

Characterization of organic aerosols at the Natura 2000 remote environment of Sanabria Lake (Spain): Evaluating the influence of African dust and regional biomass burning smoke

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HIGHLIGHTS

- GC/MS characterization of 76 polar and apolar organic compounds.
- Natural sources highly contribute to organic aerosol in the background environment.
- SOA markers predominate in warmer seasons; biomass burning tracers in cold seasons.
- African dust promote the formation of oxygenated organic compounds.
- Regional forest fires increase biomass markers and PAH concentrations.

ARTICLE INFO

Keywords:

Remote site
PM₁₀
Organic compounds
GC/MS
Biomass burning events
African dust

ABSTRACT

This work presents a thorough analysis of PM₁₀ speciated organic composition at Sanabria Lake Natural Park, a rural remote area in NW-Spain, including diacids, hydroxy and poliacids, fatty acids, alkenoic acids, sugars, sugar alcohols, n-alkanes, PAHs, quinones, hopanes, tracers of biomass burning, and biogenic secondary organic aerosol (BSOA) from isoprene and α -pinene.

PM₁₀ ambient concentrations at Sanabria (mean value of 12.2 $\mu\text{g m}^{-3}$) were within the typical range registered in regional-background air quality monitoring stations in Spain. However, the occurrence of African dust outbreaks and biomass burning events produced significant increases in the PM₁₀ levels at this monitoring site (daily mean levels of 29.2 $\mu\text{g m}^{-3}$ and 13.7 $\mu\text{g m}^{-3}$, respectively).

Major organic compounds were levoglucosan, saccharides and 2-methyltetrols, markers for biomass burning, soil dust and BSOA respectively.

SOA contributed more than 53% of the total measured organics in summer. Samples with high levels of SOA include most of the African dust events, suggesting that African dust might promote the formation of oxygenated species such as SOA derivatives in this area. This contribution decreased to a 14% in winter. Biomass burning tracers represented 37% of the analysed organic pollutants in winter, indicating that this is the main source of organic compounds in the colder seasons, mainly due to the influence of regional biomass burning events and the use of biomass as fuel in domestic heating. Hence, the fact that African dust outbreaks and biomass burning events are likely to become increasingly frequent in the context of climate change makes this type of analysis particularly relevant for assessing their impact on natural protected areas.

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<https://doi.org/10.1016/j.atmosenv.2023.119634>

Received 19 October 2022; Received in revised form 23 January 2023; Accepted 30 January 2023

Available online 2 February 2023

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1. Introduction

Atmospheric aerosols have recognized influence on climate, air quality, human health and ecosystem functioning. They can change the atmospheric radiation budget directly by scattering and absorbing radiation, and indirectly by altering the cloud processes; they represent one of the main air pollutants affecting human health and modifying nutrient availability in the different biogeochemistry systems (Wang et al., 2009; IPCC et al., 2013; WHO Regional Office for Europe, 2013; WHO, 2014; Gonçalves et al., 2014; Mahowald et al., 2017; Yli-Juuti et al., 2021).

Organic matter is a major component of atmospheric aerosols, consisting of a complex mixture of hundred of compounds that contribute 10–70% to their mass (Saxena et al., 1995). It is important to understand the organic aerosol composition to evaluate its possible health effects, their relation to photochemistry or long range atmospheric transport and the induced alteration of biogeochemical cycles (Simoneit and Mazurek, 1982; Rooge et al., 1991; Brown et al., 2002; Alves, 2008; Fu et al., 2016).

Relative contributions of primary versus secondary sources depend on the type of local emissions, meteorology and atmospheric chemical conditions (Brown et al., 2002).

At rural areas, the most important primary sources are biomass burning and particles from soil dust (Simoneit, 2004; Medeiros and Simoneit, 2007, van Drooge et al., 2015).

Biogenic secondary organic aerosols (BSOA), originated from the photooxidation of biogenic volatile organic compounds (VOCs), represent a major contribution to atmospheric aerosols in natural and rural environments, due to the large VOC emissions from vegetation (Fu and Kawamura, 2011 and references therein, Ding et al., 2014, Klyta and Czaplicka, 2020).

It is currently assumed that the main contributions to PM₁₀ regional background levels by natural sources in southern Europe are attributed to African dust intrusions (Pey et al., 2013 and references therein) and biomass burning smoke emissions from wildfires (Alves et al., 2011; Vicente et al., 2013; Faustini et al., 2015). Interestingly, the frequency and intensity of dust events in the western Mediterranean basin have increased in the last decades (Salvador et al., 2022). As a consequence of global warming, a robust increase in the area burned by wildfires is expected over Mediterranean Europe in the next decades based on climate-fire model projections (Turco et al., 2018).

There are few studies relating desert dust episodes with organic compounds. The global atmospheric transport of dust carries predominantly mineral-crustal particulate matter. However, dust can mix with organic and inorganic compounds via heterogeneous reactions or adsorption processes during long-range transport (Gonçalves et al., 2014; Fu et al., 2016 and references therein). Other studies have evaluated the effects of dust storms on the atmospheric chemistry of ozone (O₃) (Bian et al., 2003; Bonasoni et al., 2004). The results suggest a possible impact of dust on the chemistry of organic carbon species, being most susceptible the oxygenated compounds. Salisbury et al. (2006) analysed the changes induced by dust in the photochemistry of oxygenated organic compounds, such as aldehydes and ketones. These authors found that during the dust periods, the daily cycles and the absolute concentrations of some species, such as acetaldehyde, were different, although these changes could not be attributed unequivocally to heterogeneous reactions with dust.

Several studies on organic aerosols have been reported in Spain for urban, suburban and rural areas (Pindado et al., 2009; Mirante et al., 2013, 2013v; van Drooge and Grimalt, 2015; Pérez et al., 2020). However, there is a lack of this type of information for atmospheric aerosols at remote sites located far away from anthropogenic sources of air pollutants. The Sanabria Lake is the largest natural freshwater lake in the Iberian Peninsula, representing a unique ecosystem. It is located in a remote area with a very small population, situation that has allowed the maintenance of a typically oligotrophic state of the lake. Recent

planktonic diatom blooms have risen the concern about a possible shift of the trophic status (Pahissa et al., 2015). For this reason, an intensive two-year monitoring programme was launched by the water competence authorities in order to analyse the status of the lake and the main drivers that could be affecting the ecosystem functioning. Within this framework, air quality was monitored simultaneously with the limnological study, to analyse the contribution of atmospheric deposition to nutrient inputs in the Sanabria lake basin.

The main objective of this study was to characterize the molecular composition of the organic fraction of the PM₁₀ aerosol at the site. The comprehensive characterization of organic constituents in the PM₁₀ fraction can contribute to better understand the chemistry and sources of atmospheric aerosols, overcoming the existing lack of information on the current levels of organic compounds at regional background environments, and can provide insights of drivers that could be affecting ecosystem functioning in this area of high ecological value, including the influence of African dust outbreaks and biomass burning events.

2. Methodology

2.1. Study area

The Sanabria Lake is an oligotrophic water body located 1000 m.a.s.l in the Duero River Basin in NW Spain (42°07'21" N, 6°43'09" W; Fig. 1). With a glacial origin, it is located in a territory of medium and high mountains formed by acid Paleozoic rocks (granites, gneiss, slates), intensely eroded by the action of the ice during the last glaciation. According to the historic data series (1950–2011) of an adjacent meteorological station (Ribadelago Station; 42°07' N, 06°45' W) the local climate is wet Mediterranean mountain type with an annual mean temperature of 9 °C and mean annual rainfall of 1510 mm (Hernández et al., 2015).

The lake and its surrounding area are included in a Special Protection Area of the Natura 2000 Network (ES4190105 “Lago de Sanabria y alrededores”) and in the protected area “Sanabria Natural Park”. This territory is home of several endangered or endemic species, many of them related to the aquatic habitats and peatlands. Other remarkable habitats in the area are oaklands, mountain heathlands and acidic high-mountain pastures.

The Sanabria lake basin is far from important sources of pollutant emissions, but with some human pressure in the area, particularly during summer, linked to touristic activities. In its approximately 127 km², the greatest anthropogenic sources of atmospheric pollutants are traditional livestock activities and biomass combustion for home heating of the <1000 inhabitants in the catchment and closest town.

2.2. Sampling method

The sampling site was located at the Casa Forestal de la Playa de Viquiella (1020 m a.s.l.). This area corresponds to the lowest altitude in the basin and highest human activity at the Natural Park.

A high-volume sampler CAV-A/mb (MCV, Spain) equipped with a PM1025-CAV inlet was used to take 24-h samples of PM₁₀ on quartz filters Pall 2500 QAQ-UP (150 mm diameter), operating at a flow rate of 30 m³ h⁻¹. Samples were taken once a week for 18 months, changing successively the weekday, from June 2016 to December 2017. Some samples were lost due to incomplete sampling periods caused by electric power disruption. This technical problem also caused missing samplings for several weeks. A total of 41 samples were finally collected.

Prior to sampling, filters were combusted at 450 °C for 3 h and stored in baked aluminum foil packages, then weighted in a conditioned room for gravimetric analysis according to EN 12341, 2014. Finally, filters were wrapped in aluminium foil and stored at -18 °C until analysis. Blank filters were also weighted and analysed periodically with each batch of samples. A total of 10 blank filters were employed.

Meteorological parameters (wind speed and direction, precipitation,

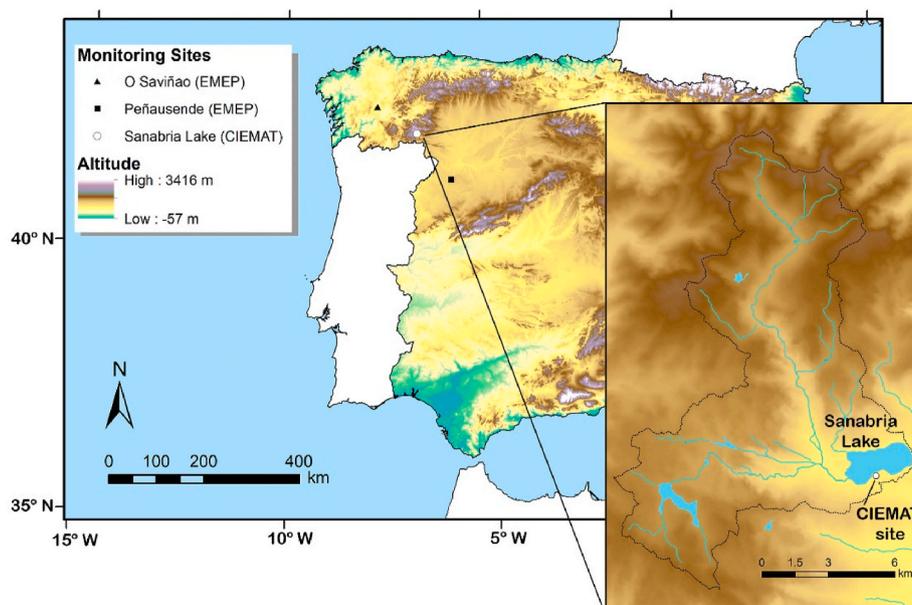


Fig. 1. Geographical location of the Sanabria sampling site and the closest EMEP air quality monitoring stations: Peñausende and O Saviñao.

radiation, air temperature and relative humidity) were continuously monitored at the sampling site. Atmospheric concentrations of ozone (O₃), ammonia (NH₃), nitrogen dioxide (NO₂) and nitric acid vapour (HNO₃) were monitored using passive samplers, following the methodology explained in García-Gómez et al. (2016). Two replicate samplers per gaseous species were exposed at 2 m during 36 consecutive periods of 2 weeks. Tube-type samplers (Radiello®; Fondazione Salvatore Maugeri, 2006) were used to measure atmospheric concentrations of NH₃, NO₂ and O₃, while badge-type samplers, manufactured following Bytnerowicz et al. (2005), were used for HNO₃. The years 2016 and 2017 constitute a dry period in the area, with an average annual rain of 894 mm, and mean temperature and relative humidity of 12.2 °C and 62.6%, respectively. Yearly mean concentrations of air pollutants (calculated for the period June 2016–May 2017) were 0.9 µg NO₂ m⁻³, 0.4 µg NH₃ m⁻³, 1.3 µg HNO₃ m⁻³ and 75.9 µg O₃ m⁻³, which are typical concentration values of Mediterranean rural areas that are far from significant sources of air pollution (García-Gómez et al., 2016). Seasonal values of meteorology and gaseous pollutants for the sampling period are shown in Table S1.

2.3. Analytical procedure

A quarter of each filter was extracted with dichloromethane:methanol (2:1; v/v) under ultrasonication, and analysed following a method previously described (Pérez et al., 2020).

In brief, 25 µl of the concentrated extract (1 mL) were derivatized with BSTFA/TMCS prior to GC/MS to analyse polar compounds (Fraction 1).

The remaining extract (975 µl) was submitted to a clean-up procedure on activated alumina and GC/MS analysed for aliphatics, hopanes, quinones and PAHs analysis (Fraction 2).

Accuracy of method was checked by analyzing SRM1649b within each batch of samples.

Blank filters were also analysed with each batch of samples. Small amounts of some analytes were encountered, typically some n-alkanes and fatty acids, which were less than 2% of compounds in real samples, or corrected to final concentrations.

MDL were calculated as three times the standard deviation of results from analysis of six blank filters, and were estimated from 0.001 ng µL to 1 for benzo(a)fluorenone to 0.17 ng µL⁻¹ for hexadecanoic acid, which

correspond to 0.01–5 ng m⁻³, assuming a sample volume of 740 m³.

Replicate analyses of six fractions of a filter sample showed that the precision of the method, expressed as relative standard deviation was below 20% for most analytes.

More detail on the method can be found in the Supplementary material.

For the analysis of crustal elements, another quarter of each filter was digested following 200.2 US-EPA method (Martin et al., 1994) and analysed by Inductively Coupled Plasma combined with Optical Emission Spectroscopy (ICP-OES) following 200.7 US-EPA method (U.S. EPA, 1994).

2.4. Identification of days with contributions of African dust and biomass burning smoke

The identification of African dust outbreaks over NW Spain during the sampling period at Sanabria was carried out by means of a well-known methodology (Escudero et al., 2007; Querol et al., 2013). It is based on the daily interpretation of air mass back-trajectories, desert dust model forecast images, satellite imagery and synoptic meteorological maps. Currently, this is one of the official methods recommended by the European Commission for detecting the appearance of African dust plumes over a given region (Commission Staff Working Paper, 2011).

The main biomass burning events that occurred in the study region were also identified, based on the output from the NAAPS (Navy Aerosol Analysis and Prediction System) Global Aerosol Model. The NAAPS is a global aerosol transport model maintained operationally by the U.S. Navy for predicting the distribution of tropospheric aerosols (<https://www.nrlmry.navy.mil/aerosol/>). This model uses geostationary satellite and MODIS fire products to detect smoke emissions produced by active burning fires, such as wildfires and the combustion of agricultural residues. More details on the model initialisation and the estimation of smoke emissions, transport and removal can be found in Giglio et al. (2003) and Reid et al. (2009).

Then, time series of daily PM₁₀ data from two regional background air-quality monitoring sites were compiled and analysed to evaluate the real impact of African dust and biomass burning smoke on surface PM levels during each identified episodic day all the sampling period long. The applied method is in accordance with the European Commission

recommendations (Commission Staff Working Paper, 2011). Peñausende (41°17'00" N; 05°52'00" W; 985 m.a.s.l.) and O Saviñao (43°13'52" N; 07°41'59" W; 506 m.a.s.l.) are stations of the Co-operative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP) located SE and NW of the Sanabria monitoring site, at a distance of about 117 and 147 km respectively (Fig. 1). They monitor background air-quality levels that are representative of a given area surrounding the station, ranging from 25 to 150 km, depending on the local topographical features (EEA, 1999).

3. Results and discussion

3.1. Atmospheric levels of PM₁₀ during the sampling period

On average, PM₁₀ levels registered at Sanabria Lake during the sampling period reached 12.2 $\mu\text{g m}^{-3}$. This value is in the lowest side of the range of regional background levels of PM₁₀ obtained at EMEP monitoring stations (12–20 $\mu\text{g m}^{-3}$) and other rural stations (14–21 $\mu\text{g m}^{-3}$) in Spain in the period 1999–2010 (Querol et al., 2012). Daily mean PM₁₀ levels registered at Peñausende and O Saviñao along the sampling period (11.9 and 11.3 $\mu\text{g m}^{-3}$, respectively) were within the same range. It suggests that despite the reduced number of samples obtained in Sanabria, compared to the initial work plan, the results obtained from the analysis of these samples are representative of the entire period.

10 samples were collected during African dust outbreaks and 9 during biomass burning events in the vicinity of the station. Half of the African events occurred in summer, while one third of the biomass burning events occurred in summer and one third in spring. On 5 occasions both types of events occurred simultaneously. During the occurrence of such events, PM₁₀ levels increased above the current levels registered in Sanabria. On average they reached 29.2 $\mu\text{g m}^{-3}$ and 13.7 $\mu\text{g m}^{-3}$ under African dust outbreaks and biomass burning events, respectively. When no events happened, mean PM₁₀ levels in Sanabria decreased to 5.8 $\mu\text{g m}^{-3}$ during the sampling period.

One of the PM₁₀ samples was obtained during an unusually intense African dust event that happened on 23-February-2017 and has been described elsewhere (Fernández et al., 2019; Oduber et al., 2019). This event caused the highest PM₁₀ value (110.6 $\mu\text{g m}^{-3}$) recorded at Sanabria during the experimental period (Fig. 2). For this reason the highest average PM₁₀ value was recorded in winter (19.3 $\mu\text{g m}^{-3}$). If this sample is excluded, the highest seasonal mean PM₁₀ value was recorded in summer (14.6 $\mu\text{g m}^{-3}$) and the lowest in winter (4.1 $\mu\text{g m}^{-3}$).

3.2. Atmospheric levels of organic compounds

The sum of quantified organic compounds on average corresponded to 2% of the total measured mass of PM₁₀ in summer samples, increasing up to 4% in autumn and winter. Total quantified organics ranged from 172 to 246 ng m^{-3} in winter and spring respectively (mean 210 ng m^{-3}). Box and whisker plots of seasonal variation of PM₁₀ and total organics are shown in Fig. 2. The higher concentrations achieved during the warmest months can be related to the higher prevalence of natural and

secondary organic compounds in the aerosol, due to the photochemical transformation of biogenic VOCs and the higher emission rates. These results are in agreement to those found in other remote areas (Sheesly et al., 2004).

Tables S2 and S3 present the mean concentrations of seventy-six measured organic compounds. Most abundant species were levoglucosan (mean 27.4 ng m^{-3}), sacharides (manitol, glucose) and SOA isoprene derivatives (2-methyltetrols), i.e. compounds associated with biomass burning, soil dust, and secondary aerosol respectively. This same trend was found by García et al. (2017) in their study of organic aerosols in the Saharan Air Layer at Izaña Observatory, located at 2400 m a.s.l. on the island of Tenerife.

A correlation analysis was performed among individual organic compounds, PM₁₀ and O₃ using the Statgraphics Centurion XVII statistical software (95% confidence, $p < 0.05$). The results obtained for the target compounds grouped by chemical families are discussed below.

Organic diacids, n-alkanes, SOA markers from isoprene and terpenes and PM₁₀ showed significant correlations with each other (>0.6), also positive with O₃ (>0.3). Alkanes and organic diacids can be either biogenic or anthropogenic in origin, whereas measured isoprene and terpene markers are proved biogenic compounds. Their correlations could indicate a preferred natural origin of all of these families in this area. In fact, the highest n-alkane concentrations at Sanabria were observed for the C27 and C29 homologs for all seasons, which suggest a vegetation source. Also, the carbon preference index (CPI), defined as the ratio between odd to even hydrocarbons (minimum during winter 1.7, up to 3.2 in summer) denotes biogenic origin. The higher CPI in summer is related to a larger influence of vegetation waxes in the aerosol (Mazurek et al., 1989; Kavouras and Stephanou, 2002; Brown et al., 2002, and references therein).

2-Methylthreitol (2 MT) and 2-methylerythritol (2 ME), 2-methylglyceric acid (2MGA) and C₅-alkene triols: cis-2-methyl-1,3,4-trihydroxy-1-butane, 3-methyl-2,3,4-trihydroxy-1-butane and trans-2-methyl-1,3,4-trihydroxy-1-butane, recognized products of oxidation of isoprene were measured (Claeys et al., 2004; Wang et al., 2005; Wu et al., 2020). The highest levels of these compounds were reached in summer (76 ng m^{-3}), with minimum during winter (4.8 ng m^{-3}), mean of 39 ng m^{-3} . These values were consistent with those found in a Japanese forest in summer and in Amazon and Hungarian forests (Alves, 2008 and references therein, Fu and Kawamura, 2011; Ding et al., 2014).

The relative contribution (percentage of abundances) of the SOA isoprene tracers according to season is shown in Fig. 3. The predominance of 2-methyltetrols (up to 94 ng m^{-3}) has been previously observed in other field studies (Li et al., 2013) and is consistent with their formation as major products in low NO_x atmospheres found in chamber studies (Ding et al., 2014 and references therein). Indeed, NO_x concentrations measured at Sanabria were always very low ($<4 \mu\text{g m}^{-3}$) during the whole period of sampling. The relative abundance of tretrols and MGA slightly decreased in the cold seasons, while C₅-alkene triols increased their proportion.

The detected α -pinene oxidation products included pinic and cis-pinonic acids, 3-hydroxyglutaric acid (HGA) and 3-methyl-1,2,3-

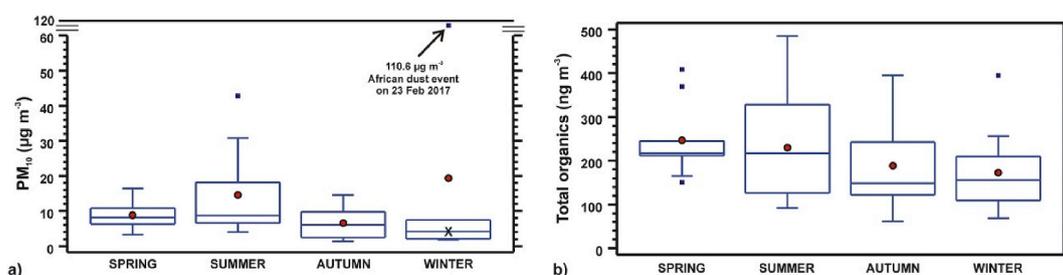


Fig. 2. Boxplots of PM₁₀ ($\mu\text{g m}^{-3}$) and total organics content (ng m^{-3}) during each season in Sanabria Natural Park. The x represents the average winter PM₁₀ value, excluding the unusually high value associated with the African dust event produced on 23 February 2017.

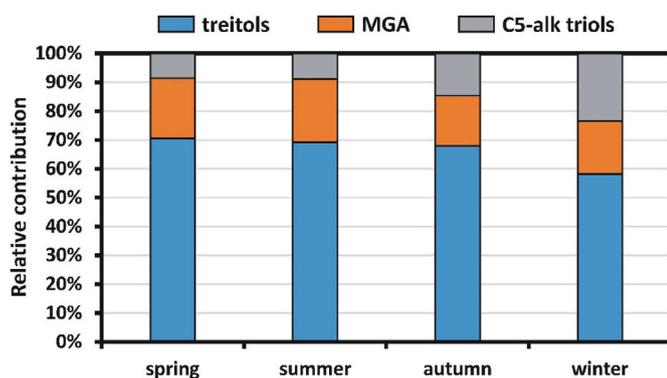


Fig. 3. Abundance (%) of the SOA isoprene tracers according to season.

butanetricarboxylic acid (MBTCA). The sum of SOA pinene tracers (mean 13 ng m^{-3}) varied from 17.2 ng m^{-3} in summer to 5.7 ng m^{-3} in winter, following all the individual compounds this seasonal trend.

In the presence of O_3 , α -pinene originates pinonic and pinic acid. Further reaction of pinic and pinonic acids originates HGA and MBTCA, so these can be considered as second generation products of oxidation of α -pinene (Claeys et al., 2007; Wu et al., 2020). Besides, all of these compounds have been reported to dominate in the fine particulate fraction except cis-pinonic acid which was preferably in the coarse fraction (Mahilang et al., 2021; Kanellopoulos et al., 2021). These factors can explain the lack of correlation found between cis-pinonic acid and their derivatives, also discussed in several field studies (Ding et al., 2011; Alier et al., 2013; Pérez et al., 2020).

A higher relative contribution (% abundance) during the cold periods was found for cis-pinonic acid, respect to the other terpene tracers, which could be explained by its transformation to MBTCA promoted by the higher temperatures and stronger radiation in the summer. In this sense, the ratio cis-pinonic acid/MBTCA can be used to establish the aging of α -pinene SOA. A higher ratio indicates less transformation of pinonic acid to MBTCA and thus relatively fresh SOA. This ratio was 4.0 in winter, and decreased to 1.4 in spring and summer, showing the higher photochemical activity in hot seasons (Ding et al., 2014).

Galactosan, mannosan, levoglucosan, dehydroabietic acid, PAHs and xilitol were highly correlated (0.7–0.9). These compounds were not related to PM_{10} or O_3 , indeed some PAHs isomers showed a negative correlation with O_3 (−0.3), which could indicate their photodegradation.

PAHs showed very low concentrations (mean value of 0.30 ng m^{-3}), which ranged from 0.54 ng m^{-3} in winter to 0.15 ng m^{-3} in summer. Quinones followed a similar trend (0.12 ng m^{-3} in winter to 0.006 ng m^{-3} in summer, mean 0.06 ng m^{-3}), pointing to the clean natural atmosphere in this area. The increase of PAHs in winter has been observed in other rural areas of Europe (van Drooge and Grimalt, 2015) and can be attributed to biomass combustion for residential heating in combination with stable atmospheric conditions. Retene, a marker of pine wood combustion was not detected in the samples, whereas benzo(b) fluoranthene was the most abundant.

The low impact of road traffic emissions in this area is related to the low levels registered of phthalic acids and hopanes (average 0.011 ng m^{-3}), which are tracers of motor vehicle exhaust gases (Glasius et al., 2022). Hopanes were only well correlated with each other (0.8) and PM_{10} (0.7).

Levoglucosan, a recognized tracer of biomass burning, was the most abundant organic compound in the analysed samples, showing values ranging from 11.8 to 59.7 ng m^{-3} in spring and winter respectively (average 29.4 ng m^{-3}). Puxbaum et al. (2007) reported similar levoglucosan concentrations (32 ng m^{-3}) at a rural site in Portugal.

Dehydroabietic acid (DHA) is a specific tracer of conifer resins. This compound has been identified in the vegetation smoke both of natural

and thermally altered aerosol particles, and is emitted in large quantities during the combustion of coniferous wood (Rooge et al., 1998; Medeiros and Simoneit, 2007). Highest concentrations were found during winter (up to 3.2 ng m^{-3}), annual mean 1.9 ng m^{-3} . These levels are much lower than those found in other rural areas of Spain affected by local biomass burning emissions (van Drooge and Grimalt, 2015; Pérez et al., 2020).

Saccharides (glucose and trehalose) and mannitol, considered molecular markers of fungal spores, and also related to soil particles were well correlated (0.8–0.9). These compounds were moderately correlated to PM_{10} (>0.4). Their higher concentrations during spring can be explained by the higher biological activities in soils, higher plant growth and contribution from pollen (Fu et al., 2012; Alier et al., 2013; Zhu et al., 2022).

Fatty acids showed positive correlations with a variety of other compounds, such as diacids, MBTCA, aliphatics, some PAHs such as phenanthrene, fluoranthene or chrysene, PM_{10} and O_3 , showing the high number of different sources, which can contribute to increase their levels.

Based on this correlation study, compounds were grouped into 14 classes according to functional groups and sources. Concentration data depending on the season and the development of biomass burning events and African dust outbreaks are summarized in Table 1.

3.3. Influence of African dust outbreaks and biomass burning events

The previous analysis of inorganic markers for traffic and crustal aerosols (Alonso del Amo et al., 2018), determined the low anthropogenic influence in this site, confirmed by the low concentrations of PAHs, hopanes and phthalic acids measured and the lack of correlation with n-alkanes. However, as it has been previously mentioned, PM_{10} levels in Sanabria significantly increased during the occurrence of African dust outbreaks and biomass burning events.

Fig. 4 represents the influence of African dust outbreaks and biomass burning events in the total organics content. A clear increase was observed during African dust episodes (278 ng m^{-3}), higher when both episodes were coincident (325 ng m^{-3}). The ANOVA test confirmed significant differences among data ($F = 4.93$, $P = 0.0056$ at 95% confidence). The multiple range test found differences for the two groups of samples affected by African dust in relation to no event samples. Gonçalves et al. (2014), analyzing the content of organic compounds in PM_{10} at Cape Verde, also found that the organic content was higher during the occurrence of African dust outbreaks. In the western Mediterranean basin, African dust episodes take place mostly in summer (Pey et al., 2013). In this season, the higher temperatures contribute to BSOA formation. In this work, 5 out of 10 samples influenced by dust were taken in summer, and two of them were also affected by biomass burning smoke emissions, so it is difficult to differentiate both effects.

However, when comparing only samples from the warmest periods, the ANOVA test also showed significant differences between the two groups of samples, those affected by African dust episodes ($F = 3.57$, $P = 0.0377$ at 95% confidence) and the unaffected samples. The results indicate that African dust events promote the increase of total organic compounds in PM_{10} .

Biomass burning tracers showed a clear seasonal trend (Fig. 5a), with maximum levels during winter (68.3 ng m^{-3}) and minimum in spring (13.8 ng m^{-3}). The ANOVA test showed significant differences ($F = 3.78$, $P = 0.0185$, 95% confidence) between warm and cold periods. The highest daily mean values were obtained from November 2016 to March 2017.5 out of the 9 biomass burning events were identified in this period. However, high levels of biomass burning tracers were also obtained in no events days, mainly in December 2016. Since it is common to use biomass as a fuel for residential heating in rural areas of Spain in the winter season, this result suggests that this source also had a clear impact on the organic PM_{10} content recorded in Sanabria.

Regarding the influence of African dust episodes and biomass burning events (Fig. 5b), ANOVA test showed also statistically

Table 1

Mean concentrations (ng m^{-3}) of analysed compounds in PM₁₀ aerosols collected at Sanabria Natural Park since June 2016 to December 2017, during each season and during the occurrence of African dust outbreaks (AD) and biomass burning events (BB) and the simultaneous development of both events (AD/BB).

ng m^{-3}	Spring (n = 9)	Summer (n = 13)	Autumn (n = 9)	Winter (n = 10)	Total (n = 41)	AD (n = 5)	BB (n = 4)	AD/BB (n = 5)	Rest of samples (n = 27)
\sum n-alkanes	17.1	18.0	12.0	11.8	15.0	18.8	19.9	20.2	12.6
\sum PAHs	0.161	0.153	0.374	0.540	0.297	0.197	0.511	0.281	0.287
\sum quinones	0.058	0.006	0.052	0.121	0.056	0.061	0.199	0.018	0.040
\sum hopanes	0.018	0.021	<0.002	<0.002	0.011	0.045	<0.002	0.025	0.003
Biomass burning tracers	13.8	16.0	40.6	68.3	33.7	13.5	79.9	75.5	22.8
Fatty acids	31.5	25.8	30.7	32.9	29.9	38.1	34.5	38.1	26.1
Alkenoic acids	9.78	6.03	11.4	6.03	8.02	9.41	7.72	6.68	8.06
Sugars	40.4	20.9	29.3	13.4	25.2	36.5	11.3	26.5	24.9
Sugar alcohols	35.4	20.3	22.1	12.2	22.0	20.8	10.8	30.4	22.4
\sum Diacids	11.6	12.6	9.44	7.67	10.5	15.8	12.0	16.6	6.15
Pthalic acids	3.04	3.70	3.49	4.07	3.60	3.14	5.65	6.18	2.90
\sum Hydroxy/polyacids	17.2	13.4	4.75	4.68	10.2	16.0	9.19	17.1	8.15
BSOA tr (isoprene)	49.1	76.0	13.6	4.85	39.0	82.9	23.3	68.6	27.8
BSOA tr (α -pinene)	17.3	17.2	10.6	5.68	13.0	23.0	13.5	19.1	9.91
Total organics	246	230	188	172	210	278	228	325	174

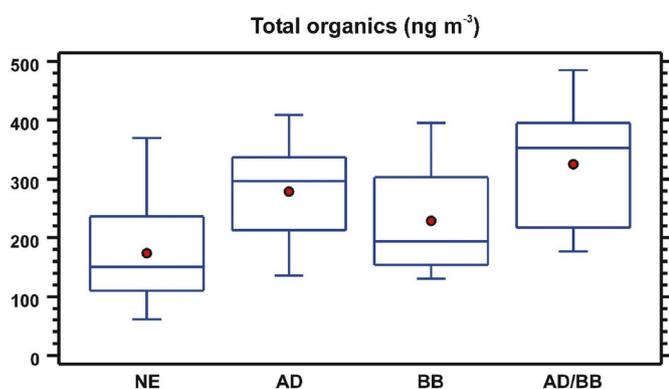


Fig. 4. Boxplots of total organics concentrations (ng m^{-3}) during the occurrence of no events (NE), African dust outbreaks (AD), biomass burning events (BB) and the simultaneous development of both events (AD/BB) in Sanabria Natural Park.

significant differences among groups ($F = 4.41$, $P = 0.0095$, 95% confidence). The multiple range test found differences for samples affected by biomass burning events and the rest of samples, as expected. The same trend was observed for PAHs.

SOA compounds showed an opposite seasonal trend, with maximum in summer and minimum in winter, for both primary and second-generation products of oxidation of terpenes, as reported in other clean environments (Deng et al., 2021). As an example, SOA isoprene tracers box and whisker plot for seasons is shown in Fig. 6a. The ANOVA test showed significant differences ($F = 9.98$, $P = 0.001$, 95% confidence) for hot and cold periods. Higher levels of these compounds were

found during African dust episodes (82.9 ng m^{-3}), as shown in Fig. 6b. Also, ANOVA test showed significant differences ($F = 3.63$, $P = 0.0215$, 95% confidence) for the samples affected by African events related to no event or biomass burning alone events. This trend could be related to the tendency of these episodes to occur during summer, when the SOA production is higher due to the elevated radiation and temperatures, but also to the enhancement of photooxidation reactions in the presence of dust. Highest concentrations of SOA isoprene and terpenes were also previously measured in samples associated to African dust (García et al., 2017).

In fact, a statistically significant linear relationship with a relatively high correlation coefficient ($r = 0.82$) between the crustal content in PM₁₀ samples, estimated as the sum of Al, Fe, Mg, Ti and Ca content, and the associated SOA isoprene concentration values has been obtained, as shown in Fig. 7.

Although it is not possible to establish unique sources for many of the studied organic compounds, SOA contributed more than 53% to the total measured organics in summer, considering the sum of dicarboxylic and hydroxycarboxylic acids, isoprene and terpene tracers. Samples with high levels of SOA include most of the African dust events, but also reflect the importance of the vegetation emission and photochemistry in the area. This contribution decreased to a 14% in winter. Biomass burning tracers, including correlated compounds (levoglucosan and its isomers, dehydroabietic acid, PAHs and xylitol) represented 37% of the analysed organic pollutants in winter, indicating that this is the main source of organic compounds in the colder seasons, mainly due to the influence of regional wildfires, agricultural waste open burning and the use of biomass in domestic heating.

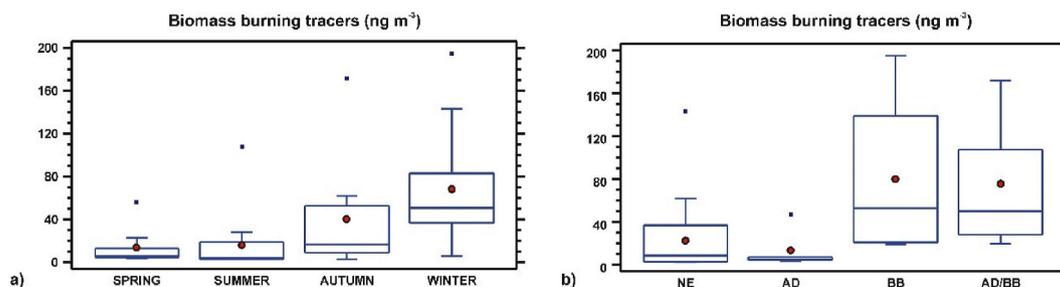


Fig. 5. Boxplots of biomass burning tracers concentrations (ng m^{-3}) during each season a) and during the occurrence of no events (NE), African dust outbreaks (AD), biomass burning events (BB) and the simultaneous development of both events (AD/BB) b) in Sanabria Natural Park.

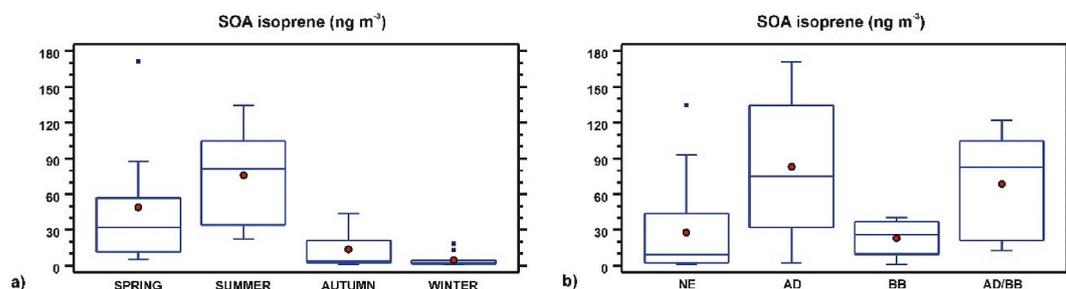


Fig. 6. Boxplots of SOA isoprene concentrations (ng m^{-3}) during each season a) and during the occurrence of no events (NE), African dust outbreaks (AD), biomass burning events (BB) and the simultaneous development of both events (AD/BB) b) in Sanabria Natural Park.

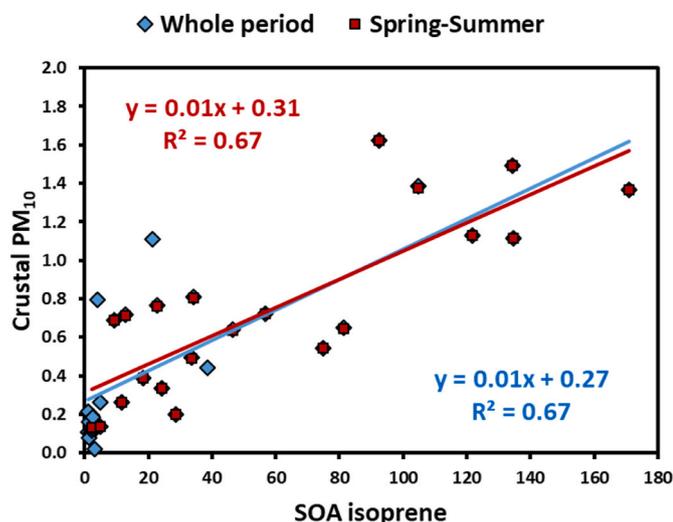


Fig. 7. Correlation between SOA isoprene tracers and crustal elements in PM_{10} .

4. Conclusions

Low mean concentrations of PM_{10} were obtained at Sanabria Lake Natural Park from June 2016 to December 2017 ($12.2 \mu\text{g m}^{-3}$), remaining in the lowest range of values registered in regional background monitoring stations of EMEP and other rural stations in Spain. The occurrence of African dust outbreaks and biomass burning events significantly increased PM_{10} concentrations.

The quantified organic compounds accounted for only a small proportion of the total mass of PM_{10} collected, ranging from 2% in summer to 4% in autumn and winter. In particular, the results showed very low concentrations of anthropogenic organic compounds, such as PAHs, hopanes and phthalic acids, indicating that the Sanabria Lake Natural Park represents a quite pristine area. In fact, plant emissions and other inputs from natural and biological sources were important sources of organic aerosol in this background natural environment.

Biomass burning smoke represented an important contribution to organic compounds in PM_{10} during winter, while SOA dominated during summer. In detail, biomass burning smoke contributed to 37% of the quantified organic compounds in winter, mainly due to house heating in combination with stable atmospheric conditions and the occurrence of wildfires and agricultural waste combustion. While biomass burning tracers and PAHs concentrations showed the maximum values at this time, the total organic compounds concentration was the smallest during the year.

SOA accounted for more than 53% of the evaluated organics in summer, which decreased to a 14% in winter. The observed predominance of 2-methyltetrols among the SOA isoprene tracers is consistent with an atmosphere with low NO_x . Their percentage slightly decreased in the cold seasons, while C5-alkene triols increased. The trend of SOA

terpenes tracers reflected a higher conversion of pinonic acid to second generation products during hot seasons. African dust events could promote the formation of SOA species due to the fact that the occurrence of these events was associated with increases of total organic compounds in PM_{10} with lower concentrations of PAHs and biomass burning tracers.

All these results demonstrate that the characterization of organic compounds in atmospheric aerosols provide relevant information on human activities that could be affecting the conservation of areas with high ecological value such as the Sanabria Lake Natural Park. The need for further research on the implications of African dust on the photochemistry and formation of SOA and biomass burning events on the levels of certain organic compounds is emphasized, especially in the current context of climate change under which the frequency of such events is expected to increase.

CRedit authorship contribution statement

Rosa Pérez-Pastor: Formal analysis, Resources, Investigation, Validation, Writing – original draft. **Pedro Salvador:** Data curation, Formal analysis, Resources, Visualization, Writing – review & editing. **Héctor García-Gómez:** Investigation, Writing – review & editing, Visualization. **Susana García-Alonso:** Methodology, Formal analysis, Validation, Writing – review & editing. **Manuel Toro:** Conceptualization, Resources, Funding acquisition, Project administration. **Begoña Artíñano:** Conceptualization, Supervision, Writing – review & editing. **Rocío Alonso:** Conceptualization, Methodology, Resources, Writing – review & editing, Project administration.

Declaration of competing interest

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.

Data availability

Data will be made available on request.

Acknowledgements

This study has been possible thanks to the Project “Control limnológico bianual intensivo del lago de Sanabria”, funded by the *Duero Hydrographic Confederation* (Ministry for the Ecological Transition and the Demographic Challenge), commissioned to the Centre for Hydrographic Studies (CEDEX), CIEMAT and other research institutions (Ref. 452-A-640.01.01/2014), to study the ecological functioning of Lake Sanabria and its basin (2015–2019). The authors especially thank to Santiago Robles Claros, Jose Carlos Vega Ureta and Héctor Calvete Sogo for their field support.

We acknowledge the Spanish Ministry for the Ecological Transition for supporting a number of research contracts to investigate the development of African Dust Outbreaks in Spain and for providing the time

series of PM₁₀ levels registered at “Peñausende” and “O Saviñao” EMEP regional background sites, the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT trajectory model (<https://www.arl.noaa.gov/hysplit/hysplit/>), the Atmospheric Modelling & Weather Forecasting Group - University of Athens (<http://forecast.uoa.gr>), the Earth Science Department - Barcelona Supercomputing Centre (<https://ess.bsc.es/bsc-dust-daily-forecast>), the Naval Research Laboratory (<https://www.nrlmry.navy.mil/aerosol/>) and the NASA (<http://modis.gsfc.nasa.gov/>) for the provision of the SKIRON, DREAM/BSCDREAM8b, NAAPs aerosol maps and the satellite imagery, respectively that were used to detect the occurrence of African dust outbreaks and wildfire events in study area.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2023.119634>.

References

- Alier, M., van Drooge, B.L., Dall'Osto, M., Querol, X., Grimalt, J.O., Tauler, R., 2013. Source apportionment of submicron organic aerosol at an urban background and a road site in Barcelona (Spain) during SAPUSS. *Atmos. Chem. Phys.* 13, 10353–10371.
- Alonso del Amo, R., García-Gómez, H., Bermejo Bermejo, V., Elvira Cózar, S., González Fernández, I., Rábago Juan-Aracil, I., Salvador Martínez, P., Artiñano Rodríguez de Torres, B., 2018. Encomienda de Gestión del CEDEX al CIEMAT para la realización del “Análisis de la entrada de nutrientes de procedencia atmosférica en el lago de Sanabria”. Final Project report. CIEMAT, Madrid, p. 103.
- Alves, C., 2008. Characterization of solvent extractable organic constituents in atmospheric particulate matter: an overview. *An. Acad. Bras. Cienc.* 80, 21–82.
- Alves, C., Vicente, A., Nunes, T., Gonçalves, C., Fernandes, A.P., Mirante, F., Tarelho, L., Sanchez de la Campa, A., Querol, X., Monteiro, C., Evtugina, M., Pio, C., 2011. Summer 2009 wildfires in Portugal: emission of trace gases and aerosol composition. *Atmos. Environ.* 45, 641–649.
- Bian, H., Zender, C.S., 2003. Mineral dust and global tropospheric chemistry: relative roles of photolysis and heterogeneous uptake. *J. Geophys. Res.* 108 (D21), 4672.
- Bonasoni, P., Cristofanelli, P., Caizolari, F., Bonafe, U., Evangelisti, F., Stohi, A., Sajani, S. Z., van Dingenen, R., Colombo, T., Balkanski, Y., 2004. Aerosol-ozone correlations during dust transport episodes. *Atmos. Chem. Phys.* 4, 1201–1215.
- Brown, S.G., Herckes, P., Ashbaugh, L., Hannigan, M.P., Kreidenweis, S.M., Collett, J.L., 2002. Characterization of organic aerosol in Big Bend National Park, Texas. *Atmos. Environ.* 36, 5807–5818.
- Bytnerowicz, A., Sanz, M.J., Arbaugh, M.J., Padgett, P.E., Jones, D.P., Davila, A., 2005. Passive sampler for monitoring ambient nitric acid (HNO₃) and nitrous acid (HNO₂) concentrations. *Atmos. Environ.* 39, 2655–2660.
- Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., O Andreae, M., Artaxo, P., Maenhaut, W., 2004. Formation of secondary organic aerosols through photooxidation of isoprene. *Science* 303, 1173–1176.
- Commission Staff Working Paper, 2011. Establishing guidelines for demonstration and subtraction of exceedances attributable to natural sources under the directive 2008/50/EC on ambient air quality and cleaner air for Europe, Brussels, 15.02.2011. SEC (2011) 208 Final. 37 pp., available at: https://www.miteco.gob.es/images/es/Directrices%20Comisi%C3%B3n-SEC%202020final-en_tcm30-186523.pdf.
- Deng, J., Gao, Y., Zhu, J., Li, L., Yu, S., Kawamura, K., Fu, P., 2021. Molecular markers for fungal spores and biogenic SOA over the Antarctic Peninsula: field measurements and modeling results. *Sci. Total Environ.* 762, 143089.
- Ding, X., He, Q.F., Shen, R.Q., Yu, Q.Q., Wang, X.M., 2014. Spatial distributions of secondary organic aerosols from isoprene, monoterpenes, β -caryophyllene, and aromatics over China during summer. *J. Geophys. Res. Atmos.* 119, 11877–11891. <https://doi.org/10.1002/2014JD021748>.
- European Environment Agency, 1999. Criteria for EUROAIRNET. The EEA air quality monitoring and information Network. In: Air Research, Kjeller, Norway, Rod Sluyter, RIVM, Bilthoven, the Netherlands and Constantin Helmis. National Observatory of Athens, Greece, p. 56. Prepared by: Steinar Larssen, Norwegian Institute for.
- EN 12341, 2014. Standard. Ambient Air. Standard Gravimetric Measurement Method for the Determination of the PM₁₀ and PM_{2.5} Mass Concentration of Suspended Particle Matter.
- Escudero, M., Querol, X., Pey, J., Alastuey, A., Pérez, N., Ferreira, F., Cuevas, E., Rodríguez, S., Alonso, S., 2007. A methodology for the quantification of the net African dust load in air quality monitoring networks. *Atmos. Environ.* 41, 5516–5524.
- Faustini, A., Alessandrini, E.R., Pey, J., Perez, N., Samoli, E., Querol, X., Cadum, E., Perrino, C., Ostro, B., Ranzi, A., Sunyer, J., Stafoggia, M., Forastiere, F., 2015. MED-PARTICLES study group. Short-term effects of particulate matter on mortality during forest fires in Southern Europe: results of the MED-PARTICLES Project. *Occup. Environ. Med.* 72 (5), 323–329.
- Fernández, A.J., Sicard, M., Costa, M.J., Guerrero-Rascado, J.L., Gómez-Amo, J.L., Molero, F., Barragán, R., Basart, S., Bortol, I.D., Bedoya-Velázquez, A.E., Utrillas, M. P., Salvador, P., Granados-Muñoz, M.J., Potes, M., Ortiz-Amezcuca, P., Martínez-Lozano, J.A., Artiñano, B., Muñoz-Porcar, C., Salgado, R., Román, R., Rocadenbosch, F., Salgueiro, V., Benavent-Oltra, J.A., Rodríguez-Gómez, A., Alados-Arboledas, L., Comerón, A., Pujadas, M., 2019. Extreme, wintertime Saharan dust intrusion in the Iberian Peninsula: Lidar monitoring and evaluation of dust forecast models during the February 2017 event. *Atmos. Res.* 228, 223–241.
- Fondazione Salvatore Maugeri, 2006. Instruction Manual for Radiello Sampler, 01/2006 <http://www.radiello.com>.
- Fu, P.Q., Kawamura, K., 2011. Diurnal variations of polar organic tracers in summer forest aerosols: a case study of a Quercus and Picea mixed forest in Hokkaido, Japan. *Geochem. J.* 45, 297–308.
- Fu, P.Q., Kawamura, K., Kobayashi, M., Simoneit, B.R.D., 2012. Seasonal variations of sugars in atmospheric particulate matter from Gosan, Jeju Island: significant contributions of airborne pollen and Asian dust in spring. *Atmos. Environ.* 55, 234–239.
- Fu, P., Zhuang, G., Sun, Y., Wang, Q., Chen, J., Ren, L., Yang, F., Wang, Z., Pan, X., Li, X., Kawamura, K., 2016. Molecular markers of biomass burning, fungal spores and biogenic SOA in the Taklimakan desert aerosols. *Atmos. Environ.* 130, 64–73.
- García, M.I., van Drooge, B.L., Rodríguez, S., Alastuey, A., 2017. Speciation of organic aerosols in the Saharian Air Layer and in the free troposphere westerlies. *Atmos. Chem. Phys.* 17, 8939–8958.
- García-Gómez, H., Aguilera, L., Izquierda-Rojano, S., Valiño, F., Àvila, A., Elustondo, D., Santamaría, J.M., Alastuey, A., Calvete-Sogo, H., González-Fernández, I., Alonso, R., 2016. Atmospheric pollutants in peri-urban forests of *Quercus ilex*: evidence of pollution abatement and threats for vegetation. *Environ. Sci. Pollut. Res.* 23, 6400–6413.
- Giglio, L., Descloitres, J., Justice, C.O., Kaufman, Y., 2003. An enhanced contextual fire detection algorithm for MODIS. *Remote Sens. Environ.* 87, 273–282.
- Glasius, M., Thomsen, D., Wang, K., Iversen, L.S., Duan, J., Huang, R.J., 2022. Chemical characteristics and sources of organosulfates, organosulfonates, and carboxylic acids in aerosols in urban Xi'an, Northwest China. *Sci. Total Environ.* 810, 151187.
- Gonçalves, C., Alves, C., Nunes, T., Rocha, S., Cardoso, J., Cerqueira, M., Pio, C., Almeida, S.M., Hillamo, R., Teinila, K., 2014. Organic characterisation of PM₁₀ in Cape Verde under Saharan dust influxes. *Atmos. Environ.* 89, 425–532.
- Hernández, A., Trigo, R.M., Pla-Rabes, S., Valero-Garcés, B.L., Jerez, S., Rico-Herrero, M., Vega, J.C., Jambriña-Enríquez, M., Giral, S., 2015. Sensitivity of two Iberian lakes to North Atlantic atmospheric circulation modes. *Clim. Dynam.* 45, 3403–3417.
- IPCC, 2013. In: Stocker, T.F., Qin, D., Plattner, G.K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (Eds.), *Climate Change 2013: the Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate*. Cambridge University Press, Cambridge, UK and New York, NY, USA, p. 1535.
- Kanellopoulos, P.G., Chrysoschou, E., Koukoulakis, K., Bakeas, E., 2021. Secondary organic aerosol markers and related polar organic compounds in summer aerosols from a sub-urban site in Athens: size distributions, diurnal trends and source apportionment. *Atmos. Pollut. Res.* 12, 1–13.
- Kavouras, I., Stephanou, E., 2002. Particle size distribution of organic primary and secondary aerosol constituents in urban, background marine, and forest atmosphere. *J. Geophys. Res. Atmos.* 107, 4069.
- Klyta, J., Czaplacka, M., 2020. Determination of secondary organic aerosol in particulate matter – Short Review. *Microchem. J.* 157, 104997.
- Li, J.J., Wang, G.H., Wang, X.M., Cao, J.J., Sun, T., Cheng, C.L., Meng, J.J., Hu, T.F., Liu, S.X., 2013. Abundance, composition and source of atmospheric PM_{2.5} at a remote site in the Tibetan Plateau, China. *Tellus B: Chem. and Phys. Meteorol.* 65, 20281 <https://doi.org/10.3402/tellusb.v65i0.20281>.
- Mahilang, M., Deb, M.K., Perviz, S., Tiwari, S., Jain, V.K., 2021. Biogenic secondary organic aerosol formation in an urban area of eastern central India: seasonal variation, size distribution and source characterization. *Environ. Res.* 195, 110802.
- Mahowald, N.M., Scanza, R., Brahney, J., Goodale, C.L., Hess, P.G., Moore, J.K., Neff, J., 2017. Aerosol deposition impacts on land and ocean carbon cycles. *Curr. Clim. Change Rep.* 3, 16–31. <https://doi.org/10.1007/s40641-017-0056-z>.
- Martin, T.D., Creed, J.T., Brockhoff, C.A., 1994. Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements. U.S. Environmental Protection Agency Report, p. 12. Revision 2.8, EMMC Version.
- Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1989. Interpretation of high-resolution GC and HPLC/MS data acquired from atmospheric organic aerosol samples. *Aerosol Sci. Technol.* 10, 408–420.
- Medeiros, P.M., Simoneit, B.R.T., 2007. Analysis of sugars in environmental samples by GC/MS. *J. Chromatogr. A* 1141, 271–278.
- Mirante, F., Alves, C., Pio, C., Pindado, O., Perez, R., Revuelta, M.A., Artiñano, B., 2013. Organic composition of size segregated atmospheric particulate matter, during summer and winter sampling campaigns at representative sites in Madrid, Spain. *Atmos. Res.* 132–133, 345–361.
- Odufer, F., Calvo, A.I., Blanco-Alegre, C., Castro, A., Nunes, T., Alves, C., Sorribas, M., Fernández-González, D., Vega-Maray, A.M., Valencia-Barrera, R.M., Lucarelli, F., Nava, S., Calzolari, G., Alonso-Blanco, E., Fraile, B., Fialho, P., Coz, E., Prevot, A.S.H., Pont, V., Fraile, R., 2019. Unusual winter Saharan dust intrusions at Northwest Spain: air quality, radiative and health impacts. *Sci. Total Environ.* 669, 213–228.
- Pahissa, J., Fernández-Enríquez, C., de Hoyos, C., 2015. Water quality of Lake Sanabria according to phytoplankton. A comparison with historical data. *Limnética* 34, 527–540.
- Pérez, R., Salvador, P., García, S., Alastuey, A., García dos Santos, S., Querol, X., Artiñano, B., 2020. Characterization of organic aerosol at a rural site influenced by olive waste biomass burning. *Chemosphere* 248, 125896.
- Pey, J., Querol, X., Alastuey, A., Forastiere, F., Stafoggia, M., 2013. African dust outbreaks over the Mediterranean Basin during 2001–2011: PM₁₀ concentrations,

- phenomenology and trends, and its relation with synoptic and mesoscale meteorology. *Atmos. Chem. Phys.* 12, 28195–28235.
- Pindado, O., Pérez, R., García, S., Sánchez, M., Galán, P., Fernández, M., 2009. Determination and sources assignment of PM_{2.5} organic aerosol in a rural area of Madrid. *Atmos. Environ.* 43, 2796–2803.
- Puxbaum, H., Caseiro, A., Sanchez-Ochoa, A., Giebl, A.K., Claeys, M., Gelencser, A., Legrand, M., Preunkert, S., Pio, C., 2007. Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. *J. Geophys. Res. Atmos.* 112, D23S05.
- Bases científico técnicas para un Plan Nacional de Mejora de la Calidad del Aire, 978-84-00-09475-1. Informe técnico. In: Querol, X., Viana, M.M., Moreno, T., Alastuey, A. (Eds.), Colección informes CSIC 3, 349. Available in: [http://www.miteco.gob.es/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/CALIDAD%20AIRE%20\(alta\) tcm30-187886.pdf](http://www.miteco.gob.es/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/CALIDAD%20AIRE%20(alta) tcm30-187886.pdf).
- Available at: Querol, X., Alastuey, A., Pey, J., Escudero, M., Castillo, S., Orío, A., González, A., Pallarés, M., Jiménez, S., Ferreira, F., Marques, F., Monjardino, J., Cuevas, E., Alonso, S., Artíñano, B., Salvador, P., de la Rosa, J., 2013. Procedimiento para identificación de episodios naturales africanos de PM₁₀ y PM_{2.5}, y la demostración de causa en lo referente a las superaciones del valor límite diario de PM₁₀ Sci. Rep. 40 <https://www.miteco.gob.es/images/es/metodologiaparaisodios naturales-revabril2013 tcm30-186522.pdf>.
- Reid, J.S., Hyer, E.J., Prins, E.M., Westphal, D.L., Zhang, J., Wang, J., Christopher, S.A., Curtis, C.A., Schmidt, C.C., Eleuterio, D.P., Richardson, K.A., Hoffman, J.P., 2009. Global monitoring and forecasting of biomass-burning smoke: description of and lessons from the Fire Locating and Modeling of Burning Emissions (FLAMBE) program. *IEEE J. Sel. Top. Appl. Earth Obs. Rem. Sens.* 2, 144–162. <https://doi.org/10.1109/JSTARS.2009.2027443>.
- Rooze, W.F., Hildemann, L.M., Mazurek, M.A., Glen, R., Cass, G.R., Simoneit, B.R.T., 1991. Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. *Environ. Sci. Technol.* 25, 1112–1125.
- Rooze, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1998. Sources of fine organic aerosol. 9. Pine, oak and synthetic log combustion in residential fireplaces. *Environ. Sci. Technol.* 32, 13–22.
- Salvador, P., Pey, J., Pérez, N., Querol, X., Artíñano, B., 2022. Increasing atmospheric dust transport towards the western Mediterranean over 1948–2020. *Climate and Atmospheric Science* 5, 34. <https://doi.org/10.1038/s41612-022-00256-4>.
- Salisbury, G., Williams, J., Gros, V., Bartenbach, S., Xu, X., Fischer, H., Kormann, R., Reus, M., Zöllner, M., 2006. Assessing the effect of a Saharan dust storm on oxygenated organic compounds at Izaña, Tenerife (July–August 2002). *J. Geophys. Res.* 111, D22303 <https://doi.org/10.1029/2005JD006840>.
- Saxena, P., Hildemann, L.M., McMurry, P.H., Seinfeld, J.H., 1995. Organics alter hygroscopic behavior of atmospheric particles. *J. Geophys. Res.* 100 (D9), 18.755–18.770.
- Sheesley, R.J., Schauer, J.J., Bean, E., Kenski, D., 2004. Trends in secondary organic aerosol at a remote site in Michigan's Upper Peninsula. *Environ. Sci. Technol.* 38, 6491–6500.
- Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of the throsphere. II. Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmos. Environ.* 16, 2139–2159.
- Simoneit, B.R.T., Elias, V.O., Kobayashi, M., Kawamura, M., Rushdi, A.I., Medeiros, P.M., Rogge, W.F., Didyk, B.M., 2004. Sugars-dominant water soluble organic compounds in soils, and characterization as tracers in atmospheric particulate matter. *Environ. Sci. Technol.* 38, 5939–5949.
- Turco, M., Rosa-Cánovas, J.J., Bedia, J., Jerez, S., Montávez, J.P., Llasat, M.C., Provenzale, A., 2018. Exacerbated fires in Mediterranean Europe due to anthropogenic warming projected with non-stationary climate-fire models. *Nat. Commun.* 9, 3821. <https://doi.org/10.1038/s41467-018-06358-z>.
- U.S. EPA, 1994. Method 200.7: "Determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emission spectrometry". Revision 4.4 (Cincinnati, OH).
- Van Drooge, B.L., Grimalt, J.O., 2015. Particle size-resolved source apportionment of primary and secondary organic tracer compounds at urban and rural locations in Spain. *Atmos. Chem. Phys.* 15, 7735–7752.
- Vicente, E.D., Alves, C., Calvo, A., Fernandez, A., Nunes, T., Almeida, S.M., Pio, C., 2013. Emission factor san detailed chemical composition of smoke particles from the 2010 wildlife season *Atmos. Environ. Times* 71, 295–303.
- Wang, W., Kourtchev, I., Graham, B., Cafmeyer, J., Maenhaut, W., Claeys, M., 2005. Characterization of oxygenated derivatives of isoprene related to 2-methyltetrols in Amazonian aerosol using trimethylsilylation and gas chromatography/ion trap mass spectrometry. *Rapid Commun. Mass Spectrom.* 19, 1343–1351.
- Wang, G., Kawamura, K., Xie, M., Hu, S., Gao, S., Cao, J., An, Z., Wang, Z., 2009. Size distributions of n-alkanes, PAHs and hopanes and their sources in the urban, mountain and marine atmospheres over East Asia. *Atmos. Chem. Phys.* 9, 8869–8882.
- WHO Regional Office for Europe, 2013. Review of evidence on health aspects of air pollution – REVIHAAP Project. Technical Report. Copenhagen: WHO Regional Office for Europe. Available from: http://www.euro.who.int/_data/assets/pdf_file/0004/193108/REVIHAAP-Final-technical-report.pdf.
- WHO, 2014. Burden of Disease from the Joint Effects of Household and Ambient Air Pollution for 2012. World Health Organization, Geneva, Switzerland.
- Wu, X., Cao, F., Haque, M.M., Fan, M.Y., Zhang, S.C., Zhang, Y.L., 2020. Molecular composition and source apportionment of fine organic aerosols in Northeast China" *Atmos. Environ. Times* 239, 117722.
- Yli-Juuti, T., Mielonen, T., Heikkinen, L., Arola, A., Ehn, M., Isokääntä, S., Keskinen, H. M., Kulmala, M., Laakso, A., Lipponen, A., Luoma, K., Millonen, S., Nieminen, T., Paasonen, P., Petäjä, T., Romakkaniemi, S., Tonttila, J., Kollola, H., Virtanen, A., 2021. Significance of the organic aerosol driven climate feedback in the boreal area. *Nat. Commun.* 12, 5637. <https://doi.org/10.1038/s41467-021-25850-7>. www.nature.com/naturecommunications.
- Zhu, R.G., Xiao, H.Y., Cheng, L., Zhu, H., Xiao, H., Gong, Y., 2022. Measurement report: characterization of sugars and amino acids in atmospheric fine particulates and their relationship to local primary sources. *Atmos. Chem. Phys.* 22, 14019–14036. <https://doi.org/10.5194/acp-22-14019-2022>.