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# Sugars in atmospheric aerosols over the Eastern Mediterranean

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## Abstract

Aerosol samples (PM<sub>10</sub>) were collected at Finokalia monitoring station in a remote area of Crete in the Eastern Mediterranean over a two-year period. They were analyzed for total organic carbon (OC), water-soluble organic carbon (WSOC) and the molecular distributions of sugars. WSOC comprised 45% of OC while the contribution of sugars to the OC and WSOC content in the PM<sub>10</sub> particles averaged 3±2% (n=218) and 11±6% (n=132), respectively. The total concentration of sugars ranged between 6 and 334 ng m<sup>-3</sup> with the two most abundant sugars over the two-year period being glucose and levoglucosan, contributing about 25% each to the total carbohydrate pool. Primary saccharides (glucose, fructose, and sucrose) peaked at the beginning of spring (21, 17 and 15 ng m<sup>-3</sup> respectively), indicating significant contributions of bioaerosols to the total organic aerosol mass. On the other hand, higher concentrations of anhydrosugars (biomass burning tracers levoglucosan, mannosan, galactosan) were recorded in winter (19, 1.4 and 0.2 ng m<sup>-3</sup> respectively) than in summer (9.1, 1.1 and 0.5 ng m<sup>-3</sup> respectively). Levoglucosan was the dominant monosaccharide in winter (37% of total sugars) while the low concentration measured in summer (19% of total sugars) was probably due to the enhanced photochemical oxidation by hydroxyl (•OH) radicals which impact anhydrosugars. Based on levoglucosan observations, biomass burning was estimated to contribute up to 13% to the annual average OC measured at Finokalia. Annual OC, WSOC and carbohydrate dry deposition fluxes for the two-year sampling period were estimated at 414, 175 and 9 mg C m<sup>-2</sup> y<sup>-1</sup> respectively. Glucose and levoglucosan accounted for 34% and 2% of the total sugar fluxes. According to our estimations, atmospheric OC and WSOC inputs account for 0.70% and 0.71%, respectively of the carbon in the annual primary production in the Cretan Sea. Considering the entire Mediterranean, dry deposition of OC can provide at least 3 times more C than riverine inputs of Rhone. Carbohydrate dry deposition flux represents up to 0.04% of the C used for the primary production in the Cretan Sea, while <0.01% for

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

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

## 1. Introduction

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

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

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

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

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

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

## 2 Experimental

### 2.1 Sampling site & procedure

Aerosol samples were collected at approximately 3m above the ground at Finokalia monitoring station (35°24'N, 25°60'E; <http://finokalia.chemistry.uoc.gr>), a remote location in the northern coast of Crete, Greece (Figure 1). The site is not impacted by local human activities but is influenced by long-range transport of continental air masses and is considered as representative of the Eastern Mediterranean atmosphere (Mihalopoulos et al., 1997; Kouvarakis et al., 2000; Gerasopoulos et al., 2005; Sciare et al., 2008; Theodosi et al., 2011). Thus it is a particularly well-suited site for the study of “aged” aerosols from Central and Eastern Europe. PM<sub>10</sub> samples were collected on pre-combusted Quartz fiber filters (Whatman and Pall, 47 mm; 550 °C overnight) during two campaigns lasting at least a full year from April 2009 to March 2010 and from October 2012 to December 2013. Overall 143 filters were collected on a 48h basis during the first campaign thus covering 80% of the year and 75 samples were collected on a 24h basis during the second campaign covering 20% of the year and resulting in a total of 218 samples. For both campaigns the sampling was uniformly distributed by

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

## **2.2 Analytical techniques**

### *2.2.1. Ion chromatography*

A portion of the quartz filters (1.5 to 2.5 cm<sup>2</sup>) was extracted in 5 to 7.5 ml of Milli-Q water in an ultrasonic bath for 45 min. The solutions obtained after the extraction were filtered using syringe filters (0.45 µm pore size) to remove any insoluble species and were then analyzed by ion chromatography for the main anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) and cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) using the technique described by Paraskevopoulou et al. (2014).

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

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

### *2.2.3. Particulate carbohydrates determination*

#### *2.2.3.a. Sample preparation*

A portion of each quartz fiber filter (4 to 9 cm<sup>2</sup>) was extracted in 6 ml of Milli-Q water by ultrasonic bath agitation for 60 min. The liquid samples extracted were immediately filtered through pre-combusted quartz wool (450 °C for 6h) packed into a pre-combusted Pasteur pipette to remove any insoluble particles including particles of the quartz filter before injection to the chromatograph on the same day. Procedural blanks collected in the field were treated and analyzed in the same manner as the samples. The results showed no contamination for any target compound. Therefore the data reported hereafter were neither corrected for the field blanks nor for the extraction recoveries.

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

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

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

#### 2.2.3.c. HPAEC – PAD analysis

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

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

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

### 3. Results

#### 3.1 OC, EC, WSOC and Ions

The concentrations of OC, WSOC and EC measured in the PM<sub>10</sub> samples ranged 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  $\mu\text{g m}^{-3}$ ) 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 results indicated that OC and EC concentrations did not exhibit a seasonal variation, remained almost constant throughout the year. Lower concentrations were observed from September till January due to wash out by rain. Similarly, WSOC concentrations did not show a clear seasonal cycle. Nevertheless, slightly higher values were measured in the summer, possibly linked with enhanced photochemistry which renders the organic fraction more water-soluble (Bougatioti et al., 2013). WSOC comprised 6.22% to 82.0% of OC with a mean of 45.1% and no distinct differences between summer (51.1%) and winter (47.2%). This contribution is lower than the  $67\pm 7\%$  reported for PM<sub>2.5</sub> at the same site (Bougatioti et al. 2011), but in the same range as the contribution of 50% for PM<sub>10</sub> samples collected at an urban site in Norway (Yttri et al., 2007).

In our samples, ions were characterized by an abundance of non-sea salt potassium  $\text{nss-K}^+$  with a range of 38.2 to 885  $\text{ng m}^{-3}$  (mean 198  $\text{ng m}^{-3}$ ). Non-sea salt potassium is a typical tracer of biomass burning (Cachier et al., 1991). The levels of oxalates were also high, in the range of 7.32 to 913  $\text{ng m}^{-3}$  (mean 277  $\text{ng m}^{-3}$ ) (Kawamura et al., 1996; Kawamura and Ikushima, 1993; Laongsri and Harrison, 2013). This was especially so in the winter/early spring and summer period. These observed  $\text{nss-K}^+$  levels indicate that Finokalia is influenced by biomass burning emissions, which corroborates well with previous investigations at the same site (Sciare et al., 2008). Our results also showed that  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  concentrations exhibited peaks during winter (3.16, 0.39 and 1.45  $\mu\text{g m}^{-3}$  respectively) and in spring/summer (5.01, 0.97 and 1.32  $\mu\text{g m}^{-3}$  respectively). The winter peak is most likely associated with anthropogenic activities such as domestic heating and long range transport. The summer peak can be attributed to the absence of precipitation in conjunction with the induced photochemical reactions during that season which lead to secondary aerosol formation in the area (Mihalopoulos et al., 1997).

### 3.2 Distribution of carbohydrates in PM<sub>10</sub> particles

In 2009-2010 total sugars concentration in PM<sub>10</sub> samples ranged from 11.1 to 334  $\text{ng m}^{-3}$  (mean 63.0  $\text{ng m}^{-3}$ ) and were higher than measurements in 2012-2013 (6.41 to 92.5  $\text{ng m}^{-3}$ ; mean 31.5  $\text{ng m}^{-3}$ ) (Figure 2). The mean total sugars concentration for both periods was 57.7  $\text{ng m}^{-3}$  (median 41.8  $\text{ng m}^{-3}$ ) and was comparable to observations at a rural site in Portugal (Pio et al., 2008), but lower compared to urban sites (71-77  $\text{ng m}^{-3}$ ) across the Mediterranean (Tel Aviv, Graham et al., 2004; Rehovot, Burshtein et al., 2011; and Barcelona, Reche et al., 2012) (Table 2). The contribution of sugars to the OC and WSOC content in the PM<sub>10</sub> particles varied from 0.18 to 22.9% with a mean of 3.30% and a median of 2.72% for OC and 1.4 to 66.6% with a mean of 10.6% and median of 7.3% for WSOC. The contribution of sugars to the OC in our samples falls in the range of values reported previously for Barcelona which ranged from 1.4 to 2.2 % with a mean of mean 2.0% (Reche et al. 2012). Similar values of 1.1 to 2.4% with a mean of 1.4% were reported for Tel Aviv (Graham et al., 2004) and for both rural (0.1

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

Anhydrosugars in particular accounted for 0 to 0.43% (mean 0.06%) of the PM<sub>10</sub> mass, 0.04-9.05% (mean 0.9%) of the OC, and 0.29-14.1% (mean 2%) of the WSOC. The highest mean contribution of anhydrosugars to the OC (1.4%) and WSOC (2.9%) was observed in winter, highlighting the strong influence of biomass burning on winter aerosols and enhanced chemical stability of levoglucosan in the atmosphere during the winter period compared to summer (see below). The above observation has also been reported for Barcelona by Reche et al. (2012) who found a significant correlation between levoglucosan, OC and K<sup>+</sup> in PM<sub>2.5</sub>, especially at night, suggesting the transport of biomass burning emissions from the regional scale towards the city.

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

### 3.3 Seasonal variation of sugars at the Finokalia site

Total sugars concentration in PM<sub>10</sub> samples showed a seasonal variation with higher values in spring (20.8-266 ng m<sup>-3</sup>, mean 77 ng m<sup>-3</sup>) and lower values in autumn (7.41-311 ng m<sup>-3</sup>, mean 39.3 ng m<sup>-3</sup>) (Figure 3).

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



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

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

## **4. Discussion**

### **4.1 Climatology**

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

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

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

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

The total sugars concentration in atmospheric aerosols (PM<sub>10</sub>) exhibited two seasonal maxima. The first one in the spring growing season and the second one in winter when leaf senescence and microbial degradation of primary saccharides occurs

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

Levogluconan in particular was by far the most dominant sugar in winter time (mean 37% of the total sugar composition; Figure 2). This suggests that biomass burning processes contribute significantly to the PM<sub>10</sub> sugar content, further highlighting the importance of these processes in the Eastern Mediterranean (Sciare et al., 2008). In addition, the low photooxidative decay of levogluconan in the atmosphere during winter time can also enhance its levels.

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

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

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

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

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

During the period studied anhydrosugar concentrations were strongly correlated (levogluconan vs mannitol,  $r=0.82$ ; levogluconan vs galactitol,  $r=0.74$ ; mannitol vs galactitol,  $r=0.63$ ;  $n=218$ ). This is presented in Table 3 and implies a common origin

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

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

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

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

#### 4.3.2 Levoglucosan to mannosan ratio: biomass burning tracers

The relative ratio of levoglucosan to mannosan (L/M) has been used for source reconstruction of combustion-derived by products in atmospheric aerosols (Schmidl et al., 2008a; Caseiro et al., 2009; Fabbri et al., 2009; Sang et al., 2013). Throughout the sampling period for our two campaigns the L/M ratio ranged from 2.28 to 88.2 in  $\text{PM}_{10}$  samples ( $15.5\pm14.8$ ; median 9.97). Despite such a wide range in the ratios we observed only a small seasonal variation of the averaged seasonal L/M ratio (spring= $15.9\pm8.9$ , median=11.2; summer= $15.5\pm13.5$ , median=10.2; autumn= $13.0\pm11.4$ , median=8.6; winter= $17.1\pm13.4$ , median=10.9).

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

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

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

#### 4.4 Non photooxidized levoglucosan concentrations

The annual variations of levoglucosan and  $\text{nss-K}^+$  concentrations are depicted in Figure 6a. A bimodal pattern is clearly observed for  $\text{nss-K}^+$  with early spring and mid-summer maxima while levoglucosan exhibits only a single maximum in winter.  $\text{nss-K}^+$  may originate from several sources such as dust and biomass burning (Mihalopoulos et al., 1997). Therefore, in order to eliminate the influence of dust transport from N. Africa on  $\text{nss-K}^+$  levels, samples under prevailing southerly and south-westerly winds were excluded and the same bimodal pattern was observed (not shown). Assuming i) that low photooxidation occurs in winter, and ii) considering identical emission sources for both levoglucosan and  $\text{nss-K}^+$  throughout the year (supported by the existence of a main common source of biomass burning in the region during the whole year, Sciare et al., 2008), we can estimate the concentration of levoglucosan before photooxidation reduces its levels using the constant L/ $\text{nss-K}^+$  slope of their linear regression equal to 0.117,  $r=0.63$  ( $0.126\pm0.08$ ; median=0.117;  $n=42$  in winter). Figure 6b depicts the daily concentrations of levoglucosan and  $\text{nssK}^+$  in  $\text{PM}_{10}$  aerosols at Finokalia indicatively during the first winter campaign (2009-2010). Figure 6c reflects the annual variability of the estimated levoglucosan concentrations which exhibit two maxima in winter/early spring and in summer, in accordance with Sciare et al. (2008) and Reche et al. (2012). These studies suggested that the Eastern Mediterranean is under the influence of biomass burning aerosols during winter/early spring and summer. It must be kept in mind that during summer levoglucosan levels were decreased by 54% due to the enhanced photooxidative decay, when both measured and estimated levoglucosan concentrations are considered ( $9.40$  and  $20.1 \text{ ng m}^{-3}$ , respectively).

#### 4.5 Relative contribution of biomass burning to OC

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

and agricultural residues (Andreae and Merlet, 2001). In this study, we used the value of 8.1% to estimate the percentage contribution of biomass and biofuel burning activities to the OC in each of the PM<sub>10</sub> aerosol samples (Table 4). The estimated levoglucosan levels were used in our calculations as discussed in the previous section.

On this basis we estimated that biomass burning in the East Mediterranean contributed annually 13% to the OC in PM<sub>10</sub> aerosols at Finokalia station (Table 4). The highest mean contributions from biomass burning were found, as expected, during winter 16.0%±10.9% (median 13%). The estimated annual contribution of 13% is in good agreement with the 14% value reported by Sciare et al. (2008) for the Mediterranean Basin. These annual mean values are also comparable to those reported for various sites affected by biomass burnings (12% Portugal, Puxbaum et al., 2007; 19-21% Barcelona, Reche et al., 2012).

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

### *4.6.1 Fluxes and carbohydrate speciation*

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

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

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

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

Among the primary sugars, glucose was the dominant monosaccharide in PM<sub>10</sub> particles (approximately 27% of the total carbohydrates concentration) with the highest

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

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

#### 4.6.2 Significance of carbohydrates deposition on the seawater productivity

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

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

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

## 5. Summary and concluding remarks

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

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

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

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

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

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**Figure captions:**

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

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

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

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

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

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

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

**Figure 8.** Organic carbon inputs from the atmosphere ( $\text{PM}_{10}$  particles) and rivers (Rhône River) in terms of OC, WSOC and sugars in the Western and Eastern Mediterranean Sea.



**Table 1.** The mean, standard deviation, median and range of measured concentrations for PM<sub>10</sub> aerosol samples, collected at Finokalia during the two campaigns (April 2009-March 2010 and October 2012-December 2013).

$\mu\text{g m}^{-3}$	PM <sub>10</sub> (n=218)			
	Mean± Stdev	Median	min	max
PM <sub>10</sub>	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 <sup>-</sup>	1.39±1.56	0.72	0.01	7.61
Br <sup>-</sup>	0.01±0.01	0.01	0.00	0.09
NO <sub>3</sub> <sup>-</sup>	1.23±0.80	1.18	0.00	4.47
PO <sub>4</sub> <sup>3-</sup>	0.23±0.33	0.12	0.00	2.74
SO <sub>4</sub> <sup>2-</sup>	3.49±1.77	3.35	0.40	8.72
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.28±0.18	0.28	0.01	0.91
Na <sup>+</sup>	1.89±1.51	1.45	0.05	10.8
NH <sub>4</sub> <sup>+</sup>	0.65±0.67	0.32	0.00	5.60
K <sup>+</sup>	0.21±0.13	0.17	0.04	0.88
Mg <sup>2+</sup>	0.31±0.20	0.21	0.00	9.67
Ca <sup>2+</sup>	1.59±2.10	0.62	0.00	16.0

977 **Table 2.** Mean and range values of carbohydrates in PM<sub>10</sub> aerosol sampled at Finokalia  
978 and other Mediterranean sites.

Sugars (ng m <sup>-3</sup> )	PM <sub>10</sub>		TSP		PM <sub>10</sub>		PM <sub>2.5</sub>	
	Mean	range	Mean	range	Mean	range	Mean	range
Xylitol	0.92	nd-4.96	-	-	-	-	-	-
Levogluconan	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)	

\*nd: not detected

\*\* Estimated concentrations from author's data.

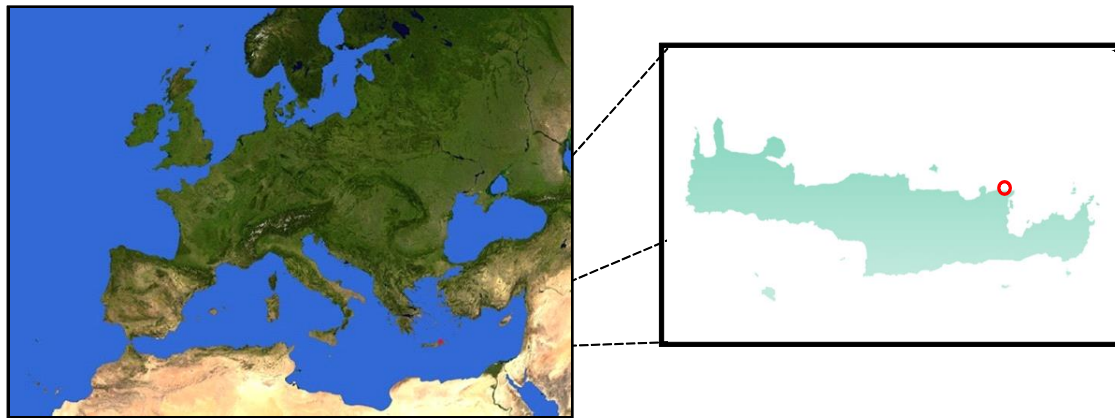
984 **Table 3.** Pearson product-moment correlation coefficient (r) between the elements  
985 analyzed in the PM<sub>10</sub> fraction collected at Finokalia sampling station (n=218). Only  
986 correlations with r greater than 0.30 are presented (p<0.001).  
987

r	PM <sub>10</sub>	Xylitol	Levogluconan	Mannitol	Mannosan	Galactosan	Arabinose	Galactose	Glucose	Mannose	Fructose	Sucrose
PM <sub>10</sub>	1.00											
Xylitol	0.72	1.00										
Levogluconan	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
NO <sub>3</sub> <sup>-</sup>												
HPO <sub>4</sub> <sup>2-</sup>											0.42	
SO <sub>4</sub> <sup>2-</sup>							0.33			0.36		
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>							0.39			0.44		
Na <sup>+</sup>		0.37	0.39		0.31		0.33		0.38			
NH <sub>4</sub> <sup>+</sup>										0.34		
nss-K <sup>+</sup>												
Mg <sup>2+</sup>		0.40			0.42							
Ca <sup>2+</sup>					0.38			0.30				

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

PM <sub>10</sub>	% 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

996 **Figure 1**

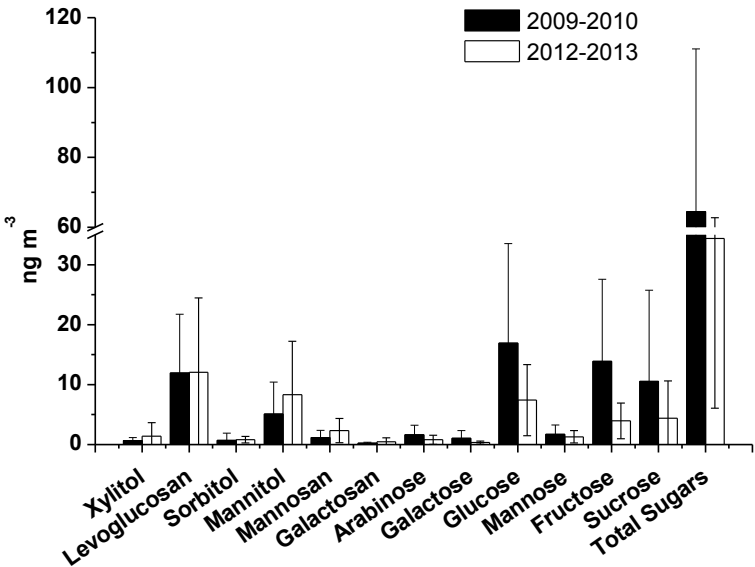


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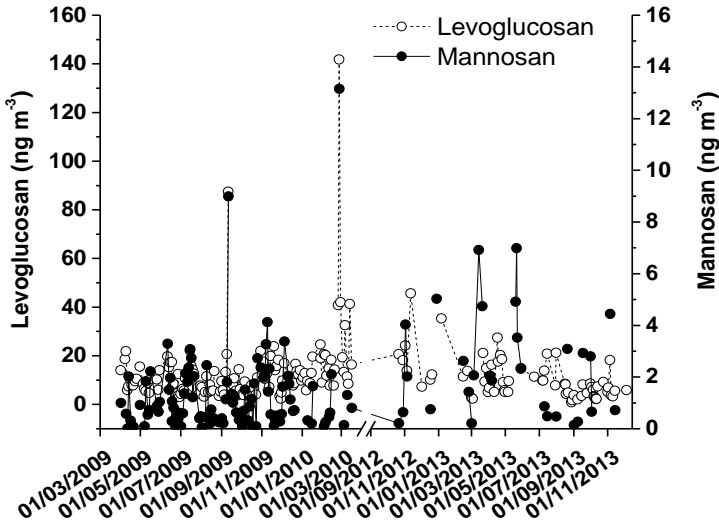
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**Figure 2**

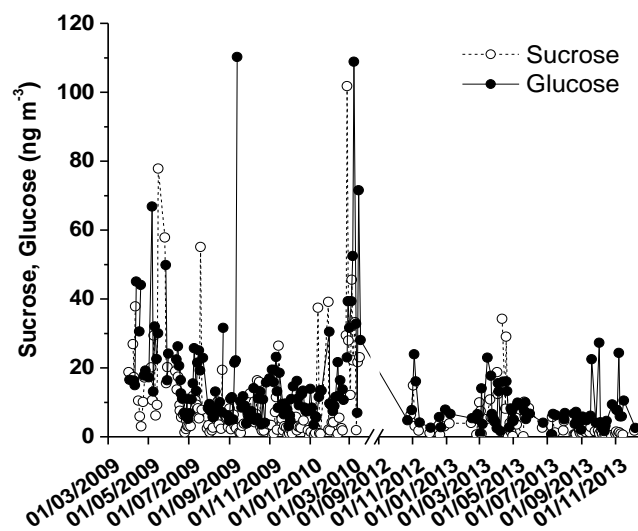
**(a) Sugars**



**(b) Anhydrosugars**



1005 (c) Primary sugars

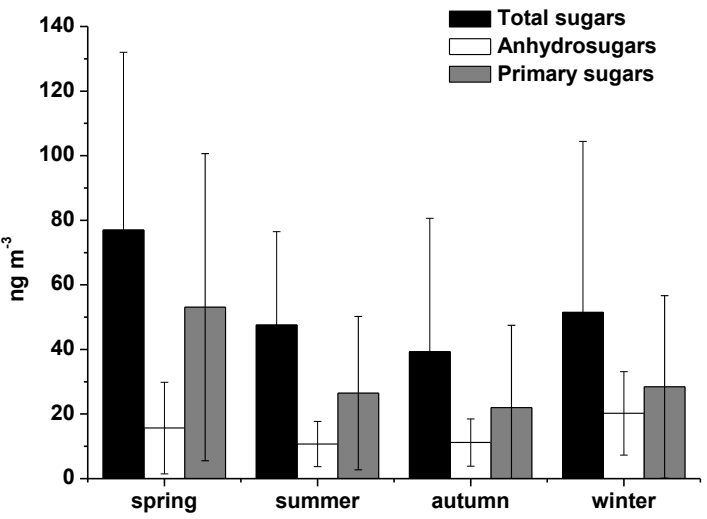


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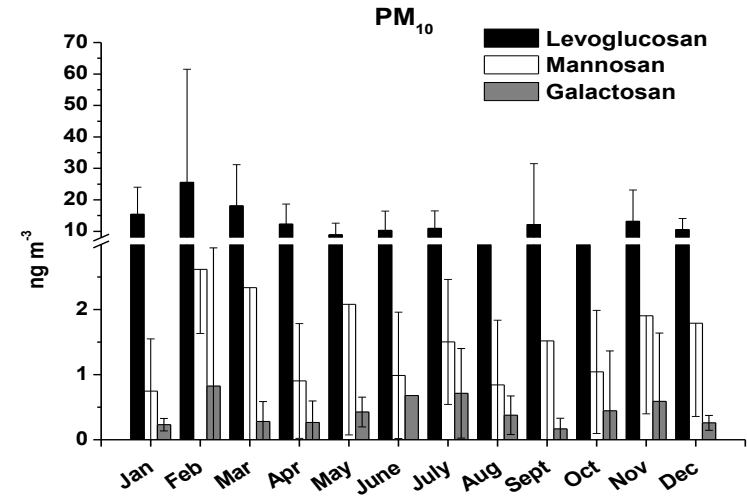
**Figure 3**



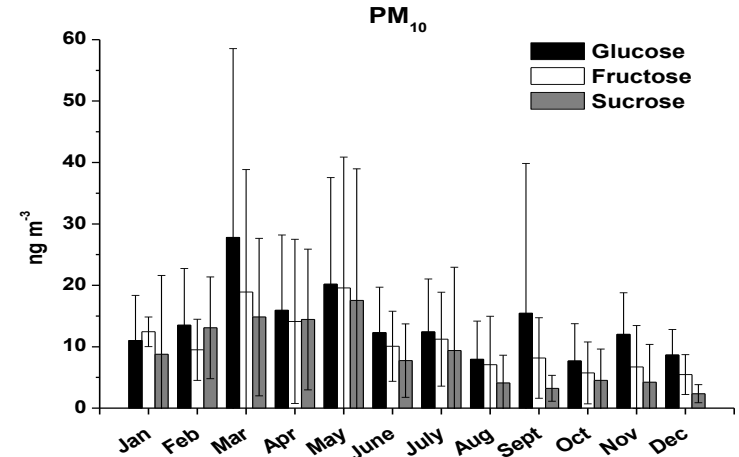


**Figure 4**

**(a) Anhydrosugars**

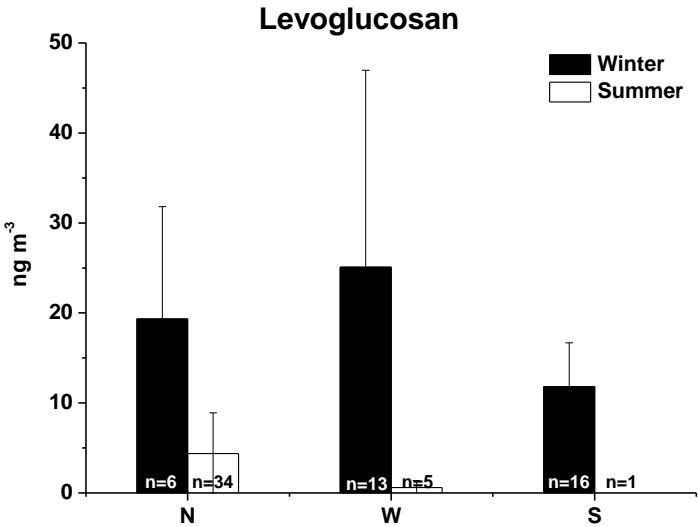


**(b) Primary sugars**

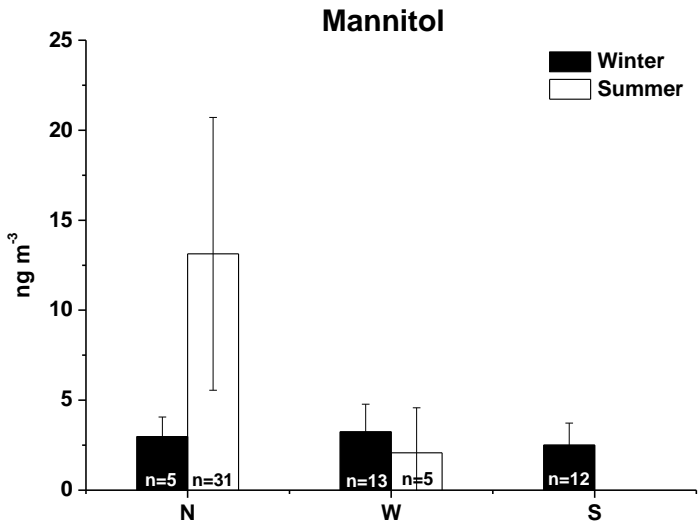


**Figure 5**

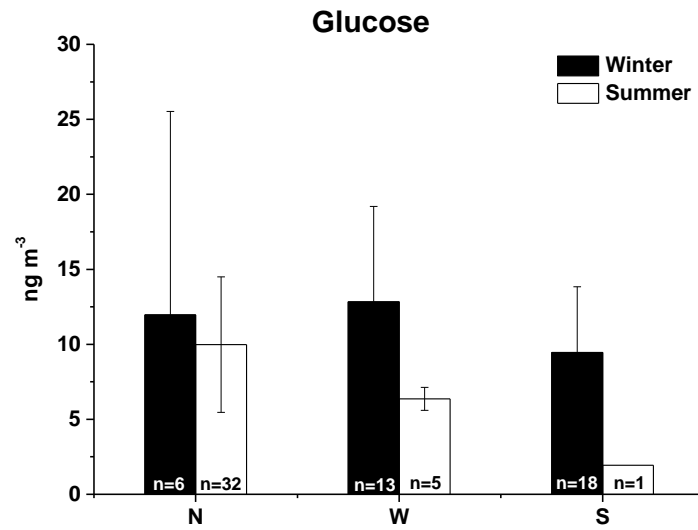
(a)



(b)



(c)



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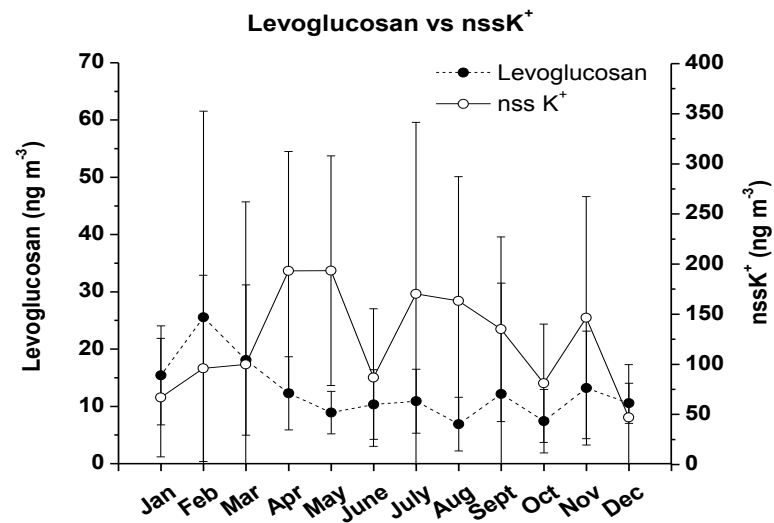
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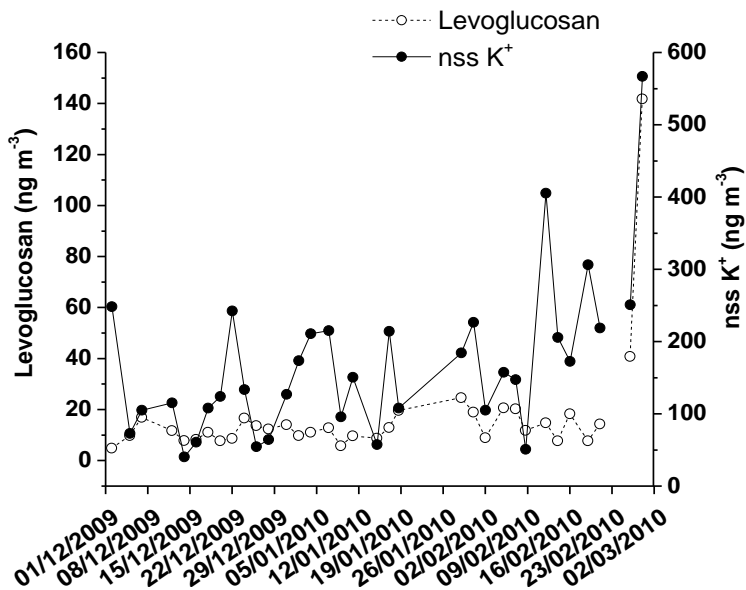
1031

**Figure 6**

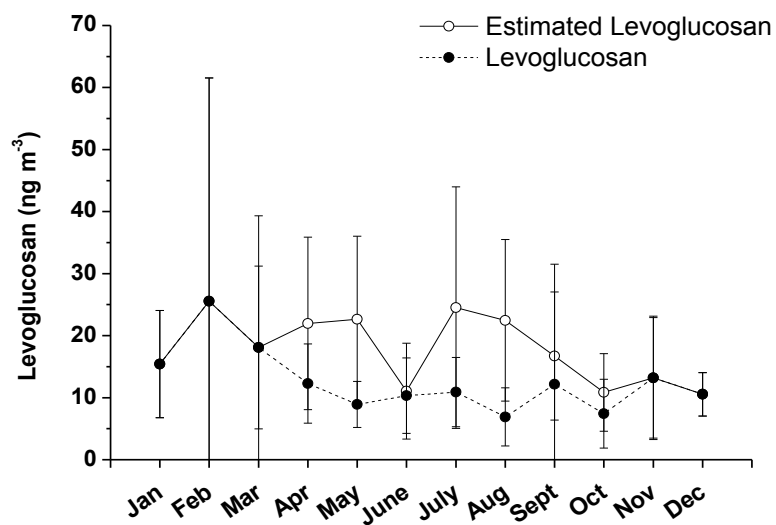
**(a)**



**(b)**



1040 (c)



1041

1042

1043

1044

1045

1046

1047

**Figure 7**

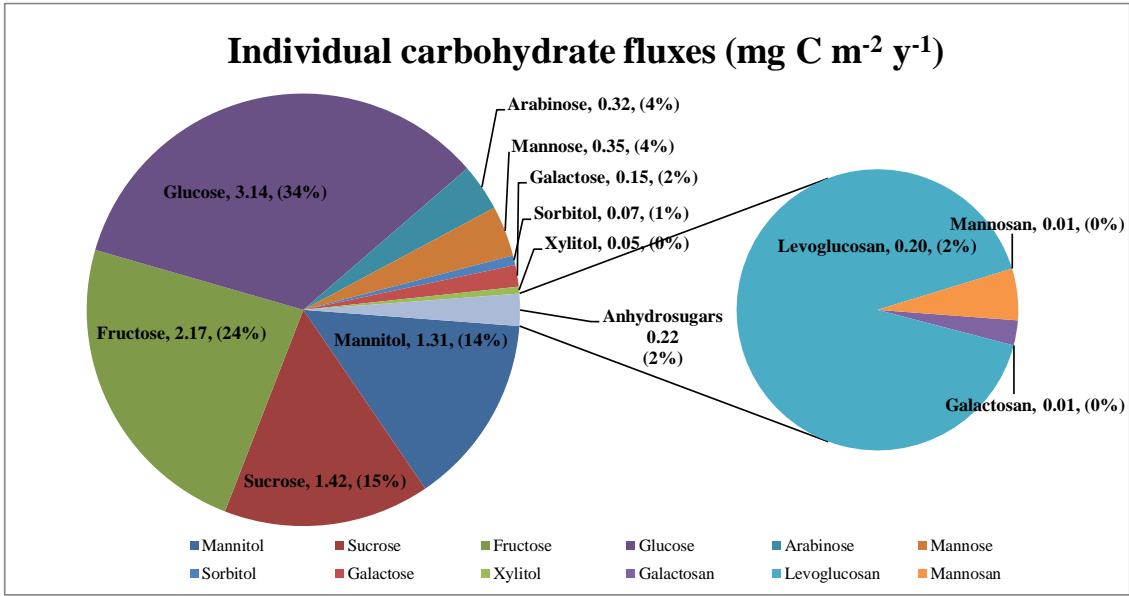
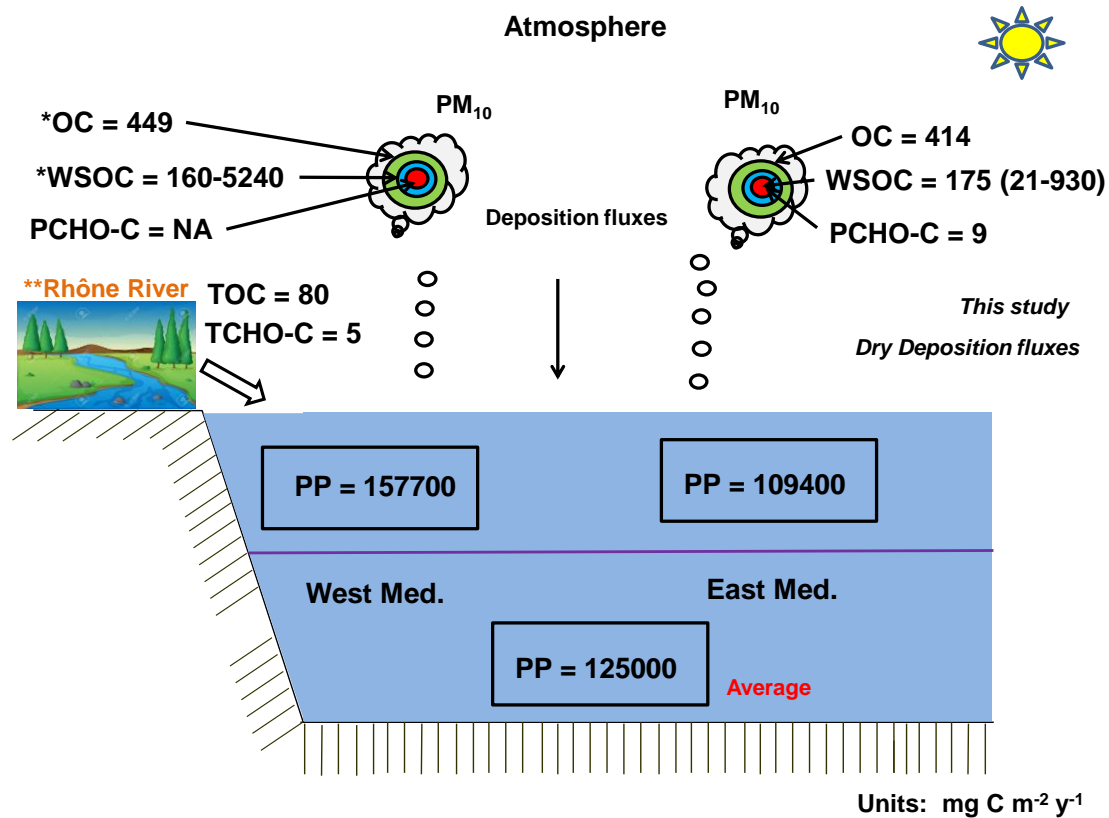


Figure 8



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)