studies (Prieto et al., 2010; Quinto et al., 2014), the “extract-discard” mode was selected to obtain
235 better performances in terms of recovery and sensitivity. In fact, Prieto et al. (Prieto et al., 2010, 2011)
236 demonstrated that by using the “extract-discard” mode, it is possible to achieve similar or higher
237 responses than those achieved with the multiple draw-eject procedure. In addition, by applying this
238 extraction mode a reduction of the mechanical stress of the MEPS syringe plunger can be obtained,
239 thus improving MEPS syringe lifetime.

240 Important parameters affecting MEPS efficiency, such as type of sorbent material and type of elution
241 solvent (Fu et al., 2012; Pereira et al., 2014; Yang et al., 2017) were investigated. A washing step
242 usually recommended between sample loading and elution step to remove matrix unwanted
243 substances (Abdel-Rehim, 2011) was not applied, since the chromatogram of the blank matrix showed
244 the absence of peaks related to the presence of interferences (Fig. S1). In addition, it should be
245 considered that the use of washing solution could affect analyte recovery (El- Beqqali et al., 2007).

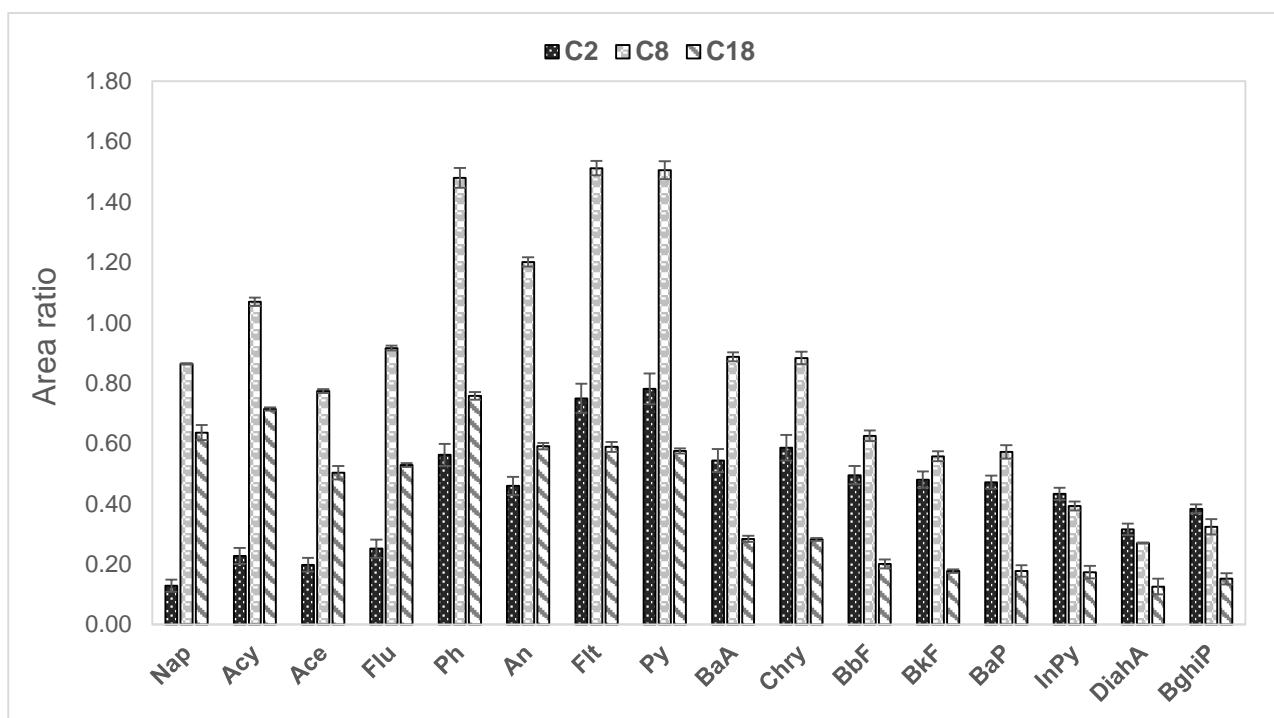
246 Preliminarily, sample loading speed and analyte elution speed were evaluated considering the
247 processing time *per* sample combined with the efficiency of analyte sorption and partition (Mendes
248 et al., 2012) and subsequent desorption process (data not shown). Taking into account the speed range
249 available on the eVol[®] device provided with a 50 μL syringe, i.e., 1.67-25.00 $\mu\text{L s}^{-1}$, extraction and
250 elution rates were found to be appropriate operating at 12.50 $\mu\text{L s}^{-1}$ and 1.67 $\mu\text{L s}^{-1}$, respectively. As
251 suggested by Abdel-Rehim (Abdel-Rehim, 2011), extraction speed in the range of 10-20 $\mu\text{L s}^{-1}$ is
252 suitable for maximizing the interactions between analytes and sorbent, thus improving the retention
253 capability of the MEPS technique. As for the elution rate, the use of the lowest speed enables a good
254 analyte elution as well as the use of a reduced solvent volume. In addition, it should be considered
255 that by operating under the selected conditions, it was possible to prevent bubbling in the syringe,
256 thus improving method repeatability. Similar results were also reported by Prieto et al. (Prieto et al.,
257 2010) which obtained optimal performance for the extraction of organic compounds including PAHs
258 when the fill and injection speed had intermediate and low values, respectively.

259 3.1.1. *Comparison of performance of different silica-based sorbents on PAH microextraction*

260 Up to date, numerous sorbents have been studied with the MEPS technique based not only on the
261 nature of the analytes, but also accounting for the sample matrix in order to achieve adequate recovery
262 (Moeder et al., 2010; Prieto et al., 2011; Pereira et al., 2014; Moein et al. 2015; Fernández et al.,
263 2017; Yang et al., 2017). In this study, selectivity towards target PAHs was assessed by evaluating
264 the extraction capability of three different types of sorbent materials packed in the MEPS BIN. Silica-
265 based reversed-phase sorbent materials are suitable for the extraction of lipophilic compounds from
266 aqueous matrix (Yang et al., 2017). In this context, a comparative evaluation of the efficiency of the
267 C2, C8 and C18 sorbent phases for the enrichment of the analytes from water samples was carried
268 out. In this first investigation step, dichloromethane was used as eluting solvent since previous studies
269 reported its high elution efficiency for the determination of PAHs in water samples (Ma et al., 2010;

270 Fu et al., 2012; Paszkiewicz et al., 2018). Afterwards, the effect of other elution solvents on extraction
271 recovery was evaluated for the selected sorbent phase.

272 Fig. 1 shows that C8-BIN exhibited better performance for most of the analytes, particularly for two,
273 three- and four-ring PAHs due to the highest sorption/partition capacity, whereas for InPy, DiahA
274 and BghiP the highest yield was achieved using C2-BIN. This behaviour could be explained taking
275 into account the stronger retention of the heaviest PAHs on the C8 sorbent compared to C2, revealing
276 a less effective elution process. By contrast, C18-BIN showed the lowest yield for PAHs with four-
277 or more aromatic rings. This result is consistent with the non-polar nature of C18 phase characterized
278 by the presence of longer alkyl chain, providing stronger retention of more hydrophobic compounds
279 and then poor recovery when eluting with reduced solvent volume (Oleszczuk and Baran, 2004;
280 Buszewska-Forajta et al., 2018). Taking into account a wide range of log K_{ow} values of the herein
281 considered analytes (ranging from 3.30 (naphthalene) to 6.95 (indeno[1,2,3-cd]pyrene) (Miller et al.,
282 1984), C8-BIN is proposed as a most suitable MEPS sorbent material being characterized by a more
283 balanced performance for this application than C2-BIN and C18-BIN.



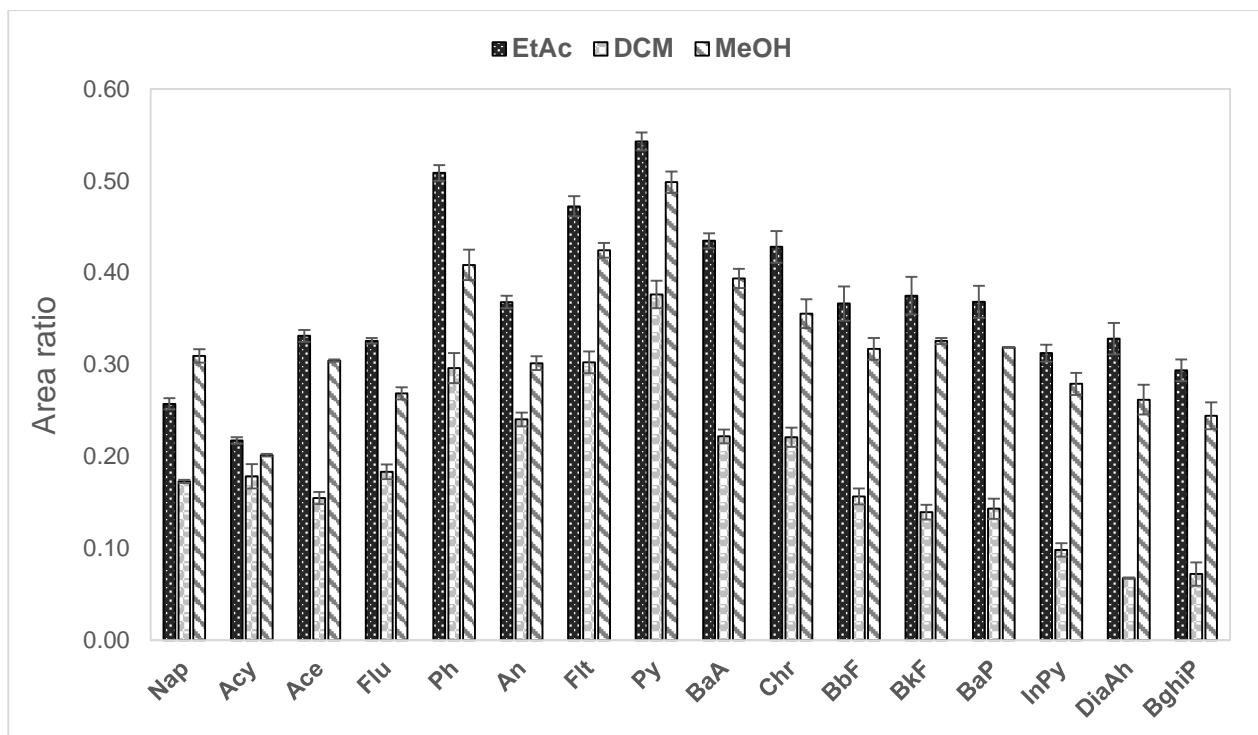
284

285 **Fig. 1** Comparison of extraction efficiency of the MEPS C2-BIN, C8-BIN and C18-BIN sorbents. Sample
286 spiked concentration, 500 ng L⁻¹; pump cycles of sample loading, 40 × 50 μL; speed of sample loading, 12.50

287 $\mu\text{L s}^{-1}$; pump cycles of eluent, $10 \times 10 \mu\text{L}$; elution solvent, dichloromethane; speed of elution solvent; $1.67 \mu\text{L}$
288 s^{-1} .

289 3.1.2. Comparison of performance of different desorption solvents on PAH microextraction

290 The type of elution solvent is a further parameter affecting the performance of MEPS (Moein et al.,
291 2015). The effect of DCM, EtAc and MeOH was studied for the elution of the 16 PAHs from C8-
292 BIN performing three independent replicate experiments for each solvent. As shown in Fig. 2, the
293 best recovery for all target analytes except for Nap was observed when using EtAc. The lowest
294 response obtained by DCM could be ascribed to residual water on the sorbent particles packed in the
295 BIN after sample loading despite the drying step, thus resulting in an unsatisfactory recovery of PAHs
296 being DCM immiscible with water. MeOH has been previously reported as elution solvent in MEPS
297 procedures for PAH extraction using silica-based sorbents (El-Beqqali et al., 2006; Fu et al., 2012;
298 Quinto et al., 2012, 2014). However, in our study MeOH responses were lower than EtAc except for
299 naphthalene, which presents the lowest octanol/water partition coefficient (K_{ow}) (Miller et al., 1984),
300 thus facilitating its desorption by using MeOH. The effect of solvents was tested carrying out a one-
301 way ANOVA followed by Bonferroni *t*-test for multiple comparisons. ANOVA highlighted the
302 presence of significant differences ($p < 0.05$) between mean responses. Afterwards, *t*-test revealed
303 that EtAc exhibited similar or higher extraction yield ($p < 0.05$) (except for Nap) compared to MeOH.
304 On the basis of these findings, EtAc was used as elution solvent.



305

306 **Fig. 2** Comparison of extraction efficiency as a function of elution solvent (DCM, EtAc, MeOH). Sample
 307 spiked concentration, 250 ng L⁻¹; pump cycles of sample loading, 40 × 50 μL; speed of sample loading, 12.50
 308 μL s⁻¹; pump cycles of eluent, 10 × 10 μL; type of BIN, C8; speed of elution solvent; 1.67 μL s⁻¹.

309 *3.2. Microextraction optimization by experimental design*

310 Once the loading and elution speeds were adjusted and after the selection of sorbent and elution
 311 solvent, the number of both loading and elution cycles were optimized using a FCD.

312 As for the number of loading cycles, ideally the proper concentration factor for the analytes should
 313 be achieved with a reduced number of loading cycles to avoid long extraction times (Pereira et al.,
 314 2014). The calculated regression models used to estimate the optimal extraction conditions for the 16
 315 PAHs are shown in Table 2. The variable x_1 , when significant, indicates an increase in the GC-MS
 316 response of PAHs in correspondence to a high number of loading cycles, whereas a reduced number
 317 of elution steps is suitable to obtain a satisfactory recovery.

318

319 **Table 2**
 320 Regression coefficients of the polynomial functions calculated by optimization procedure.

PAHs	Regression models
------	-------------------

Nap	$y = 574 (\pm 30) + 118 (\pm 39)x_1 - 230 (\pm 39)x_2$
Acy	$y = 666 (\pm 34) + 104 (\pm 43)x_1 - 283 (\pm 43)x_2$
Ace	$y = 499 (\pm 27) + 96 (\pm 34)x_1 - 200 (\pm 34)x_2$
Flu	$y = 569 (\pm 32) + 111 (\pm 40)x_1 - 240 (\pm 40)x_2$
Phe	$y = 848 (\pm 50) + 152 (\pm 64)x_1 - 375 (\pm 64)x_2$
Ant	$y = 640 (\pm 41) + 122 (\pm 51)x_1 - 296 (\pm 51)x_2$
Flt	$y = 798 (\pm 46) + 145 (\pm 58)x_1 - 359 (\pm 58)x_2$
Py	$y = 819 (\pm 46) + 138 (\pm 58)x_1 - 350 (\pm 58)x_2$
BaA	$y = 489 (\pm 34) - 193 (\pm 43)x_2$
Chr	$y = 495 (\pm 34) - 199 (\pm 43)x_2$
BbF	$y = 304 (\pm 28) + 74 (\pm 35)x_1 - 198 (\pm 35)x_2$
BkF	$y = 301 (\pm 28) + 74 (\pm 35)x_1 - 173 (\pm 35)x_2$
BaP	$y = 325 (\pm 34) - 181 (\pm 43)x_2$
InPy	$y = 201 (\pm 23) - 204 (\pm 29)x_2$
DiahA	$y = 133 (\pm 25) - 159 (\pm 31)x_2$
BghiP	$y = 212 (\pm 23) - 216 (\pm 29)x_2$

322 x_1 : number of loading cycles.

323 x_2 : number of elution cycles.

324 Finally, the optimal conditions for the simultaneous extraction of the investigated PAHs were
 325 identified by using the multicriteria method of desirability functions, resulting in 80 loading cycles
 326 and 3 elution cycles. The developed procedure achieved a global desirability $D = 0.91$ and good single
 327 desirability values always higher than 0.9, proving method feasibility for the simultaneous extraction
 328 of the target analytes. The method can be considered also time efficient with an average time of 20
 329 min *per* sample if compared to previously reported MEPS procedures, requiring a higher number of
 330 loading and elution cycles. (Quinto et al., 2012, 2014).

331 3.3. Analytical performance of the MEPS-GC-MS method

332 The validation parameters such as linearity, LOD, LOQ, trueness and precision were evaluated for
 333 the GC-MS determination of the 16 target PAHs under the above-mentioned optimal extraction
 334 conditions. Enrichment factors were also calculated to assess the extraction capabilities of the C8
 335 sorbent, obtaining good EFs values ranging from 64 (± 7) for Ace to 129 (± 18) for Phe. For
 336 confirmation purposes, EFs were also calculated using a concentration of 20 ng L⁻¹, obtaining results
 337 comparable with those calculated using a concentration of 50 ng L⁻¹.

338 As shown in Table 3, the developed method achieved excellent LOD values at the low ng L^{-1} level
 339 for all the target compounds, demonstrating its capability for the analysis of PAHs at ultra-trace
 340 levels. These values are comparable with those reported in previous studies (Quinto et al., 2012,
 341 2014), which validated the MEPS-based method on spiked ultrapure water. Good linearity was
 342 verified by applying Mandel's fitting test in the LOQ – 150 ng L^{-1} range for all the analytes. Precision
 343 studies showed RSDs% for repeatability in the 0.3–11% range at the lowest concentration (15 ng L^{-1})
 344 and in the 0.1–10% range at the highest concentration level (150 ng L^{-1}). As for intermediate
 345 precision, RSD values always lower than 15% were found (Table S1). Recovery rates in the 77.6 (\pm
 346 0.1)–120.8 (± 0.1)% range ($n = 10$) were obtained (Table S2), thus proving good trueness of the
 347 developed method. The selectivity of the method was also evaluated testing the absence of interfering
 348 peaks at the retention times of the target PAHs when analyzing a blank sample and a snow sample,
 349 as shown in Figs. S1 and S3.

350 Similarly to Quinto et al. (Quinto et al., 2012, 2014), the present method was developed, optimized
 351 and validated for the determination of very diverse chemical compounds with a wide range of physical
 352 and chemical properties, whereas other MEPS procedures only concerned low-molecular weight
 353 PAHs (El-Beqqali et al., 2006; Fu et al., 2012) (Table 4). In addition, the achieved LODs were
 354 obtained by extracting low sample volume, i.e. 4 mL, representing a further improvement in temporal
 355 resolution records compared to other studies on PAHs contamination in polar sites using very large
 356 sample volume (7 – 10 L) (Fuoco et al., 2012; Vecchiato et al., 2015). Finally, the herein described
 357 method revealed advantageous due to the use of a commercially available and cost-effective sorbent
 358 phase that could be reused more than 300 times.

359 **Table 3**
 360 Analytical parameters of the MEPS-GC-MS method.

PAHs	LOD (ng L^{-1})	LOQ (ng L^{-1})	$b_0(\pm s_{b_0})$	$b_1(\pm s_{b_1})$
Nap	1.1	3.6	0.088 (± 0.003)	0.00248 (± 0.00004)
Acy	1.3	4.3	0.026 (± 0.005)	0.0023 (± 0.0001)
Ace	1.4	4.7	-	0.0036 (± 0.0001)
Flu	0.7	2.4	0.03 (± 0.01)	0.0027 (± 0.0001)

Phe	0.3	1.1	0.17 (\pm 0.01)	0.0029 (\pm 0.0001)
Ant	1.3	4.2	0.07 (\pm 0.01)	0.0030 (\pm 0.0001)
Flt	0.3	1.1	0.05 (\pm 0.01)	0.0039 (\pm 0.0002)
Py	0.4	1.4	0.06 (\pm 0.02)	0.0044 (\pm 0.0002)
BaA	0.6	1.9	0.04 (\pm 0.01)	0.0036 (\pm 0.0001)
Chr	0.5	1.7	0.04 (\pm 0.01)	0.0061 (\pm 0.0001)
BbF	2.5	8.4	0.06 (\pm 0.02)	0.0032 (\pm 0.0002)
BkF	2.5	8.3	-	0.0064 (\pm 0.0002)
BaP	3.8	12.5	0.09 (\pm 0.02)	0.0040 (\pm 0.0003)
InPy	3.5	11.5	0.05 (\pm 0.01)	0.0034 (\pm 0.0001)
DiahA	4.6	15.3	-	0.0042 (\pm 0.0001)
BghiP	4.2	13.9	0.07 (0.02)	0.0037 (\pm 0.0002)

361 Calibration curve equation: $y = b_0 + b_1x$.

362 (-): intercept not statistically significant.

363 **Table 4**

364 Comparison of the developed method with other MEPS methods for the determination of PAHs.

Analytes	Extraction mode	Sorbent material	Sample loading condition ^a	Elution condition ^a	LOQ (ng L ⁻¹)	Technique	Reference
5 PAHs	Draw-eject	C8	60 × 50 μ L (20 μ L s ⁻¹)	1 × 30 μ L (20 μ L s ⁻¹)	5	GC-MS	El-Beqqali et al. (2006)
8 PAHs	Draw-eject	C18	40 × 50 μ L (5 μ L s ⁻¹)	1 × 50 μ L (3 μ L s ⁻¹)	2.5 – 27.5	GC-MS	Fu et al. (2012)
16 PAHs	Draw-eject	C8	300 × 50 μ L (1.67 μ L s ⁻¹)	20 × 50 μ L (1.67 μ L s ⁻¹)	1.6 – 6.2	GC-MS	Quinto et al. (2012)
16 PAHs	Extract-Discard	C8	90 × 50 μ L (4 μ L s ⁻¹)	1 × 50 μ L (4 μ L s ⁻¹)	0.8 – 2.0	GC-MS	Quinto et al. (2014)
16 PAHs	Extract-Discard	C8	80 × 50 μ L (12.50 μ L s ⁻¹)	3 × 10 μ L (1.67 μ L s ⁻¹)	1.1 – 15.3	GC-MS	This work

365 ^a Number of pulled/pushed cycles × aspirated volume (speed)

366 3.4. Applicability of the MEPS-GC-MS method to the analysis of Antarctic snow samples

367 The applicability of the developed method was proven by carrying out the determination of PAHs in
368 five surface snow samples kindly provided by PNRA and collected during the 2020 – 2021 austral
369 summer in Antarctica at four sites on the coast of Victoria Land (Fig. 3). Sample A was collected
370 nearby the meteorological station of Icaro Camp (74°42'37" S, 164°07'05" E); samples B and E were
371 from the area of the scientific research base “Enigma Lake” (74°43' S, 164°01' E); samples C and D
372 were collected near Cape Phillips (73°03' S, 169°36' E) and Adélie Cove (74°45' S, 164°00' E),
373 respectively. The latter is a colony of about 13 - 15 thousand nests of Adélie penguins.

374 As shown in Table 5, PAHs with more than four aromatic rings were not detected in the investigated
375 samples. This could be ascribed to the low presence of high-molecular weight PAHs in snow matrix
376 being more lipophilic and less water soluble than lighter PAHs (Korosi et al., 2015). The covered
377 Σ_{16} PAHs concentrations for each sample revealed values ranging from 24 to 39 ng L⁻¹, with the lowest
378 concentration detected at site D corresponding to Adélie Cove. However, among the different sites
379 considered, comparable Σ_{16} PAHs concentrations were observed, even for the most distant located
380 area (Cape Phillips). Nap and Flu presented the highest concentration level compared to the other
381 analytes in all sampling sites (41 and 42% of the total Σ_{16} PAHs, respectively). Nap and Flu are main
382 components of diesel fuel (Dandajeh et al., 2019), therefore our results are in agreement with other
383 studies describing the presence of regional environmental pollution around scientific stations due to
384 ship operations and fuel combustion (Bargagli, 2008; Kukučka et al., 2010; Vecchiato et al., 2015).
385 In addition, the total Σ_{16} PAHs concentration found in the analysed samples is 158 ng L⁻¹, very similar
386 to that achieved by Vecchiato et al. (Vecchiato et al., 2015) who attributed the major contribution to
387 the anomalous Nap concentration detected in the sample collected at Mid Point, assuming a possible
388 PAH distribution by the wind from a twin-otter refueling point. These considerations support the
389 hypothesis of PAHs contamination influenced by local sources.

390 In general, it can be stated that Antarctic contamination level for PAHs is low compared to other
391 remote areas. For a frame of reference, the found PAH concentrations were compared to those
392 determined in other remote areas, e.g. Caucasus and Alps. Vecchiato et al. (Vecchiato et al., 2020)
393 measured PAHs concentrations in the ice core drilled in 2009 at the western plateau of Elbrus
394 obtaining the most recent Elbrus PAH concentrations at the top of the core in the 112 - 166 ng L⁻¹
395 range. Gabrieli et al. (Gabrieli et al., 2010b) examined the seasonal snowpack from Eastern Italian
396 Alps in 2004-2005. Σ PAHs concentration in high altitude sites (>1700 m a.s.l.) was in the 20 – 59 ng
397 L⁻¹ range. The highest Σ PAHs concentration was 290 ng L⁻¹ in valley bottom urban area. Finally,
398 when comparing different remote environments it should be noted that the differences of

399 contamination level reflect the influence for each sampling site of their regional sources as well as
 400 the deposition regime and the emission pattern of PAHs.

401 **Table 5**
 402 Concentrations of PAHs detected in the Antarctic snow samples

PAHs	Icaro (A)	Enigma (B)	Cape Phillips (C)	Adélie Cove (D)	Enigma2 (E)
Nap	11.2	8.8	7.8	6.7	6.0
Acy	n.d.	n.d.	7.1	n.d.	7.4
Ace	n.d.	n.d.	n.d.	n.d.	n.d.
Flu	10.1	7.8	8.1	7.7	8.5
Phe	n.d.	n.d.	n.d.	n.d.	n.d.
Ant	n.d.	n.d.	n.d.	n.d.	n.d.
Flt	5.2	6.2	5.2	5.1	5.3
Py	4.3	5.7	4.2	4.4	4.2
BaA	n.d.	6.9	n.d.	n.d.	n.d.
Chr	n.d.	3.5	n.d.	n.d.	n.d.
BbF	n.d.	n.d.	n.d.	n.d.	n.d.
BkF	n.d.	n.d.	n.d.	n.d.	n.d.
BaP	n.d.	n.d.	n.d.	n.d.	n.d.
InPy	n.d.	n.d.	n.d.	n.d.	n.d.
DiahA	n.d.	n.d.	n.d.	n.d.	n.d.
BghiP	n.d.	n.d.	n.d.	n.d.	n.d.

403 All data in ng L⁻¹.
 404 n.d.: not detected.

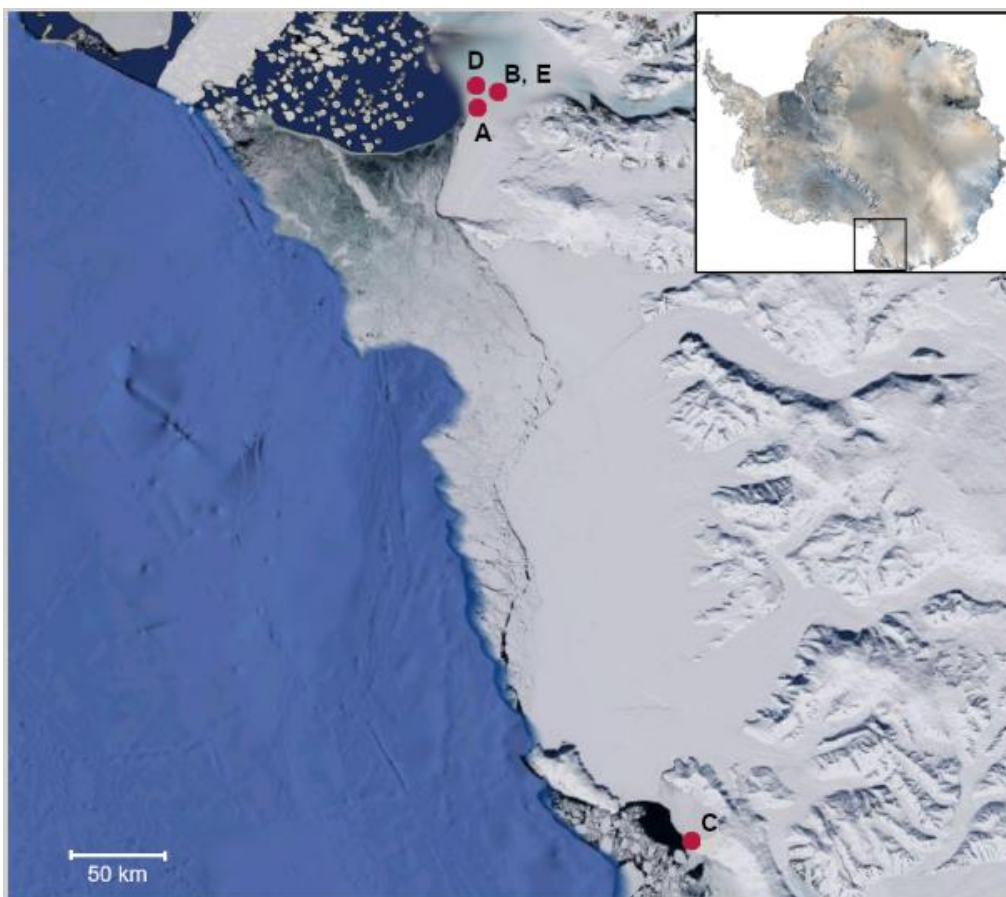


Fig. 3 Sampling sites of surface snow in Antarctica

405

406

407 4. Conclusions

408 An eco-friendly semi-automated MEPS-GC-MS method was successfully devised, validated and
 409 applied for the first time to the extraction of the 16 US-EPA priority PAHs from Antarctic snow
 410 samples at ultra-trace levels. The optimized method based on the use of silica-C8 sorbent exhibited
 411 high extraction efficiency allowing highly sensitive analysis of environmentally important PAHs in
 412 snow samples. The semi-automatic sample preparation provided high precision and reduced sample
 413 handling avoiding potential contamination during the extraction procedure. An additional advantage
 414 of the proposed method relies on the reduced sample volume, representing a promising tool to meet
 415 challenges of high temporal resolution records in paleoclimatic investigations.

416 The optimized method proved to be suitable for ultra-trace analysis of PAHs in snow samples
 417 collected in four sites in Antarctica revealing a likely contribution of local pollution sources to PAHs

418 contamination of Antarctic environment. Future applications of the developed MEPS method for
419 ultra-trace analysis of PAHs in snow/ice and ice cores from polar regions could provide
420 paleoenvironmental records in order to assess the occurrence and global contamination with PAHs
421 and other emerging contaminants.

422

423 **Acknowledgements**

424 This work was supported by the projects “Innovative Analytical Methods to study biogenic and
425 anthropogenic proxies in Ice COres” funded by the MIUR Progetti di Ricerca di Rilevante Interesse
426 Nazionale (PRIN) - grant 2017EZNJWN and “Emerging COntaminants in Antarctic Snow: sources
427 and TRAnsport” (ECO AS:TRA) funded by the MIUR Programma Nazionale di Ricerca in Antartide
428 (PNRA) - grant PNRA18_00229.

429 This work has also benefited from the framework of the COMP-HUB Initiative, funded by the
430 ‘Departments of Excellence’ program of the Italian Ministry for Education, University and Research
431 (MIUR, 2018-2022).

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