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Application for marine and atmospheric samples**

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1 **Simultaneous determination of neutral sugars, alditols and anhydrosugars**  
2 **using anion-exchange chromatography with pulsed amperometric**  
3 **detection: Application for marine and atmospheric samples**

4  
5  
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## 24 **Abstract**

25 An improved high-performance anion-exchange chromatography with pulsed  
26 amperometric detection (HPAEC-PAD) method is described for the simultaneous  
27 determination of neutral sugars (hexoses, pentoses and deoxysugars), alditols and  
28 anhydrosugars commonly found in atmospheric and marine samples. The method uses a  
29 CarboPac MA1 column, at a flow rate of  $0.3 \text{ mL min}^{-1}$ , and a NaOH gradient (250-700 mM).  
30 The proposed method applies a temperature gradient (from 25 to 28 °C) to the column for the  
31 first 30 min of the analysis, followed by a constant temperature at 28 °C until the end of the  
32 analysis. These analytical conditions allowed the separation of 15 out of 17 carbohydrates in  
33 75 min with resolution factors better than 0.5 for the critical pairs levoglucosan/arabitol,  
34 galactosan/arabinose, arabinose/mannose and glucose/xylose.

35 The application of this method to field samples revealed that anhydrosugars represented  
36 53% of total neutral carbohydrates (TCHO) in total suspended atmospheric particles (TSP),  
37 whereas they were detected for the first time in marine particulate organic matter (POM) and  
38 high-molecular-weight dissolved organic matter (HMWDOM) samples accounting 2% and  
39 3% of TCHO, respectively. Levoglucosan and/or galactosan were the major anhydrosugars in  
40 all samples however, their concentrations are undoubtedly underestimated because hydrolysis  
41 was applied to the marine samples prior to the HPAEC-PAD analysis. Despite this  
42 underestimation, their presence in the marine samples clearly indicates possible terrestrial  
43 input most likely via atmospheric deposition as these compounds are considered terrestrial  
44 burning biomass tracers. Finally, deoxysugars were also detected for the first time in the TSP  
45 sample representing 1% of TCHO, while alditols accounted for 0.4% and 0.3% of TCHO in  
46 POM and HMWDOM, respectively.

47

48

## 49 **1. Introduction**

50 Carbohydrates are among the most abundant organic molecules on the earth because they  
51 are detected in all marine and terrestrial ecosystems (Giorio et al., 2018; He et al., 2010;  
52 Mopper, 1977; Mopper et al., 1980; Panagiotopoulos and Sempéré, 2005a; Repeta et al.,  
53 2015; Theodosi et al., 2018). The determination of carbohydrates at the molecular level has  
54 been often used to determine different biogeochemical signatures such as terrestrial inputs in  
55 coastal marine environments (Cowie and Hedges, 1984; da Cunha et al., 2002;  
56 Panagiotopoulos et al., 2014), organic matter sources (He et al., 2010; Panagiotopoulos et al.,  
57 2012; Wicks et al., 1991), and decomposition pathways (Amon et al., 2001; Giroldo et al.,  
58 2003; Hedges et al., 1994; Opsahl and Benner, 1999).

59 Previous environmental studies on atmospheric suspended particulate matter (PM<sub>2.5-10</sub>)  
60 showed that carbohydrates account for 0.2–3% and 0.7–11% of organic carbon (OC) and  
61 water-soluble organic carbon (WSOC), respectively (Theodosi et al., 2018; Tsai et al., 2015;  
62 Yang et al., 2005). The dominant carbohydrates reported in aerosols are glucose and sucrose  
63 released by terrestrial plants (Medeiros et al., 2006; Samaké et al., 2019), levoglucosan,  
64 galactosan and mannosan from biomass burning processes (Bhattarai et al., 2019; Simoneit et  
65 al., 2004, 1999), as well as mannitol and arabitol from airborne fungal spores and/or various  
66 vascular plants (Bauer et al., 2008; Samaké et al., 2019). Other minor carbohydrates reported  
67 in aerosols include some neutral sugars (e.g., arabinose, fructose, galactose, and mannose) and  
68 alditols (e.g., xylitol and sorbitol; Barbaro et al. 2015; Theodosi et al. 2018). It is worth noting  
69 that fucose and rhamnose, two important deoxysugars consistently found in bacterial  
70 heteropolysaccharides (Giroldo et al., 2003), soil organic matter (Bock et al., 2007),  
71 freshwater ecosystems (Cheng and Kaplan, 2003) as well as vascular plants (Opsahl and  
72 Benner, 1999) have never been reported in atmospheric samples.

73 Monomeric constituents of carbohydrates after acid hydrolysis (e.g., fucose, rhamnose,  
74 arabinose, galactose, glucose, mannose and xylose) have also been detected in the marine  
75 environment. As revealed by chromatographic techniques, these monosaccharides account for  
76 10–15%, <10% and <20% in particulate, dissolved and sedimentary organic carbon,  
77 respectively (Panagiotopoulos and Sempéré, 2005a and references therein). These  
78 monosaccharides have also been reported in marine high-molecular-weight dissolved organic  
79 matter (HMWDOM) at equimolar concentrations although <sup>1</sup>H nuclear magnetic resonance  
80 spectroscopy (NMR) showed the presence of much broader spectra of carbohydrates  
81 including unhydrolyzed polysaccharides and methylated sugars (Panagiotopoulos et al.,  
82 2007). Other minor carbohydrate classes also reported in marine samples include amino  
83 sugars (Benner and Kaiser, 2003; Kaiser and Benner, 2009) and uronic acids (Bergamaschi et  
84 al., 1999; Engel and Händel, 2011; Hung et al., 2001).

85 Surprisingly, alditols and anhydrosugars, two major carbohydrate categories consistently  
86 found in aerosols and ice cores (Gambaro et al., 2008; Giorio et al., 2018), have scarcely been  
87 reported in marine samples despite the growing evidence that dry or wet atmospheric  
88 deposition is an important process between the atmospheric and marine compartments  
89 (Pantelaki et al., 2018; Zheng et al., 2018). It is worth noting that only Panagiotopoulos et al.  
90 (2013) have identified anhydrosugars (levoglucosan, mannosan, and galactosan) in surface  
91 marine HMWDOM, in addition to the seven neutral sugars described above. This finding  
92 raises questions about the possible sources of anhydrosugars in marine water (terrestrial vs  
93 marine), which have been recently examined using compound-specific carbon isotopes  
94 analysis (Nouara et al., 2019). Nevertheless, to the best of our knowledge a well-established  
95 technique for the measurement of anhydrosugars and alditols does not exist for marine  
96 samples. Moreover, the lack of information about deoxysugars in atmospheric samples

97 hinders our understanding of their dynamics and clearly points to the need for a universal  
98 method to measure these carbohydrates in any environmental sample.

99 High-performance anion-exchange chromatography with pulsed amperometric detection  
100 (HPAEC-PAD) is the most employed chromatographic technique for the analysis of  
101 carbohydrates in environmental samples (Benner and Kaiser, 2003; Caseiro et al., 2007;  
102 Iinuma et al., 2009; Mopper et al., 1992; Panagiotopoulos and Sempéré, 2005a; Sempéré et  
103 al., 2008). However, simple carbohydrates (e.g., monosaccharides) are not ionized in the same  
104 manner in alkaline media used in the HPAEC mobile phase, and therefore different  
105 concentrations of NaOH must be applied to separate these monosaccharide families (e.g.,  
106 alditols, neutral sugars, and uronic acids). Due to this “limitation”, most environmental  
107 applications of the HPAEC-PAD technique have focused on one family of carbohydrates  
108 (e.g., neutral sugars, or amino sugars) and few attempts have been made to date to separate a  
109 much broader spectrum of carbohydrate categories in the same run (Engel and Händel, 2011).

110 The main objective of the present study is to establish a universal HPAEC-PAD method  
111 capable of simultaneously identifying several carbohydrate families including neutral sugars,  
112 alditols and anhydrosugars commonly found in terrestrial and marine ecosystems. This  
113 objective was achieved after the evaluation of the performance of two different anion-  
114 exchange columns and the optimization of the mobile phase concentration, column  
115 temperature and flow rate. The proposed method was validated in three different  
116 environmental matrices, namely, total suspended atmospheric particles (TSP), marine  
117 particulate organic matter (POM), and marine HMWDOM.

## 118 **2. Materials and procedures**

### 119 *2.1. Reagents*

120 Carbohydrate standards were purchased from Sigma-Aldrich or Interchim, at their purest  
121 available grade (>98%). A mixture of standard solutions at concentrations ranging from 50

122 nM to 10  $\mu$ M was prepared by dilution with ultrapure water of a standard stock solution (1  
123 mM) of neutral sugars (fucose, rhamnose, arabinose, galactose, glucose, mannose, xylose,  
124 fructose and ribose), alditols (xylitol, arabitol, sorbitol and mannitol), anhydrosugars  
125 (levoglucosan, mannosan and galactosan), and one disaccharide (sucrose). All the prepared  
126 solutions including the stock solution were stored in the dark at  $-25$   $^{\circ}$ C until use. Despite that  
127 no degradation was observed after melting and refrozen, the standard solutions (50 nM–10  
128  $\mu$ M) were renewed after 2 weeks. The HCl solution (37%, Sigma-Aldrich) diluted with  
129 ultrapure water to 1 M was used for sample hydrolysis, while the NaOH solution (50% w/v in  
130 H<sub>2</sub>O, low carbonate; PanReac AppliChem ITW Reagents) diluted with ultrapure water was  
131 used for the mobile phase of the HPAEC-PAD chromatography. The ultrapure water used in  
132 this work was produced by a Millipore Milli-Q system (Molsheim, France).

133

## 134 2.2. *Sampling and extraction of carbohydrates*

### 135 2.2.1. *TSP*

136 The aerosol sample was collected on a precombusted (450  $^{\circ}$ C, 6 h) weighed Whatman  
137 quartz fiber filter (20.3 cm  $\times$  25.4 cm, nominal retention size, 0.7  $\mu$ m) using an automatic  
138 sampler (Tisch Environmental USA; flow rate 85 m<sup>3</sup> h<sup>-1</sup>). The sample was collected from  
139 March 10th to March 17th of 2016, from the rooftop of the Endoume Marine Station  
140 (Marseille; 43 $^{\circ}$  16' N - 5 $^{\circ}$  21' E). After collection, the sample was dried for 24 h in a  
141 desiccator, weighed, and then stored in a freezer at  $-25$   $^{\circ}$ C in precombusted aluminum foil  
142 (450  $^{\circ}$ C, 6 h). A 1-cm<sup>2</sup> section of the filter was extracted with 6 mL ultrapure water in an  
143 ultrasonic bath for 1 h and filtered through a Pasteur pipette packed with quartz wool (both  
144 precombusted at 450  $^{\circ}$ C for 6 h) to remove any remaining particles, and then analyzed  
145 immediately (Theodosi et al., 2018). The recovery yields of the extraction procedure were  
146 estimated after the extraction of a precombusted (450  $^{\circ}$  C, 6 h) Whatman quartz fiber filter

147 spiked with a standard mixture of neutral carbohydrates spanning a concentration range from  
148 100 to 1000 nM (Theodosi et al., 2018). The obtained yields of neutral sugars for all the  
149 concentrations tested were between 101 and 119% ( $n = 5$ ). The abovementioned analytical  
150 procedure allowed the extraction and identification only of the free neutral sugars present in  
151 the TSP sample and as such the composition of combined sugars was not determined in this  
152 study.

153

### 154 2.2.2. *Marine POM*

155 Sinking particles (marine POM) were collected over seven-day periods from January 6th to  
156 March 3rd, 2013, in the upwelling system located offshore of Lima (Peru) in the Pacific  
157 Ocean ( $12^{\circ} 02' S - 77^{\circ} 40' W$ ), using sediment traps (PPS3, Technicap) deployed in the  
158 oxycline/upper oxygen minimum zone (OMZ) layer at a depth of 34 m (Bretagnon et al.,  
159 2018). To avoid the bio-degradation of POM, a solution of seawater with 5% formaldehyde  
160 was added to the bottom of the collection chamber. After trap recovery, the living and dead  
161 swimmers were carefully removed so that only detrital particles remained in the sample.  
162 These detrital particles (marine POM) were stored in the dark at 4 °C in the initial chambers  
163 used in the trap. On land, the samples were filtered through 25 mm precombusted (450 °C, 6  
164 h) Whatman GF/F filters, freeze-dried, and subsequently stored in the dark at 4 °C until  
165 further analysis. Five portions (40–60 mg each) of each of the five samples obtained from the  
166 respective collection chambers of the sediment trap were pooled together, resulting in ~265  
167 mg dry POM powder. To release neutral sugars, the POM powder was hydrolyzed with 1 M  
168 HCl at 100 °C for 20 h (Panagiotopoulos et al., 2014). The acid-soluble fraction recovered  
169 after centrifugation (2000 rpm) was then transferred into a precombusted (450 °C, 6 h) glass  
170 vial, and the acid was removed from the sample by three successive lyophilizations. The POM  
171 recovery (by weight) after acid hydrolysis was 84%. A part of the final dry powder was



172 weighed (25.61 mg), redissolved in 1 mL ultrapure water and filtered through a Pasteur  
173 pipette packed with quartz wool (both precombusted at 450 °C for 6 h). The filtrate was  
174 diluted 500 times with ultrapure water and filtered again to remove any remaining particles  
175 prior to injection into the chromatographic system.

176

### 177 2.2.3. *Marine HMWDOM*

178 The surface (15 m) seawater sample was collected from the Hawaii area (19° 43' N - 156°  
179 03' W) in December 2003 and processed at Woods Hole Oceanographic Institution (USA) as  
180 described by Panagiotopoulos et al. (2013). Briefly, the sample (8640 L) was filtered through  
181 0.8 µm and 0.2 µm dual cartridge filters, and then ultrafiltered using a cross-flow  
182 ultrafiltration system. The concentrated sample (40 L) that included the HMWDOM was  
183 further desalted by diafiltration with ultrapure water to a final volume of 2 L and freeze dried  
184 to obtain a fluffy white powder. The carbon composition of the HMWDOM collected was  
185 35% by weight, with a carbon/nitrogen ratio of 16. A part of the resultant HMWDOM powder  
186 (104 mg) was hydrolyzed to release the neutral sugars with 1 M HCl at 100 °C for 20 h, then  
187 the hydrolysis was stopped by placing the sample in an ice bath. The HCl was removed from  
188 the sample by lyophilization (3 times; final pH = 7). Then, a portion of the sample (55.83 mg)  
189 was redissolved in 1 mL ultrapure water, filtered through a Pasteur pipette packed with quartz  
190 wool (both precombusted at 450 °C for 6 h) and stored frozen at -20 °C. Before analysis, the  
191 sample was diluted 3 times with ultrapure water.

192

### 193 2.3. *Chromatographic system*

194 Carbohydrate analysis was performed using a Thermo-Dionex ICS-3000 anion-exchange  
195 chromatograph (HPAEC) equipped with a 250-µL injection loop and a pulsed amperometric  
196 detector (PAD). The waveform used for pulsed amperometric detection was the standard

197 quadruple potential for carbohydrate analysis (Panagiotopoulos et al., 2012). The ultrapure  
198 water used to prepare the mobile phase was sparged with high purity N<sub>2</sub> for 30 min prior to  
199 use. The mobile phase consisted of ultrapure water (eluent A) and NaOH at 1 M (eluent B)  
200 prepared by dilution in degassed ultrapure water. The eluents were kept continuously under  
201 pure N<sub>2</sub> pressure to avoid exposure to atmospheric CO<sub>2</sub>, which can cause a drastic decrease in  
202 column selectivity and loss of sugar resolution. In addition, an on-line degasser (RFIC eluent  
203 degasser, Thermo Fisher) was added before the analytical column to decrease interference  
204 from dissolved oxygen (Cheng and Kaplan, 2001).

205 In this study, two anion-exchange analytical columns were tested for sugar separation: a  
206 CarboPac MA1 (7.5 μm, 4 × 250 mm; Thermo Fisher) and a CarboPac PA1 (10 μm, 4 × 250  
207 mm; Thermo Fisher), both fitted with their corresponding guard column (4 × 50 mm; Thermo  
208 Fisher). The Chromeleon software (Thermo Fisher) was used for processing and data  
209 acquisition. The performance of the chromatographic separation (resolution factor, R<sub>s</sub>)  
210 between the two-carbohydrate species A and B is calculated according to the following  
211 formula:

$$212 \quad R_s = 2 [(t_R)_B - (t_R)_A] \times [W_A + W_B]^{-1}$$

213 Where (t<sub>R</sub>)<sub>A</sub> and (t<sub>R</sub>)<sub>B</sub> are the retention times of the two species A and B, respectively, and  
214 W<sub>A</sub> and W<sub>B</sub> are their corresponding peak widths.

### 215 **3. Results and discussion**

#### 216 *3.1. Method optimization*

217 Although previous investigations described the simultaneous discrimination of some  
218 neutral sugars, alditols and anhydrosugars using CarboPac PA1 or CarboPac MA1 columns  
219 (Caseiro et al., 2007; Iinuma et al., 2009), the analytical HPAEC-PAD conditions used in  
220 previous studies were unable to fully resolve the 17-carbohydrate mixture assessed in the

221 present study. Application of the analytical protocol using the CarboPac MA1 column in  
222 Iinuma et al. (2009) revealed that the critical monosaccharide groups that required a further  
223 efficient separation were, by elution order: (a) levoglucosan, arabitol, fucose and rhamnose,  
224 (b) mannosan and sorbitol, (c) mannose, arabinose and galactosan, and (d) glucose and  
225 xylose. The optimization of the method therefore involved evaluating the effects of basic  
226 chromatographic parameters (flow rate, mobile phase composition and column temperature)  
227 to achieve optimal separation of the 17-carbohydrate mixture. Charged carbohydrates (e.g.,  
228 uronic acids and phosphorylated sugars) were not considered in this study because they  
229 require different mobile phase conditions compared to neutral carbohydrates using  
230 CH<sub>3</sub>COONa as the eluent (Engel and Händel, 2011; Hu et al., 2012).

231

### 232 *3.1.1. Column selection*

233 Although several types of anion-exchange columns are available for carbohydrate analysis  
234 (CarboPac PA10, 20, 100 and 200; Ronkart et al. 2007; Meyer et al. 2008; Raessler et al.  
235 2010; Raessler 2011), the most recommended are: (1) the CarboPac PA1 column for analysis  
236 of neutral sugars (Cheng and Kaplan, 2001; Kerhervé et al., 2002; Panagiotopoulos et al.,  
237 2012; Panagiotopoulos and Sempéré, 2005a; Theodosi et al., 2018), and (2) the CarboPac  
238 MA1 column for analysis of alditols, anhydrosugars and neutral sugars (Iinuma et al., 2009;  
239 Jung et al., 2014; Zhang et al., 2013).

240 The CarboPac PA1 column is well-suited for the analysis of neutral monosaccharides.  
241 However, when alditols and anhydrosugars are included in the same run, a NaOH gradient is  
242 required because these compounds are eluted at lower NaOH concentrations (<1 mM)  
243 compared to neutral monosaccharides (>15 mM). However, the use of a NaOH gradient  
244 causes disequilibrium of the baseline signal, which further results in a positive (Sullivan et al.,

245 2011) or a negative peak (Caseiro et al., 2007; Theodosi et al., 2018) that may potentially  
246 mask sugar peaks that are eluted within this time window.

247 The CarboPac MA1 column was introduced much later than the CarboPac PA1 column  
248 and, to date, has never been applied to marine samples. Nevertheless, its macroporous  
249 stationary phase has a higher anion-exchange capacity over the CarboPac PA1 column (1450  
250  $\mu\text{eq}/\text{column}$  vs  $100 \mu\text{eq}/\text{column}$ ), which further allows the use of gradient conditions without  
251 affecting the baseline stability (Iinuma et al., 2009; Zhang et al., 2013). Moreover, because  
252 the CarboPac MA1 column operates at high NaOH elution conditions ( $>200 \text{ mM}$ ), the pH  
253 values of the mobile phase are  $>12.5$  and as such all the hemiacetal groups of sugars are  
254 deprotonated. This further increases the retention of sugars on the column and thus results in a  
255 better resolution (Thermo Fisher, Technical Note 20). Finally, the higher baseline stability of  
256 the CarboPac MA1 column over the CarboPac PA1 column offers an additional advantage in  
257 terms of the retention time of chromatographic peaks, which does not significantly shift over  
258 successive injections (Gremm and Kaplan, 1997). Due to these reasons, this study was  
259 conducted using the CarboPac MA1 column and different chromatographic parameters (flow  
260 rate, etc.) were appropriately adjusted for separation of different classes or sugars.

261

### 262 *3.1.2. Optimization of flow rate, mobile phase and column temperature*

263 According to the manufacturer, the CarboPac MA1 column operates at a recommended  
264 range of flow rates of  $0.2\text{--}0.5 \text{ mL min}^{-1}$ , and the flow rate is generally fixed at  $0.4 \text{ mL min}^{-1}$   
265 for environmental applications (Iinuma et al., 2009; Jung et al., 2014; Li et al., 2016).  
266 Nevertheless, the latter authors did not report co-elution problems because they did not  
267 consider fucose, rhamnose, arabinose, sorbitol and xylose in their standards. To overcome the  
268 co-elution problem, we first decreased the flow rate to  $0.3 \text{ mL min}^{-1}$ . This resulted in a slight

269 improvement in the separation of the above compounds, and therefore this flow rate was  
270 maintained for all further improvements.

271 Previous investigations employing the CarboPac MA1 column used NaOH concentrations  
272 ranging from 300 to 800 mM (Andersen and Sørensen, 2000) to elute alditols, anhydrosugars,  
273 and some neutral sugars (Iinuma et al., 2009). Nonetheless, such conditions were not optimal  
274 for the 17 carbohydrates considered in this study. Therefore, different NaOH gradient tests  
275 were performed at a fixed column temperature of 25 °C and a flow rate of 0.3 mL min<sup>-1</sup>. The  
276 improved separation of the first seven eluted monosaccharides (xylitol, levoglucosan, arabitol,  
277 fucose, rhamnose, sorbitol and mannosan) was achieved by applying an NaOH gradient  
278 ranging from 250 mM to 350 mM in the first 30 min (Fig. 1 a, Table 1). Unfortunately, fucose  
279 and rhamnose were not resolved ( $R_s = 0$ ) under these conditions despite additional  
280 adjustments of the NaOH gradient. The 250 to 350 mM gradient was then followed by a 15  
281 min-NaOH gradient increasing from 350 to 450 mM that allowed an acceptable separation  
282 (with resolution factors close to or higher than 1) of mannitol, galactosan, arabinose and  
283 mannose.

284 Following the chromatographic separation after 45 min, the NaOH concentration was  
285 increased from 450 to 700 mM and held for 55 min to elute glucose, xylose, galactose and  
286 fructose. Under these elution conditions, the xylose/galactose and galactose/fructose pairs  
287 were fully resolved ( $R_s > 1.5$ ), while the glucose/xylose pair was partially resolved ( $R_s = 0.3$ ).  
288 Additional tests of decreasing or increasing the final NaOH concentration (700 mM) did not  
289 improve the glucose/xylose resolution. Finally, by prolonging the 700 mM NaOH  
290 concentration for an additional 20 min, the last two carbohydrates (ribose and sucrose) were  
291 eluted with excellent resolution ( $R_s = 8.1$ ). After 75 min, the column was equilibrated for 20  
292 min with the initial NaOH concentration (250 mM). Regeneration and clean-up of the column

293 were not necessary, because the high NaOH concentration (700 mM) reached at the end of the  
294 analysis was sufficient to restore column performance.

295 Because pairs of levoglucosan/arabitol, fucose/rhamnose, galactosan/arabinose,  
296 arabinose/mannose and glucose/xylose were completely or partially overlapped under the  
297 NaOH gradient conditions optimized above, we also explored the effect of temperature on the  
298 resolution of these monosaccharide pairs. Earlier investigations have shown that temperature  
299 plays an important role in monosaccharide separation using the CarboPac PA1 column and  
300 that sub-ambient temperatures strongly affect the resolution of closely eluting  
301 monosaccharide pairs, notably fucose/rhamnose and mannose/xylose (Panagiotopoulos et al.,  
302 2001). The results of this study indicated that glucose co-eluted with xylose at temperatures  
303  $<20\text{ }^{\circ}\text{C}$ , while arabinose overlapped with mannose at  $>30\text{ }^{\circ}\text{C}$ . Moreover, fucose and rhamnose  
304 always co-eluted under both these temperature conditions. Overall, these results suggest that  
305 sub-ambient temperature conditions do not have a significant impact on the separation of the  
306 abovementioned carbohydrate pairs on the CarboPac MA1 column.

307 By narrowing the temperature range between 25 and 30  $^{\circ}\text{C}$ , we found that these  
308 monosaccharide pairs were better resolved (except the fucose/rhamnose pair which again co-  
309 eluted), as shown by their corresponding resolution factors (Fig. 2). The results showed that  
310 except for the arabinose/mannose ( $R_s = 0.4$ ) and fucose/rhamnose pairs ( $R_s = 0$ ), the resolution  
311 factors for the levoglucosan/arabitol ( $R_s = 0.7$ ), galactosan/arabinose ( $R_s = 1.3$ ), and  
312 glucose/xylose ( $R_s = 0.6$ ) pairs were significantly improved at a temperature of 28  $^{\circ}\text{C}$ .  
313 Therefore, a temperature gradient was applied between 25 and 28  $^{\circ}\text{C}$  for the first 30 min of  
314 analysis. The latter temperature was maintained for the next 45 min to distinguish the  
315 galactosan/arabinose, arabinose/mannose and glucose/xylose pairs (Table 1, Table A 1; Fig. 1  
316 a). After 75 min, the temperature was reset to 25  $^{\circ}\text{C}$  during column re-equilibration (20 min)  
317 until the next injection.

318 *3.2. Linearity, detection limit, precision and blanks*

319 The optimized method showed a linear response for all monosaccharides ( $R^2 > 0.999$ ) over  
320 a concentration range of 50 nM to 10  $\mu$ M, which is typical for environmental monosaccharide  
321 concentrations. The detection limits calculated at a signal-to-noise ratio (S/N) of three were  
322 4–51 nM for neutral sugars, 2–15 nM for alditols and 8–32 nM for anhydrosugars (Table A  
323 1), in agreement with previous studies using different elution conditions and anion-exchange  
324 columns for monosaccharide determination (Caseiro et al., 2007; Iinuma et al., 2009;  
325 Panagiotopoulos et al., 2001; Theodosi et al., 2018). The high detection limit obtained for  
326 fructose (51 nM), also observed in a previous study (Iinuma et al., 2009), is probably due to  
327 the low detector response toward this compound. The precision of the method was calculated  
328 by performing six identical runs with the standard mixture of the 17 carbohydrates (50 nM  
329 each). The relative standard deviation (RSD%) ranged from 1.8 to 16.6% for the peak area  
330 and from 0.2 to 1.7% for the retention time (Table A 1). The procedural blank for the marine  
331 POM consisted of a 25-mm Whatman GF/F filter (precombusted at 450 °C for 6 h),  
332 hydrolyzed in the same manner as the samples. Similarly, the procedural blank for the TSP  
333 consisted of a Whatman quartz fiber filter (precombusted at 450 °C for 6 h) extracted with the  
334 ultrapure water. The results showed no detectable sugars in blanks (Fig. S 1).

335

336 *3.3. Comparison with the CarboPac PA1 column*

337 The final optimized MA1-HPAEC-PAD method (Table 1, Fig. 1 a) was compared with a  
338 different method employing the CarboPac PA1 column (Caseiro et al., 2007; Theodosi et al.,  
339 2018). The chromatogram obtained with the latter column (Fig. 1 b) showed that, at low  
340 NaOH concentrations (1 mM; 0–15 min), xylitol, sorbitol, mannitol and mannosan peaks  
341 were partially resolved, while the arabitol/levoglucosan and galactosan/fucose pairs  
342 completely overlapped. Similar observations were made at high NaOH concentrations (19

343 mM; 15–53 min) for rhamnose/arabinose, mannose/xylose and ribose/sucrose pairs. Based on  
344 the above co-elutions, these results clearly suggest that loss of molecular level information  
345 may occur when a sample containing all of the abovementioned monosaccharides is analyzed  
346 with the CarboPac PA1 column. Moreover, these co-elutions may further induce erroneous  
347 quantification of these monosaccharides. Overall, these results indicate that the CarboPac  
348 MA1 column is more appropriate than the CarboPac PA1 column for environmental  
349 applications in terms of monosaccharide resolution and baseline stability.

350

### 351 3.4. *Application to environmental samples*

352 The method established in this study was tested on three different environmental matrices  
353 including TSP, marine POM and HMWDOM. The chromatograms of these matrices are  
354 presented in Fig. 3 and indicated the presence of large quantities of monosaccharides (Table  
355 2).

#### 356 3.4.1. *TSP*

357 The major carbohydrate classes identified in the TSP sample included anhydrosugars and  
358 disaccharides, followed by neutral sugars and alditols. The sum of their concentration was 563  
359  $\text{ng m}^{-3}$ , representing the total neutral carbohydrate (TCHO) content recorded in the TSP  
360 sample. The results of this study showed that levoglucosan ( $261 \text{ ng m}^{-3}$ ) and sucrose ( $178 \text{ ng}$   
361  $\text{m}^{-3}$ ) were among the major neutral carbohydrates (Table 2; Fig. 3 a), which is in agreement  
362 with other studies of European urban atmospheres (Yttri et al., 2007). Anhydrosugars  
363 represented 53% of TCHO in the TSP sample and were dominated by levoglucosan and  
364 mannosan, which accounted for 87% and 10% of the anhydrosugar pool, respectively (Fig. 4  
365 a). Galactosan was also detected in the TSP sample but in lower concentrations (Table 2).



366 Neutral sugars accounted for 11% of the TCHO pool (Fig. 4 a) with fructose and glucose  
367 exhibiting the highest concentrations (Fig. 4 a, Table 2). The presence of these neutral sugars  
368 in the TSP sample strongly supports the influence of biogenic emission, which is typical of  
369 plants growth during spring (Fu et al., 2012; Medeiros et al., 2006). Other minor neutral  
370 sugars found in the TSP sample included the arabinose, mannose and xylose (Table 2).  
371 Finally, alditols represented the least abundant carbohydrate class, accounting for 4% of  
372 TCHO in the TSP sample (Fig. 4 a). The alditols decreased in abundance in the order of  
373 xylitol, mannitol, arabitol and sorbitol (Table 2), and their presence in the sample indicates  
374 inputs from fungal spores and/or microbial activities (Bauer et al., 2008; Dahlman et al.,  
375 2003; Loos et al., 1994).

376 Although fucose and rhamnose co-eluted under the current HPAEC-PAD conditions, they  
377 were also identified and quantified in the aerosol sample for the first time and accounted for  
378 1% of TCHO and 8% of neutral sugars. Fucose and rhamnose may have multiple sources in  
379 atmospheric particles including soil organic matter (Gunina and Kuzyakov, 2015; Ogner,  
380 1980; Simoneit et al., 2004), vascular plants (Bianchi, 2007; Popper et al., 2004; Schädel et  
381 al., 2010), microorganisms and bacteria (Cowie and Hedges, 1984; Fox et al., 1993; Petit et  
382 al., 2013), while recent studies indicated that marine sources via water/air exchange may also  
383 be an important contributor (Rastelli et al., 2017).

384 Nevertheless, field measurements using gas chromatography (Alves et al., 2011) or nuclear  
385 magnetic resonance spectroscopy (Chalbot et al., 2013) identified only fucose or rhamnose  
386 but never simultaneously reported both sugars in atmospheric samples. On the other hand,  
387 studies using HPAEC-PAD have never reported fucose and rhamnose in atmospheric  
388 particles, probably because of the co-elution of these deoxysugars with other  
389 monosaccharides (fucose with galactosan and rhamnose with arabinose after analysis with the

390 CarboPac PA1 column; Fig. 1 b). Therefore, the presence of fucose and rhamnose in the  
391 sample has never been thoroughly assessed to date.

392 The lack of data on deoxysugars in atmospheric samples may also be related to their  
393 original structure. As deoxysugars are mostly found in bacterial lipopolysaccharides (Perry et  
394 al., 1996; Weckesser et al., 1970; Zdorovenko et al., 2007) and/or plant structural  
395 polysaccharides (Colombini et al., 2002; Grössl et al., 2005; Popper et al., 2004; Schädel et  
396 al., 2010), they are either not efficiently recovered after water extraction (case of  
397 lipopolysaccharides) or are recovered in the water phase but cannot be released from  
398 carbohydrate polymer (case of structural polysaccharides) as no hydrolysis is applied.

#### 399 3.4.2. *Marine POM*

400 The major carbohydrate classes identified in the marine POM sample included the neutral  
401 sugars followed by anhydrosugars and alditols. The sum of their concentration was 16.2 mg  
402 g<sup>-1</sup>. Neutral sugars accounted for 98% of the TCHO pool (Fig. 4 b) and were dominated by  
403 galactose (5.7 mg g<sup>-1</sup>) and glucose (3.8 mg g<sup>-1</sup>) (Table 2; Fig. 3 b). These monosaccharides  
404 were followed by fructose (2.0 mg g<sup>-1</sup>) and fucose/rhamnose (co-eluted; 1.8 mg g<sup>-1</sup>) while  
405 xylose, mannose and arabinose exhibited concentrations <1 mg g<sup>-1</sup>. These results are in good  
406 agreement with previously reported monosaccharide patterns for marine POM in several  
407 oceanic regimes (Hernes et al., 1996; Panagiotopoulos and Sempéré, 2005b; Skoog and  
408 Benner, 1997). Fructose and ribose, occasionally reported in marine POM samples due to  
409 their low recovery after acid hydrolysis (Borch and Kirchman, 1997; Panagiotopoulos and  
410 Sempéré, 2005a), were also identified in this sample (Table 2). This finding most likely  
411 indicates the presence of storage polysaccharides (fructans) and nonstructural labile  
412 compounds such as RNA or nucleotides originating from marine organisms (Cowie and  
413 Hedges, 1984; Haug and Mykelstad, 1976; Hicks et al., 1994; Panagiotopoulos and Sempéré,  
414 2005b). Alternatively, fructose may originate from sucrose. As sucrose was not detected in

415 the marine POM sample (the same holds for the HMWDOM sample), this most likely implies  
416 its complete hydrolysis under the acid conditions used for its extraction, which results in two  
417 monosaccharides (fructose and glucose).

418 The proposed analytical method allowed the identification and quantification of alditols  
419 (0.4% of TCHO) and anhydrosugars (2% of TCHO), the two monosaccharide families that  
420 have been largely overlooked to date in marine environmental studies (Fig. 4 b). The results  
421 showed that xylitol was the major alditol type detected in the POM sample, followed by  
422 sorbitol, while arabitol and mannitol were not detected in the sample (Table 2). Alditols are  
423 generally reported as terrestrial tracers derived from fungal spores and/or microbial activities  
424 (Dahlman et al., 2003; Vandeska et al., 1995), therefore, their presence in the marine POM  
425 sample may suggest possible terrestrial input (van Pinxteren et al., 2012). Alternatively,  
426 alditols may have marine origin. As carbohydrates are an important fraction of the organic  
427 matter produced by marine primary production or released into the environment via  
428 degradation processes, it is highly possible that alditols are also part of the carbohydrate pool.  
429 Nevertheless, additional measurements using compound-specific  $^{13}\text{C}$  analysis are warranted to  
430 test this hypothesis and constrain the sources of alditols in the marine waters.

431 Compositionally, anhydrosugars were dominated by galactosan followed by levoglucosan  
432 and mannosan, which represented for 63%, 25% and 13% of total anhydrosugars, respectively  
433 (Fig. 4 b). The dominance of galactosan over levoglucosan has also been reported for sea  
434 surface microlayer samples in Baltic sea (van Pinxteren et al., 2012) during different seasons  
435 of the year however, more data are warranted in the same time from both atmospheric and  
436 marine compartments to validate/confirm these findings.

437 However, the anhydrosugar concentrations found in this sample (and in the HMWDOM  
438 sample) are most likely underestimated because these compounds are converted to their  
439 respective hexoses after acid hydrolysis (Blanco et al., 2018). Indeed, in an additional set of

440 experiments to investigate whether the hydrolysis conditions affect the stability of  
441 monosaccharides, we performed acid hydrolysis (1 M HCl, 100 °C, 20 h) on a standard  
442 monosaccharide mixture containing neutral sugars, alditols and anhydrosugars. The results  
443 showed that levoglucosan, mannosan and galactosan were completely converted to glucose,  
444 mannose and galactose, respectively, while minimal loss was observed for neutral sugars and  
445 alditols (Fig. S 2), which is consistent with previous studies (Skoog and Benner, 1997; Wang  
446 et al., 2016).

447 Overall, these results revealed that the concentration of anhydrosugars is biased in  
448 environmental samples if these sugars are acid-extracted (POM and HMWDOM sample).  
449 Therefore, an alternative extraction method should be considered (e.g., extraction with water  
450 or MeOH). Despite the possible underestimation of the amount of the anhydrosugars found in  
451 the marine POM, their presence in this sample clearly indicates an external input, most likely  
452 via atmospheric deposition, as shown by the isotopic signature ( $\delta^{13}\text{C}$ ) of levoglucosan and  
453 mannosan pointing to a terrestrial origin (Nouara et al., 2019).

454

### 455 3.4.3. *Marine HMWDOM*

456 The major carbohydrate classes identified in the HMWDOM sample included the neutral  
457 sugars followed by anhydrosugars and alditols. The sum of their concentration was 766  $\mu\text{g}$   
458  $\text{g}^{-1}$ . Neutral sugars accounted for 97% of the TCHO pool in the HMWDOM (Fig. 4 c). The  
459 results of this study revealed that fucose & rhamnose (300  $\mu\text{g g}^{-1}$ ), glucose (122  $\mu\text{g g}^{-1}$ ),  
460 mannose (103  $\mu\text{g g}^{-1}$ ), galactose (83  $\mu\text{g g}^{-1}$ ), xylose (74  $\mu\text{g g}^{-1}$ ), and arabinose (34  $\mu\text{g g}^{-1}$ )  
461 were among the major monosaccharides, which agrees with the neutral sugar pattern reported  
462 in previous studies (Aluwihare et al., 1997; Repeta et al., 2002) (Table 2; Fig. 3c). Fructose  
463 and ribose were also quantified in the HMWDOM sample, and similar to POM, they most  
464 likely originate from storage polysaccharide or RNA.

465 Anhydrosugars accounted for 3% of TCHO and were dominated by levoglucosan,  
466 galactosan and mannosan, which represented 61%, 22% and 17% of total anhydrosugars,  
467 respectively (Fig. 4 c). The lower concentration of anhydrosugars in the HMWDOM sample  
468 (the same holds for the POM sample) compared to the TSP sample maybe due to the high  
469 dilution occurring at sea and also to photodegradation processes by OH\* radicals which take  
470 place in the atmosphere for these compounds (Hoffmann et al., 2010; Lai et al., 2014). In  
471 addition, as suggested for marine POM, the concentration of anhydrosugars in HMWDOM is  
472 most likely biased due to the acid extraction procedure. The presence of the anhydrosugars in  
473 the sample may indicate possible input of terrestrial organic matter (burning biomass tracers),  
474 although additional studies using  $\delta^{13}\text{C}$  are warranted to confirm this hypothesis. Finally, the  
475 least abundant carbohydrate class was the alditols, which accounted 0.3% of TCHO and  
476 represented by mannitol and xylitol (Fig. 4 c).

477

#### 478 **4. Conclusions**

479 The results of this study indicated that under the optimized analytical conditions, neutral  
480 sugars, alditols, and anhydrosugars commonly found in most environmental samples can be  
481 analyzed with a single run in 75 min with satisfactory resolution except for the  
482 fucose/rhamnose pair that completely co-eluted. These deoxysugars were identified for the  
483 first time in the TSP sample by this improved HPAEC-PAD technique, which will facilitate  
484 future investigations by shedding light on bacterial and/or microorganism activities on  
485 atmospheric samples. However, additional deconvolution of these deoxysugars signals using  
486 the traditional HPAEC-PAD method for neutral sugar determination (Panagiotopoulos et al.,  
487 2001) might also be useful.

488 The proposed improved HPAEC-PAD method allowed, for the first time, the identification  
489 and quantification of anhydrosugars and alditols in marine samples (marine POM and

490 HMWDOM). These two carbohydrate families have largely been overlooked in the dissolved  
491 free monosaccharide pool (DFMS), and, to the best of our knowledge, they have never been  
492 reported in marine DOM. Indeed, anhydrosugars and alditols can easily be extracted from  
493 seawater using cation and anion-exchange resins (Kirchman et al., 2001; Mopper et al., 1992;  
494 Sempéré et al., 2008; Skoog and Benner, 1997; van Pinxteren et al., 2012) in the same manner  
495 as neutral sugars. However, because the subsequent PA1-HPAEC-PAD analysis has always  
496 been performed at >15 mM NaOH to elute the neutral sugars; anhydrosugars and alditols  
497 always co-elute at time window of 2–5 min, therefore, they have never been identified in the  
498 DFMS pool.

499 On the other hand, dissolved combined monosaccharides (DCHO) or polysaccharides in  
500 marine samples are generally measured as their monomeric constituents that are released after  
501 acid hydrolysis. Thus, if anhydrosugars are present in the sample, they will be counted in the  
502 hexose pool as the sample is hydrolyzed. Therefore, we recommend that DCHO analysis  
503 always be preceded or accompanied by the analysis of DFMS to evaluate the contribution of  
504 anhydrosugars – if present – in the sample. This strategy is particularly critical for samples  
505 from coastal areas that receive significant terrestrial inputs, particularly in wintertime, and are  
506 characterized by strong influence from wood burning.

507 The proposed HPAEC method provides an acceptable resolution for most of the  
508 carbohydrates examined, and therefore its coupling with mass spectrometry may further help  
509 with the structural elucidation and confirmation of the analyzed carbohydrates. Moreover, its  
510 high potential may further be explored in other environmental matrices, including sediments,  
511 seawater, and marine biota, which will provide a more complete profile of carbohydrates in  
512 the environment. This complete profile, in turn, may be helpful to improve our understanding  
513 on carbohydrate dynamics in the marine and terrestrial ecosystems and potentially better  
514 evaluate the impact of biomass burning processes on marine waters.

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851 **Table and Figure captions**

852 **Table 1:** Optimal analytical conditions for the simultaneous analysis of neutral sugars,  
853 alditols, anhydrosugars and sucrose

854 **Table 2.** Carbohydrate composition in atmospheric TSP, marine POM and marine  
855 HMWDOM samples. The carbohydrate concentrations presented in this table are not  
856 corrected for losses during the hydrolysis or the extraction procedure (see materials and  
857 methods), and therefore they should be considered as minimum concentrations found in  
858 the samples.

859 **Fig. 1.** HPAEC-PAD chromatograms of a standard mixture of 17 monosaccharides (1  $\mu\text{M}$   
860 each) obtained with the (a) CarboPac MA1 column after optimization according to Table  
861 1 (Peak identification: 1 = xylitol, 2 = levoglucosan, 3 = arabitol, 4 = fucose/ rhamnose,  
862 5 = sorbitol, 6 = mannosan, 7 = mannitol, 8 = galactosan, 9 = arabinose, 10 = mannose,  
863 11 = glucose, 12 = xylose, 13 = galactose, 14 = fructose, 15 = ribose, 16 = sucrose) and  
864 (b) CarboPac PA1 column (Peak identification: 1 = xylitol, 2 = arabitol/levoglucosan, 3  
865 = sorbitol, 4 = mannitol, 5 = mannosan, 6 = galactosan, 7 = fucose, 8 =  
866 rhamnose/arabinose, 9 = galactose, 10 = glucose, 11 = mannose/xylose, 12 = fructose, 13  
867 = ribose/sucrose). The dotted line and secondary axis indicate the NaOH gradient. The  
868 analytical HPAEC-PAD conditions for the CarboPac PA1 column are as follows: flow  
869 rate  $0.7 \text{ mL min}^{-1}$ , 0–15 min : 1 mM NaOH; 15–38 min : 19 mM NaOH (curve 5),  
870 column temperature  $17 \text{ }^\circ\text{C}$  and detector temperature  $20 \text{ }^\circ\text{C}$  (Theodosi et al., 2018).

871 **Fig. 2.** The resolution of levoglucosan/arabitol ( $\blacklozenge$ ), fucose/rhamnose ( $\times$ ), galactosan/arabinose  
872 ( $\blacksquare$ ); arabinose/mannose ( $\blacktriangle$ ), and glucose/xylose ( $\bullet$ ) pairs with fixed temperatures (25,  
873 28 and  $30 \text{ }^\circ\text{C}$ ) applied during the whole HPAEC-PAD run under the optimized mobile  
874 phase and flow rate conditions.

875 **Fig. 3.** HPAEC-PAD chromatograms according to Table 1 of (a) total suspended atmospheric  
876 particles (TSP), (b) marine particulate organic matter (POM) and (c) marine high-  
877 molecular-weight dissolved organic matter (HMWDOM). Peak identification: 1 =  
878 xylitol, 2 = levoglucosan, 3 = arabitol, 4 = fucose/rhamnose, 5 = sorbitol, 6 = mannosan,  
879 7 = mannitol, 8 = galactosan, 9 = arabinose, 10 = mannose, 11 = glucose, 12 = xylose,  
880 13 = galactose, 14 = fructose, 15 = ribose, 16 = sucrose.

881 **Fig. 4.** Relative abundances (%) of neutral sugars, alditols, anhydrosugars and disaccharides  
882 within the TCHO pool for (a) total suspended atmospheric particles (TSP), (b) marine  
883 particulate organic matter (POM) and (c) marine high-molecular-weight dissolved  
884 organic matter (HMWDOM). The relative abundances (%) of levoglucosan, galactosan  
885 and mannosan within the anhydrosugar pool are given as well for the abovementioned  
886 environmental samples.

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900 **Table 1**901 Optimal analytical conditions for the simultaneous analysis of neutral sugars, alditols, anhydrosugars  
902 and sucrose.

Parameters	Conditions	
Column	CarboPac MA1 (250 × 4 mm I.D.), Thermo Fisher	
Eluent flow rate (mL min <sup>-1</sup> )	0.3	
Detector temperature (°C)	25	
Sample loop size (μL)	250	
Injection volume (μL)	230	
Column oven temperature (°C)	25–28	(0–30 min); curve 5
	28	(30–75 min)
	25	(75–95 min)
NaOH gradient (mM)	250–350	(0–30 min) ; curve 5
	350–450	(30–45 min) ; curve 5
	450–700	(45–55 min) ; curve 5
	700	(55–75 min)
	250	(75–95 min)

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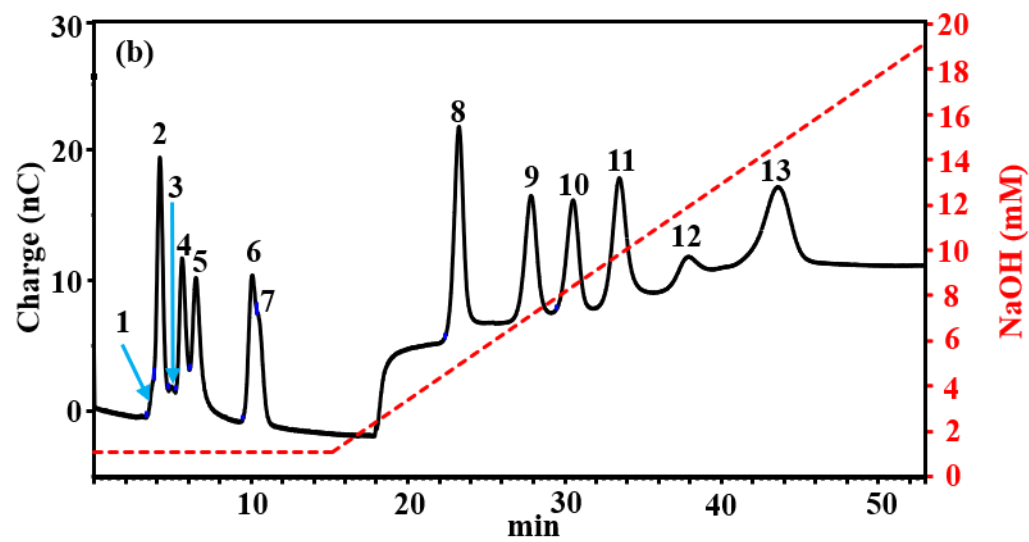
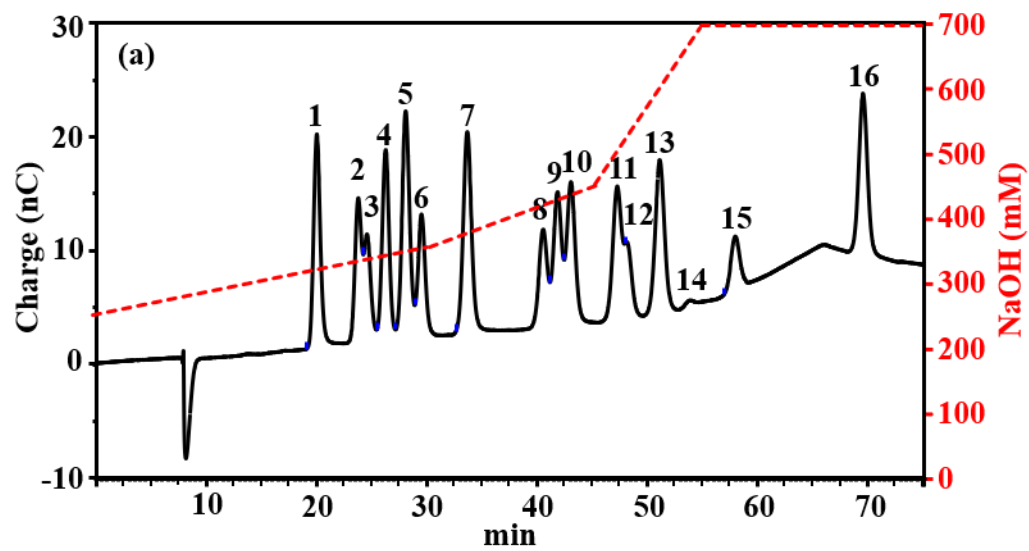
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905 **Table 2**906 Carbohydrate composition in atmospheric TSP, marine POM and marine HMWDOM samples. The  
907 carbohydrate concentrations presented in this table are not corrected for losses during the hydrolysis or  
908 the extraction procedure (see materials and methods), and therefore they should be considered as  
909 minimum concentrations found in the samples.

Carbohydrate	TSP (ng m <sup>-3</sup> )	POM (mg g <sup>-1</sup> )	HMWDOM (μg g <sup>-1</sup> )
Xylitol	11	0.05	0.13*
Levoglucozan	261	0.08	12
Arabitol	3.4	ND	ND
Fucose & Rhamnose	5.0	1.8	300
Sorbitol	1.9	0.02	ND
Mannosan	30	0.04	3.4
Mannitol	7.8	ND	2.3
Galactosan	9.4	0.2	4.4
Arabinose	2.1	0.1	34
Mannose	1.2	0.8	103
Glucose	15	3.8	122
Xylose	1.2	0.9	74
Galactose	ND	5.7	83
Fructose	36	2.0	11
Ribose	ND	0.7	19
Sucrose	178	ND	ND

910 ND = Not detected

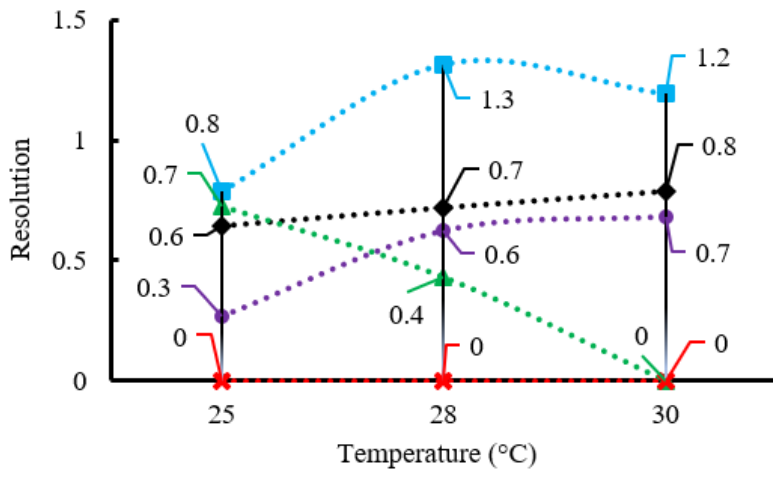
911 \* Xylitol concentration was outside the calibration range (50-1000 nM) but ~6 times higher than its  
912 detection limit (Table A 1), thus it was quantified with an uncertainty of ~24%.



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FIGURE 1





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**FIGURE 2**

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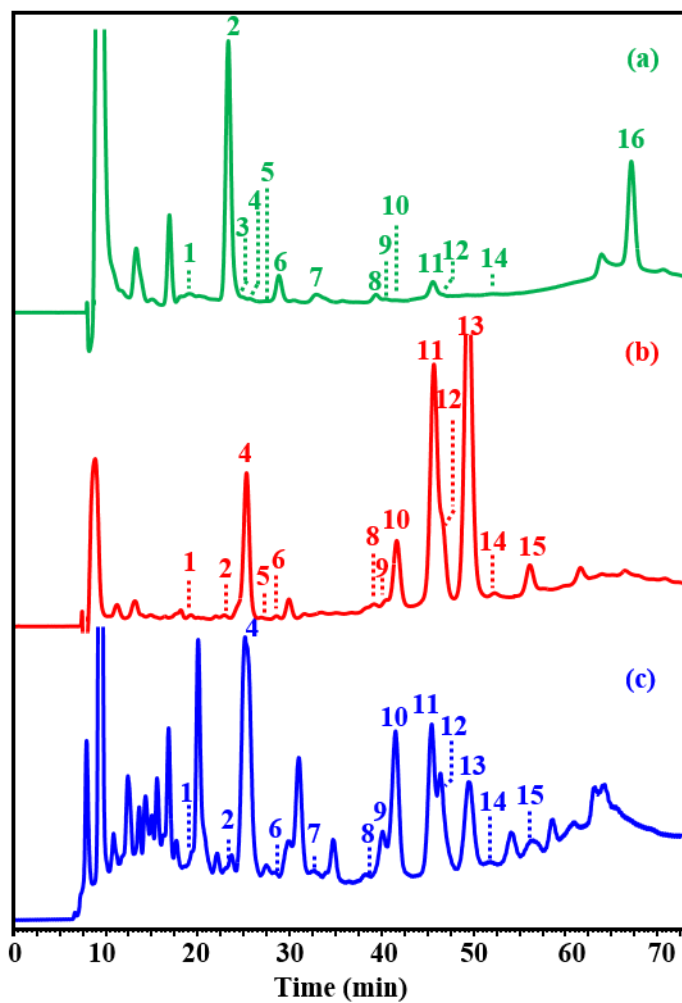
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**FIGURE 3**

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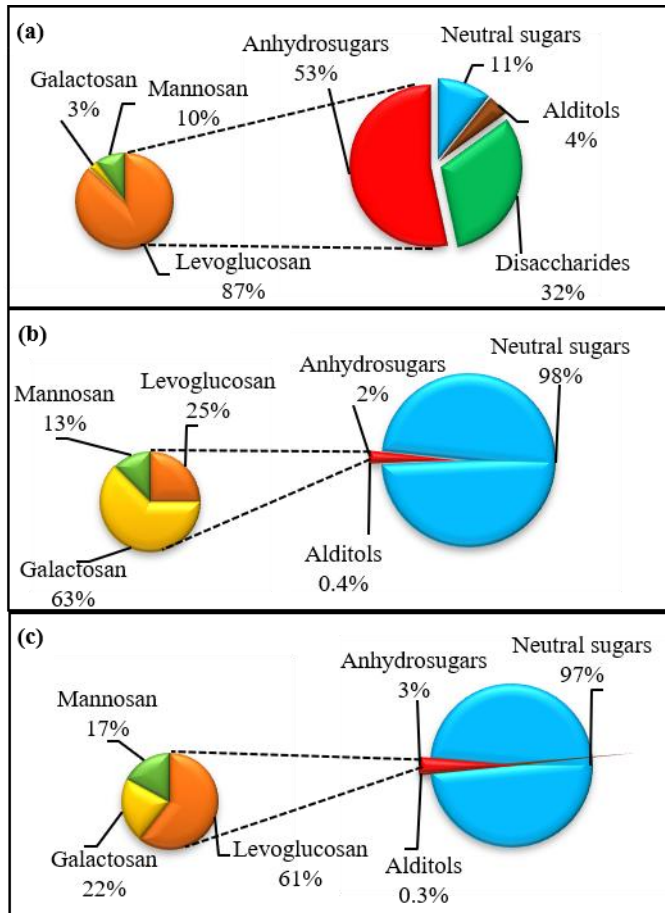
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**FIGURE 4**

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*Supplemental Information for*

**Simultaneous determination of neutral sugars, alditols, and anhydrosugars using anion-exchange chromatography with pulsed amperometric detection: Application for marine and atmospheric samples**

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09<sup>th</sup> May 2019

979 **Table of Contents**

980

981 **Table S 1.** HPAEC-PAD performance after optimization (Table 1). The average retention time ( $t_R$ ),  
982 and resolution factor ( $R_s$ ) of the carbohydrate standards is given at 1  $\mu$ M level ( $n = 3$ ). The relative  
983 standard deviations (RSD) of peak area and retention time of the same standards is calculated at 50  
984 nM level ( $n = 6$ ), except for fructose (1  $\mu$ M level;  $n = 6$ ). The detection limit (DL) was calculated at  
985 signal to noise ratio of 3.....45

986

987 **Fig S 1.** Example of HPAEC-PAD chromatograms of procedural blanks (a) ultrapure water (b) TSP  
988 blank and (c) POM blank. Blanks were prepared in triplicate for each sample (TSP and marine POM)  
989 and run according to the method established in Table 1.....46

990

991 **Fig S 2.** High-performance liquid chromatography with refractive index detection (HPLC-RI)  
992 chromatograms of a monosaccharide mixture (1 mM each) before hydrolysis (black solid line) and  
993 after hydrolysis (red dotted line) with 1 M HCl under 100 °C for 20 h. Peak identification : 1 =  
994 glucose, 2 = xylose, 3 = galactose & rhamnose, 4 = galactosan, 5 = arabinose & fucose, 6 = mannose,  
995 7 = fructose, 8 = mannitol, 9 = levoglucosan, 10 = xylitol, 11 = sorbitol, 12 = mannosan. The  
996 analytical HPLC-RI conditions are given in Nouara et al. (2019) and are as follows: cation exchange  
997 column in  $Pb^{2+}$  form, isocratic elution with ultrapure water at 0.6 mL  $min^{-1}$ , column temperature 75  
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1008 HPAEC-PAD performance after optimization (Table 1). The average retention time ( $t_R$ ), and  
 1009 resolution factor ( $R_s$ ) of the carbohydrate standards is given at 1  $\mu$ M level ( $n = 3$ ). The relative  
 1010 standard deviations (RSD) of peak area and retention time of the same standards is calculated at 50  
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 1012 signal to noise ratio of 3.

<b>Carbohydrate</b>	<b><math>t_R</math> (min)</b>	<b><math>R_s</math></b>	<b>Area RSD (%)</b>	<b><math>t_R</math> RSD (%)</b>	<b>DL (nM)</b>
Xylitol	19.9	3.1	5.6	0.2	2
Levoglucozan	23.8	0.6	4.0	0.5	8
Arabitol	24.4	1.3	6.7	0.4	13
Fucose & Rhamnose	26.0	1.3	6.5	0.3	17
Sorbitol	27.8	1.2	5.0	0.3	15
Mannosan	29.3	3.2	1.9	0.3	18
Mannitol	33.3	5.1	2.7	0.4	7
Galactosan	40.2	0.8	9.3	0.4	32
Arabinose	41.4	0.7	4.9	0.4	7
Mannose	42.6	2.4	1.8	0.3	6
Glucose	46.7	0.5	4.4	0.3	9
Xylose	47.7	1.6	6.7	0.3	24
Galactose	50.5	1.7	5.2	0.6	4
Fructose	53.1	3.0	16.6	1.7	51
Ribose	57.2	8.1	6.0	0.4	13
Sucrose	68.9	-	5.8	0.7	13

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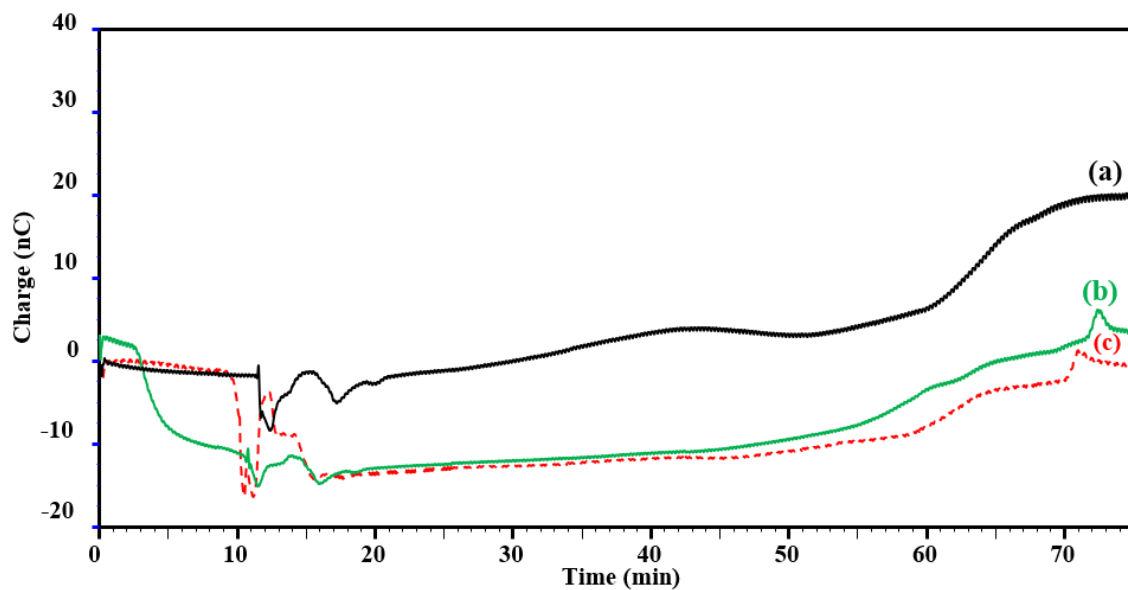
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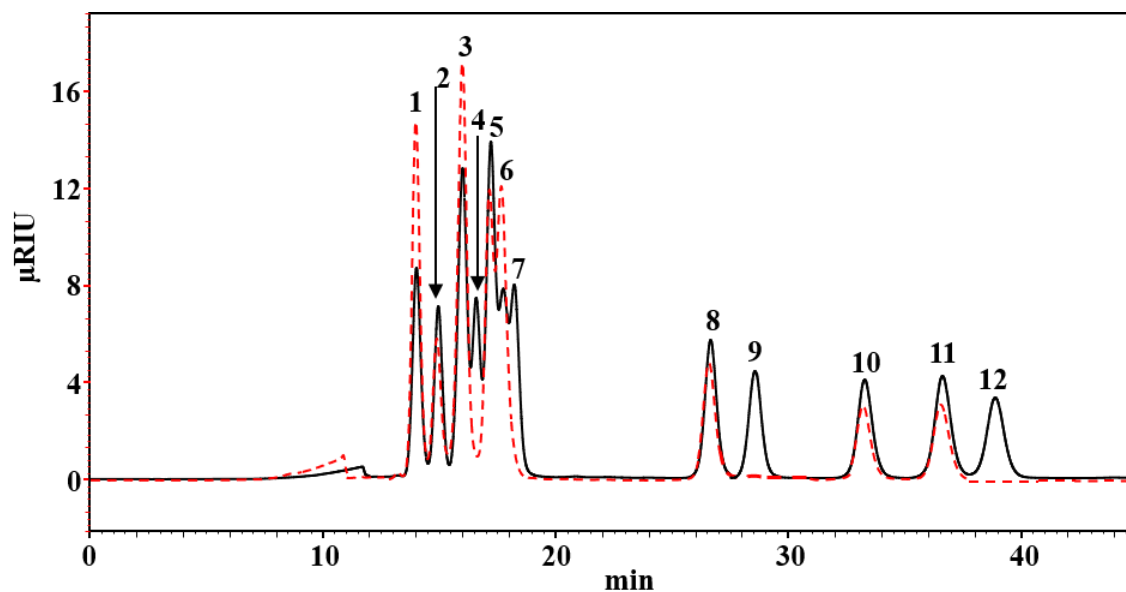
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