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# One-year study of airborne sugar compounds: cross-interpretation with other chemical species and meteorological conditions

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## Abstract

The daily evolution of seventeen sugar compounds (seven saccharides, seven alcohol-saccharides and three anhydrosaccharides) in atmospheric aerosol samples collected between 9 March 2016 and 14 March 2017 was studied in León (Spain). The main links between the concentration of sugar compounds and various chemical species, pollen, fungal spores and meteorological conditions were studied. The results showed that in spring, when high levels of metabolic activity of the plants occur and temperatures increase, glucose, sucrose, 2-methyl-erythritol, mannitol, arabitol and inositol, are significantly correlated with airborne pollen concentration. Between spring and autumn, *Alternaria* air concentrations is significantly correlated with temperatures, arabitol and sorbitol + adonitol concentrations. Furthermore, during rainy days, *Alternaria* is also correlated with mannitol. In autumn, lower temperatures cause an increase in the concentrations of levoglucosan, mannosan and galactosan, probably due to the increased use of domestic heating devices. These anhydrosugars and arabinose, fructose and glucose, are significantly correlated with K, NO<sub>3</sub><sup>-</sup>, EC, OC, Cu, Zn, Se, Pb, V and Ni, while mannosan also correlates with As, showing that these anhydrosaccharides can be emitted from different anthropogenic sources. Precipitation causes an increase in glucose and sucrose concentrations, due to the break of pollen particles that produce hundreds of fine size particles. Besides, precipitation causes an increase in arabitol concentration, due to the release and growth of fungi.

**Keywords:** bioaerosols, meteorological conditions, tracers, sugar compounds

## 1. Introduction

Atmospheric bioaerosols comprise a variety of biological particles that include bacteria, fungi, fungal spores, pollen and allergenic pollens, arthropod allergens (e.g., from mites and cockroaches), pet allergens, algae, amoebae and viruses (Després et al., 2012; Douwes et al., 2008; Fröhlich-Nowoisky et al., 2016). They play an important role in human health and atmospheric processes. Pollen allergens are considered to be primarily glycoproteins that are released into the atmosphere in the form of exudates. Thus, it is the glucidic fraction that triggers the allergic responses, so an interaction of sugars with other particles, biotic or not, can clearly increase the symptoms of respiratory allergies (Dall'Antonia et al., 2014). The presence of high levels of pollen in the atmosphere has been related to allergic respiratory diseases, such as asthma, rhinitis, and atopic dermatitis (D'Amato et al., 2007; Fröhlich-Nowoisky et al., 2016; Fukutomi and Taniguchi, 2015). In particular, among fungal spores, the specie *Alternaria alternata* can be considered one of the most allergenic species. The main allergen produced by this fungal spore is the Alt a 1 acid glycoprotein (16.4 kDa and 15.3 kDa band), which is found in the cytoplasm and cellular wall of mold and mycelial spores. It is related to the development of asthma and rhinitis, as well as to epidemics of asthma exacerbation (Armentia et al., 2019; Fukutomi and Taniguchi, 2015), although its true biological function remains unknown.

Sugar compounds (saccharides, alcohol-saccharides and anhydrosaccharides) represent an important part of the water-soluble organic fraction in the atmospheric aerosol (Barbaro et al., 2019; Burshtein et al., 2011; Simoneit et al., 2004; Wang et al., 2018; Yttri et al., 2007). These organic compounds can have their origin in different anthropogenic and natural sources, including biomass combustion and/or biogenic primary emissions (Table S1).

Dust storms have been reported to be a natural source of bioaerosols and sugar compounds such as arabitol, mannitol, sucrose and tehalose (found in many anhydrobiotic organism), due to the resuspension of soil material and biogenic sources like pollen and fungal spores (Kumar et al., 2017; Oduber et al., 2020, 2019b). Anhydrosaccharides, levoglucosan, galactosan and mannosan, which originate from the pyrolysis of cellulose and hemicellulose, and potassium, located in the cytoplasm of plants, are used as biomass burning tracers (Vicente and Alves, 2018). Arabitol and mannitol, responsible for the energy storage in fungi, have been pointed out as biomarkers of fungal spores in the air (Bauer et al., 2008; Burshtein et al., 2011; Medeiros et al., 2006). Nevertheless, high concentrations of alcohol-saccharides have also been observed in plant tissues. Mannitol is found in more than 70 different families of plants, as well as bacteria. Similarly, sorbitol is the primary photosynthetic metabolite of sucrose in many species, for example of the Rosaceae family, including all of the genus *Malus*, *Pyrus* and *Prunus* (apples, pears and stone fruits, respectively)

(Dumschott et al., 2017). Sucrose, fructose and glucose are free sugars found in high concentrations in plant tissues and are major contributors to pollen (Fu et al., 2012; Medeiros et al., 2006; Simoneit et al., 2004; Speranza et al., 1997). Besides, a small fraction of fructose, glucose and other less studied saccharides, such as arabinose, galactose, xylose, xylitol and ribose, has been observed in smoke samples from biomass burning (Alves et al., 2011; Medeiros et al., 2006; Vicente et al., 2013).

The atmospheric concentrations of bioaerosols are also affected by meteorological conditions. Temperature, wind speed, relative humidity and precipitation are parameters that influence the airborne concentration of fungal spores, plants flowering and pollination periods (Fernández-González et al., 1993; Filali Ben Sidel et al., 2015; Grinn-Gofroń et al., 2019; Makra et al., 2014; Oduber et al., 2019a; Sabo et al., 2015). Although the impact of precipitation on different sugar compounds have not been examined in detail until now, to better understand atmospheric processes, it may be important to assess the behaviour of these constituents after a rain event. For example, the below-cloud scavenging (BCS) process has a direct impact on the aerosol concentration in the air (i.e. Blanco-Alegre et al., 2018; Castro et al., 2010; Cugnon et al., 2018). This process depends on several features of rainfall, such as raindrop size distribution and rainfall rate, and on the local/regional concentration of the particles and gases in the atmosphere (Celle-Jeanton et al., 2009; Xu et al., 2017). The scavenging of different species, mainly inorganic, and the relationship with the intensity and volume of precipitation, has been studied by several authors in different regions of the world (i.e. Blanco-Alegre et al., 2019; Calvo et al., 2012; Custódio et al., 2014; Pan and Wang, 2015; Uchiyama et al., 2017). Even though a washing effect by rain has been observed for several aerosols, certain particles as pollen can swell and rupture producing hundreds of fine-size particles (D'Amato et al., 2007), increasing the concentration of sugar compounds in the atmosphere.

It is important to know under what meteorological conditions sugar compounds are emitted and what chemical and biological markers are well correlated with them. This will allow to determine the natural and/or anthropogenic origin of these compounds. This type of studies is only possible if a long-term study is carried out, considering the meteorological parameters, chemical composition and biogenic contribution of atmospheric particles. Thus, this study aims to: i) evaluate, between March 2016 and March 2017 in León (Spain), the daily and seasonal evolution of seventeen sugar compounds in the PM<sub>10</sub> fraction: arabinose, fructose, galactose, glucose, ribose, sucrose, xylose, adonitol, arabitol, 2-methylerythritol, myoinositol, mannitol, sorbitol, xylitol, galactosan, levoglucosan and mannosan; ii) establish the correlation with meteorological parameters, with some biological markers (pollen and fungal spore concentrations) and with chemical markers (K, As, Se, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Pb, Zn, etc.); iii) finally, estimate the impact of precipitation on the concentration of sugar compounds.

To our knowledge, only a few studies have evaluated the temporal evolution of the main sugar compounds in particulate matter and much less have related their concentrations in the environment

to meteorological conditions, mainly under rain weather, to some biological tracers and to other chemical species.

## 2. Experimental

### 2.1. Sampling

#### 2.1.1. Site

The city of León is located in the northwest of the Iberian Peninsula (42° 36' N, 05° 35' W and 838 m a.s.l) and is characterised by a continental type climate with influence of the Mediterranean. Winters are cold and long, with average temperatures of  $5 \pm 3$  °C, while summers are warm with average temperatures of  $20 \pm 4$  °C. Spring is the season with the highest amount of rain, while summer is usually a dry season with frequent storms (Castro et al., 2010; Fernández-Raga et al., 2017).

The sampling campaign was carried out in a suburban area located in the northeast of León city, Spain (Fig. S1), more specifically, at the terrace of the Faculty of Veterinary at the University of León. The sampling site is characterised by the absence of large emitting industries and a high contribution of biomass burning and fossil fuel emissions, due to the high traffic flow in the vicinity of the sampling area and the use of domestic heating devices in the city centre and in nearby towns (Blanco-Alegre et al., 2019; Oduber et al., 2018). In addition, León is greatly affected by primary biological emissions from the surroundings. Furthermore, numerous forests with many types of vegetation, whose pollination contributes to a high concentration of pollen, are about 30 km north from the city (Calvo et al., 2018; Oduber et al., 2019a). Approximately 30 km south of the city, extensive agricultural areas are located, which can represent a significant source of fungi due to rotting fruits or when crops are harvested.

#### 2.1.2. $PM_{10}$

$PM_{10}$  samples were collected every 24 hours, beginning at 1200 UTC every day between 9 March 2016 and 14 March 2017. For traceability in  $PM_{10}$  measurements (Aggarwal et al., 2013), the sampling was carried out following the procedures established in the standard EN 12341: 2014 by using a low volume sampler (TECORA, ECHOPM), with a sampling flow rate of 2.3 m<sup>3</sup> h<sup>-1</sup> (referred to normal temperature and pressure conditions) and equipped with 47 mm diameter Teflon filters. Furthermore, a high-volume sampler (CAV-Mb), operating with a flow rate of 30 m<sup>3</sup> h<sup>-1</sup> and equipped with 150 mm diameter quartz filters (prebaked at 600 °C for 6 hours) was also used. After sampling, quartz filters were folded and stored in aluminium foil (also baked), while Teflon filters were stored in Petri dishes. Both types of filters were stored in the freezer at -18 °C until

analysis. A total of 325 samples of each, Teflon and quartz filters, were collected throughout the sampling campaign.

After and before the sampling filters were weighted ( $\pm 0.00001$  g) in an electronic semi-micro balance (Mettler Toledo, XPE105DR). Quartz filters were used for the determination of the  $PM_{10}$  mass by the gravimetric method. Following the quality assurance/quality control (QA/QC) procedures described for sample collection, filter transport and handling, and filter weighing in the Normative EN 12341 of the European Committee for Standardization (2014), the balance and filters were conditioned for 24 hours in a room with controlled relative humidity ( $< 50\%$ ) and temperature ( $20\text{ }^{\circ}\text{C}$ ), and the microbalance was auto calibrated before each session, according to the instructions of the manufacturer.

The time period for each season was considered as follows: spring from 20 March to 20 June, summer from 21 June to 21 September and autumn from 22 September to 20 December and winter from 21 December to 19 March.

### 2.1.3. Bioaerosols and allergenic fraction

Atmospheric bioaerosol (particles between 2 and  $20\text{ }\mu\text{m}$  in diameter) sampling was performed continuously by using a Hirst volumetric trap (Hirst, 1952) mod. Lanzoni VPPS 2000, placed in the sampling location described in section 2.1.1. The complete sampling system contains a motor, a vacuum pump, a orifice, a rotating drum, a wind vane, a clockwork system and an impaction support. The wind vane allows permanent rotation of the trap head so that the orifice faces the wind. The suction pump works 24 h a day and continuously throughout the year at the same flow rate ( $10\text{ L min}^{-1}$ ). A 345 mm Melinex tape impregnated with a silicone fluid was exposed for seven days inside the sampler. The Melinex tape was attached to a drum with a driving speed of  $2\text{ mm h}^{-1}$  regulated by means of a clockwork mechanism. The daily analysis of the samples was carried out according to the Spanish Aerobiological Network (Galan et al. 2007), based on four parallel longitudinal transects along the slides. The pollen count by optical microscopy is possible due to their appearance stained with fuchsine.

The atmospheric aerosol for the quantification of the allergenic fraction was sampled with a low-volume sampler Burkard Multi-Vial Cyclone (Burkard Manufacturing Co. Ltd.) and with a suction rate of  $16.5\text{ L min}^{-1}$ . Atmospheric particles were collected dry directly into a 1.5 mL Eppendorf vial every 24 h and stored at  $-20\text{ }^{\circ}\text{C}$ .

### 2.1.4. Rainfall parameters

Rain variables were measured by a laser disdrometer (Laser Precipitation Monitor, LPM) of *Thies Clima*, which registered raindrops between 0.125 and 8 mm in 22 drop size ranges, on a 1-minute basis (Fernández-Raga et al., 2009). From the data provided by the LPM, the following

rainfall variables were obtained: precipitation intensity, accumulated precipitation, number of drops, volume swept by falling drops, mean and standard deviation of raindrop sizes.

## 2.2. Analytical techniques

### 2.2.1. Particulate sugar compounds

A portion of each quartz filter, with an area of about 14.14 cm<sup>2</sup>, was used for the determination of 17 sugar compounds: 7 saccharides (arabinose, fructose, galactose, glucose, ribose, sucrose and xylose), 7 alcohol-saccharides (adonitol, arabitol, 2-methylerythritol, myo-inositol, mannitol, sorbitol and xylitol) and 3 anhydrosaccharides (galactosan, levoglucosan and mannosan).

Sugar compounds were extracted with 3 mL of ultra-pure Milli-Q water with ultrasonic agitation. The extracts were filtered with a 0.2 µm pore PTFE syringe filter and transferred to glass vials for injection into the chromatograph on the same day. The analysis of the 17 sugar compounds was carried out by means of a Thermo Scientific Dionex<sup>TM</sup> ICS-5000 ion chromatograph equipped with a CarboPac® PA-1 (2 × 250 mm) anion-exchange analytical column. The methodology is based on Caseiro et al. (2007) and Piazzalunga et al. (2010), using multi-step gradient conditions with ultra-pure Milli-Q water and two solutions of NaOH (200 mM and 5 mM). The methodology allowed a good separation of sixteen of the seventeen sugars analysed. The alcohol-sugars, sorbitol and adonitol co-eluted in the same retention time, so the results obtained for these two compounds are shown as a sum of both as SA.

### 2.2.2. Organic and elemental carbon analysis

Two quartz filter punches, 9 mm in diameter each, were used to determine organic carbon (OC) and elemental carbon (EC) by using the thermal-optical system developed by the University of Aveiro (Portugal), following the methodology described by Alves et al. (2015) and Pio et al. (2011).

### 2.2.3. Water-soluble ions

Half of each Teflon filter was used to extract water-soluble ions with 6 mL ultra-pure Milli-Q water with ultrasonic agitation. The extracts were filtered with a 0.2 µm pore size PTFE syringe filter and stored in glass vials in the refrigerator until analysis. The determination of water-soluble ions was carried out by means of a Thermo Scientific Dionex<sup>TM</sup> ICS-5000 ion chromatograph. Cations (Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) were separated with an IonPac® CS16 (4 × 250 mm) column and using a solution of 30 mM of methanesulphonic (MSA) as mobile phase. Anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were separated with an IonPac® AS11 (4 × 250 mm) column and with a solution of 30 mM of potassium hydroxide (KOH) as mobile phase.

### 2.2.4. Trace elements



The other half of the Teflon filters was used for the determination of major trace elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Pb), using the PIXE technique (Particle-Induced X-ray Emission) described by Lucarelli et al. (2015).

### 2.2.5. Allergenic fraction

The quantification of the aeroallergen Alt a 1 was carried out following the method described by Fernández-González et al. (2019, 2010), which implies modifications of the methods previously described by Moreno-Grau et al. (2006) and Takahashi et al. (2001). The methodology for the determination of the allergenic fraction related to Alt a 1 protein, consists of two stages: extraction and quantification.

In the extraction phase, atmospheric particle samples, previously collected in Eppendorf tubes, were centrifuged at 14000 r.p.m. and subsequently extracted with a phosphate buffer solution (50 mM pH 7.0), NaCl 150 mM, EDTA 3 mM, Tween 20 at 0.005% and  $\text{NH}_4\text{HCO}_3$  125 mM. The extract was separated by centrifugation at 4000 r.p.m. for 10 minutes and both the supernatant and the sediment were stored separately at  $-20^\circ\text{C}$ .

The content of Alt a 1 protein in the extracted samples was quantified using a double sandwich ELISA (Enzyme Linked Immuno Sorbent Assay) method. The ELISA plates (Greiner, Frickenhausen, Germany) were coated with the antibody corresponding to Alt a 1 in a phosphate buffered saline (PBS) solution. Once the incubation period was over, the content of the plates was emptied and a PBS solution was added with 1% Bovine Serum Albumin (BSA) and 0.05% Tween-20 (PBS-BSA-T). The plates were incubated for 1 hour, and then their contents were emptied to perform 3 successive washes with a PBS solution with 0.1% BSA and 0.1% Tween-20 (PBS-B-T). Finally, the enzymatic activity was determined by adding o-phenylenediamine and measuring the absorbance of the resulting solutions with a plate reader. The quantification of the allergen was carried out by interpolating the absorbance values in a linear calibration curve.

Concerning the QA/QC, in the analytical techniques described in this section, the following analytical checks were carried out: i) a duplicate analysis was carried out every 10 samples, ii) the extraction and analysis of blank filters were carried out, iii) the detection and quantification limits were determined from the blank filters, iv) every 10 or 15 samples a known standard was analyzed to check the quantification. Furthermore, quality control for the entire database of ions was verified by calculating the ion balance.

## 2.3. Scavenging coefficient



The scavenging coefficient was evaluated through the following equation:

$$\Delta C = \frac{C_2 - C_1}{C_1} \times 100 \quad (1)$$

where  $C_2$  and  $C_1$  are the concentration of the studied sugar compound after and before the precipitation event, respectively. Sugar compound concentrations before and after the precipitation event were obtained as a mean value, calculated from the concentrations registered 2 days before and 2 days after the event, respectively. Consequently, a negative  $\Delta C$  indicates effective scavenging.

#### 2.4. Additional data

Weather information (temperature, precipitation and relative humidity) was recorded in the sampling location with an automatic meteorological station. Additional weather information (insolation and wind) was obtained from the database of the National Agency for Meteorology ([www.aemet.es](http://www.aemet.es)). For the statistical treatment, SPSS software (IBM Statistics Software V. 24) was used. The Kruskal-Wallis non-parametric test (Kruskal and Wallis, 1952) followed by Dunn test (Dunn, 1964) was applied in order to determine the eventual statistically significant differences ( $p < 0.05$ ). Furthermore, the correlations were calculated using the non-parametric Pearson rank correlation method (significance level  $p < 0.05$ ).

### 3. Results and discussion

#### 3.1. Annual evolution of sugar compounds in PM<sub>10</sub>

During the sampling campaign the annual mean PM<sub>10</sub> concentration was  $23 \pm 8 \mu\text{g m}^{-3}$ , with concentrations ranging between 4 and  $59 \mu\text{g m}^{-3}$ . The total sugar concentrations in PM<sub>10</sub> ranged between 1.3 and  $1052 \text{ ng m}^{-3}$ , with an annual mean of  $64 \pm 108 \text{ ng m}^{-3}$  (Table S2), which represents 0.3 % of PM<sub>10</sub>. Spring was the season with the highest daily and mean total sugar concentrations ( $1052$  and  $122 \pm 193 \text{ ng m}^{-3}$ , respectively), and the non-parametric Kruskal-Wallis test showed that there are statistically significant differences between the total sugar concentration in spring and the rest of the seasons. In contrast, winter was the season with the lowest total sugar concentration ( $41 \pm 47 \text{ ng m}^{-3}$ ). Theodosi et al. (2018) reported similar annual values, in a rural site in Greece, with a total mean concentration of  $57.7 \text{ ng m}^{-3}$ . Shahid et al. (2019) showed a total mean concentration of  $2100 \text{ ng m}^{-3}$ , in a study carried out in an urban site of Pakistan in December. Emygdio et al. (2018) reported a total mean sugar concentration of  $363.2 \text{ ng m}^{-3}$ , in Brazil, between autumn and winter.

Moreover, Liu et al. (2016) documented a total sugar concentration of  $792 \text{ ng m}^{-3}$  in Beijing, China, between 2010 and 2011. The differences are probably due to the quantification of compounds not entirely coincident, the variety of sources, the period of sampling, the weather conditions and the impact of long-range and local events that may affect sugar levels at each location. Besides, in temperate regions, early spring is the period of greatest plant activity, when most species restart vegetative growth and flowering occurs. All this implies important movements of cellulose during plant development. In León, high levels of sugar compounds in the atmosphere, caused by anthropogenic and biogenic emissions, is common throughout the year. Between autumn and winter, biomass burning emissions are frequent due to the use of domestic heating devices (Blanco-Alegre et al., 2019). In spring and summer, pollen and airborne spores are present because of the flowering and pollination of the large mass of plants and sporulation of fungi surrounding the city (Calvo et al., 2018; Fernández-González et al., 1993; Oduber et al., 2019a).

The monthly evolution of the sugar compounds shows higher concentrations of arabinose, fructose, glucose, ribose, sucrose, xylose, arabitol, 2-methylerythritol and myo-inositol between May and July (Fig. S3). The maximum mean seasonal concentration of arabinose, fructose, glucose, ribose and sucrose was observed in spring ( $1.08, 50.25, 10, 28 \text{ ng m}^{-3}$ , respectively) (Fig. S2, Table S2), and the Kruskal-Wallis test showed that there are statistically significant differences between the concentration of these sugar compounds in spring and the rest of the seasons, except summer. All these saccharides, except ribose and xylose, are significantly correlated ( $r > 0.6$ ), indicating a common origin. These saccharides can be abundantly emitted as primary biogenic aerosol particles (fungal spores, pollen, bacteria, and plant fragments) (Medeiros et al., 2006; Rathnayake et al., 2017; Theodosi et al., 2018). Therefore, the higher concentrations of these saccharides between May and July could be linked to the main pollen season in León (Fernández-González et al., 1993; Oduber et al., 2019a) and to the continuous lawn mowing around the sampling point, which implies the breakage of the vegetal tissues of numerous herbaceous plants, with the release of sugars to the atmosphere.

Between October and February, galactose, mannitol, SA, galactosan, levoglucosan and mannosan, showed the highest concentrations, while arabitol and xylitol also exhibited an important contribution during these months. Levoglucosan, mannosan and galactosan (significantly correlated,  $r > 0.5$ ) showed highest mean seasonal concentration in autumn and winter (Fig. S2, Table S2), with significant differences between the concentration in these two seasons and those in spring and summer. These anhydrosaccharides are usually related to biomass burning emissions (Vicente and Alves, 2018), which are frequent between autumn and early spring, due to wood burning for domestic heating purposes in León. Moreover, during summer, the Iberian Peninsula is often affected by forest fires. Thus, emissions from wildfires may contribute to the enhancement of anhydrosugar levels in the atmosphere during this season.

Higher concentrations of fructose, sucrose and glucose during summer, and higher concentrations of anhydrosugars during winter, were also reported by Wang et al. (2018) in an urban station of Xi'an, China. The same behaviour was observed by Yttri et al. (2007) in a suburban station of Norway, showing concentrations of sucrose, levoglucosan, mannosan and galactosan in winter of 5.3, 605, 167 and 4 ng m<sup>-3</sup>, respectively, and 20, 47, 10 and 3 ng m<sup>-3</sup>, respectively, in summer. Both studies found that the increase in the anhydrosugar concentrations during cold seasons can be due to an increase in the use of domestic heating devices, together with the stagnation caused by the low boundary layer.

### 3.2. Sugar compounds vs meteorological parameters

Insolation showed a significant correlation with glucose ( $r = 0.1$ , Table S3). However, when evaluated by season, it is observed that this correlation increases up to 0.3, also showing a correlation with arabinose ( $r = 0.4$ ) and arabitol ( $r = 0.5$ ) in spring. Glucose, sucrose, 2-metylerythritol and mannitol revealed a significant positive correlation with mean temperatures (T), with  $r$  between 0.1 and 0.5. The same behaviour was observed for these sugar compounds and minimum and maximum temperatures ( $T_{\text{Min}}$ ,  $T_{\text{Max}}$ , respectively). In spring, arabinose, fructose, galactose, glucose, sucrose, arabitol, 2-metylerythritol, inositol and mannitol are positively correlated with T and  $T_{\text{Max}}$  ( $r > 0.5$ ). Fernández-González et al. (1993) observed that the airborne pollen concentration in León is greatly affected by temperatures and reported that pollen concentrations have maximum values with temperatures between 20 and 25 °C, which are usual between spring and summer in León. Furthermore, Calvo et al. (2018) and Fernández-González et al. (1993) also reported that in León the maximum pollen concentration is reached between late-spring and early-summer, due to the high concentration of several pollen types (*Quercus*, *Pinus*, *Salix*, *Plantago*, *Ericaceae*, *Leguminosae*, *Urticaceae* and *Poaceae*).

The anhydrosaccharides displayed a negative significant correlation with T in spring (galactosan and levoglucosan) and with  $T_{\text{Max}}$  in autumn (galactosan). Due to the low temperatures and high relative humidity between late-autumn and early-spring in León (Table 1), the use of heating devices is very common, causing increased levels of anhydrosugars due to emissions from biomass-based domestic heating devices.

Wind speed affected air sugar concentrations particularly in spring, when winds are at their strongest in León (Table 1). In this season, arabinose, glucose, sucrose, arabitol, 2-metylerythritol and mannitol are negatively correlated with wind speed ( $0.3 < r < 0.6$ ). However, during summer, the concentration of sucrose increases with increasing wind speed. This fact could be related with the location of the source. Airborne particles emitted far from the sampling location need high wind speeds to reach the monitoring site, so aerosol concentrations increase with wind speed.

Nevertheless, a decrease in concentrations with increasing wind speed suggests sources close to the sampling site, with the greatest impact in stagnant atmospheric conditions (Carslaw et al., 2006; Yu et al., 2004).

**Table 1.** Seasonal mean values for insolation, wind speed (ws), temperature (T), minimum temperature ( $T_{\text{Min}}$ ), maximum temperature ( $T_{\text{Max}}$ ), relative humidity (RH), total accumulated precipitation and rain days in León (Spain) during the sampling period.

	Winter	Spring	Summer	Autumn
Insolation ( $\text{h day}^{-1}$ )	$6 \pm 4$	$9 \pm 4$	$13 \pm 2$	$6 \pm 4$
ws ( $\text{m s}^{-1}$ )	$0.9 \pm 0.7$	$1.1 \pm 0.8$	$0.6 \pm 0.3$	$0.6 \pm 0.4$
T ( $^{\circ}\text{C}$ )	$5 \pm 3$	$11 \pm 5$	$21 \pm 3$	$10 \pm 4$
$T_{\text{Min}}$ ( $^{\circ}\text{C}$ )	$0 \pm 3$	$5 \pm 4$	$12 \pm 3$	$4 \pm 4$
$T_{\text{Max}}$ ( $^{\circ}\text{C}$ )	$12 \pm 4$	$17 \pm 5$	$30 \pm 3$	$16 \pm 6$
RH (%)	$70 \pm 12$	$63 \pm 11$	$41 \pm 8$	$71 \pm 11$
Precipitation (mm)	131.5	155.1	15.3	69.4
Rain days	31	24	6	23

### 3.3. Sugar compounds and precipitation

In order to evaluate the effect of precipitation on the concentrations of sugar compounds, a total of 41 precipitation events were studied during the sampling campaign. Table 2 shows the main characteristics of these events.

**Table 2.** Mean monthly intensity, accumulated precipitation and duration of precipitation events in León during the sampling period

Month	Number of events	Intensity ( $\text{mm h}^{-1}$ )	Precipitation (mm)	Duration (h)
January	5	$0.4 \pm 0.2$	21	$12 \pm 8$
February	6	$1.1 \pm 0.4$	97	$14 \pm 2$
March	1	0.2	1	5
April	11	$0.7 \pm 0.4$	93	$9 \pm 6$
May	4	$1.1 \pm 0.4$	38	$10 \pm 6$
June				
July				
August	3	$2 \pm 2$	6	$5 \pm 4$
September				
October	3	$0.61 \pm 0.07$	15	$10 \pm 2$
November	3	$0.5 \pm 0.3$	10	$9 \pm 5$
December	5	$0.5 \pm 0.3$	20	$9 \pm 5$

Although for some of the sugar compounds, a decrease in the concentration after a precipitation event is observed (Fig. 1), there are some cases (glucose, mannosan, fructose, sucrose, ribose, SA,

mannitol and arabitol) in which an increase is registered. As D'Amato et al., (2007) pointed out that, during periods of rain, pollen particles can swell and break, producing hundreds of fine-size particles, and increasing the population of the airborne modes, which may persist in the atmosphere for weeks after precipitation (Bigg et al., 2015; Morris et al., 2017). This can be due to the hydration of the pollen grains and to the release of glycidic molecules (associated or not with proteins) from the cytoplasm or to the rupture of some pollen spores and / or bacteria walls, if there are very strong pressure changes (Fernández-González et al., 2010).

Arabitol, SA and mannitol also showed a substantial increase in their concentrations after a rain event. These saccharides are used as tracers for airborne fungal spores, and rain could trigger mechanisms of passive and/or active release and/or promote the growth of fungi, germination and growth of hyphae (Schulthess and Faeth, 1998). Wet conditions that follow rainfall events are favourable for the active release of fungal spores, causing an increase in their concentrations in the air (Rodríguez-Rajo et al., 2005; Van Osdol et al., 2004).

**Fig. 1.** Mean scavenging coefficients (boxes) and standard deviations (whiskers) for each sugar compound during the sampling campaign in León.

Significant positive correlations between  $\Delta C$  of glucose and several rain parameters (mean intensity, swept volume and drop mean size) were observed (Table S4). Furthermore, raindrops larger than 3 mm correlated significantly with  $\Delta C$  for this sugar, while for smaller raindrops, the correlation shows a (non-significant) washing effect. A similar pattern is observed for fructose for raindrops larger than 4 mm. Mannosan concentration raises significantly after rain with increasing mean rain intensities, accumulated precipitations and drop mean sizes. For larger raindrop sizes, a positive correlation with  $\Delta C$  is also registered. These results could support the existence of a threshold raindrop size above which the release of sugar compounds prevails over the scavenging process.

### 3.4. Sugar compounds vs biomarkers

The total pollen concentration was positively correlated with arabinose, fructose, glucose, sucrose and myo-inositol ( $r > 0.4$ , Table S5). The polar plots of these sugar compounds (Fig. S4), showed that from March to May, the main source is located mainly in the third and fourth quadrant, probably due to the numerous forests with many types of vegetation about 30 km north from the city. Graham et al. (2003) also reported higher glucose, fructose and sucrose concentrations

coinciding with higher pollen, fern spores and insect counts, in Amazonia in 2001. Medeiros et al. (2006) observed that, in Howland Forest, United States, glucose was the most abundant monosaccharide during the growing season, while galactose and arabinose increased between spring and mid-summer, as observed in this study (Fig. S3), reflecting the synthesis of primary sugars at the beginning of the plant growing season. The Pearson correlation of total pollen concentration with fructose, glucose and sucrose increases in spring ( $r > 0.4$ ), coinciding with the main pollen season (Fig. 2).

**Fig. 2.** Daily evolution of the total pollen concentration and sum of concentrations of sugar compounds: myo-inositol, 2-methylerythritol, arabitol, arabinose, fructose, galactose, glucose, mannitol, ribose, and sucrose, in León during the sampling campaign.

Mannitol was also significantly correlated with pollen concentration in spring ( $r = 0.4$ ). Burshtein et al. (2011) explained that, although mannitol is common in fungi, it is also abundant in various families of plants. Therefore, the correlations observed could be attributed to high levels of metabolic activity of plants during the flowering period. Moreover, in winter only glucose and mannosan showed a correlation with pollen. According to Fernández-González et al. (1993), the pollen calendar of León displays high levels of three types (*Crupessaceae*, *Alnus glutinosa* and *Corylus avellane*) in winter. This result probably indicates that these pollen types can emit higher concentrations of glucose than fructose and sucrose, compared to the emissions of typical spring-summer pollens.

The fungal spore, *Alternaria*, showed significant positive correlations with T, T<sub>Min</sub> and T<sub>Max</sub> (~0.4) and a negative relationship with RH (-0.3) between spring and autumn. Fernández et al. (1998) described that the *Alternaria* fungal spore has an optimal growth with mean temperatures between 22 and 28 °C. Furthermore, Rathnayake et al. (2016) reported high positive correlations between fungal spore tracers and mean temperature ( $r = 0.8$ ,  $p < 0.01$ ), confirming that the proliferation of fungi is favoured by high temperatures (around 23 and 27 °C). Besides, Filali Ben Sidel et al. (2015) found that this fungal spore is released under high temperature and low relative humidity conditions, corroborating the correlation observed in this study. However, *Alternaria* only correlated significantly with some of the sugars, such as arabitol and SA (in autumn), and levoglucosan (in winter), which probably indicates the presence of these sugars in the spore walls, and their release once the sporangia have decomposed.

Considering only rainy days, *Alternaria* was significantly correlated only with mannitol ( $r = 0.50$ , Table S6), and with Alt a 1 ( $r = 0.90$ ), which is the most important allergen of spores of this genus and that can be released under different environmental conditions (Hong et al., 2005; Skóra et al., 2015; Twaroch et al., 2012). Several authors indicated that relative humidity and rainfall in

previous days could favour the release and/or growth of fungal spores (Gosselin et al., 2016; Rodríguez-Rajo et al., 2005; Van Osdol et al., 2004). Moreover, during rainy days, ribose and sucrose also showed a significant correlation with pollen concentrations. This result indicates that the release of these saccharides is assisted by rain.

### 3.5. Sugar compounds vs other chemical species

Species related to biomass burning emissions, such as K,  $\text{NO}_3^-$  and OC (Reche et al., 2012; Urban et al., 2012; Zhang et al., 2010) were significantly correlated with levoglucosan, mannosan and galactosan ( $0.3 < r < 0.5$ ), suggesting a common origin. These correlations are even higher when analysed during autumn, when the Pearson coefficients ranged between 0.4 and 0.8, while in spring and summer the anhydrosaccharides do not present a significant relationship with these species (Table S5). Fig. 3 shows that the concentrations of levoglucosan, mannosan and galactosan, as well as  $\text{NO}_3^-$ , K and Pb, peak between December and March, when an increase in the use of residential heating appliances take place in León. Between September and February, the main source contribution of levoglucosan and mannosan is located at NE and SW (Fig. S4), where the city centre and the conurbation are located, suggesting a possible contribution from heating devices to the emission of these sugar compounds. Arabinose, fructose and glucose are also correlated with K,  $\text{NO}_3^-$  and OC in autumn. Biomass burning emissions can cause an increase in several sugar compounds, such as glucose, arabinose, ribose, arabitol, etc. (Medeiros et al., 2006; Vicente et al., 2013). The glucose-to-levoglucosan ratio can be used to determine the major source of glucose, since levoglucosan is used as a biomass burning tracer. In this study an annual mean of 1.7 and a considerable decrease of this ratio in autumn (1.3) and winter (0.5) was observed. Previous studies have proposed a value of approximately 4.5 for smoke-free samples, and close to 0.9 for smoke samples (Barbaro et al., 2015; Medeiros et al., 2006). In the city of León, the glucose/levoglucosan ratios only exceeded the value of 4.5 in 11 days: 8 in spring, 1 in summer and 2 in autumn, suggesting that smoke particles are an important source of glucose in the remaining days.

**Fig. 3.** Daily evolution of K, Pb,  $\text{NO}_3^-$  (concentration  $\times 0.1$ ) and the sum of concentrations of sugar compounds: levoglucosan, mannosan and galactosan, represented as biomass burning + fossil fuel, in León during the sampling campaign.

Anhydrosaccharides, mannosan and levoglucosan, are also correlated with some traffic emission tracers such as EC, OC, Cu, Zn, Se, Pb, V and Ni (Calvo et al., 2013; Manousakas et al., 2017), with  $r > 0.2$ . These correlations are even better when only the autumn is analysed ( $r > 0.4$ ), whereas in the other seasons no significant relationships between these species and anhydrosaccharides were



obtained. Although levoglucosan and mannosan are usually associated with biomass burning emissions, these results show that they can also be related to fossil fuel and/or traffic emissions. Alves et al. (2020) reported that both the shredded tiny tyre chips and the wear particles that form from the interaction between tyres and pavement, can release appreciable amounts of levoglucosan. Cellulose fibres are mixed with rubber compounds in the tyre vulcanisation process. The temperatures reached in the friction between the tyres and the pavements during vehicle running are probably enough to convert part of the cellulose fibres into sugars. In autumn, mannosan was correlated with As, which is a coal combustion marker (Vejahati et al., 2010). Yan et al. (2018) found that coal combustion is a source of anhydrosugars (levoglucosan, mannosan and galactosan) and suggested that levoglucosan cannot be used as a distinct source marker for biomass burning in cities where coal is still used. León has a coal-fired power station (located 30 km north of the city) and domestic coal-fired devices are still used in the province, so coal burning can be a significant source of particulate matter in the region. On rainy days, it was also observed that mannosan, mannitol, arabinose and fructose correlated with some of the fossil fuel tracers, probably due to an increase in traffic flow and/or use of residential heating devices in those days.

Sulphate and ammonium were correlated with arabitol, mannitol, fructose and levoglucosan in spring ( $r > 0.3$ ;  $p < 0.05$ ), while these ions were highly correlated with mannosan in autumn ( $r > 0.7$ ;  $p < 0.01$ ) and in winter ( $r > 0.5$ ;  $p < 0.01$ ), suggesting a possible common origin. Ammonium-sulphate is formed from the photo-oxidation of  $\text{SO}_2$  from fossil fuel combustion (Alastuey et al., 2004; Qin et al., 2017). In addition,  $\text{SO}_4^{2-}$  and  $\text{NH}_4$  are formed by the progressive gas-to-particle conversion of the components emitted by biomass burning (Balasubramanian et al., 1999).

Mineral-related elements (Al, Si, Zn) showed a positive correlation with glucose, sucrose, arabitol, myo-inositol and mannitol ( $0.3 < r < 0.8$ ) in spring. As already mentioned, in spring high levels of pollen are registered in León. Thus, the observed correlation is probably related to soil resuspension and/or dust intrusions, which can transport high amounts of biological particles (Oduber et al., 2019b).

#### 4. Conclusions

The daily evolution of seventeen sugar compounds in aerosol samples, collected between 9 March 2016 and 14 March 2017 was analysed. The concentration database of the sugar compounds has allowed to determine its natural and/or anthropogenic origin, based on the association with other variables, such as several other chemical species, pollen, fungal spores and meteorological conditions. During the sampling campaign, the total sugar concentrations in  $\text{PM}_{10}$  ranged between 1.3 and 1052  $\text{ng m}^{-3}$ , with an annual mean of  $64 \pm 108 \text{ ng m}^{-3}$ , accounting for 0.3 % of the  $\text{PM}_{10}$  mass concentration.

Pearson correlations between the analysed sugar compounds, meteorological parameters, other chemical species and biological tracers (pollen and *Alternaria* concentrations), showed that:

- In spring, when a high metabolic activity of plants occurs and temperature increases, sugar compounds (glucose, sucrose, 2-methyl-erythritol, mannitol, arabitol and inositol) correlated with airborne pollen concentrations. Glucose, sucrose, arabitol, myo-inositol and mannitol were also correlated with Al, Si and K, pointing to soil resuspension and/or dust intrusions as emission sources in this season. However, the use of glucose and arabinose as a pollen tracer should be done with great care, because they can also be related to biomass burning emissions.
- Between spring and autumn, *Alternaria* air concentrations increased with rising temperatures and decreasing relative humidity, due to the proliferation of fungi. In autumn, arabitol and sorbitol + adonitol can be used as tracers for this fungal species. Moreover, on rainy days, mannitol and the allergen Alt a 1, were correlated with *Alternaria*, which probably indicates that mannitol is a good tracer for *Alternaria* in wet periods.
- In autumn, lower temperatures cause an increase in the concentrations of levoglucosan, mannosan and galactosan, due to the increasing use of residential heating devices. In this season, these anhydrosugars and arabinose, fructose and glucose, presented significant relationships with K, NO<sub>3</sub><sup>-</sup> and OC (biomass burning tracers). Furthermore, mannosan and levoglucosan were correlated with EC, O<sub>2</sub>, Cu, Zn, Se, Pb, V and Ni, which are traffic and fossil fuel combustion markers. In autumn, mannosan was also correlated with As, a coal combustion marker. Thus, the selection of these anhydrosaccharides as tracers of biomass burning during the cold season, may be overestimating the contribution of that source, due to the contribution from other anthropogenic emissions.

Precipitation can cause an increase in glucose and sucrose concentrations, due to the breakage of pollen particles that can release sugar compounds bonded to hundreds of fine size grains. Rainfall can also cause an increase in arabitol concentrations owing to the release and growth of fungi. The increase of glucose concentration after rain showed a significant positive correlation with mean rainfall intensity, swept volume and drop mean size. Concretely, raindrops larger than 3 mm increased glucose concentration, while smaller raindrops produced a (non-significant) washing effect. The behaviour of fructose was similar for raindrops larger than 4 mm. This fact could suggest the existence of a threshold raindrop size that split both processes: washing and release of sugar compounds. Nevertheless, further studies are needed in order to validate this hypothesis.

The study of concentrations and origin of atmospheric bioaerosols is increasingly necessary of their health consequences. This work reveals that the association of sugar compounds with biological and non-biological tracers and with meteorological conditions is a necessary tool to assign the origin of water-soluble organic compounds, helping to assess the bioaerosol levels in the

air. To avoid overestimating or wrongly assigning a source, monitoring of multiple parameters and the combined assessment of all of them must be made.

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### Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Graphical abstract:

### Highlights

- The daily evolution of 17 sugar compounds in atmospheric aerosol was studied in León
- Mannosan and levoglucosan are linked with traffic and fossil fuel combustion markers
- Precipitation can cause an increase in glucose, sucrose and arabitol concentrations.
- On rainy days, mannitol is a good tracer for *Alternaria*
- Some sugar compounds are correlated with rain intensity, swept volume and drop size

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