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► **To cite this version:**

C. Theodosi, Christos Panagiotopoulos, A. Nouara, P. Zarmpas, P. Nicolaou, et al.. Sugars in atmospheric aerosols over the Eastern Mediterranean. *Progress in Oceanography*, 2018, MERMEX special issue, 163, pp.70-81. 10.1016/j.pocean.2017.09.001 . hal-01657239

HAL Id: hal-01657239

<https://hal.science/hal-01657239v1>

Submitted on 22 Jan 2018

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1 Sugars in atmospheric aerosols over the Eastern Mediterranean

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17 Abstract

18 Aerosol samples (PM₁₀) were collected at Finokalia monitoring station in a remote
19 area of Crete in the Eastern Mediterranean over a two-year period. They were analyzed
20 for total organic carbon (OC), water-soluble organic carbon (WSOC) and the molecular
21 distributions of sugars. WSOC comprised 45% of OC while the contribution of sugars
22 to the OC and WSOC content in the PM₁₀ particles averaged 3±2% (n=218) and
23 11±6% (n=132), respectively. The total concentration of sugars ranged between 6 and
24 334 ng m⁻³ with the two most abundant sugars over the two-year period being glucose
25 and levoglucosan, contributing about 25% each to the total carbohydrate pool. Primary
26 saccharides (glucose, fructose, and sucrose) peaked at the beginning of spring (21, 17
27 and 15 ng m⁻³ respectively), indicating significant contributions of bioaerosols to the
28 total organic aerosol mass. On the other hand, higher concentrations of anhydrosugars
29 (biomass burning tracers levoglucosan, mannosan, galactosan) were recorded in winter
30 (19, 1.4 and 0.2 ng m⁻³ respectively) than in summer (9.1, 1.1 and 0.5 ng m⁻³
31 respectively). Levoglucosan was the dominant monosaccharide in winter (37% of total
32 sugars) while the low concentration measured in summer (19% of total sugars) was
33 probably due to the enhanced photochemical oxidation by hydroxyl (•OH) radicals
34 which impact anhydrosugars. Based on levoglucosan observations, biomass burning
35 was estimated to contribute up to 13% to the annual average OC measured at Finokalia.
36 Annual OC, WSOC and carbohydrate dry deposition fluxes for the two-year sampling
37 period were estimated at 414, 175 and 9 mg C m⁻² y⁻¹ respectively. Glucose and
38 levoglucosan accounted for 34% and 2% of the total sugar fluxes. According to our
39 estimations, atmospheric OC and WSOC inputs account for 0.70% and 0.71%,
40 respectively of the carbon in the annual primary production in the Cretan Sea.
41 Considering the entire Mediterranean, dry deposition of OC can provide at least 3 times
42 more C than riverine inputs of Rhone. Carbohydrate dry deposition flux represents up
43 to 0.04% of the C used for the primary production in the Cretan Sea, while <0.01% for

44 the entire Mediterranean. OC and WSOC contributions in the order of 0.33% and
45 0.14% for the whole basin further underline a minor contribution of the atmosphere in
46 the carbon cycle of the Mediterranean Sea.

47

48 **Key words:** Atmospheric aerosol; sugars; anhydrosugars; biomass burning; Eastern
49 Mediterranean Sea

50

51

52 **1. Introduction**

53 Atmospheric aerosols consist of inorganic and organic substances including gases,
54 dust, spores and bacteria (Putaud et al., 2004; Bauer et al., 2008; Koçak et al., 2012).
55 They affect air quality, interact with light and atmospheric water, and impact on
56 visibility and climate (Tragou and Lascaratos, 2003; Vrekoussis et al., 2005; Pitari et
57 al., 2015). Identified organic compounds are generally present in fine particles (< 2.5
58 μm) and account for about 2 to 11 % of the organic carbon (OC) in the atmosphere,
59 implying that most of the organic content is uncharacterized (Fu et al. 2013).
60 Interestingly enough, a similar mass percentage was reported for seawater
61 (Panagiotopoulos and Sempéré, 2005).

62 Previous investigations identified the main organic components of aerosols
63 originating from land as being lipids of higher plant waxes, primary saccharides and
64 biomass burning tracers such as levoglucosan, mannosan, and galactosan (Simoneit et
65 al., 2004; Bauer et al., 2008). In some cases these organics account for more than half
66 of the organic carbon in both particulate matter, PM_{10} and $\text{PM}_{2.5}$ in winter (Simoneit
67 and Elias, 2000; Simoneit, 2002; Caseiro et al., 2009; Yttri et al., 2009). Lipid
68 biomarkers have previously been employed to determine the sources of organic matter
69 in atmospheric particles and, more recently, to evaluate the degradation processes
70 (biotic/abiotic) occurring during the transit of these biomarkers from continental land
71 masses into the oceans and the water column (Kawamura, 2003; Sempéré and
72 Kawamura, 2003; Rontani et al., 2011). However, Marchand and Rontani (2001)
73 showed that lipid biomarkers are not always source-specific. In order to assess the
74 sources of these compounds, additional information from compound-specific isotopic
75 measurements (use of stable isotopes ^{13}C) is required.

76 Unlike lipids-indicators, anhydrosugars (levoglucosan, mannosan, and galactosan)
77 are source specific indicators. In particular levoglucosan is the single most abundant
78 compound generated during thermal breakdown of cellulose (Simoneit et al. 1999;
79 Simoneit and Elias 2000). Anhydrosugars are produced in large quantities by
80 anthropogenic activities such as agricultural waste and residential wood combustion
81 (Fine et al. 2002; Kostenidou et al. 2013) and also by forest fires (Alves et al. 2011) and
82 have been detected in atmospheric aerosols in the remotest of areas (Fu et al. 2013). In
83 addition, the relative abundance of anhydrosugars may characterize the wood burning
84 sources, particularly hardwood versus softwood combustion (Schmidl et al., 2008a;
85 Caseiro et al., 2009; Sang et al., 2013) or residential versus natural fireplace
86 combustion (Fine et al., 2004). Other sugar compounds reported in atmospheric
87 aerosols include primary saccharides (e.g. fructose, sucrose, and glucose) and sugar

88 alcohols (e.g. mannitol, sorbitol, and xylitol) originating from various sources including
89 plants, spores and bacteria (Jaenicke, 2005; Bauer et al., 2008; Deguillaume et al.,
90 2008).

91 The Mediterranean basin hosts < 1% of the world's population. It is subject to
92 various anthropogenic impacts such as pollution related to urbanization and industrial
93 activities. Moreover, extensive forest fires and dust plumes occurring in Southern
94 Europe significantly impact aerosol levels in the Mediterranean environment and
95 modify the carbohydrate content of aerosols (Sciare et al., 2008; Kanakidou et al.,
96 2011; Reche et al., 2012). Atmospheric inputs are a potential source of organic matter
97 and micronutrients in seawater (Theodosi et al., 2010a; The MerMex Group, 2011;
98 Theodosi et al., 2013a, b; Guieu et al., 2014; Violaki et al., 2015). Dissolved organic
99 carbon (DOC) plays a key role in carbon export from the surface down to the meso and
100 bathypelagic layers (Sohrin and Sempéré, 2005; Santinelli et al., 2010; Santinelli et al.,
101 2013). Organic carbon deposition by wet and dry deposition into the Mediterranean Sea
102 ranges from 10 to 20 x 10¹⁰ mol C year⁻¹ (Copin-Montégut, 1993).

103 Despite their mass abundance in aerosols few measurements of OC, WSOC and
104 other organic compounds including sugars have been reported for the Mediterranean
105 atmosphere. This study aims to provide, for the first time, data on the carbohydrate
106 content of atmospheric aerosols at a remote site in the Eastern Mediterranean (Finokalia
107 sampling station of the University of Crete). Carbohydrate data and their seasonal
108 variations along with other parameters such as OC, elemental carbon (EC), WSOC and
109 ions are presented. Emphasis is given to the annual variability of levoglucosan which
110 enables the quantification of the relative contribution of biomass burning emissions to
111 the OC in the Eastern Mediterranean.

112

113

114 **2 Experimental**

115

116 **2.1 Sampling site & procedure**

117 Aerosol samples were collected at approximately 3m above the ground at Finokalia
118 monitoring station (35°24'N, 25°60'E; <http://finokalia.chemistry.uoc.gr>), a remote
119 location in the northern coast of Crete, Greece (Figure 1). The site is not impacted by
120 local human activities but is influenced by long-range transport of continental air
121 masses and is considered as representative of the Eastern Mediterranean atmosphere
122 (Mihalopoulos et al., 1997; Kouvarakis et al., 2000; Gerasopoulos et al., 2005; Sciare et
123 al., 2008; Theodosi et al., 2011). Thus it is a particularly well-suited site for the study of
124 “aged” aerosols from Central and Eastern Europe. PM₁₀ samples were collected on pre-
125 combusted Quartz fiber filters (Whatman and Pall, 47 mm; 550 °C overnight) during
126 two campaigns lasting at least a full year from April 2009 to March 2010 and from
127 October 2012 to December 2013. Overall 143 filters were collected on a 48h basis
128 during the first campaign thus covering 80% of the year and 75 samples were collected
129 on a 24h basis during the second campaign covering 20% of the year and resulting in a
130 total of 218 samples. For both campaigns the sampling was uniformly distributed by

131 season with a total of 57 samples in spring, 49 in summer, 62 in autumn and 50 in
132 winter.

133

134 **2.2 Analytical techniques**

135 *2.2.1. Ion chromatography*

136 A portion of the quartz filters (1.5 to 2.5 cm²) was extracted in 5 to 7.5 ml of Milli-
137 Q water in an ultrasonic bath for 45 min. The solutions obtained after the extraction
138 were filtered using syringe filters (0.45 µm pore size) to remove any insoluble species
139 and were then analyzed by ion chromatography for the main anions (Cl⁻, NO₃⁻, SO₄²⁻,
140 HPO₄²⁻ and C₂O₄²⁻) and cations (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) using the technique
141 described by Paraskevopoulou et al. (2014).

142

143 *2.2.2. OC, EC, and WSOC analysis*

144 All quartz filters were analyzed for OC and EC according to the Thermal Optical
145 Transmission (TOT) technique of Birch and Cary (1996), using a Sunset Laboratory
146 OC/EC Analyzer with small modifications in the temperature program (Theodosi et al.
147 2010b; Paraskevopoulou et al., 2014). For this the EUSAAR- 2 (European Supersites
148 for Atmospheric Aerosol Research) protocol was applied (Cavalli et al., 2010). During
149 the first (OC) phase the sample (1 or 1.5 cm²) was kept in a helium atmosphere and
150 heated in four steps at 200, 300, 450 and 650 °C. In the second phase the sample was
151 heated to 500, 550, 700 and 850 °C in He/O₂ atmosphere. The detection limit of the
152 analysis was 0.26 and 0.05 µg C cm⁻² for OC and EC respectively. For WSOC analysis
153 a part of the filter (3 cm²) was extracted with 15 ml of Milli-Q water in ultrasonic bath
154 for 45 min. The sample extract was filtered and analyzed for WSOC using a TOC-
155 VCSH Shimadzu organic carbon analyzer (Theodosi et al., 2010b). Only filters from
156 the first campaign April 2009 to March 2010 were analyzed for WSOC. The reported
157 results for OC, EC and WSOC were blank corrected.

158

159 *2.2.3. Particulate carbohydrates determination*

160 *2.2.3.a. Sample preparation*

161 A portion of each quartz fiber filter (4 to 9 cm²) was extracted in 6 ml of Milli-Q
162 water by ultrasonic bath agitation for 60 min. The liquid samples extracted were
163 immediately filtered through pre-combusted quartz wool (450 °C for 6h) packed into a
164 pre-combusted Pasteur pipette to remove any insoluble particles including particles of
165 the quartz filter before injection to the chromatograph on the same day. Procedural
166 blanks collected in the field were treated and analyzed in the same manner as the
167 samples. The results showed no contamination for any target compound. Therefore the
168 data reported hereafter were neither corrected for the field blanks nor for the extraction
169 recoveries.

170

171 *2.2.3.b. Reagents and standards - calibration*

172 Standard stock solutions at a concentration of 1 mM were prepared for each of the
173 twelve carbohydrates namely: xylitol, levoglucosan, sorbitol, mannitol, mannosan,
174 galactosan, arabinose, galactose, glucose, mannose, fructose and sucrose (Sigma-

175 Aldrich). Calibrations were performed on serial dilutions from the above stock solution
176 by dissolving the twelve individual carbohydrates in Milli-Q water. All individual and
177 composite standard solutions were stored at 4 °C in the dark. For quantitative
178 determination, two calibration curves were established with standard concentrations
179 ranging from 50 to 1000 nM and from 1 to 7.5 µM. The correlation coefficients were
180 always higher than 0.99 ($R^2 > 0.99$) for all carbohydrates in both calibration curves.

181

182 2.2.3.c. HPAEC – PAD analysis

183 The liquid extracts were analyzed using an improved high-performance anion-
184 exchange chromatography (HPAEC) with pulsed amperometric detection (PAD)
185 method to quantify the twelve sugar compounds in atmospheric aerosols. Sugars were
186 separated in an anion exchange column (Carbopac PA-1; 250 mm×4 mm) and detected
187 by an electrochemical detector (ED40-Dionex) set in the pulsed amperometric mode
188 (standard quadruple-potential). The detector and column compartments were
189 maintained at 20 °C and 17 °C, respectively. Data acquisition and processing were
190 performed using the Chromeleon software. Further details of the HPAEC–PAD system
191 can be found in Panagiotopoulos et al. (2001; 2012).

192 For the separation and cleaning, three eluents were used for the HPAEC mobile
193 phase: 20mM NaOH (eluent A), Milli-Q water (eluent B) and 1.0 M NaOH (eluent C).
194 Low-carbonate sodium hydroxide solutions (NaOH) were used for the HPAEC mobile
195 phase. All solutions were sparged with helium for at least 30 min before use to remove
196 dissolved gases and were kept continuously under pure helium pressure. The complete
197 run time was approximately 53 min using a flow rate of 0.7 mL min⁻¹. The elution
198 profile included an isocratic elution for 15 min at 1 mM NaOH to detect anhydrosugars
199 and sugar alcohols followed by gradient at 19 mM NaOH for 38 min to elute the
200 primary sugars (Caseiro et al., 2009). Then, the column was flushed with 1 M NaOH
201 for 30 min and re-equilibrated with 1 mM NaOH for 19 min before the injection of the
202 next sample.

203 In order to evaluate the precision of the method, both in terms of retention time and
204 the peak area of each carbohydrate detected, the coefficient of variation (CV), defined
205 as the ratio of the standard deviation to the mean value, was determined. The results
206 showed that repeated injections (n = 6) of a standard solution of 50 nM of each sugar
207 resulted in a CV range of 0.05-0.81% (mean 0.27%) for the retention time and 2.46-
208 11.2% (mean 6.54%) for the peak area. The detection limit of the method for the
209 various carbohydrates was estimated at 25 nM. The recovery of the whole analytical
210 procedure was evaluated by extracting and analyzing five times pre-combusted quartz
211 blank filters spiked with mixtures of the sugar standards at four different concentrations
212 (100, 250, 500 and 1000 nM). The recoveries for all sugar concentrations were in the
213 range of 101–119% (mean 111%) for the 60 min extraction time.

214

215 3. Results

216 3.1 OC, EC, WSOC and Ions

217 The concentrations of OC, WSOC and EC measured in the PM₁₀ samples ranged
218 from 0.27 to 10.3 $\mu\text{g m}^{-3}$ (mean 1.93 $\mu\text{g m}^{-3}$) for OC; 0.09 to 4.37 $\mu\text{g m}^{-3}$ (mean 0.86 μg
219 m^{-3}) for WSOC, and 0.02 to 3.26 $\mu\text{g m}^{-3}$ (mean of 0.34 $\mu\text{g m}^{-3}$) for EC (Table 1). The
220 results indicated that OC and EC concentrations did not exhibit a seasonal variation,
221 remained almost constant throughout the year. Lower concentrations were observed
222 from September till January due to wash out by rain. Similarly, WSOC concentrations
223 did not show a clear seasonal cycle. Nevertheless, slightly higher values were measured
224 in the summer, possibly linked with enhanced photochemistry which renders the
225 organic fraction more water-soluble (Bougiatioti et al., 2013). WSOC comprised 6.22%
226 to 82.0% of OC with a mean of 45.1% and no distinct differences between summer
227 (51.1%) and winter (47.2%). This contribution is lower than the $67\pm 7\%$ reported for
228 PM_{2.5} at the same site (Bougiatioti et al. 2011), but in the same range as the contribution
229 of 50% for PM₁₀ samples collected at an urban site in Norway (Yttri et al., 2007).

230 In our samples, ions were characterized by an abundance of non-sea salt potassium
231 nss-K⁺ with a range of 38.2 to 885 ng m^{-3} (mean 198 ng m^{-3}). Non-sea salt potassium is
232 a typical tracer of biomass burning (Cachier et al., 1991). The levels of oxalates were
233 also high, in the range of 7.32 to 913 ng m^{-3} (mean 277 ng m^{-3}) (Kawamura et al., 1996;
234 Kawamura and Ikushima, 1993; Laongsri and Harrison, 2013). This was especially so
235 in the winter/early spring and summer period. These observed nss-K⁺ levels indicate
236 that Finokalia is influenced by biomass burning emissions, which corroborates well
237 with previous investigations at the same site (Sciare et al., 2008). Our results also
238 showed that SO₄²⁻, NH₄⁺, and NO₃⁻ concentrations exhibited peaks during winter (3.16,
239 0.39 and 1.45 $\mu\text{g m}^{-3}$ respectively) and in spring/summer (5.01, 0.97 and 1.32 $\mu\text{g m}^{-3}$
240 respectively). The winter peak is most likely associated with anthropogenic activities
241 such as domestic heating and long range transport. The summer peak can be attributed
242 to the absence of precipitation in conjunction with the induced photochemical reactions
243 during that season which lead to secondary aerosol formation in the area (Mihalopoulos
244 et al., 1997).

245

246 **3.2 Distribution of carbohydrates in PM₁₀ particles**

247 In 2009-2010 total sugars concentration in PM₁₀ samples ranged from 11.1 to 334
248 ng m^{-3} (mean 63.0 ng m^{-3}) and were higher than measurements in 2012-2013 (6.41 to
249 92.5 ng m^{-3} ; mean 31.5 ng m^{-3}) (Figure 2). The mean total sugars concentration for both
250 periods was 57.7 ng m^{-3} (median 41.8 ng m^{-3}) and was comparable to observations at a
251 rural site in Portugal (Pio et al., 2008), but lower compared to urban sites (71-77 ng m^{-3})
252 across the Mediterranean (Tel Aviv, Graham et al., 2004; Rehovot, Burshtein et al.,
253 2011; and Barcelona, Reche et al., 2012) (Table 2). The contribution of sugars to the
254 OC and WSOC content in the PM₁₀ particles varied from 0.18 to 22.9% with a mean of
255 3.30% and a median of 2.72% for OC and 1.4 to 66.6% with a mean of 10.6% and
256 median of 7.3% for WSOC. The contribution of sugars to the OC in our samples falls in
257 the range of values reported previously for Barcelona which ranged from 1.4 to 2.2 %
258 with a mean of mean 2.0% (Reche et al. 2012). Similar values of 1.1 to 2.4% with a
259 mean of 1.4% were reported for Tel Aviv (Graham et al., 2004) and for both rural (0.1

260 to 3.1%, mean 0.8%) and an urban (0.2 to 3.8%, mean 1%) background sites in Norway
261 (Yttri et al., 2007).

262 Anhydrosugars in particular accounted for 0 to 0.43% (mean 0.06%) of the PM₁₀
263 mass, 0.04-9.05% (mean 0.9%) of the OC, and 0.29-14.1% (mean 2%) of the WSOC.
264 The highest mean contribution of anhydrosugars to the OC (1.4%) and WSOC (2.9%)
265 was observed in winter, highlighting the strong influence of biomass burning on winter
266 aerosols and enhanced chemical stability of levoglucosan in the atmosphere during the
267 winter period compared to summer (see below). The above observation has also been
268 reported for Barcelona by Reche et al. (2012) who found a significant correlation
269 between levoglucosan, OC and K⁺ in PM_{2.5}, especially at night, suggesting the transport
270 of biomass burning emissions from the regional scale towards the city.

271 Among the sugars identified, levoglucosan and glucose exhibited the highest
272 concentrations, ranging from 0.89 to 142 ng m⁻³ (mean 12.6 ng m⁻³) and from 0.48 to
273 110 ng m⁻³ (mean 13.5 ng m⁻³) respectively. On average these two accounted for about
274 25% each to the total sugars concentration as shown in Table 2 and Figure 2. Fructose
275 and sucrose concentrations ranged from below the detection limit to 102 ng m⁻³ and
276 were the next most abundant accounting for 18% and 15% respectively of total sugars.
277 Mannitol accounted for 10% of total carbohydrates, whereas arabinose, galactose, and
278 mannose represented < 4% of total sugars and their concentrations ranged from below
279 the detection limit to 13.5 ng m⁻³ (Table 2; Figure 2). Our results also showed higher
280 levels of glucose, fructose, and sucrose in the 2009-2010 campaign (accounting for
281 61% of total sugars) relative to the 2012-2013 campaign (48% of total sugars). This
282 further indicates significant inter-annual variation for these compounds from their
283 sources (Figure 2). Levoglucosan, mannitol, mannosan, glucose and sucrose
284 concentrations measured at the Finokalia remote coastal station were 2 to 8 times lower
285 than those recorded in urban areas across the Mediterranean Sea (Graham et al., 2004;
286 Burshtein et al., 2011; Reche et al., 2012) as also shown in Table 2 and Figure 2.
287 Concentrations of mannitol and glucose in our study were similar to those recorded in
288 European cities (Yttri et al., 2007; Pio et al., 2008). However, levoglucosan and
289 mannosan concentrations at Finokalia are much lower (16 and 34 times respectively)
290 than those at a background site in Norway (Yttri et al., 2007).

291

292 **3.3 Seasonal variation of sugars at the Finokalia site**

293 Total sugars concentration in PM₁₀ samples showed a seasonal variation with higher
294 values in spring (20.8-266 ng m⁻³, mean 77 ng m⁻³) and lower values in autumn (7.41-
295 311 ng m⁻³, mean 39.3 ng m⁻³) (Figure 3).

296 The observed concentrations of anhydrosugars (Figure 3; Figure 4a) were higher in
297 winter (mean for levoglucosan and mannosan of 18.6 and 1.96 ng m⁻³ respectively) than
298 in summer (9.08 and 1.10 ng m⁻³). This is in agreement with previous investigations in
299 other European sites for the three anhydrosugar isomers (Yttri et al., 2007; Burshtein et
300 al., 2011; Reche et al., 2012). Xylitol and sorbitol closely followed anhydrosugar
301 patterns and were higher in winter than in summer. In contrast, mannitol concentrations
302 showed a maximum in late summer to early autumn, decreased in winter and peaked

303 again in late spring. A similar seasonal pattern has been reported by Burshtein et al.
304 (2011) for Israel in the Eastern Mediterranean.

305 Our results also showed that glucose, fructose and sucrose exhibited their highest
306 concentrations during spring and then decreased as the growing season progressed
307 (Figure 4b). These results reflect the biosynthesis of these compounds during spring
308 and are consistent with previous investigations (Medeiros et al., 2006; Pio et al., 2008).
309 A similar pattern was observed for arabinose, galactose, and mannose.

310

311 **4. Discussion**

312 **4.1 Climatology**

313 To better understand the seasonal variability of sugars in our site as well as the
314 factors controlling their variability a short overview of air masses and aerosol sources
315 prevailing in the area is presented.

316 Five-day back-trajectories were computed using the Hysplit Dispersion Model
317 (Hybrid Single-Particle Lagrangian Integrated Trajectory) and used to determine the
318 source region of air masses arriving at the site during the studied period. Over the
319 course of a year, the northern sector is the most important with almost half of the air
320 masses arriving at Finokalia originating from Central and Eastern Europe as well as
321 part of western Turkey. During the warm periods when the photochemical activity is at
322 its highest the contribution of this sector reaches up to 75%. During the cold season the
323 prevalence of the N/NW sector is less pronounced and important transport from the
324 southern sector is responsible for Sahara dust transport (S/SW winds; occurrence up to
325 20%). The latter, takes place during the transition periods (spring/autumn)
326 (Mihalopoulos et al., 1997). Previous works have also indicated that due to strong
327 winds prevailing in the area contribution from local sources is very limited and that the
328 site is mainly influenced by “aged” aerosols transported to Finokalia from Central and
329 Eastern Europe (North/Northwestern winds) as well as from Sahara Desert (S/SW
330 winds) (Mihalopoulos et al, 1997).

331 The site is also strongly influenced by long-range transport of biomass burning
332 emissions during spring and summer, as it has been reported by Sciare et al. (2008).
333 Fires from countries from Central and Eastern Europe as well as countries bordering the
334 Black Sea (Bulgaria, Romania, Moldavia, Ukraine, and Russia) are expected to have a
335 significant impact over the E. Mediterranean since they are located in the northern wind
336 sector of Crete Island, reaching its highest contribution during the warm periods. These
337 fires are most likely to correspond to agricultural waste burning practices (post-
338 harvesting for the summer months) (Sciare et al., 2008). In addition forest fires from the
339 Mediterranean can also influence the site (Bougiatioti et al., 2014).

340

341 **4.2 Seasonal variability of total and individual sugars in the Eastern** 342 **Mediterranean**

343 The total sugars concentration in atmospheric aerosols (PM₁₀) exhibited two
344 seasonal maxima. The first one in the spring growing season and the second one in
345 winter when leaf senescence and microbial degradation of primary saccharides occurs

346 (Figure 3). During the dry season (spring, summer), the prevailing meteorological
347 conditions (e.g. no rain) along with the enhanced emission from primary sources (e.g.
348 vascular plants) may be responsible for the high concentrations (Figure 4b). In winter
349 the high sugar concentrations are most likely related to the high anhydrosugar content
350 of the samples (Figures 3 and 4a).

351 Levoglucosan in particular was by far the most dominant sugar in winter time
352 (mean 37% of the total sugar composition; Figure 2). This suggests that biomass
353 burning processes contribute significantly to the PM₁₀ sugar content, further
354 highlighting the importance of these processes in the Eastern Mediterranean (Sciare et
355 al., 2008). In addition, the low photooxidative decay of levoglucosan in the atmosphere
356 during winter time can also enhance its levels.

357 Indeed recent data from laboratory and field studies have provided compelling
358 evidence that levoglucosan is not inert in the atmosphere and that one of the potentially
359 strongest degradation pathways is the photochemical oxidation by •OH radicals
360 (Hennigan et al., 2010; Hoffmann et al., 2010; Mochida et al., 2010). Previous
361 investigations indicated that the 24-hour mean •OH concentrations at the Finokalia
362 station in the Eastern Mediterranean during summertime (August) are of the order of
363 $4.5 \pm 1.1 \times 10^6 \text{ cm}^{-3}$ (Berresheim et al., 2003). Such high •OH values imply a lifetime
364 for levoglucosan of 6 to 7h (3h if only daytime is considered) which results in the
365 significant degradation of levoglucosan during long-range transport in summer. This
366 explains the low summer levels of levoglucosan (Figure 4a).

367 Mannitol concentrations increased throughout the growing season, peaking in
368 summer and early autumn, indicating an input from primary biogenic sources such as
369 airborne fungal spores, algae and/or various vascular plants (Pashynska et al. 2002;
370 Bauer et al., 2008; Cheng et al., 2009). Glucose, fructose and sucrose concentrations
371 followed the mannitol pattern and were higher in spring (Figure 4b). This seasonality is
372 consistent with sucrose being an important sugar in developing flower buds (Bieleski et
373 al., 1995), while sucrose and glucose are the most abundant storage and photosynthetic
374 carbohydrates in plants (e.g. pollen, plant walls, fruit and their fragments; Pacini et al.,
375 2006).

376 Figure 5 presents the variability of the three main sugars levoglucosan, mannitol
377 and glucose, representing the three main sources: biomass burning, primary biogenic
378 sources and fungal spores as a function of air masses origin for summer and winter. Air
379 masses origin can impact sugar and anhydrosugar levels mainly during summer time,
380 with the highest levels observed under northern air masses influence (Russia, Ukraine,
381 Bulgaria and Turkey) and the lowest under the southern one (Sahara desert). It worth
382 noting that the lower levoglucosan levels observed during summer time are most
383 probably due to the enhanced photooxidation of this compound (see discussion below).

384

385 **4.3 Carbohydrate origins at the Finokalia station**

386 *4.3.1 Correlations between carbohydrates, ions, OC, EC and WSOC*

387 During the period studied anhydrosugar concentrations were strongly correlated
388 (levoglucosan vs mannosan, $r=0.82$; levoglucosan vs galactosan, $r=0.74$; mannosan vs
389 galactosan, $r=0.63$; $n=218$). This is presented in Table 3 and implies a common origin

390 for these compounds. Investigating these correlations on a seasonal basis (not shown)
391 the highest correlations were found to be in winter ($r=0.93-0.95$; $n=50$) reflecting their
392 common sources such as residential wood, coal, and agricultural waste burning
393 (Simoneit et al., 1999; Simoneit et al., 2004). These results are further supported by a
394 positive correlation of $nss-K^+$ (typical biomass tracer) with anhydrosugars during
395 winter ($r=0.61, 0.54$ and 0.71 for $nss-K^+$ vs levoglucosan, mannosan and galactosan,
396 respectively; $n=50$).

397 Anhydrosugars also correlated significantly with OC ($r=0.33-0.41$; $n=205$) and
398 WSOC ($r=0.34-0.69$; $n=132$) during the entire sampling period (Table 3). Notably,
399 significant relations of all three anhydrosugars were obtained with OC during winter
400 ($r=0.67, 0.74$ and 0.68 for levoglucosan, mannosan and galactosan respectively; $n=50$)
401 and summer ($r=0.58$ and 0.48 for levoglucosan and mannosan; $n=49$). A similar pattern
402 was also observed for WSOC during winter ($r=0.85-0.90$; $n=50$). The above results
403 clearly indicate that biomass-burning emissions from regional sources in wintertime are
404 important contributors of OC and WSOC in PM_{10} .

405 Sugars in general and anhydrosugars in particular did not exhibit any significant
406 correlation with ions throughout the sampling period (Table 3). The exception was
407 levoglucosan during the winter which exhibited linear correlations with major ions such
408 as $nss-K^+$ that are, as mentioned above, possibly associated with biomass burning
409 processes.

410 Our results also showed linear correlations ($r=0.48-0.78$; Table 3; $n=218$) among
411 the main primary sugars (i.e. fructose, glucose, and sucrose). These have been proposed
412 as markers for fugitive dust from biologically active surface soils (Simoneit et al., 2004;
413 Bauer et al., 2008). Primary sugars were strongly correlated to each other during
414 summer ($r=0.79-0.89$; $n=49$, $p<0.001$), inferring to their common biological origin
415 during that period. Significant correlations were also observed in summer between the
416 primary sugars, glucose and fructose versus arabinose and galactose (glucose vs
417 arabinose, $r=0.66$; glucose vs galactose, $r=0.61$; fructose vs galactose, $r=0.78$; $n=49$)
418 again indicating a common continental source.

419

420 4.3.2 Levoglucosan to mannosan ratio: biomass burning tracers

421 The relative ratio of levoglucosan to mannosan (L/M) has been used for source
422 reconstruction of combustion-derived by products in atmospheric aerosols (Schmidl et
423 al., 2008a; Caseiro et al., 2009; Fabbri et al., 2009; Sang et al., 2013). Throughout the
424 sampling period for our two campaigns the L/M ratio ranged from 2.28 to 88.2 in PM_{10}
425 samples (15.5 ± 14.8 ; median 9.97). Despite such a wide range in the ratios we observed
426 only a small seasonal variation of the averaged seasonal L/M ratio (spring= 15.9 ± 8.9 ,
427 median=11.2; summer= 15.5 ± 13.5 , median=10.2; autumn= 13.0 ± 11.4 , median=8.6;
428 winter= 17.1 ± 13.4 , median=10.9).

429 As indicated above, levoglucosan is subject to intense photochemical oxidation
430 reactions by $\cdot OH$ radicals especially in summer (lifetime of about 3h during daytime).
431 Our results indicated that the L/M ratio shows no significant seasonal variation which
432 further suggests that photochemistry has little or no impact on the L/M values. This
433 suggests that mannosan, which is an epimer of levoglucosan (an isomer that differs in

434 the position 2 of the $\cdot\text{OH}$ function, i.e axial vs equatorial) may be subject to the same
435 photochemical reactions with perhaps slightly different kinetics.

436 The most common hardwoods in Crete are olive trees, while beech and pine trees
437 are classified as softwoods. The reported L/M ratios are: for softwood=3-10,
438 hardwood=15-25, herbaceous tissues=25-50, crop residues>40 (Schmidl et al., 2008a,
439 b; Engling et al., 2009, 2014; Mkoma et al., 2013). The range of L/M values observed
440 throughout the sampling period (2.3 to 88.2; median 10), with relatively small seasonal
441 variation (between 13 and 17), could suggest the existence of a common source of
442 biomass burning in the region during the whole year which cannot be clearly
443 characterized in terms of the type of wood being burnt only on the basis of the L/M
444 ratio. Indeed, as it has been previously reported by Sciare et al. (2008). Finokalia
445 station is mainly affected by biomass burning emissions from agricultural wastes (post-
446 harvest wheat residual) from Central and Eastern Europe and countries surrounding the
447 Black Sea with contribution from forest fires (especially during summer).

448

449 **4.4 Non photooxidized levoglucosan concentrations**

450 The annual variations of levoglucosan and nss-K^+ concentrations are depicted in
451 Figure 6a. A bimodal pattern is clearly observed for nss-K^+ with early spring and mid-
452 summer maxima while levoglucosan exhibits only a single maximum in winter. nss-K^+
453 may originate from several sources such as dust and biomass burning (Mihalopoulos et
454 al., 1997). Therefore, in order to eliminate the influence of dust transport from N.
455 Africa on nss-K^+ levels, samples under prevailing southerly and south-westerly winds
456 were excluded and the same bimodal pattern was observed (not shown). Assuming i)
457 that low photooxidation occurs in winter, and ii) considering identical emission sources
458 for both levoglucosan and nss-K^+ throughout the year (supported by the existence of a
459 main common source of biomass burning in the region during the whole year, Sciare et
460 al., 2008), we can estimate the concentration of levoglucosan before photooxidation
461 reduces its levels using the constant L/ nss-K^+ slope of their linear regression equal to
462 0.117, $r=0.63$ (0.126 ± 0.08 ; median=0.117; $n=42$ in winter). Figure 6b depicts the daily
463 concentrations of levoglucosan and nssK^+ in PM_{10} aerosols at Finokalia indicatively
464 during the first winter campaign (2009-2010). Figure 6c reflects the annual variability
465 of the estimated levoglucosan concentrations which exhibit two maxima in winter/early
466 spring and in summer, in accordance with Sciare et al. (2008) and Reche et al. (2012).
467 These studies suggested that the Eastern Mediterranean is under the influence of
468 biomass burning aerosols during winter/early spring and summer. It must be kept in
469 mind that during summer levoglucosan levels were decreased by 54% due to the
470 enhanced photooxidative decay, when both measured and estimated levoglucosan
471 concentrations are considered (9.40 and 20.1 ng m^{-3} , respectively).

472

473 **4.5 Relative contribution of biomass burning to OC**

474 The L/OC ratio has been previously used to estimate the contributions of biomass
475 burning sources in aerosols (Andreae and Merlet, 2001). Calculated L/OC ratios show
476 small variation, typically ranging from 8.0 to 8.2% for the various sources of biomass
477 burning emissions such as savanna, grassland, tropical and extratropical forests, biofuel

478 and agricultural residues (Andreae and Merlet, 2001). In this study, we used the value
479 of 8.1% to estimate the percentage contribution of biomass and biofuel burning
480 activities to the OC in each of the PM₁₀ aerosol samples (Table 4). The estimated
481 levoglucosan levels were used in our calculations as discussed in the previous section.

482 On this basis we estimated that biomass burning in the East Mediterranean
483 contributed annually 13% to the OC in PM₁₀ aerosols at Finokalia station (Table 4).
484 The highest mean contributions from biomass burning were found, as expected, during
485 winter 16.0%±10.9% (median 13%). The estimated annual contribution of 13% is in
486 good agreement with the 14% value reported by Sciare et al. (2008) for the
487 Mediterranean Basin. These annual mean values are also comparable to those reported
488 for various sites affected by biomass burnings (12% Portugal, Puxbaum et al., 2007;
489 19-21% Barcelona, Reche et al., 2012).

490

491 **4.6 Dry Deposition fluxes of carbohydrates in the Mediterranean Sea**

492 *4.6.1 Fluxes and carbohydrate speciation*

493 In order to investigate the atmospheric input of carbon in the form of carbohydrates
494 in the Cretan Sea we calculated the bulk deposition fluxes (F_x) of the individual sugar
495 concentrations (C_x) using their specific settling velocities (V_d) and the following
496 equation:

$$497 \quad F_x = C_x \cdot V_d \quad (1)$$

498 In the past, a number of approaches have been applied to calculate dry atmospheric
499 deposition flux, including mass-size distributions in the aerosol population, usually
500 evaluated from virtual impactors (Bergametti, 1987), from theoretical models (Dulac et
501 al., 1989), the deployment of surrogate collectors (Dolske and Gatz, 1985; Baeyens et
502 al., 1990) or the difference between total deposition and wet deposition measurements
503 (Migon et al., 1997).

504 Unpublished data from the Finokalia station indicated that anhydrosugars are
505 mainly associated with the fine fraction particles (PM₁) whereas primary sugars with
506 the coarse fraction, which is in agreement with previous investigations (Schkolnik et
507 al., 2005; Fuzzi et al., 2007; Bauer et al., 2008; Deguillaume et al., 2008). For this
508 reason, we assumed different deposition velocities for coarse and fine particles of 2 cm
509 s⁻¹ and 0.1 cm s⁻¹ respectively (Theodosi et al., 2010a). It is well known that there is no
510 widely accepted values for deposition velocities and uncertainty in the used values can
511 be as high as 100%. However, works performed at Finokalia for nutrients and trace
512 metals with size segregated aerosol sampling and by comparing their fluxes with other
513 methods (Kouvarakis et al., 2001; Theodosi et al., 2010) found that deposition
514 velocities values of 2 cm s⁻¹ and 0.1 cm s⁻¹ for coarse and fine particles respectively can
515 be considered as best guess for flux estimates for the area. Our calculation give rise to
516 an annual total sugar fluxes of 9.19 mg C m⁻² y⁻¹. Primary sugars (7.55 mg C m⁻² y⁻¹)
517 and sugar alcohols (1.43 mg C m⁻² y⁻¹ of which 1.31 mg C m⁻² y⁻¹ was mannitol)
518 exhibited higher deposition fluxes than anhydrosugars (0.22 mg C m⁻² y⁻¹) (Figure 7).

519 Among the primary sugars, glucose was the dominant monosaccharide in PM₁₀
520 particles (approximately 27% of the total carbohydrates concentration) with the highest

521 deposition flux ($3.14 \text{ mg C m}^{-2} \text{ y}^{-1}$) accounting for 34% of the total carbohydrates flux
522 (Figures 2, 7). A similar glucose flux percentage (approximately 33% of the
523 carbohydrates) was reported for dissolved and particulate carbon delivered by the
524 Rhone River in the western Mediterranean Sea (Panagiotopoulos et al., 2012).
525 Although marine dissolved carbohydrate measurements are not available for the
526 Mediterranean Sea, literature data from the Pacific and Arctic Ocean suggest that
527 glucose is also the dominant sugar in marine surface waters accounting for 25 to 50%
528 of total carbohydrates (Skoog and Benner, 1997; Sempéré et al., 2008; Panagiotopoulos
529 et al., 2014). These results may therefore indicate that external carbohydrate inputs
530 from the atmosphere and rivers may potentially contribute to sustaining the level of
531 glucose in dissolved organic matter (DOM).

532 The above derived dry deposition fluxes of carbohydrates can be extrapolated to the
533 entire Mediterranean Sea with surface area of $2.5 \times 10^6 \text{ km}^2$ ($1.67 \times 10^6 \text{ km}^2$ for the
534 Eastern Mediterranean and $0.86 \times 10^6 \text{ km}^2$ for the Western Mediterranean; Candela et
535 al., 1989). Although such extrapolation is prone to a high uncertainty (factor of 2 at
536 least), an order of magnitude estimation is always useful especially when a comparison
537 to other sources is required. On this basis dry deposition carbohydrate fluxes are equal
538 to $2.30 \times 10^{10} \text{ g C y}^{-1}$ ($0.19 \times 10^{10} \text{ moles C y}^{-1}$) and glucose flux equal to $0.79 \times 10^{10} \text{ g C}$
539 y^{-1} ($0.07 \times 10^{10} \text{ moles C y}^{-1}$). Our results indicate that atmospheric inputs from dry
540 deposition alone could contribute almost twice the total carbohydrate input of the
541 Rhone River into the Mediterranean Sea ($0.11 \times 10^{10} \text{ moles C y}^{-1}$, (Panagiotopoulos et
542 al., 2012).

543

544 *4.6.2 Significance of carbohydrates deposition on the seawater productivity*

545 The annual carbohydrates fluxes calculated for the two-year sampling period are
546 equal to $9.19 \text{ mg C m}^{-2} \text{ y}^{-1}$ ($13.5 \text{ mg C m}^{-2} \text{ y}^{-1}$ during April 2009 to March 2010 and
547 $4.95 \text{ mg C m}^{-2} \text{ y}^{-1}$ during October 2012 to December 2013). Given that OC and WSOC
548 are distributed mainly in the fine mode with a fine to coarse ratio of 70/30 (Koulouri et
549 al., 2008, Bougiatioti et al., 2013) the annual dry deposition fluxes of OC and WSOC
550 are $414 \text{ mg C m}^{-2} \text{ y}^{-1}$ (n= 205) and $175 \text{ mg C m}^{-2} \text{ y}^{-1}$ (n=132) respectively (Figure 8).
551 Total carbohydrates thus account for 2% and 5% of these fluxes respectively. Assuming
552 that these values are valid for the entire Mediterranean basin, dry deposition OC and
553 WSOC input to the sea of 1 and $0.42 \times 10^{12} \text{ g C y}^{-1}$ can be estimated, respectively.
554 Direct measurements of total OC (TOC) in rainwater at Crete in the Eastern
555 Mediterranean indicate that wet deposition can account for $1.5 \times 10^{12} \text{ g C y}^{-1}$
556 (Economou and Mihalopoulos, 2002). Similar values of 0.4 to $13.1 \times 10^{12} \text{ g C y}^{-1}$ were
557 obtained for total (wet plus dry) atmospheric fluxes at Cap Ferrat (Pulido-Villena et al.,
558 2008). Sempéré et al. (2000) estimated the total (dissolved plus particulate) OC fluxes
559 of the Rhone River to the Mediterranean Sea to be $2.7 \times 10^{10} \text{ moles C y}^{-1}$ ($0.3 \times 10^{12} \text{ g}$
560 C y^{-1}). This suggests that the total TOC input from atmospheric deposition could be up
561 to 9 times higher than the Rhone river inputs.

562 Considering an annual primary production (PP) of $24.8 \text{ g C m}^{-2} \text{ y}^{-1}$ for the South
563 Aegean Sea (upper 50 m at four stations; Ignatiades, 1988), atmospheric carbohydrate
564 dry deposition accounts for about to 0.37‰ of this PP, and OC and WSOC about 0.70

565 and 0.71% respectively. Taking an average annual PP of $125 \text{ g C m}^{-2} \text{ y}^{-1}$ for the entire
566 Mediterranean (Antoine et al., 1995; The MerMex Group, 2011; Figure 8) our results
567 indicate that OC, WSOC and carbohydrate contributions to PP are of the order of
568 0.33%, 0.14% and $<0.01\%$, respectively.

569

570 **5. Summary and concluding remarks**

571 The role of biomass combustion and primary bio-particles in atmospheric PM_{10}
572 aerosol in the Eastern Mediterranean over a two-year period was estimated by studying
573 sugar tracers. Sugars concentration ranged from 6 to 334 ng m^{-3} and their average
574 contributions to the OC and WSOC pools were 3 and 11% respectively. Averaging over
575 the two-year study period, glucose and levoglucosan were the two most abundant
576 sugars and contributed equally about 25% of the total sugar concentration in PM_{10}
577 aerosols. Fructose, sucrose and mannitol represented 18%, 15% and 10% of total
578 carbohydrates concentrations, respectively, while the contribution of the remaining
579 sugars was less than 4%.

580 The concentration of primary saccharides (sum of glucose, fructose and sucrose)
581 peaked at 53 ng m^{-3} during spring and then decreased as the growing season progressed
582 (22 ng m^{-3}), reflecting the biosynthesis of these compounds by terrestrial vascular
583 plants. On the other hand, the highest concentrations of anhydrosugars (sum of
584 levoglucosan, galactosan, and mannosan) were recorded in winter (20 ng m^{-3}) rather
585 than in summer (11 ng m^{-3}) due to enhanced photochemical oxidation by $\cdot\text{OH}$ radicals.
586 Levoglucosan, which is associated with biomass combustion, was the dominant
587 monosaccharide in winter (37% of total sugars) with lower concentrations in the
588 summer (19% of total sugars). We estimate that atmospheric oxidation by $\cdot\text{OH}$
589 decreases levoglucosan levels by 54% during summer. The levoglucosan
590 concentrations estimated assuming no photooxidation of levoglucosan in summer
591 exhibit a bimodal cycle with two maxima (winter/early spring and summer). These
592 results clearly highlight the importance of such processes in the Eastern Mediterranean
593 Sea.

594 The annual mean contribution of biomass burning to OC in the Eastern
595 Mediterranean was equal to 13% in PM_{10} . Levoglucosan to mannosan ratios varied
596 between 13 and 17 for different seasons, indicating possibly a common source of
597 biomass burning in the region during the whole year. Annual deposition fluxes of total
598 carbohydrates in PM_{10} particles were estimated to be $9.19 \text{ mg C m}^{-2} \text{ y}^{-1}$. Glucose and
599 levoglucosan accounted for 34% and 2%, respectively of the total fluxes indicating
600 different deposition fluxes of primary sugars and anhydrosugars in the Cretan Sea.

601 By considering the annual PP in the Cretan Sea our results indicate OC, WSOC and
602 sugar contributions of the order of 0.70%, 0.71 and 0.04% respectively. While, for the
603 entire Mediterranean their dry deposition represents up to 0.33%, 0.14% and $<0.01\%$ of
604 the C used for the PP respectively.

605 Finally TOC input from total atmospheric deposition could be up to 9 times higher
606 than the Rhone river inputs highlighting the important role of the atmosphere on the
607 Mediterranean Sea carbon cycle.

608

609 **Acknowledgements**

610 This work was funded by the project PANOPLY (Pollution Alters Natural aerosol
611 composition: implications for Ocean Productivity, cLimate and air qualItY). C.
612 Theodosi acknowledges financial support from the State Scholarship Foundation (ΠΕ2-
613 SHORT TERMS-19904) within the framework for action “State Scholarships
614 Foundation’s mobility grants program for the short term training in recognized
615 scientific/research centers abroad for doctoral candidates or postdoctoral researchers in
616 Greek universities or research centers”. This study was carried out as a part of the OT-
617 MED-Labex (AIOLOS project) within WP4 MERMEX/MISTRALS and contributes to
618 the international SOLAS project. We are grateful to Elvira Pulido, co-leader of WP4-
619 MERMEX for suggestions on the manuscript.

620

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- 919

920 **Figure captions:**

921

922 **Figure 1.** Location of the remote background sampling site at Finokalia, Crete, Greece.

923

924 **Figure 2.** (a) Mean values of individual sugars and total sugars concentrations (ng m^{-3})
925 in PM_{10} aerosol samples collected at Finokalia station during both 2009-2010 and
926 2012-2013 sampling campaigns. Error bars represent the standard deviation of the
927 concentrations, time series of (b) levoglucosan, mannosan and (c) sucrose, glucose in
928 PM_{10} aerosols at Finokalia for both sampling campaigns.

929

930 **Figure 3.** Seasonal variability of sugar composition (mean \pm standard deviation) of
931 aerosols collected at the Finokalia station during both sampling periods 2009-2010 and
932 2012-2013. Total sugars composition represents the sum of all sugars measured. Total
933 anhydrosugar (levoglucosan, mannosan, and galactosan) and primary sugar (glucose,
934 fructose, and sucrose) concentrations are also given.

935

936 **Figure 4.** Mean seasonal cycle of concentrations for (a) anhydrosugars: levoglucosan,
937 mannosan and galactosan and (b) primary sugars: glucose, fructose and sucrose,
938 calculated from daily values for the periods April 2009 to March 2010 and October
939 2012 to December 2013.

940

941 **Figure 5.** (a) Levoglucosan, (b) mannitol and (glucose) variability as a function of air
942 masses origin for winter and summer.

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944 **Figure 6.** (a) Temporal variation of levoglucosan and nssK^+ , (b) time series of
945 levoglucosan and nssK^+ in PM_{10} aerosols at Finokalia for the winter period December
946 2009 to February 2010 and (c) temporal variation of measured and estimated
947 levoglucosan concentrations in PM_{10} aerosol at Finokalia.

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949 **Figure 7.** Estimated carbohydrate fluxes ($\text{mg C m}^{-2} \text{y}^{-1}$) for the Eastern Mediterranean
950 during both campaigns (April 2009 to March 2010 and October 2012 to December
951 2013), divided into primary sugars, sugar alcohols, and anhydrosugars. Numbers in
952 parentheses provide the relative contribution of the individual sugar to the total
953 carbohydrate flux.

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955 **Figure 8.** Organic carbon inputs from the atmosphere (PM_{10} particles) and rivers
956 (Rhône River) in terms of OC, WSOC and sugars in the Western and Eastern
957 Mediterranean Sea.

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962 **Table 1.** The mean, standard deviation, median and range of measured concentrations
 963 for PM₁₀ aerosol samples, collected at Finokalia during the two campaigns (April 2009-
 964 March 2010 and October 2012-December 2013).

965

$\mu\text{g m}^{-3}$	PM ₁₀ (n=218)			
	Mean± Stdev	Median	min	max
PM ₁₀	31.6±32.1	22.0	6.28	235
OC	1.93±1.26	1.68	0.27	10.3
EC	0.34±0.31	0.27	0.02	3.26
WSOC (n=132)	0.86±0.61	0.80	0.09	4.37
Cl ⁻	1.39±1.56	0.72	0.01	7.61
Br ⁻	0.01±0.01	0.01	0.00	0.09
NO ₃ ⁻	1.23±0.80	1.18	0.00	4.47
PO ₄ ³⁻	0.23±0.33	0.12	0.00	2.74
SO ₄ ²⁻	3.49±1.77	3.35	0.40	8.72
C ₂ O ₄ ²⁻	0.28±0.18	0.28	0.01	0.91
Na ⁺	1.89±1.51	1.45	0.05	10.8
NH ₄ ⁺	0.65±0.67	0.32	0.00	5.60
K ⁺	0.21±0.13	0.17	0.04	0.88
Mg ²⁺	0.31±0.20	0.21	0.00	9.67
Ca ²⁺	1.59±2.10	0.62	0.00	16.0

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977 **Table 2.** Mean and range values of carbohydrates in PM₁₀ aerosol sampled at Finokalia
 978 and other Mediterranean sites.

Sugars (ng m ⁻³)	PM ₁₀		TSP		PM ₁₀		PM _{2.5}	
	Mean	range	Mean	range	Mean	range	Mean	range
Xylitol	0.92	nd-4.96	-	-	-	-	-	-
Levoglucozan	12.6	0.89-142	80	39-140	-	-	60	20-100
Sorbitol	0.72	nd-5.81	-	-	-	-	-	-
Mannitol	5.81	nd-47.2	12	8-21	49.2 (winter) 15.1 (summer)	5.57-138	-	-
Mannosan	1.53	nd-13.2	4	2-9.7	-	-	6	2-10
Galactosan	0.36	nd-3.66	4	1.5-6	-	-	5	1-9
Arabinose	1.37	nd-13.5	-	-	-	-	-	-
Galactose	0.91	nd-9.69	-	-	-	-	-	-
Glucose	13.5	0.48-110	21	12-27	-	-	-	-
Mannose	1.71	nd-11.7	-	-	-	-	-	-
Fructose	10.4	0.83-81.0	-	-	-	-	-	-
Sucrose	8.44	nd-102	28	8-59	-	-	-	-
Total Sugars	57.7		77		-		71	
Sampling	24 months (n=218)		11 days/Dec (n=9)		12 month (n=60)		2months/Feb-Mar (202)	
Location	E. Mediterranean (rural site; Finokalia, GR)		E. Mediterranean (urban site; Tel Aviv, IL)		E. Mediterranean (urban site; Rehovot, IL)		W. Mediterranean (urban site; Barcelona, ES)	
Reference	This study		Graham et al. (2004) **		Burshtein et al. (2011)		Reche et al. (2012)	

979 *nd: not detected

980 ** Estimated concentrations from author's data.

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984 **Table 3.** Pearson product-moment correlation coefficient (r) between the elements
 985 analyzed in the PM₁₀ fraction collected at Finokalia sampling station (n=218). Only
 986 correlations with r greater than 0.30 are presented (p<0.001).

987

r	PM ₁₀	Xylitol	Levoglucozan	Mannitol	Mannosan	Galactosan	Arabinose	Galactose	Glucose	Mannose	Fructose	Sucrose
	1.00											
Xylitol	0.72	1.00										
Levoglucozan	0.31	0.74	1.00									
Mannitol		0.31		1.00								
Mannosan	0.41	0.91	0.82	0.35	1.00							
Galactosan	0.35	0.88	0.74		0.63	1.00						
Arabinose	0.02	0.61	0.49		0.33	0.37	1.00					
Galactose							0.35	1.00				
Glucose			0.48	0.36	0.43		0.57	0.58	1.00			
Mannose		0.44	0.51	0.57	0.43	0.50	0.86		0.34	1.00		
Fructose							0.32	0.49	0.78		1.00	
Sucrose		0.47	0.47		0.31	0.62			0.48		0.56	1.00
OC		0.45	0.41	0.31	0.33	0.41	0.48	0.31		0.47		0.41
EC	0.36	0.30						0.58				
WSOC	0.35	0.81	0.48		0.34	0.69	0.45			0.56	0.16	0.43
NO₃⁻												
HPO₄²⁻											0.42	
SO₄²⁻							0.33			0.36		
C₂O₄²⁻							0.39			0.44		
Na⁺		0.37	0.39		0.31		0.33		0.38			
NH₄⁺										0.34		
nss-K⁺												
Mg²⁺		0.40			0.42							
Ca²⁺					0.38			0.30				

988 **Table 4.** Annual and seasonal percentage contributions of biomass/biofuel burning to
 989 the OC from the levoglucosan estimated when neglecting daytime oxidation by OH
 990 radicals (measured levoglucosan in parenthesis) for the samples collected during 2009-
 991 2010 and 2012-2013 at Finokalia sampling station.

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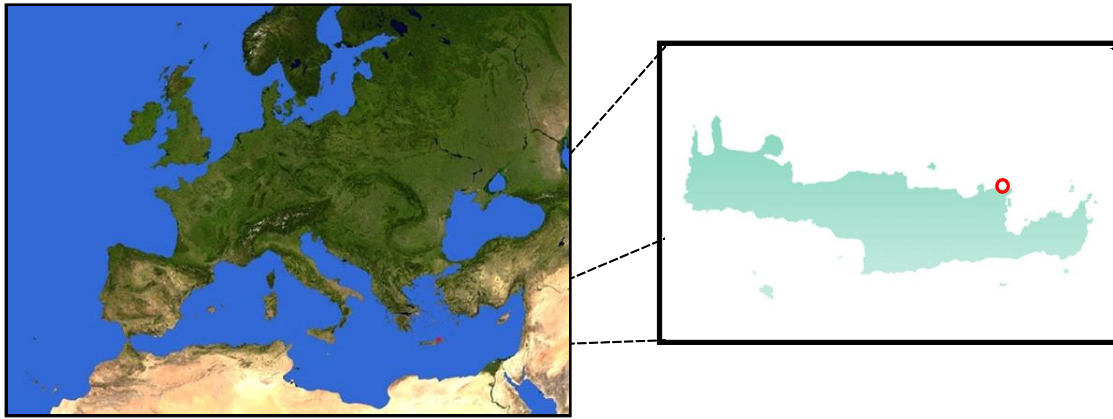
PM ₁₀	% Contribution of biomass burning to OC	
	Mean	min-max
Annual	13 (9)	6-18
Spring	12 (8)	0.3-46
Summer	12.5 (5)	0.7-50
Autumn	11 (7)	0.3-28
Winter	16 (16)	2-53

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996 **Figure 1**

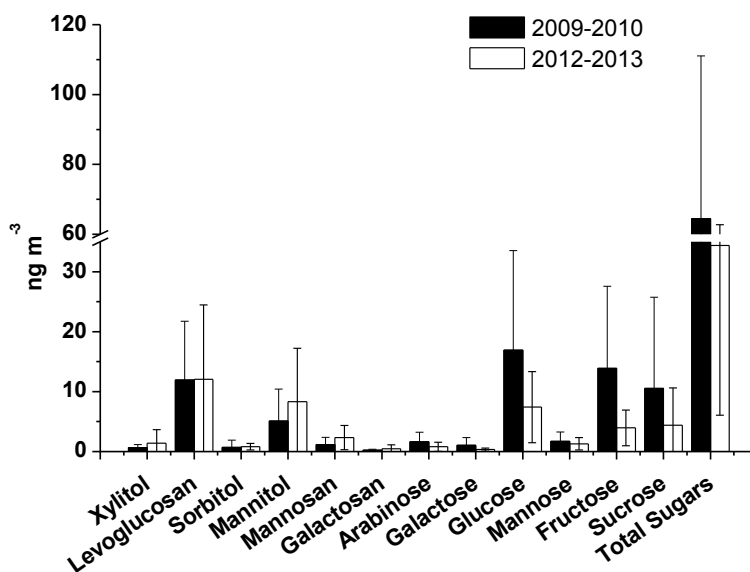


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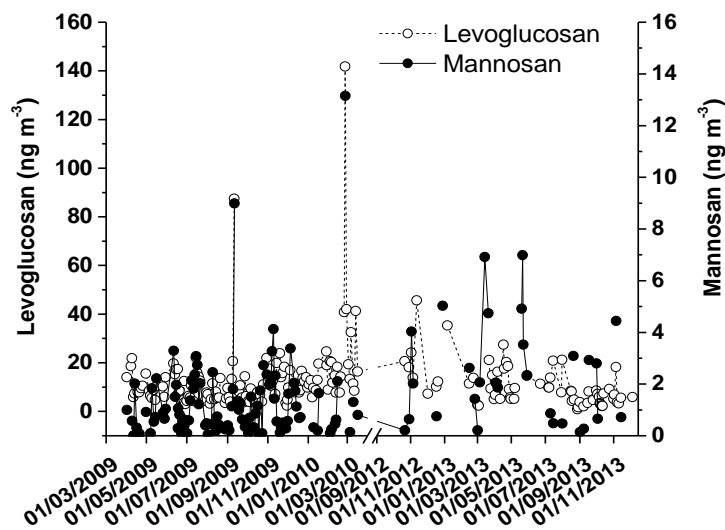
999 **Figure 2**

1000 **(a) Sugars**



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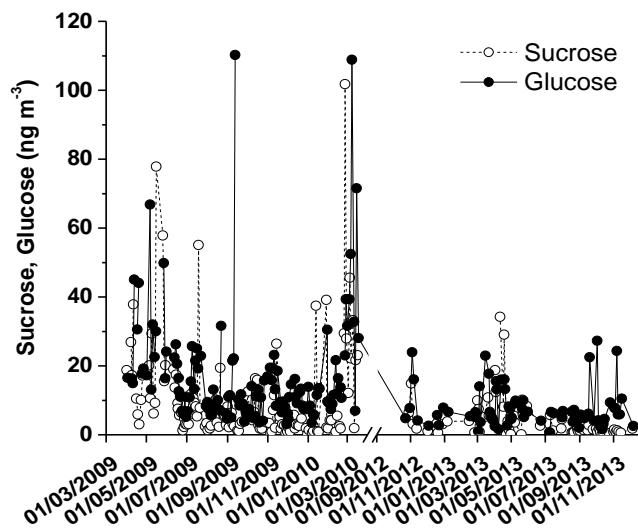
1002 **(b) Anhydrosugars**



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1005 (c) Primary sugars



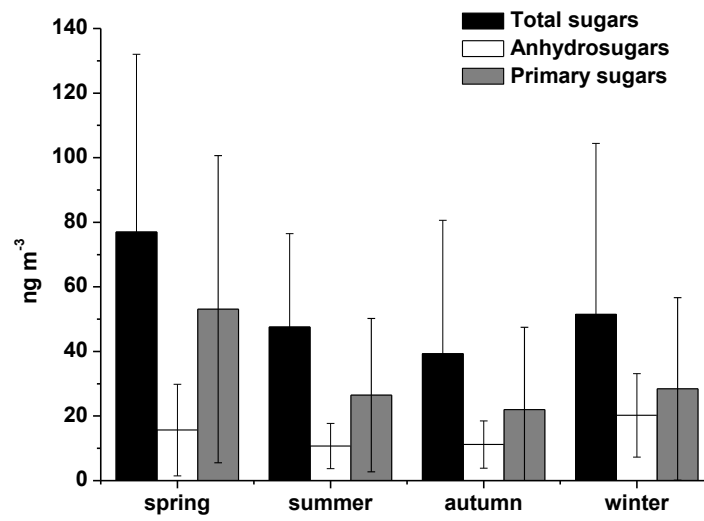
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1009 **Figure 3**

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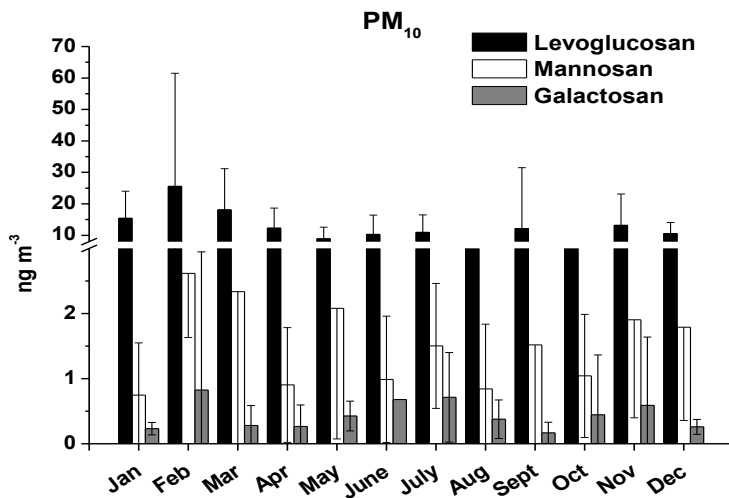
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1015 **Figure 4**

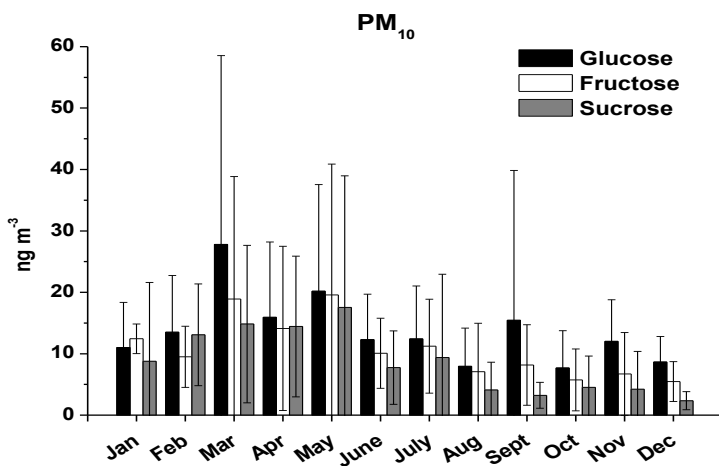
1016 **(a) Anhydrosugars**



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1019 **(b) Primary sugars**

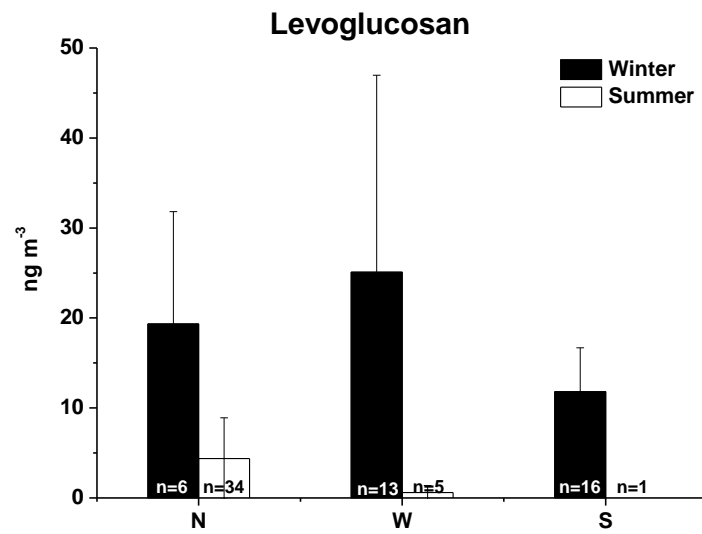


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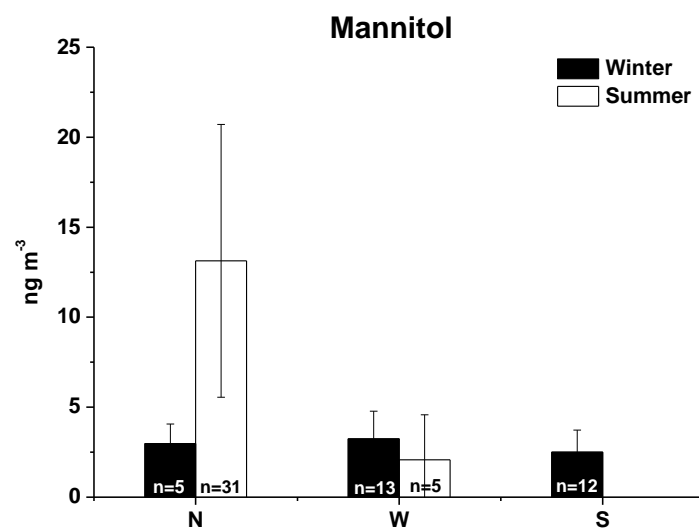
1022 **Figure 5**

1023 (a)



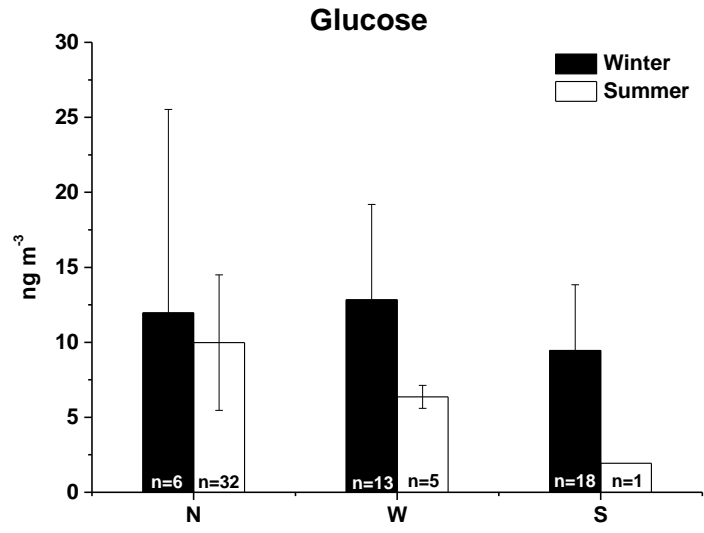
1024

1025 (b)



1026

1027 (c)

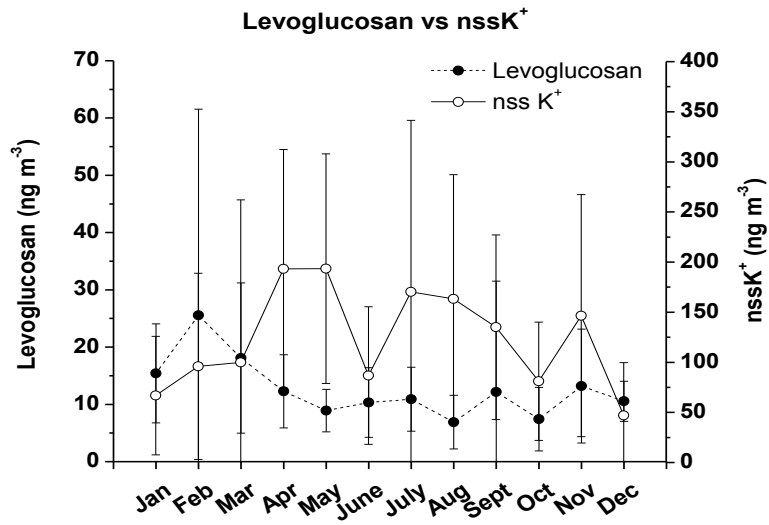


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1032 **Figure 6**

1033 (a)

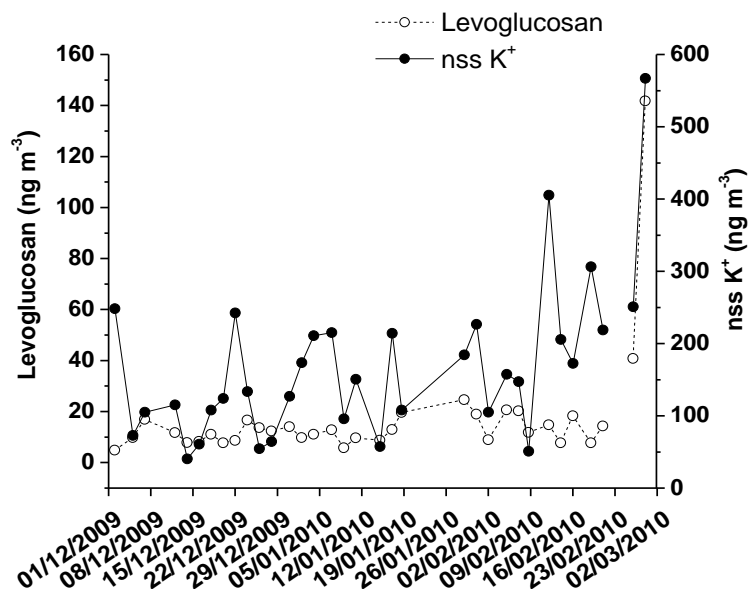
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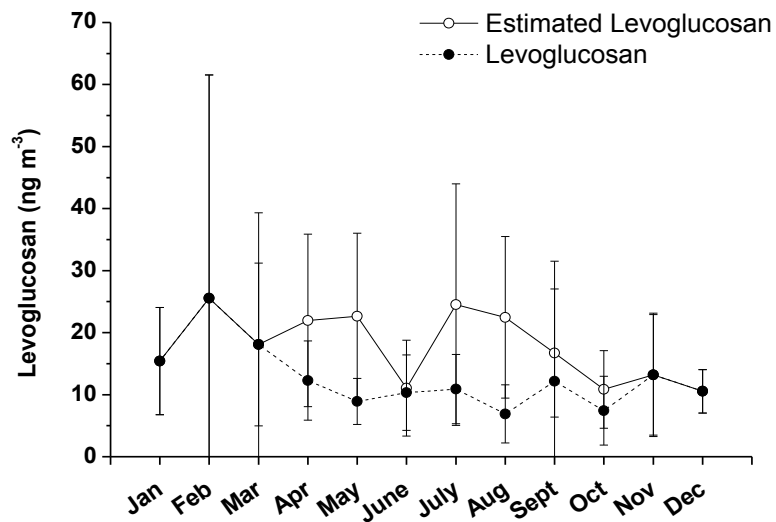
1037 (b)



1038

1039

1040 (c)



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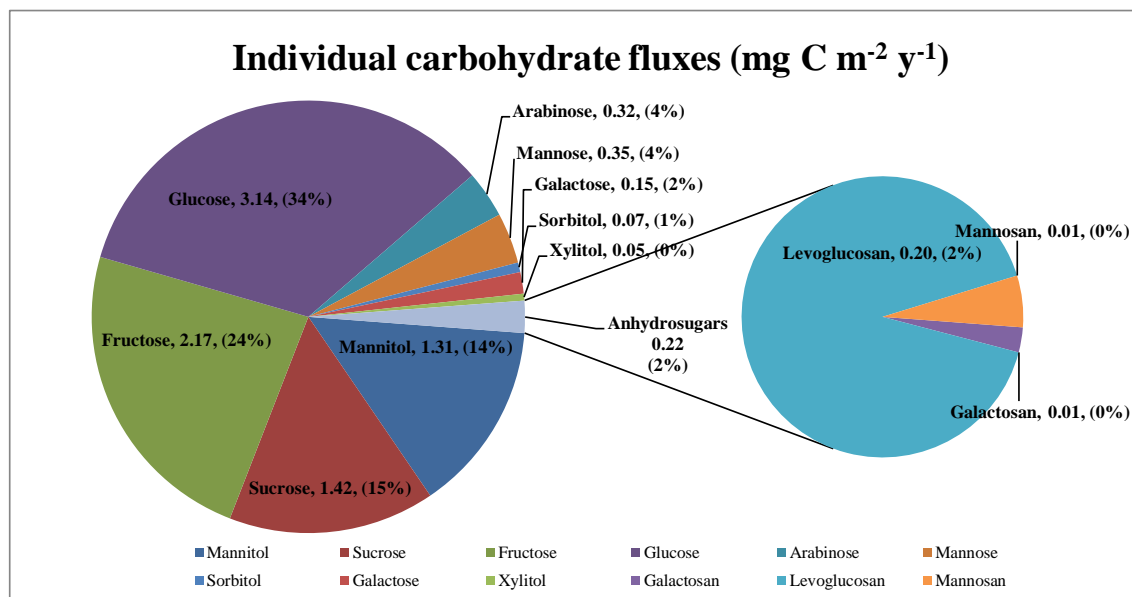
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1048 **Figure 7**

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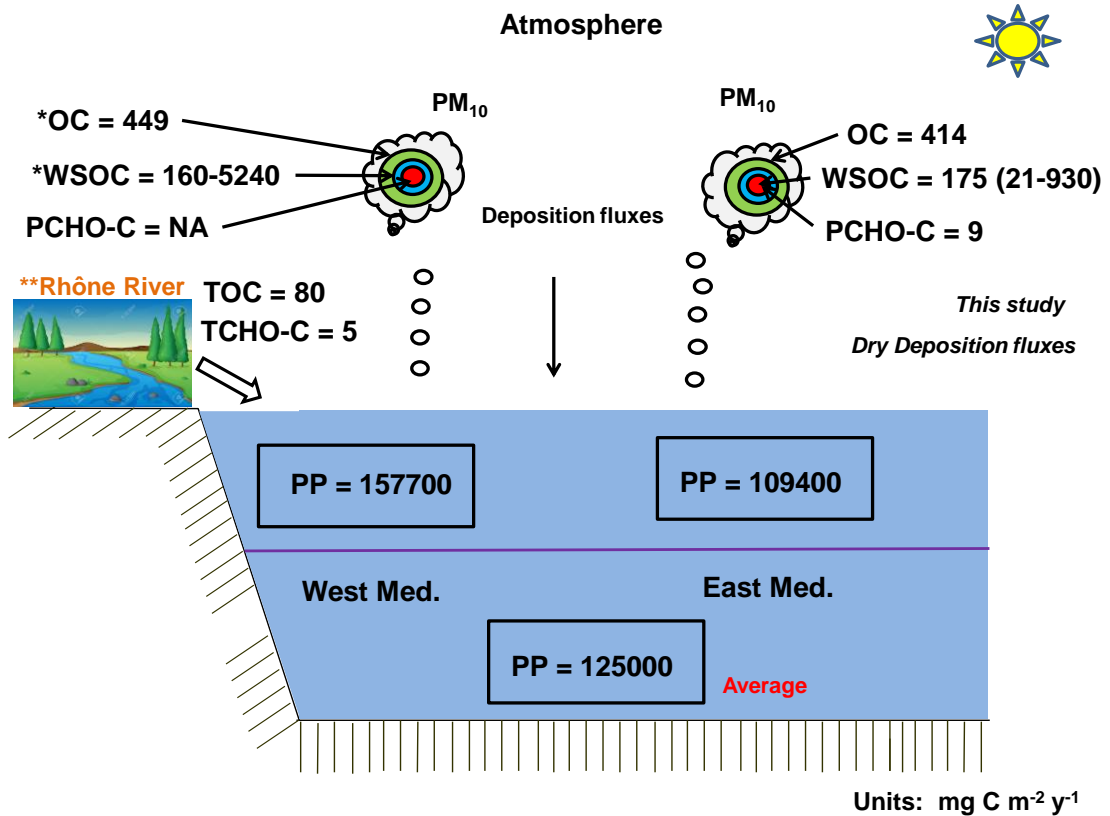
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1053 **Figure 8**

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NA: not available

PCHO-C = particulate sugar-carbon;

TCHO-C = total sugar-carbon (particulate + dissolved)

PP data from Antoine et al., 1995

**OC data from Pey et al. (2009) and WSOC data from Pulido-Villena et al. (2008)*

*** TOC, TCHO-C data from Panagiotopoulos et al. (2012)*