Contents lists available at ScienceDirect



Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv



Diurnal source apportionment of organic and inorganic atmospheric particulate matter at a high-altitude mountain site under summer conditions (Sierra Nevada; Spain)

Clara Jaén^a, Gloria Titos^{b,c}, Sonia Castillo^{b,c}, Andrea Casans^{b,c}, Fernando Rejano^{b,c}, Alberto Cazorla^{b,c}, Javier Herrero^{b,c}, Lucas Alados-Arboledas^{b,c}, Joan O. Grimalt^a, Barend L. van Drooge^{a,*}

^a Institute of Environmental Assessment and Water Research (IDAEA-CSIC), c/Jordi Girona 18-26, 08034 Barcelona, Spain

^b Andalusian Institute for Earth System Research (IISTA), University of Granada, Avenida del Mediterráneo sn, 18071 Granada, Spain

^c Department of Applied Physics, Sciences Faculty, University of Granada, Avenida Fuentenueva sn, 18071 Granada, Spain

HIGHLIGHTS

- Detection of inorganic and organic compounds in PM₁₀ in a high-mountain site.
- Combined source apportionment resolves five PM₁₀ sources.
- Atmospheric transport dominates PM composition.
- Diurnal transport within the boundary layer with mountain breezes was observed.
- Small contributions from local pollution sources were detected.

ARTICLE INFO

Editor: Pavlos Kassomenos

Keywords: Air pollution High-mountain Particulate matter Organic PM Inorganic PM Source apportionment GRAPHICALABSTRACT



ABSTRACT

High-altitude mountain areas are sentinel ecosystems for global environmental changes such as anthropogenic pollution. In this study, we report a source apportionment of particulate material with an aerodynamic diameter smaller than 10 μ m (PM₁₀) in a high-altitude site in southern Europe (Sierra Nevada Station; SNS (2500 m a.s.l.)) during summer 2021. The emission sources and atmospheric secondary processes that determine the composition of aerosol particles in Sierra Nevada National Park (Spain) are identified from the concentrations of organic carbon (OC), elemental carbon (EC), 12 major inorganic compounds, 18 trace elements and 44 organic molecular tracer compounds in PM₁₀ filter samples collected during day- and nighttime. The multivariate analysis of the joint dataset resolved five main PM₁₀ sources: 1) Saharan dust, 2) advection from the urbanized valley, 3) local combustion, 4) smoke from a fire-event, and 5) aerosol form regional recirculation with high contribution of particles from secondary inorganic and organic aerosol formation patterns typical of mountainous areas. Although a local pollution source was identified, the contribution of this source to PM₁₀, OC and EC was

* Corresponding author.

E-mail address: barend.vandrooge@idaea.csic.es (B.L. van Drooge).

https://doi.org/10.1016/j.scitotenv.2023.167178

Received 31 May 2023; Received in revised form 8 September 2023; Accepted 16 September 2023 Available online 18 September 2023

0048-9697/© 2023 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC license (http://creativecommons.org/licenses/by-nc/4.0/).

small. Our results evidence the strong influence of middle- and long-range transport of aerosols, mainly from anthropogenic origin, on the aerosol chemical composition at this remote site.

1. Introduction

Atmospheric particulate matter (PM) has negative effects on human health and ecosystems, and influences the radiation balance and cloud formation processes with positive and negative climate feedbacks (Forster et al., 2007; Landrigan et al., 2018; O'Connor et al., 2021; Pope and Dockery, 2006). The physico-chemical properties of the aerosols and their chemical composition are complex, dynamic, and highly variable due to the influence of many factors, including biogenic and anthropogenic emissions, atmospheric processes, and meteorological conditions (Brines et al., 2019; Jaén et al., 2021; van Drooge et al., 2018). These factors are relevant for the ultimate impact of PM on human health, ecosystems, and climate change (Villasclaras et al., 2022; Yuan et al., 2019). Previous studies underscored the need to examine the PM speciation, i.e., the identification of differences in PM composition through time and to relate the observed changes to the main emission sources and transformation processes during atmospheric transport, including the formation of secondary aerosols.

The chemical composition of PM and source contribution has been comprehensively studied from the analysis of inorganic and organic molecular tracer compounds. The multivariate analysis of these tracer compounds by Positive Matrix Factorization (PMF) and Multivariate Curve Resolution (MCR-ALS) allowed estimating source contributions, such as vehicle exhaust, vehicle non-exhaust, waste incineration, biomass burning, heavy oil combustion, soil dust, and biogenic and anthropogenic secondary aerosols, with acceptable analytical uncertainties (Alier et al., 2013; Amato et al., 2016; Brines et al., 2019; Pérez Pastor et al., 2020; Tauler et al., 2009; van Drooge et al., 2018; van Drooge and Grimalt, 2015; Viana et al., 2008). These studies showed that the contributions of emission sources and secondary aerosol processing to PM air pollution differed remarkably among sites and through time, such as the abundance of biomass burning aerosols (e.g. anhydrosugars, K) in cold seasons and rural sites, compared to warm seasons and metropolitan areas; abundance of secondary aerosol contributions (e.g. methyltetrols from isoprene oxidation, SO_4^{2-} , NO_3^{-} , NH^+) in summer and background areas, compared to urban traffic sites; an overall abundance of traffic emissions (e.g. hopanes, Ba, Cu) in metropolitan areas compared background areas.

Remote areas, such as high mountains, provide information on the global background air quality, and air pollution sources after mid- and long-range atmospheric transport (Bukowiecki et al., 2021; Chen et al., 2021; Diémoz et al., 2019; García et al., 2017; Prats et al., 2022). Moreover, these regions allocate important freshwater reservoirs whose ecosystems may be affected by air pollution (Jarque et al., 2015). Air pollution is transported over long distances to these sites, but these remote sites may also receive contaminants carried by anabatic winds from the valleys along the mountain slopes during the daytime (Fu et al., 2014; Kunwar et al., 2019). In contrast, during nighttime, the katabatic winds and the low mixing layer height can isolate the highest parts of the mountain from potential emissions from the low-lands, being often in nearly free tropospheric conditions (Diémoz et al., 2019; Lang et al., 2015; Rampanelli et al., 2004; Wagner et al., 2015). Nevertheless, even under these conditions air pollution that was transported to higher altitudes, such as biomass burning smoke, may still affect mountain sites during nighttime (Fu et al., 2012; Zhu et al., 2018). Studies on the effectiveness of these processes on the transport of PM air pollution to remote high-altitude mountain sites are less abundant than studies near low-altitude source emission areas. Besides practical reasons due to the remoteness of these sites, the determination of PM origins in remote high-mountain areas is challenging due to the distance from potential emission sources and the mixing-based features of PM after atmospheric

transport (Chu et al., 2021; García et al., 2017; Hernandez et al., 2019; Kumari et al., 2020). On the other hand, many air pollution and climate monitoring stations could be affected by increasing anthropogenic activities in their vicinity, which may alter their representativeness as remote background atmospheres (Bukowiecki et al., 2021).

The use of molecular organic compounds as tracers of specific sources is of special interest as they can provide information about the contributions of primary organic aerosols (POA), that are emitted directly into the atmosphere, as well as secondary organic aerosols (SOA), that are formed in the atmosphere after oxidation of gas-phase precursors from biogenic and anthropogenic sources. The compounds analyzed in this study include tracers of biomass burning (levoglucosan, galactosan and mannosan), soil/vegetation dust (alpha-glucose, betaglucose, mannitol, sorbitol, as well as n-alkanes), vehicle emission (hopanes, n-alkanes), incomplete combustion of organic matter (Polycyclic Aromatic Hydrocarbons (PAH) and their derivatives), α-pinene secondary organic aerosol (cis-pinonic acid, 3-hydroxyglutaric acid, and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)), isoprene secondary organic aerosol (2-methyltetrols and 2-methylglyceric acid), secondary anthropogenic organic aerosol (phthalic acid), and dicarboxylic acids, such as succinic acid, that are mainly of secondary origin from oxidation of organic compounds, but part can be primary, from sources such as traffic, biomass burning smoke and vegetation (Alier et al., 2013; Jaén et al., 2021; Schauer et al., 2002; Simoneit et al., 1991b; van Drooge and Grimalt, 2015). The condensational formation and growth of new particles in the remote areas also determines the composition of the PM in those sites and results in complex mixtures with usually higher SOA contributions (Jimenez et al., 2009). Additionally, mountain fluxes may facilitate the introduction of these particles in the free troposphere where they can be transported through the atmosphere over long distances (García et al., 2014).

The current study is focused on the chemical composition of PM_{10} in a remote high-altitude mountain site located in the Sierra Nevada National Park, in south-eastern Europe (Sierra Nevada Station; SNS (2500 m a.s.l.)). The study is based on an intensive summer field campaign (BioCloud) to determine the contribution of the emission sources and atmospheric processes influencing PM, organic carbon (OC) and elemental carbon (EC). The transformations of the primary emitted compounds into the secondary organic aerosol, secondary inorganic aerosol (SIA) and the influence of the meteorological conditions in these processes are specifically considered.

2. Measurements and methods

2.1. Sampling site

This study has been developed in the AGORA (Andalusian Global ObseRvatory of the Atmosphere) observatory (https://atmosphere.ugr. es/en/about/presentation/agora), in particular in the Sierra Nevada Station (SNS; 37.10° N, 3.39° W; 2500 m a.s.l.) situated on the northern slope of the Sierra Nevada Mountain Range, 5 km from the Veleta summit (3396 m a.s.l.) and 20 km south-east from the city of Granada (Fig. 1). AGORA is part of the Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS-ERIC (https://actris.eu)).

The strong insolation conditions and thermal fluctuations due to the high altitude and the complex orography results in a semi-arid terrain. The mountain range has several valleys that can canalize the air upwards and might favor the advection of pollution from urbanized areas. The most populated city in the region is Granada at a horizontal distance of 20 km with an altitude difference of 1800 m from SNS (Fig. 1). Due to the location of SNS with respect to the valley, prevalent wind directions

are mainly westerly and southerly, which may favor the transport of pollutants from lower altitudes, i.e. the city of Granada and its metropolitan area as observed by previous studies on the transport of black carbon in the area (Casquero-Vera et al., 2020; Rejano et al., 2021). A ski-station and an urbanization are located at 3 km from the SNS station.

This site can receive atmospheric PM driven by mesoscale phenomena such as Saharan dust intrusions from North Africa or regional transport from the European continent. The Saharan Dust episodes imply high PM levels (Israelevich et al., 2012) and can involve different atmospheric processes such as the absorption of SO₂ and NO₂ gases to increase the amounts of sulfates and nitrates in the dust particles (Abdelkader et al., 2015). Furthermore, new particle formation (NPF) events are frequent during daytime in the area (Casquero-Vera et al., 2020). Thus, the atmosphere in the SNS station is characteristic of the south-western European free troposphere and is also a sentinel site for the transport of the aerosol particles from middle and long-range distances. However, the influence of local sources related with human activities, vegetation or soil dust must also be considered.

2.2. Filter sampling

Sampling took place from June 10th to July 7th of 2021. PM_{10} samples (n = 57) were collected with a high-volume sampler (MCV, model CAV-A/MSb) at 30 m³/h on 150 mm diameter quartz microfiber filters (2500QAT-UP, Pallflex, Pall Corporate). Sampling schedule was from 10 h to 18 h and from 18 h to 10 h (UTC time, being local time UTC + 2) to identify the diurnal trends of the PM_{10} composition. The first daytime sampling period was chosen to capture those conditions when the site might be affected by transported aerosol particles from the valley and/or subject of new particle formation processes, while the second could be more representative of free tropospheric conditions.

Filters were conditioned and treated pre- and post-sampling. After sampling, the filters were stored at -20 °C until analysis.

2.3. Chemical analyses

The filters were weighted using standard gravimetric methods, and treated and analyzed to determine the levels of major and trace elements as described in Querol et al. (2001). Half of each filter was acid digested (2.5 mL HNO₃: 5 mL HF: 2.5 mL HClO₄) for the analysis of 8 major elements (Al, Ca, K, Na, Mg, Fe, Ti and Mn) by means of ICP-OES (Agilent model 5110), and 18 trace elements (Li, V, Cr, Ni, Cu, Zn, As, Rb, Sr, Mo, Ba, La, Ce, Sn, Sb, and Pb) by means of ICP-MS (Agilent model 7900). The average precision and accuracy for most of the elements were found within the normal analytical errors which were controlled by repeated analysis of blank filters and NIST-1633b (fly ash) reference standard material in both ICP techniques. The accuracy and detection limit were 2 % and 1.5 ng/m³, respectively, for ICP-OES, and 3 % and 0.01–11 ng/m³, respectively, for ICP-MS.

A quarter part of each filter was leached with MilliQ-grade deionized water at 90 °C to determine the content of major soluble anions (SO₄²⁻, NO₃, and Cl⁻) and NH₄⁴ (Querol et al., 2002) by ion chromatography (Methrom883 Basic IC Plus). The accuracy and detection limit of the ion chromatography measurements were 10 % and 0.4 μ g/m³, respectively.

A portion of 1.5 cm² of each filter was used for analysis of organic and elemental carbon (OC and EC) by a Thermal-Optical transmission technique, using a Sunset Laboratory OC-EC Analyzer with the EUSAAR_2 protocol (Cavalli et al., 2010). SiO₂, Al₂O₃ and CO₃²⁻ were indirectly determined on the basis of empirical factors (Querol et al., 2004). Quality control was implemented through use of an external sucrose aqueous solution which ensured the consistent operation of the



Fig. 1. Sampling location in Sierra Nevada and topographic profile from the city of Granada. Source: Google Earth.

instrument and the quality of the measurements.

One quarter of each filter (minus the 1.5 cm² OC/EC punch) was used to analyze organic molecular tracer compounds that can be used to elucidate the contribution of different primary and secondary sources to PM. A total of 44 organic compounds were quantified. These compounds consisted of 11 secondary products (including isoprene and α -pinene oxidation products), 2 hopanes from traffic emissions, 9 n-alkanes, 7 saccharides (including biomass burning tracers), 10 PAH, 4 quinones (oxygenated PAHs) and 1 phthalate ester. The analytical method used is described in more detail in previous works (Fontal et al., 2015; van Drooge et al., 2023; van Drooge and Grimalt, 2015). Briefly, the filter fractions were spiked with deuterated PAHs (anthracene-d10, fluoranthene-d10, pyrene-d10, benzo[a]anthracene-d12, chrysene-d12, benzo[b]fluoroanthene-d12, benzo[a]pyrene-d12, indeno[1,2,3-cd] pyrene-d12, benzo[ghi]perylene-d12), nC24-d50, levoglucosan-d7 and succinic acid- d_4 . They were then extracted with a dichloromethane: methanol 1:1 ν/v mixture (3 \times 10 mL) by ultra-sonication. Then, the extract was filtered and concentrated by rotovaporation and with a gentle stream of nitrogen to a final volume of 0.5 mL. To analyze the polar compounds (saccharides and acids), and aliquot of 25 µL of the extract was evaporated to dryness in a conical vial and derivatized by adding 25 µL of BSTFA and 10 µL of pyridine to obtain the trimethylsilylderivatives (TMS). These aliquots were analyzed by GC-MS (Agilent Technologies) in full scan mode equipped with a HP-5MS 60 m capillary column. For the analysis of the rest of compounds, the remaining extract was extracted with 3 \times 0.5 mL of n-hexane, then concentrated to 25 μ L with a stream of nitrogen and injected in a Q-Exactive GC Orbitrap MS (Agilent Technologies) in full scan mode equipped with a HP-5MS 30 m capillary column. Compounds were identified by their chromatographic retention times, mass spectra and quantified with authentic analytical standards by means of internal standard calibration which takes into consideration the extraction and recovery process and the variability of the analysis. Recoveries for all compounds were higher than 50 %. In addition, 3 field blanks were processed and were between 0 % and 28 %of the sample levels. Sample levels were blank corrected. The accuracy of the analytical procedures was 15 %, while the limits of detection (LOD) ranged between 0.03 and 3 ng/m^3 for acids and saccharides; 0.05 and 2 ng/m³ for n-alkanes; 0.1 and 18 pg/m³ for PAHs; 6 and 11 pg/m³ for hopanes, based on the mean concentration of three field blanks plus 3 times their standard deviation. Detection frequencies above LOD ranged from 72 % to 100 % for the individual compounds.

2.4. Air mass trajectories clustering

For the synoptic air mass transport study, 96 h backward trajectories were computed with NOAA HYSPLIT model (Rolph et al., 2017; Stein et al., 2015) at 1500 m a.g.l. using the meteorological fields from the NCEP/NCAR Global Reanalysis Data (Kalnay et al., 1996). The hourly endpoints from the 704 trajectories were used to create 72 h-clusters with the HYSPLIT clustering algorithm. This method groups the trajectories minimizing the difference between trajectories in that group, i.e. giving the lowest increase in the total spatial variance (Draxler et al., 2022). In this study, 6 clusters were considered to illustrate the origin of the air masses arriving to the sampling site. The number of clusters was identified by examination of the percentage change of the total spatial variance by step-wise decrease of the number of clusters (74 % from 6 to 5) and by interpretation of the geographical significance of the added clusters.

2.5. Source apportionment method

Bilinear decomposition of the original compound dataset (77 compounds in 57 samples) was performed with the Multivariate Curve Resolution—Alternating Least Square (MCR-ALS 2.0) method under non-negativity constraints using MATLAB (Jaumot et al., 2015, 2005; Tauler, 1995). This source apportionment technique is based on the D =

 $CS^{T} + E$ matrix equation to decompose an initial normalized compounds-samples matrix (D) into one matrix of sample scores for each of the reduced number of components (C), one matrix of the compound loads for each of the reduced number of components (S^T) and, a residual data matrix with data not explained by the model (E). To perform the decomposition, half of the limit of detection was used in the few cases that compound concentrations were below this limit. The number of different components was selected considering the logic interpretability of the chemical composition (profiles) in terms of emission source or atmospheric processing. In MCR-ALS, the explained variance of the components is overlapped and not orthogonal. This feature facilitates the physical interpretation of the results in comparison with orthogonal decomposition methods as environmental sources are almost never orthogonal. Previous studies have successfully applied this MCR-ALS decomposition for the source apportionment of PM (Alier et al., 2013; Jaén et al., 2021; van Drooge et al., 2022). This decomposition is equivalent to the one obtained with PMF (Tauler et al., 2009) although both methods differ in the decomposition algorithms and the normalization of loading scores profiles.

2.6. Meteorological data

In addition, meteorological data was measured at the site by an Automatic Weather Station (AWS). This AWS was equipped with an EE181 Air Temperature and Relative Humidity Probe, a Hukseflux LP02-05 pyranometer for solar radiation, a Vaisala PTB110 barometer, a Young Wind Monitor 05103 for wind speed and direction, and a Geonor T200B all-weather rain gauge with Alter wind shield for liquid and solid precipitation. Datasets of 5 min were recorded for each variable for the whole period of this study.

3. Results and discussion

3.1. PM composition

Table 1 shows the maximum, minimum, overall average, daytime average, and nighttime average concentrations of the PM constituents analyzed in this study. The table also includes the results of the Welch two sample *t*-test for the significance of the differences between mean day and night measurements. PM_{10} ranged from 3.13 to 54.03 µg/m³ exceeding in some occasions the 24-hour WHO air quality guidelines and the EU limit value for air quality (Council Directive 2008/50/EC, 2008; World Health Organization, 2021). This high PM_{10} concentrations occurred during a Saharan dust event, as explained in the following paragraph. The measured concentrations agree with PM_{10} concentrations previously reported in high mountain sites in southern Europe (Galindo et al., 2017; Moretti et al., 2021; Moroni et al., 2015; Ripoll et al., 2014; Tositti et al., 2013).

The highest PM₁₀ concentrations were measured from June 11th to June 16th and were associated with a Saharan dust intrusion as confirmed by satellite imagery (Fig. S 2). This episode was also reflected in high concentrations of elements related with Earth's crust such as CO_3^{2-} , SiO₂, Al₂O₃, calcium (Ca), magnesium (Mg) potassium (K) and iron (Fe) with maxima that have been previously observed in dust episodes in Spain (Galindo et al., 2017; Nicolás et al., 2008). In some cases, these compounds showed an increase of >500 % in samples with high PM concentrations when comparing to non-intrusion samples (Table S 1). This is also observed for Ti which has been reported as indicator of Saharan dust events in previous studies (Galindo et al., 2020; Nicolás et al., 2008). Nevertheless, during the rest of the field campaign, dust resuspension from local arid regions of Sierra Nevada also contributed to increase in the concentrations of these crustal elements. No differences between day and night samples in PM10 of crustal elements were observed.

Transformations of emissions from industry, agriculture and traffic may lead to the formation of secondary inorganic aerosols (SIA) which is

Table 1

Maximum, minimum, overall average, daytime average, and nighttime average concentrations of the air quality indicators, and analyzed compounds (n = 57). *P*-value for the Welch two sample *t*-test between Day and Night samples performed with R software is also shown. LOD: Limit of detection.

Variable	All samp	les ($n = 5$	7)		Filtered ^a $(n = 47)$				
	Max	Min	Average	Average	Average	<i>p</i> -Value	Average	Average	<i>p</i> -Value
				day	night	(day–night)	day	night	(day–night)
(µg/m ³)									
PM	54.03	3.13	15.59	16.27	14.89	0.668	13.57	9.20	0.010
OC	5.35	0.22	2.38	2.97	1.77	< 0.001	2.87	1.40	< 0.001
EC	1.05	0.01	0.22	0.26	0.18	0.108	0.24	0.13	< 0.001
CO3 SIO	7.28	0.27	1.89	2.06	1.72	0.421	1.70	1.04	0.003
AleOe	23.75	0.32	4.02	4.32	4.92	0.682	2.94	2.00	0.608
PO_{4}^{3-}	0.16	0.01	0.06	0.07	0.06	0.132	0.06	0.04	< 0.001
NO ₃	3.65	0.08	0.88	1.11	0.65	0.010	1.07	0.48	0.002
NH ₄ ⁺	0.29	0.00	0.10	0.12	0.07	0.004	0.12	0.05	0.001
SO_4^{2-}	2.73	0.13	0.79	0.91	0.66	0.057	0.87	0.53	0.015
Ca	3.20	0.11	0.85	0.93	0.77	0.400	0.77	0.47	0.002
K	1.19	0.04	0.29	0.30	0.29	0.856	0.24	0.17	0.040
Na	0.57	0.03	0.24	0.27	0.21	0.143	0.25	0.16	0.031
Mg Fe	2 29	0.04	0.23	0.27	0.23	0.470	0.22	0.13	0.413
	2.2)	0.00	0.17	0.15	0.19	0.799	0.02	0.27	0.115
(m = (m ³)									
(ng/m ⁻)	2.74	0.02	0 52	0.50	0.52	0.949	0.24	0.28	0.402
Ti	2.74	0.02 5.21	0.52 45.81	41.86	49 91	0.648	27 46	25.24	0.403
V	6.84	0.14	1.59	1.62	1.56	0.895	1.25	0.87	0.098
Cr	61.44	0.20	8.35	10.18	6.44	0.161	11.07	5.15	0.037
Mn	38.62	1.04	8.38	8.05	8.72	0.787	5.70	4.89	0.516
Ni	10.76	0.08	2.37	2.98	1.73	0.012	2.52	1.24	< 0.001
Cu	8.38	0.12	2.07	2.58	1.54	0.005	2.47	1.32	0.007
Zn	171.43	0.92	12.57	11.73	13.45	0.777	10.88	6.16	0.002
As	0.78	0.03	0.21	0.22	0.21	0.839	0.18	0.15	0.450
Sr	17.35	0.11	5.35	6.38	4 29	0.070	5.79	2.50	< 0.001
Mo	26.58	1.24	8.38	11.51	5.14	< 0.001	11.19	4.80	<0.001
Sn	1.69	0.06	0.34	0.47	0.22	< 0.001	0.47	0.18	< 0.001
Sb	1.20	0.00	0.19	0.22	0.16	0.254	0.22	0.11	0.006
Ва	29.11	2.10	8.81	9.58	8.00	0.360	8.13	5.13	< 0.001
La	2.56	0.05	0.55	0.55	0.56	0.920	0.39	0.31	0.311
Ce	5.11	0.13	1.13	1.11	1.14	0.930	0.79	0.64	0.326
PD Succipic acid (SA)	5.04	0.16	1.89	1.88	1.89	0.971	1.62	1.37	0.402 <0.001
Phthalic acid (PHA)	5.10	<lod< td=""><td>1.34</td><td>1.85</td><td>0.81</td><td>< 0.001</td><td>1.87</td><td>0.81</td><td>< 0.001</td></lod<>	1.34	1.85	0.81	< 0.001	1.87	0.81	< 0.001
Glutaric acid (GLU)	5.06	0.33	2.53	3.27	1.76	< 0.001	3.37	1.56	<0.001
Azelaic acid (AZA)	3.27	0.28	1.51	2.04	0.97	< 0.001	2.00	0.83	< 0.001
2-Metylglyceric acid (2MGA)	48.51	1.11	14.93	19.86	9.82	0.002	19.32	8.27	0.003
2-Methylthreitol (2MT1)	49.85	1.57	15.84	21.36	10.13	< 0.001	20.33	8.38	< 0.001
2-Methylerythritol (2MT2)	116.41	5.11	42.39	58.25	25.96	< 0.001	54.71	21.86	< 0.001
Cis pinonic acid (CPA)	17.63	1.03	7.58	10.87	4.17	<0.001	10.64	3.46	<0.001
3-Methyl-1 2 3-butanetricarboxylic acid	9 79	0.19	3.99	4.94	2.02	<0.013	4 98	3.08 2.17	<0.001
(MBTCA)	5.75	0.11	0.10	1.05	2.10	0.001	1.90	2.17	<0.001
Malic acid (MA)	21.63	0.47	7.97	9.75	6.13	0.016	10.45	6.27	0.012
Galactosan (GAL)	0.73	0.04	0.28	0.33	0.23	0.028	0.35	0.22	0.014
Mannosan (MANNO)	0.91	<lod< td=""><td>0.22</td><td>0.27</td><td>0.18</td><td>0.081</td><td>0.29</td><td>0.17</td><td>0.052</td></lod<>	0.22	0.27	0.18	0.081	0.29	0.17	0.052
Levoglucosan (LEV)	6.33	0.20	1.54	1.78	1.28	0.124	1.85	1.10	0.037
Alpha-glucose (AGL)	17.68	1.49	6.11	7.63	4.53	0.002	7.68	3.92	<0.001
Mannitol (MANNI)	20.01	0.67	0.98 7 54	9.07	5.22	0.001	0.03 9.38	4.02	0.001
Sorbitol (SOR)	0.87	<lod< td=""><td>0.40</td><td>0.54</td><td>0.26</td><td>< 0.001</td><td>0.55</td><td>0.25</td><td>< 0.001</td></lod<>	0.40	0.54	0.26	< 0.001	0.55	0.25	< 0.001
nC23	10.96	<lod< td=""><td>3.59</td><td>4.85</td><td>2.29</td><td>< 0.001</td><td>4.89</td><td>2.42</td><td>< 0.001</td></lod<>	3.59	4.85	2.29	< 0.001	4.89	2.42	< 0.001
nC24	6.13	0.82	2.94	3.48	2.38	< 0.001	3.40	2.39	0.009
nC25	9.85	1.38	4.71	5.97	3.41	< 0.001	5.82	3.36	< 0.001
nC26	4.33	1.06	2.68	3.24	2.09	< 0.001	3.18	2.14	< 0.001
nC27	8.44	1.33	4.14	5.19	3.04	< 0.001	5.13	2.88	< 0.001
11628 nC29	0.01 18.24	0.79	2.01 6.62	3.37 8.06	1.81	<0.001	3.30 7.85	1.83	<0.001
nC30	10.24	1.00	3.86	5.00	2.19	<0.001	7.85 5.49	2.12	< 0.001
nC31	18.54	1.86	6.60	8.49	4.64	< 0.001	8.30	4.04	<0.001
Bis(2-ethylhexyl)phthalate (DEHP)	31.06	<lod< td=""><td>14.27</td><td>18.88</td><td>9.49</td><td>< 0.001</td><td>18.20</td><td>8.98</td><td>< 0.001</td></lod<>	14.27	18.88	9.49	< 0.001	18.20	8.98	< 0.001
$\left(\log/m^3\right)$									
Benz[a]anthracene (BAA)	48.39	<lod< td=""><td>7.44</td><td>3.67</td><td>11.34</td><td>0.003</td><td>3.35</td><td>10.48</td><td>0.007</td></lod<>	7.44	3.67	11.34	0.003	3.35	10.48	0.007
Chrysene + triphenylene (C + T)	158.05	<lod< td=""><td>28.03</td><td>15.13</td><td>41.40</td><td>0.003</td><td>14.34</td><td>43.30</td><td>0.006</td></lod<>	28.03	15.13	41.40	0.003	14.34	43.30	0.006
Benzo[b+j+k] fluoranthene (BBJKFL)	147.30	<lod< td=""><td>21.00</td><td>16.00</td><td>26.18</td><td>0.076</td><td>14.26</td><td>19.83</td><td>0.123</td></lod<>	21.00	16.00	26.18	0.076	14.26	19.83	0.123

(continued on next page)

Table 1 (continued)

Variable	All samples ($n = 57$)						Filtered ^a $(n = 47)$		
	Max	Min	Average	Average day	Average night	<i>p</i> -Value (day–night)	Average day	Average night	p-Value (day–night)
Benzo[<i>a</i>]fluoranthene (BAFL)	27.03	<lod< td=""><td>3.39</td><td>2.61</td><td>4.21</td><td>0.128</td><td>2.26</td><td>2.91</td><td>0.271</td></lod<>	3.39	2.61	4.21	0.128	2.26	2.91	0.271
Benzo[e]pyrene (BEP)	50.31	0.38	8.77	6.33	11.30	0.019	5.92	9.63	0.033
Perylene (PY)	4.69	<lod< td=""><td>0.90</td><td>0.77</td><td>1.03</td><td>0.226</td><td>0.65</td><td>0.72</td><td>0.616</td></lod<>	0.90	0.77	1.03	0.226	0.65	0.72	0.616
Indeno[123cd]pyrene (IP)	85.52	0.90	10.04	8.95	11.17	0.505	7.92	6.62	0.410
Benzo[ghi]perylene (BGHIP)	108.15	1.85	15.10	14.86	15.34	0.925	14.48	10.95	0.445
3-Methylchrysene (3MC)	34.80	<lod< td=""><td>5.72</td><td>1.71</td><td>9.87</td><td>< 0.001</td><td>1.76</td><td>11.08</td><td>< 0.001</td></lod<>	5.72	1.71	9.87	< 0.001	1.76	11.08	< 0.001
6-Methylchrysene (6MC)	10.61	<lod< td=""><td>1.71</td><td>0.45</td><td>3.02</td><td>< 0.001</td><td>0.46</td><td>3.30</td><td>< 0.001</td></lod<>	1.71	0.45	3.02	< 0.001	0.46	3.30	< 0.001
9,10-Anthraquinone (ANQ)	101.03	<lod< td=""><td>31.32</td><td>29.21</td><td>33.51</td><td>0.452</td><td>29.46</td><td>34.69</td><td>0.417</td></lod<>	31.32	29.21	33.51	0.452	29.46	34.69	0.417
2-Methylanthraquinone (2MANQ)	29.16	0.98	7.24	4.43	10.16	0.002	4.32	10.49	0.005
Benzo[b]fluorenone (BBF)	29.24	<lod< td=""><td>7.33</td><td>4.20</td><td>10.58</td><td>< 0.001</td><td>4.06</td><td>10.17</td><td>0.003</td></lod<>	7.33	4.20	10.58	< 0.001	4.06	10.17	0.003
Benzanthrone (BA)	19.75	<lod< td=""><td>2.86</td><td>1.51</td><td>4.26</td><td>0.002</td><td>1.32</td><td>3.41</td><td>0.007</td></lod<>	2.86	1.51	4.26	0.002	1.32	3.41	0.007
17a(H)21β(H)-29-norhopane (norHOP)	67.85	<lod< td=""><td>30.93</td><td>41.89</td><td>19.59</td><td>< 0.001</td><td>39.62</td><td>20.35</td><td>< 0.001</td></lod<>	30.93	41.89	19.59	< 0.001	39.62	20.35	< 0.001
17a(H)21β(H)-hopane (HOP)	53.26	7.26	26.50	34.67	18.03	< 0.001	33.26	18.87	< 0.001

^a Samples with outliers in PM, OC, or EC were eliminated. Those were eliminated following the interquartile range (IQR) criterion which considers outliers observations outside the $[q0.25 - 1.5 \cdot IQR; q0.75 + 1.5 \cdot IQR]$ interval.

reflected in the increased occurrence of SO_4^{2-} , NO_3^- , NH_4^+ . These ions were found in SNS in slightly lower concentrations than those previously reported in the Iberian Peninsula in urban and rural background environments (Querol et al., 2008; Titos et al., 2014, 2012). The concentrations were similar to those observed for NO_3^- and NH_4^+ in remote sites in the Canary Islands, Greece or the Tibetan Plateau (García et al., 2017; Li et al., 2013; Ren et al., 2018; Theodosi et al., 2018) but SO_4^{2-} was less abundant than in these studies. SO_4^{2-} was in similar concentrations in day and night periods, while NO_3^- and NH_4^+ occurred in significantly higher concentrations during daytime, likely influenced by atmospheric transport during daytime and the diurnal secondary processes previously related with new particle formation in the studied sampling site (Casquero-Vera et al., 2020).

The difference between day and night of secondary inorganic aerosols is associated with atmospheric conditions. During the day, a higher temperature and intensity of solar radiation favor photochemical reactions for the formation of secondary compounds. However, at night, lower temperatures reduce the decomposition processes of thermally unstable compounds. The ionic balance of anions and cations in the water extraction was calculated in order to determine the associations of these ions (Fig. S 3). Nitrate was observed mainly in the form of calcium and sodium nitrate, and ammonium nitrate concentrations were negligible. Sulfate was present mainly as calcium sulfate and ammonium sulfate. Some of these compounds, as well as the carbonates, are associated with crustal origin due to the arid conditions of Sierra Nevada. All these ionic compounds show slightly higher values during day-time, evidencing the importance of secondary aerosol formation promoted by the atmospheric conditions (upslope transport of pollutants and resuspended material, higher temperatures and solar radiation).

The concentrations observed for the trace metals was generally lower than those previously reported in the city of Granada (Titos et al., 2014) and similar to those found in Mt. Cimone in Italy in 2004 (2100 m a.s.l. (Marenco et al., 2006)) and Mt. Atlas in Morocco (2165 m a.s.l. (Deabji et al., 2021)). Some trace metals, such as Cu, Ni, Mo, and Sn, which are associated with traffic, i.e. vehicle exhaust, brake, tire or pavement abrasion (Amato et al., 2011; Schauer et al., 2006; Wåhlin et al., 2006) showed higher daytime concentrations, while others, such as Sb, Ba, Zn, Ti, Li, and Rb showed no diurnal trend. Pb and As, more related to industrial emissions (Querol et al., 2008), did not have significant concentration differences between both day and nighttime periods, and were found in small concentrations. These observations, together with the SIA diurnal trend mentioned above, were consistent with higher occurrence of secondary processes during sunlight hours mixed with some traffic emissions reaching the station after upslope transport through the valley and natural emissions, such as resuspension of soil dust and crustal material.

The OC and EC mass concentrations were considerably low compared to urban areas in southern Europe (Dinoi et al., 2017; Galindo et al., 2019; Giannossa et al., 2022; Querol et al., 2013), similar to rural background sites from the Iberian Peninsula (Querol et al., 2013) and higher than those measured in other remote mountain sites like Izaña in the Canary Islands (2367 m a.s.l.; (García et al., 2017)), Pico Island in the Azores (2225 m a.s.l.; (Dzepina et al., 2015)) or Monte Curcio in Italy (1780 m a.s.l.; (Dinoi et al., 2017; Moretti et al., 2021)). Higher concentrations of OC and EC were observed during daytime, likely connected with transport within the planetary boundary layer. This diurnal trend was also observed for most of the organic compounds studied here. Both the acids that represent anthropogenic secondary organic aerosols (AnthSOA; SA and PHA) and the biogenic secondary organic aerosol tracers (i.e., SOA tracers of α-pinene oxidation; CPA, 3HGA and MBTCA, and SOA tracers of isoprene oxidation; 2MGA, 2MT1 and 2MT2) showed significantly higher concentrations during the daytime indicating higher biogenic and anthropogenic emissions from gas phase precursors and enhanced transformation into secondary products combined with atmospheric transport mechanisms, such as upslope winds. The mean concentrations of AnthSOA (SA: 9.22, PHA: 1.34 ng/m³) were similar to those reported in a rural background site in the north-east Spain in summer (SA: 15.5, PHA: 2.5 ng/m³; (Jaén et al., 2021)) and in remote sites in Tenerife (SA: 6.5, PHA: 3.2 ng/m³; (García et al., 2017)) and Sanabria Lake (SA: 5.4, PHA: 3.0 ng/m³; (Pérez-Pastor et al., 2023)) but lower than those observed in Mount Tai (China; SA: 57, PHA: 20 ng/m³; (Wang et al., 2009)). The dominant SOA compounds (Table 1) originated from isoprene oxidation (2MGA, 2MT1 and 2MT2). They were found in concentrations slightly higher than in these remote sites and in the Tibetan Plateau (Pérez-Pastor et al., 2023; Ren et al., 2018; Wang et al., 2009) but lower than in the rural background sites. The α -pinene SOA also showed similar concentrations than in these studies. In all cases, the higher concentrations of CPA indicated contributions from a relatively fresh SOA as CPA is generated by oxidation of α -pinene in presence of O3 while 3HGA and MBTCA are products of further oxidation of CPA (Claeys et al., 2007).

The biomass burning tracers (GAL, MAN and LEV) were present in low concentrations, compared to wintertime levels in the low-lands of Granada (Titos et al., 2017; van Drooge et al., 2022) when biomass burning is a more common practice. They did not show a diurnal trend. Levoglucosan was the dominant compound, and its concentration was in the range of those observed in Izaña (Tenerife; 0.75 ng/m³; (García et al., 2017)), and other remote sites in Europe at summer, such as the high mountain sites of Schauinsland (Germany; 1205 m a.s.l.; 12.3 ng/m³) and Puy de Dôme (France; 1205 m a.s.l.; 7.1 ng/m³), and in the marine environment of the Azores (2.0 ng/m³) (Puxbaum et al., 2007). In addition, LEV/(MAN + GAL) ratios ranged from 0.8 to 5.6 and are in

Science of the Total Environment 905 (2023) 167178

agreement with softwood combustion emissions ratios reported in the literature (Engling et al., 2006; Fine et al., 2004). In particular, the average ratio was 3.0 which coincides with the one reported by van Drooge et al. (2014) in the Iberian Peninsula as a representative ratio for residual summertime biomass burning aerosols. Thus, the small amounts of those tracers found in the high-altitude site can be considered background levels in the region.

Other primary organic compounds, such as aliphatic hydrocarbons (n-alkanes) showed a clear diurnal trend, and the highest concentrations were observed for odd carbon compounds (nC27, nC29 and nC31), related to higher plant contributions. The carbon preference index of biogenic/pyrogenic *n*-alkanes is expressed as the ratio of odd/even carbon-numbered alkanes from nC24 to nC31. CPI values >1 indicate higher contributions of higher plants, while CPI values close to 1 indicate predominant fossil fuel contributions (Mazurek and Simoneit, 1984; Rogge et al., 1993; Simoneit et al., 1991a). In any case, the average carbon preference index (CPI) for the whole period was 1.9, suggesting higher plant contributions to be slightly more dominant over fossil fuel contributions. Notwithstanding, the organic tracer compounds for vehicle emissions (hopanes: norHOP and HOP) were also higher during daytime and could be related to low intensity local traffic or mid-range air pollution from the city of Granada. Higher

a)

concentrations of these hopanes were observed in a remote site in Tenerife (norHOP: 70, HOP: $60 \rho g/m^3$; (García et al., 2017)) while lower concentrations were observed in the remote site of Sanabria Lake (norHOP: 5, HOP: $6 \rho g/m^3$; (Pérez-Pastor et al., 2023)) and some rural background sites in Spain (Jaén et al., 2021).

The PAH, both parent compounds and quinones, were found in the low $\rho g/m^3$ concentrations, which agreed with results from other remote mountain sites in Spain and Europe (García et al., 2017; Pérez-Pastor et al., 2023; van Drooge et al., 2012). It is interesting to remark that 9,10-anthraquinone, a product of anthracene photo degradation (Alam et al., 2014), was one of the dominant PAHs which could reflect high influence of PAH photooxidation during transport to this remote site. However, some of these compounds reflecting incomplete combustion of organic matter were found in significantly higher concentration in nighttime (Table 1) which could be related to some local source.

The day-night trends of the compounds may be affected by the presence of extreme events during the sampling period such as the Saharan dust intrusion mentioned above. To unmask possible diurnal patterns of the studied compounds the dataset was filtered by eliminating the 10 samples in which PM_{10} , OC, or EC concentrations were identified as outliers by the interquartile range criterion. Most of these samples were indeed related to the Saharan dust intrusion. Those results



Fig. 2. Mean air-mass trajectory for each cluster (lines) and individual air-masses trajectory points (dots) for the 6 clusters retrieved with Hysplit (a). Wind-scatter plots of each cluster with the measured wind in SNS at the trajectory end time (b to g). Wind velocity in m/s.

(Table 1) indicate a clear daytime peak concentration of PM and EC. The same trend was observed for many of the typical Earth crustal elements except SiO₂, Al₂O₃ and Fe. Other major inorganic compounds and trace metals such as PO_4^{3-} , SO_4^{2-} , Cr, Zn, Sr, Sb and Ba were also statistically higher during daytime which agrees with higher anthropogenic activity and upward airmass transport during this time of the day. Nevertheless, trends in organic compounds barely change when eliminating the rare or extreme events.

3.2. Air mass cluster analysis

The origin of the air masses can help to identify the sources of pollution and to assess possible influences of meteorology on the compounds transported to the studied site. The air-mass back trajectory analysis computed with the NOAA Hysplit model showed 6 relevant air mass clusters (Fig. 2a). Four clusters had their origin in the Atlantic Ocean, one in the Iberian Peninsula and another one in north Africa. The long-range Atlantic cluster, 4 % of the trajectories of the sampling period, showed air masses transported over long distances through the ocean from the North-west and was therefore related with strong winds (Fig. 2d). The cluster of mid-range Atlantic trajectories (17 %) had similar origin, but the air masses were transported eastward at lower wind speeds and the short-range Atlantic cluster (20 %) covered a shorter distance and some trajectories passed over Africa. On the other side, the North Atlantic cluster (14 %) transported air masses from the Celtic Sea and some regions of north-Europe. The Local-Mediterranean cluster (28 %) was composed of trajectories enclosed between the Iberian Peninsula and North Africa and was characterized by short-distance transport of the air masses. Finally, the North-African cluster encompassed 16 % of the trajectories that travelled over arid zones of North Africa.

The measured wind scatter plots in SNS (Fig. 2b to g) show the hourly

average of wind velocity and direction at the trajectory endtime for all trajectories of each cluster. The plots showed that all clusters except the North African corresponded to a local WSW dominant wind direction which coincided with the valley of the mountain range connecting the city of Granada with the sampling site. As expected, clusters with west-Atlantic origin were related to stronger winds than the Local-Mediterranean and North Atlantic ones. In the North African wind distribution (Fig. 2g), SE winds prevailed which agreed with a southern advection from the Saharan desert (Fig. 2g). Moreover, although most of the records indicated weak winds, there were also strong winds reaching the station during the African advection.

3.3. Source apportionment analysis and synoptic meteorological conditions

The bilinear decomposition of the dataset performed with MCR-ALS method resolved 5 different components with 94 % of explained variance. The chemical profiles of these components are shown in Fig. 3 and were used to assess the PM sources. Fig. 4 shows the scores of these MCR-ALS components in each sampling period together with the meteorological data registered in the SNS station. The data is also shown with the dominant trajectory cluster of each period in the x axis. Moreover, the source apportionment was also performed at day and night databases separately and similar loading profiles were obtained for the 5 components (Fig. S 4). These components in the separate analysis correlate very well with the complete database for Valley PM, Saharan dust PM and Regional PM (Fig. S 5 from a to f) while correlation is weaker for the components with lower explained variances (Fire PM and Local Combustion PM; Fig. S 5 from g to j). Given the resolution of the components, the whole database was used for the rest of the study.



Fig. 3. Compound loads for each component in MCR-ALS decomposition.



Fig. 4. Meteorological data (Temperature, Relative Humidity, precipitation, wind speed and wind direction) and MCR-ALS component scores for the sampling period. Colored date axis indicates the cluster dominating each sampling period and the grey and yellow shadows the diurnal and nocturnal sampling periods.

3.3.1. Valley PM

The component involving highest explained variance (39 %) was related with air pollution transport through the valley which connects with Granada metropolitan area (named as Valley PM). It consisted of hopanes (62 %), and n-alkanes (45 %), being the most abundant those with shorter chains and even number of carbon atoms. Both groups of compounds are indicators of vehicle emissions, suggesting atmospheric transport from the lower altitudes through the valley to the SNS as road traffic is one of the main aerosol sources in Granada metropolitan area (Titos et al., 2014; van Drooge et al., 2022). The PAH contributions to this component were very low and the 9,10-anthaquinone was the dominant compound of this family. This component also contained 34 % of the OC and contributions from some trace metals such as Mo, which can be released by vehicles through engine wear (Gonet and Maher, 2019) among other sources and other metals such as Ni, Cr, Cu and Ba that can be attributed to fuel combustion and brake and tire abrasion (Schauer et al., 2006; Wåhlin et al., 2006). This component also

contained a high contribution of bis(2-ethylhexyl) phthalate (53 %), which is a plasticizer classified as a Category 1B reprotoxin and technically banned since 2015 (Council Directive 20212/18/EU, 2012) and suggest the active transport of plastic particles to the high mountain site. Moreover, the presence of secondary organic aerosols in this component, i.e. SOA tracers of isoprene oxidation (2MGA (7 %), 2MT1 (35 %) and 2MT2 (39 %)) indicate that mid-range transport from anthropogenic emission source areas towards the sampling site is mixed with biogenic isoprene SOA generated in secondary processes in the atmosphere.

Higher concentrations of this component during daytime (Table 1; Fig. 4) are clearly observed which is consistent with the upward mountain breezes that transport air pollution from the valley, including the city of Granada (Ortiz-Amezcua et al., 2022; Rejano et al., 2021). The highest scores were observed at the end of the sampling period when western winds enhanced this upward transport along the valleys.

3.3.2. Saharan dust PM

The second component during the campaign (31 % of explained variance) is related with Saharan dust PM, as it is mainly composed by inorganic material, predominantly earth crustal elements such as CO_3^{2-} , SiO₂, Al₂O₃, Ca, K, and Fe. It contains the 52 % of the inorganic major elements and the 50 % of the trace elements. The contribution SIA is consistent with aging of the aerosols during atmospheric transport. This Saharan dust component contributed for 57 % of the PM₁₀ which is again consistent with the high concentrations of PM in these events. In addition, the component shows higher abundance of biologically synthesized n-alkanes (nC27, nC29 and nC31) indicating a primary biogenic emission of these compounds in the air masses advected from north Africa.

This component is observed in higher contribution on the days characterized by North African trajectories reaching the sampling station. However, a portion of it is also associated with the Short-range Atlantic cluster (Figs. 2a and 4). A Saharan dust intrusion was observed between June 11th and June 16th, which is the period of highest scoring of this component. The small contribution of mineral dust in the rest of the days of the campaign is probably due to the mechanical abrasion of the semi-arid zones of the mountain range.

3.3.3. Regional PM

The third component (31 % of explained variance) is represented by secondary pollutants, both inorganic (SO_4^{2-} , NO_3^{-} , NH_4^{+} ; 40 %) and organic (SA, PHA, GLU, AZA, 2MGA, 2MT1, 2MT2, CPA, 3HGA, MBTCA, MA; 42 %) and the saccharides (GAL, MANNO, LEV, AGL, BGL, MANNI, SOR; 56 %). This component is related with regional air transport, and the highest scores correspond to local Mediterranean trajectories. The component also contains 35 % of the Na, tracer of marine aerosol, which agrees with the regional circulation of this air mass. The contribution of n-alkanes with a typical profile of biogenic sources is consistent with the input of the emissions of the mountain range and its surroundings.

The highest scores of this component are related with the low wind speed, indicating recirculation of air in the region and the aging of pollutants in the air mass (Fig. 4). The trajectory clusters also show substantial contributions during days with North Atlantic trajectories. Also, the diurnal trend indicates secondary aerosol formation during the sunlight hours which could be linked to new particle formation as observed in Sierra Nevada in previous studies (Casquero-Vera et al., 2020; Rejano et al., 2021). On the contrary, the contribution of this component with strong western winds at the end of the sampling period is low.

3.3.4. Fire PM

The fourth component (14 % of explained variance) consisted of compounds that could be related to combustion sources (Fire PM), 42 % of the PAHs and 60 % of the EC. It also had high loads of trace metals related to industrial activities such as Zn, Sb and Pb (Querol et al., 2008) and contributions of some quinones.

Generally, this component showed background contribution to PM, but it had a very high score on the night between June 30th and July 1st which coincides with a major fire that started at 17:20 (UTC) in an industrial polygon at the foot of the mountain range, at 23 km distance from the sampling site (Javier Morales, 2021). The smoke affected the night sample and the impact of this fire was reduced progressively in the next days. This short-term event, and anecdotic example, shows the effects of emissions from lower areas on the air quality in Sierra Nevada National Park. Moreover, these kind of fires events represent a threat to the ecosystems of the mountain range as the composition of this component implied high concentrations of PAHs, quinones, Zn and Sb, that can also be deposited in soils and transferred to subsoil water.

3.3.5. Local combustion PM

The fifth component (12 % of variance) contained 48 % of the PAHs and 64 % of the quinones, both tracers of incomplete combustion. It also

contained 22 % of the biomass burning tracers and an alkane profile of combustion sources (predominance of shorter chains). Besides these primary emission organic tracer compounds, the presence of SOA tracers and inorganic compounds is nearly absent, suggesting the presence of a local combustion source with low impact on PM and OC. The component most likely represents an unidentified local combustion source.

One peculiar feature of this component is the temporal profile along the samples, which is dominant in some nights that seem to be separated by two days and does not present any clear relation with the meteorological factors or the trajectory origins. This trend may reflect some local combustion source operating some nights.

3.3.6. PM sources and air-mass origin

The percentual contributions of each component to the different airmass clusters are shown in Fig. 5a. The Regional PM was the dominant component in the Local-Mediterranean and North Atlantic clusters (33 % and 38 %, respectively) that were linked to weak winds and recirculation of air masses in the region. The Local-Mediterranean cluster had also a significant contribution of the Valley PM component (29%) and the Fire component (18 %). The Long-range Atlantic cluster was dominated by the Valley PM (39 %) and Regional PM (26 %) components whereas the Mid-range Atlantic was clearly dominated by Valley PM (57 %) and had small contributions from the other components. On the other side, the Short-range Atlantic cluster did not have a dominant source as comparable contributions from Valley PM (25 %), Regional PM (21 %), Saharan dust (26 %), and Local combustion (21 %) were observed. However, the relatively high contribution from Saharan dust PM might be related to the trajectories of this cluster reaching the station from Africa (Fig. 2a). Finally, as expected, the North African cluster was clearly dominated by the Saharan dust component (57 %).

The diurnal trend of each component evidences the strong daytime relation of Valley PM with an 78 % of the contribution on this component during daytime. The Regional PM also presented higher loads at daytime (67 %) while Saharan dust component was equally present in both periods (49 % day and 51 % night). On the contrary, the Local combustion component was clearly related with nighttime hours with an 83 % of the contribution, as well as the Fire PM with a 58 % for night periods (Fig. 5b and c). These trends are also reflected by when studying the diurnal trends by cluster (Fig. 5b and c) as Valley PM boxplots are dominant during daytime (Fig. 5b) while Local combustion boxplots are dominant during nighttime (Fig. 5c) for all clusters. However, North Atlantic and Local-Mediterranean clusters had significant contribution of Regional PM for both periods and the highest scores for Saharan dust PM are registered for the North African cluster for both periods and for the Short-range Atlantic during the day. In general terms, higher scores are observed during daytime agreeing with higher biogenic and anthropogenic activity influencing the sampling site and lower scores are observed at nighttime when the sampling site is in nearly free tropospheric conditions, except for the influence of the local source.

3.3.7. Contribution of components to PM, OC and EC

The contribution of each component to PM, OC, and EC is shown in Fig. 6. Despite its relatively short duration, the Saharan Dust component shows the highest contribution to PM (57 %). On the contrary, the contribution of Saharan dust to OC and EC is relatively small (17 % and 5 %, respectively). This component is followed by the Fire event PM which, despite being a short-time and accidental phenomenon that only lasted 1 day, had a significant impact on air quality in Sierra Nevada as it involved 15 % of PM, 22 % of OC and 60 % of EC for the whole studied period. Moreover, the identification of several toxic compounds in this source evidence the impact that these kinds of events have in the ecosystems of the natural park.

Regional PM contributes to 14 % of the PM in the sampling site and the percentage increases in OC and EC (23 % and 24 %, respectively) as it contains many SOA species. This is probably the most representative component of background pollution in SNS as it may represent the



Fig. 5. a) Percentages of MCR-ALS components contributions to each air trajectory cluster. b) Day samples scores boxplots for each cluster by MCR-ALS components. c) Night samples scores boxplots for each cluster by MCR-ALS components.



Fig. 6. Percentages of MCR-ALS components contribution to PM, OC and EC.

secondary aerosol processes in the free troposphere with limited influence from anthropogenic pollution sources, both local and from the valley. The influence of anthropogenic sources is best expressed by the Valley PM component which contributes to 34 % of the OC as it is mainly composed by n-alkanes, organic tracers of traffic emissions (hopanes) and secondary organic aerosols. Nevertheless, the contributions to PM and EC are relatively small (8 % and 11 %, respectively). Furthermore, the Local Combustion PM source has overall low contributions to these overall indicators, despite being one of the dominant sources during certain nights.

4. Conclusions

This study focuses on the organic and inorganic aerosol composition at a high-altitude mountain site of southern Europe. The Sierra Nevada National Park constitutes the highest mountainous area of southern Europe, being an important biodiversity hotspot in the Mediterranean area with great ecological interest. During the measurement campaign (June-July 2021), PM₁₀ samples were collected during day and nighttime to identify the main aerosol sources affecting the site. Overall, low concentrations of PM, OC and EC were found, especially compared with more populated areas, and in the range of other remote or mountain-top sites. Earth crust elements registered very high levels, but limited to the days affected by Saharan dust intrusion. The diurnal transport within the boundary layer was reflected in higher concentrations of traffic tracers and anthropogenic SIA and SOA during the day which indicates an active transport of aerosols from the more populated areas in the lower lands of the mountain range. Moreover, the higher concentrations observed for biogenic SOA during sunlight hours reinforces idea of the new particle formation events that may occur in the upper layers of the atmosphere. This trend is also reflected in PM, OC and EC concentrations which are higher during the day when the extreme events are not considered.

The source apportionment was performed over a matrix of 57 samples and 77 compounds, and identified five main contributors to PM in the SNS site; Saharan dust, Valley PM transported from the area of Granada, Regional PM, an anecdotal fire event, and a local combustion source near the vicinity of the sampling site. The Valley PM component had mixed composition with secondary products indicating an aging of pollutants during transport which was also observed in the Saharan dust component. The Regional component had the highest contribution of the SOA from the secondary products of both anthropogenic and biogenic activity. The fire event, evidenced the transport of a fire smoke episode from lower areas to the high mountains. The local combustion source was not related with any mid- or long-range transport and pointed to a local emission near the SNS site.

A clear relation with the air mass origin and the chemical composition of PM was observed. Trajectories belonging to local Mediterranean and north Atlantic clusters were related to weak winds and were influenced by inputs from the Iberian Peninsula most of the time. Consequently, they had a highest contribution of the Regional PM component. On the other hand, East Atlantic clusters (long, mid and short-range) implied a highest transport of traffic aerosols from the city of Granada. Finally, a consistent relation was observed between the North African trajectories and the Saharan dust component.

The contribution of the identified sources to the air quality indicators indicated a small contribution of local pollution sources to PM, OC and EC. The transport of the pollution originating from short- and mid-range sources dominates the site and is favored during daytime by local circulations of air driven by the mountain-valley breeze and increasing height of the planetary boundary layer. Saharan dust outbreaks can lead to significant increases in PM levels, which can affect the air quality as well as have an ecological impact in the area, leading to dust deposition on the vegetation and/or in the snowpack. Furthermore, sporadic events, such as fires can pose a risk to the air quality of the national park, as evidenced in this study, with transport of toxic compounds during an accidental short-term fire event. Comprehensive knowledge of the organic aerosol chemistry is of great importance in assessing anthropogenic influences and evaluating the aerosol effect on climate (radiative forcing as well as aerosol-cloud interactions processes). The study presented here offers new insights into the organic and inorganic composition of the south European free troposphere during summertime, as well as the impact of mid- and long-range transport of aerosol particles. Further studies are needed to understand the aerosol sources over longer time periods (winter versus summer conditions), the effect of these sources in the local air quality and biodiversity, and the impact of aerosol sources on climate.

CRediT authorship contribution statement

Clara Jaén: Investigation, Formal analysis, Visualization, Writing – original draft. **Gloria Titos:** Supervision, Conceptualization, Funding acquisition, Writing – review & editing. **Sonia Castillo:** Investigation, Writing – review & editing. **Andrea Casans:** Investigation, Writing – review & editing. **Fernando Rejano:** Investigation, Writing – review & editing. **Alberto Cazorla:** Investigation, Funding acquisition, Writing – review & editing. **Javier Herrero:** Investigation, Writing – review & editing. **Lucas Alados-Arboledas:** Funding acquisition, Writing – review & editing. **Joan O. Grimalt:** Funding acquisition, Writing – review & editing. **Barend L. van Drooge:** Formal analysis, Supervision, Conceptualization, Writing – review & editing.

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

Technical assistance from Roser Chaler and Alexandre Garcia is acknowledged. We acknowledge the use of imagery from the NASA Worldview application (https://worldview.earthdata.nasa.gov), part of the NASA Earth Observing System Data and Information System (EOSDIS).

Funding

This work was supported by the CuanTox (CTM2015-71832-P), Intempol (PGC2018-102288-B-I00) and BioCloud project (RTI2018.101154.A.I00) funded by MCIN/AEI/10.13039/ 501100011033 and FEDER "ERDF a way of making Europe" and NUCLEUS project (PID2021-128757OB-I00) funded by MCIN/AEI/ 10.13039/501100011033 and the "European Union NextGenerationEU/PRTR". The study was partially funded by the European Union's Horizon 2020 research and innovation program through project ACTRIS.IMP (grant agreement No 871115) and ATMO_ACCESS (grant agreement No 101008004), by the Spanish Ministry of Science and Innovation through projects ELPIS (PID2020-120015RB-I00), and ACTRIS-España (RED2022-134824-E), by the Junta de Andalucía Excellence project ADAPNE (P20-00136) and AEROPRE (P-18-RT-3820). This research was partially supported by University of Granada Plan Propio through Singular Laboratory AGORA (LS2022-1) and Scientific Units of Excellence Program (grant no. UCE-PP2017-02). IDAEA-CSIC is a Severo Ochoa Centre of Research Excellence (Spanish Ministry of Science and Innovation, CEX2018-000794-S). Funding from Gen-Catalunya, Research Group 2021SGR00986, eralitat de is acknowledged.

C.J. thanks the financial support from a Training of University Teachers (FPU 19/06826) grant from the Ministry of Science and Innovation (Spain).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.167178.

References

- Abdelkader, M., Metzger, S., Mamouri, R.E., Astitha, M., Barrie, L., Levin, Z., Lelieveld, J., 2015. Dust-air pollution dynamics over the eastern Mediterranean. Atmos. Chem. Phys. 15, 9173–9189. https://doi.org/10.5194/acp-15-9173-2015
- Alam, M.S., Delgado-Saborit, J.M., Stark, C., Harrison, R.M., 2014. Investigating PAH relative reactivity using congener profiles, quinone measurements and back trajectories. Atmos. Chem. Phys. 14, 2467–2477. https://doi.org/10.5194/acp-14-2467-2014.
- 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. https://doi.org/10.5194/acp-13-10353-2013.
- Amato, F., Pandolfi, M., Moreno, T., Furger, M., Pey, J., Alastuey, A., Bukowiecki, N., Prevot, A.S.H., Baltensperger, U., Querol, X., 2011. Sources and variability of inhalable road dust particles in three European cities. Atmos. Environ. 45, 6777–6787. https://doi.org/10.1016/j.atmosenv.2011.06.003.
- Amato, F., Alastuey, A., Karanasiou, A., Lucarelli, F., Nava, S., Calzolai, G., Severi, M., Becagli, S., Gianelle, V.L., Colombi, C., Alves, C., Custódio, D., Nunes, T., Cerqueira, M., Pio, C., Eleftheriadis, K., Diapouli, E., Reche, C., Minguillón, M.C., Manousakas, M.I., Maggos, T., Vratolis, S., Harrison, R.M., Querol, X., 2016. AIRUSE-LIFE+: a harmonized PM speciation and source apportionment in five southern European cities. Atmos. Chem. Phys. 16, 3289–3309. https://doi.org/ 10.5194/acp-16-3289-2016.
- Brines, M., Dall'Osto, M., Amato, F., Minguillón, M.C., Karanasiou, A., Grimalt, J.O., Alastuey, A., Querol, X., van Drooge, B.L., 2019. Source apportionment of urban PM₁ in Barcelona during SAPUSS using organic and inorganic components. Environ. Sci. Pollut. Res. 26, 32114–32127. https://doi.org/10.1007/s11356-019-06199-3.
- Bukowiecki, N., Brem, B.T., Wehrle, G., Močnik, G., Affolter, S., Leuenberger, M., Coen, M.C., Hervo, M., Baltensperger, U., Gysel-Beer, M., 2021. Elucidating local pollution and site representativeness at the Jungfraujoch, Switzerland through parallel aerosol measurements at an adjacent mountain ridge. Environ. Res. Commun. 3, 21001. https://doi.org/10.1088/2515-7620/abe987.
- Casquero-Vera, J.A., Lyamani, H., Dada, L., Hakala, S., Paasonen, P., Román, R., Fraile, R., Petäjä, T., Olmo-Reyes, F.J., Alados-Arboledas, L., 2020. New particle formation at urban and high-altitude remote sites in the south-eastern Iberian Peninsula. Atmos. Chem. Phys. 20, 14253–14271. https://doi.org/10.5194/acp-20-14253-2020.
- Cavalli, F., Viana, M., Yttri, K.E., Genberg, J., Putaud, J., 2010. Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. Atmos. Meas. Tech. 3, 79–89. https://doi.org/10.5194/amt-3-79-2010.
- Chen, W.R., Singh, A., Pani, S.K., Chang, S.Y., Chou, C.C.K., Chang, S.C., Chuang, M.T., Lin, N.H., Huang, C.H., Lee, C. Te, 2021. Real-time measurements of PM_{2.5} watersoluble inorganic ions at a high-altitude mountain site in the western North Pacific: impact of upslope wind and long-range transported biomass-burning smoke. Atmos. Res. 260, 105686. https://doi.org/10.1016/j.atmosres.2021.105686.
- Chu, B., Dada, L., Liu, Y., Yao, L., Wang, Y., Du, W., Cai, J., Dällenbach, K.R., Chen, X., Simonen, P., Zhou, Y., Deng, C., Fu, Y., Yin, R., Li, H., He, X.C., Feng, Z., Yan, C., Kangasluoma, J., Bianchi, F., Jiang, J., Kujansuu, J., Kerminen, V.M., Petäjä, T., He, H., Kulmala, M., 2021. Particle growth with photochemical age from new particle formation to haze in the winter of Beijing, China. Sci. Total Environ. 753, 142207. https://doi.org/10.1016/j.scitotenv.2020.142207.

Claeys, M., Szmigielski, R., Kourtchev, I., der Veken, P., Vermeylen, R., Maenhaut, W., Jaoui, M., Kleindienst, T.E., Lewandowski, M., Offenberg, J.H., et al., 2007. Hydroxydicarboxylic acids: markers for secondary organic aerosol from the photooxidation of α-pinene. Environ. Sci. Technol. 41, 1628–1634. https://doi.org/ 10.1021/es0620181.

Council Directive 2008/50/EC, 2008. DIRECTIVE 2008/50/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 May 2008 on Ambient Air Quality and Cleaner Air for Europe. In: Official Journal of the European Union L 152/1-L 152/42.

Council Directive 2012/18/EU, 2012. Seveso III Directive: DIRECTIVE 2012/18/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 4 July 2012 on the Control of Major-accident Hazards Involving Dangerous Substances, Amending and Subsequently Repealing Council Directive 96/82/EC. In: Official Journal of the European Union L 197/1-L 197/37.

Deabji, N., Fomba, K.W., El Hajjaji, S., Mellouki, A., Poulain, L., Zeppenfeld, S., Herrmann, H., 2021. First insights into northern Africa high-altitude background aerosol chemical composition and source influences. Atmos. Chem. Phys. 21, 18147–18174. https://doi.org/10.5194/acp-21-18147-2021.

Diémoz, H., Barnaba, F., Magri, T., Pession, G., Dionisi, D., Pittavino, S., Tombolato, I.K. F., Campanelli, M., Ceca, L.S. Della, Hervo, M., Di Liberto, L., Ferrero, L., Gobbi, G. P., 2019. Transport of Po Valley aerosol pollution to the northwestern Alps-part 1: phenomenology. Atmos. Chem. Phys. 19, 3065–3095. https://doi.org/10.5194/acp-19-3065-2019.

Dinoi, A., Cesari, D., Marinoni, A., Bonasoni, P., Riccio, A., Chianese, E., Tirimberio, G., Naccarato, A., Sprovieri, F., Andreoli, V., Moretti, S., Gulli, D., Calidonna, C.R., Ammoscato, I., Contini, D., 2017. Inter-comparison of carbon content in PM_{2.5} and PM₁₀ collected at five measurement sites in Southern Italy. Atmosphere 8, 243. https://doi.org/10.3390/atmos8120243.

Draxler, R., Stunder, B., Rolph, G., Stein, A., Taylor, A., Zinn, S., Loughner, C., Crawford, A., 2022. HYSPLIT USER's GUIDE [WWW Document]. URL. https://www. arl.noaa.gov/documents/reports/hysplit_user_guide.pdf.

- Dzepina, K., Mazzoleni, C., Fialho, P., China, S., Zhang, B., Owen, R.C., Helmig, D., Hueber, J., Kumar, S., Perlinger, J.A., Kramer, L.J., Dziobak, M.P., Ampadu, M.T., Olsen, S., Wuebbles, D.J., Mazzoleni, L.R., 2015. Molecular characterization of free tropospheric aerosol collected at the Pico Mountain Observatory: a case study with a long-range transported biomass burning plume. Atmos. Chem. Phys. 15, 5047–5068. https://doi.org/10.5194/acp-15-5047-2015.
- Engling, G., Carrico, C.M., Kreidenweis, S.M., Collett, J.L., Day, D.E., Malm, W.C., Lincoln, E., Min Hao, W., Iinuma, Y., Herrmann, H., 2006. Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection. Atmos. Environ. 40, S299–S311. https://doi.org/10.1016/j.atmosenv.2005.12.069.
- Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical characterization of Fine particle emissions from the fireplace combustion of wood types grown in the Midwestern and Western United States. Environ. Eng. Sci. 21, 387–409. https://doi.org/10.1089/ 109287504323067021.
- Fontal, M., van Drooge, B.L., López, J.F., Fernández, P., Grimalt, J.O., 2015. Broad spectrum analysis of polar and apolar organic compounds in submicron atmospheric particles. J. Chromatogr. A 1404, 28–38. https://doi.org/10.1016/j. chroma.2015.05.042.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., van Dorland, R., Bodeker, G., Boucher, O., Collins, W.D., Conway, T.J., Dlugokencky, E., Elkins, J.W., Etheridge, D., Foukal, P., Fraser, P., Geller, M., Joos, F., Keeling, C.D., Kinne, S., Lassey, K., Lohmann, U., Manning, A.C., Montzka, S., Oram, D., O'Shaughnessy, K., Piper, S., Plattner, G.-K., Ponater, M., Ramankutty, N., Reid, G., Rind, D., Rosenlof, K., Sausen, R., Schwarzkopf, D., Solanki, S.K., Stenchikov, G., Stuber, N., Takemura, T., Textor, C., Wang, R., Weiss, R., Whorf, T., 2007. Changes in atmospheric constituents and in radiative forcing. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the 4th Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press. Cambridge University

- Press, Cambridge, United Kingdom and New York, USA.
 Fu, P.Q., Kawamura, K., Chen, J., Li, J., Sun, Y.L., Liu, Y., Tachibana, E., Aggarwal, S.G., Okuzawa, K., Tanimoto, H., Kanaya, Y., Wang, Z.F., 2012. Diurnal variations of organic molecular tracers and stable carbon isotopic composition in atmospheric aerosols over Mt. Tai in the North China Plain: an influence of biomass burning. Atmos. Chem. Phys. 12, 8359–8375. https://doi.org/10.5194/acp-12-8359-2012.
- Fu, P., Kawamura, K., Chen, J., Miyazaki, Y., 2014. Secondary production of organic aerosols from biogenic VOCs over Mt. Fuji, Japan. Environ. Sci. Technol. 48, 8491–8497. https://doi.org/10.1021/es500794d.

Galindo, N., Yubero, E., Nicolás, J.F., Crespo, J., Varea, M., Gil-Moltó, J., 2017. Regional and long-range transport of aerosols at Mt. Aitana, Southeastern Spain. Sci. Total Environ. 584–585, 723–730. https://doi.org/10.1016/j.scitotenv.2017.01.108.

Galindo, N., Yubero, E., Clemente, A., Nicolás, J.F., Navarro-Selma, B., Crespo, J., 2019. Insights into the origin and evolution of carbonaceous aerosols in a mediterranean urban environment. Chemosphere 235, 636–642. https://doi.org/10.1016/j. chemosphere.2019.06.202.

Galindo, N., Yubero, E., Clemente, Á., Nicolás, J.F., Varea, M., Crespo, J., 2020. PM events and changes in the chemical composition of urban aerosols: a case study in the western Mediterranean. Chemosphere 244, 125520. https://doi.org/10.1016/j. chemosphere.2019.125520.

García, M.I., Rodríguez, S., González, Y., García, R.D., 2014. Climatology of new particle formation at Izaña mountain GAW observatory in the subtropical North Atlantic. Atmos. Chem. Phys. 14, 3865–3881. https://doi.org/10.5194/acp-14-3865-2014.

García, M.I., Van Drooge, B.L., Rodríguez, S., Alastuey, A., 2017. Speciation of organic aerosols in the Saharan Air Layer and in the free troposphere westerlies. Atmos. Chem. Phys. 17, 8939–8958. https://doi.org/10.5194/acp-17-8939-2017.

- Giannossa, L.C., Cesari, D., Merico, E., Dinoi, A., Mangone, A., Guascito, M.R., Contini, D., 2022. Inter-annual variability of source contributions to PM₁₀, PM_{2.5}, and oxidative potential in an urban background site in the central Mediterranean. J. Environ. Manag. 319, 115752. https://doi.org/10.1016/j.jenvman.2022.115752.
- Gonet, T., Maher, B.A., 2019. Airborne, vehicle-derived Fe-bearing nanoparticles in the urban environment: a review. Environ. Sci. Technol. 53, 9970–9991. https://doi. org/10.1021/acs.est.9b01505.
- Hernandez, A.J., Morales-Rincon, L.A., Wu, D., Mallia, D., Lin, J.C., Jimenez, R., 2019. Transboundary transport of biomass burning aerosols and photochemical pollution in the Orinoco River Basin. Atmos. Environ. 205, 1–8. https://doi.org/10.1016/j. atmosenv.2019.01.051.
- Israelevich, P., Ganor, E., Alpert, P., Kishcha, P., Stupp, A., 2012. Predominant transport paths of Saharan dust over the Mediterranean Sea to Europe. J. Geophys. Res. Atmos. 117, 1–11. https://doi.org/10.1029/2011JD016482.
- Jaén, C., Villasclaras, P., Fernández, P., Grimalt, J.O., Udina, M., Bedia, C., van Drooge, B.L., 2021. Source apportionment and toxicity of PM in urban, sub-urban, and rural air quality network stations in Catalonia. Atmosphere 12, 744. https://doi. org/10.3390/atmos12060744.
- Jarque, S., Quirós, L., Grimalt, J.O., Gallego, E., Catalan, J., Lackner, R., Piña, B., 2015. Background fish feminization effects in European remote sites. Sci. Rep. 5, 1–6. https://doi.org/10.1038/srep11292.
- Jaumot, J., Gargallo, R., De Juan, A., Tauler, R., 2005. A graphical user-friendly interface for MCR-ALS: a new tool for multivariate curve resolution in MATLAB. Chemom. Intel. Lab. Syst. 76, 101–110. https://doi.org/10.1016/j.chemolab.2004.12.007.

Jaumot, J., de Juan, A., Tauler, R., 2015. MCR-ALS GUI 2.0: new features and applications. Chemom. Intel. Lab. Syst. 140, 1–12. https://doi.org/10.1016/j. chemolab.2014.10.003.

- Javier Morales, 2021. Un incendio arrasa las cuatro naves de un almacén de jamones en Otura [WWW Document]. Ideal. URL. https://www.ideal.es/granada/incendio-arras a-cuatro-20210701234819-nt.html (accessed 5.25.23).
- Jimenez, J.L., Canagaratna, M.R., Donahue, N.M., Prevot, A.S.H., Zhang, Q., Kroll, J.H., DeCarlo, P.F., Allan, J.D., Coe, H., Ng, N.L., et al., 2009. Evolution of organic aerosols in the atmosphere. Science 326, 1525–1529. https://doi.org/10.1126/ science.1180353.
- Kalnay, E., Kanamitsu, M., Kistler, R., Collins, W., Deaven, D., Gandin, L., Iredell, M., Saha, S., White, G., Woollen, J., Zhu, Y., Chelliah, M., Ebisuzaki, W., Higgins, W., Janowiak, J., Mo, K.C., Ropelewski, C., Wang, J., Leetmaa, A., Reynolds, R., Jenne, R., Joseph, D., 1996. The NCEP/NCAR 40-year reanalysis project. Bull. Am. Meteorol. Soc. 77, 437–472. https://doi.org/10.1175/1520-0477(1996)077<0437: TNYRP>2.0.CO;2.
- Kumari, S., Lakhani, A., Kumari, K.M., 2020. Transport of aerosols and trace gases during dust and crop-residue burning events in Indo-Gangetic Plain: influence on surface ozone levels over downwind region. Atmos. Environ. 241, 117829. https://doi.org/ 10.1016/j.atmosenv.2020.117829.
- Kunwar, B., Kawamura, K., Fujiwara, S., Fu, P., Miyazaki, Y., Pokhrel, A., 2019. Dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in atmospheric aerosols from Mt. Fuji, Japan: implication for primary emission versus secondary formation. Atmos. Res. 221, 58–71. https://doi.org/10.1016/j.atmosres.2019.01.021.
- Landrigan, P., Fuller, R., Haines, A., Watts, N., McCarthy, G., 2018. Pollution prevention and climate change mitigation: measuring the health benefits of comprehensive interventions. Lancet Planet. Health 2, e515–e516. https://doi.org/10.1016/S2542-5196(18)30226-2.
- Lang, M.N., Gohm, A., Wagner, J.S., 2015. The impact of embedded valleys on daytime pollution transport over a mountain range. Atmos. Chem. Phys. 15, 11981–11998. https://doi.org/10.5194/acp-15-11981-2015.
- 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. Phys. Meteorol. 65, 20281. https://doi.org/10.3402/tellusb.v65i0.20281.
- Marenco, F., Bonasoni, P., Calzolari, F., Ceriani, M., Chiari, M., Cristofanelli, P., D'Alessandro, A., Fermo, P., Lucarelli, F., Mazzei, F., Nava, S., Piazzalunga, A., Prati, P., Valli, G., Vecchi, R., 2006. Characterization of atmospheric aerosols at Monte Cimone, Italy, during summer 2004: source apportionment and transport mechanisms. J. Geophys. Res. Atmos. 111, 1–15. https://doi.org/10.1029/ 2006JD007145.
- Mazurek, M.A., Simoneit, B.R.T., 1984. Characterization of biogenic and petroleumderived organic matter in aerosols over remote, rural and urban areas. In: Identif. and Anal of Org Pollut in Air, pp. 353–370.
- Moretti, S., Tassone, A., Andreoli, V., Carbone, F., Pirrone, N., Sprovieri, F., Naccarato, A., 2021. Analytical study on the primary and secondary organic carbon and elemental carbon in the particulate matter at the high-altitude Monte Curcio GAW station, Italy. Environ. Sci. Pollut. Res. 28, 60221–60234. https://doi.org/ 10.1007/s11356-021-15014-x.
- Moroni, B., Castellini, S., Crocchianti, S., Piazzalunga, A., Fermo, P., Scardazza, F., Cappelletti, D., 2015. Ground-based measurements of long-range transported aerosol at the rural regional background site of Monte Martano (Central Italy). Atmos. Res. 155, 26–36. https://doi.org/10.1016/j.atmosres.2014.11.021.
- Nicolás, J., Chiari, M., Crespo, J., Orellana, I.G., Lucarelli, F., Nava, S., Pastor, C., Yubero, E., 2008. Quantification of Saharan and local dust impact in an arid Mediterranean area by the positive matrix factorization (PMF) technique. Atmos. Environ. 42, 8872–8882. https://doi.org/10.1016/j.atmosenv.2008.09.018.
- O'Connor, F.M., Luke Abraham, N., Dalvi, M., Folberth, G.A., Griffiths, P.T., Hardacre, C., Johnson, B.T., Kahana, R., Keeble, J., Kim, B., Morgenstern, O., Mulcahy, J.P., Richardson, M., Robertson, E., Seo, J., Shim, S., Teixeira, J.C., Turnock, S.T., Williams, J., Wiltshire, A.J., Woodward, S., Zeng, G., 2021. Assessment of pre-industrial to present-day anthropogenic climate forcing in

C. Jaén et al.

UKESM1. Atmos. Chem. Phys. 21, 1211–1243. https://doi.org/10.5194/acp-21-1211-2021.

Ortiz-Amezcua, P., Martínez-Herrera, A., Manninen, A.J., Pentikäinen, P.P., O'connor, E. J., Guerrero-Rascado, J.L., Alados-Arboledas, L., 2022. Wind and turbulence statistics in the urban boundary layer over a mountain–valley system in Granada, Spain. Remote Sens. 14, 2321. https://doi.org/10.3390/rs14102321.

Pérez Pastor, R., Salvador, P., García Alonso, S., Alastuey, A., García Dos Santos, S., Querol, X., Artíñano, B., 2020. Characterization of organic aerosol at a rural site influenced by olive waste biomass burning. Chemosphere 248, 125896. https://doi. org/10.1016/j.chemosphere.2020.125896.

Pérez-Pastor, R., Salvador, P., García-Gómez, H., García-Alonso, S., Toro, M., Artíñano, B., Alonso, R., 2023. 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. Atmos. Environ. 298, 119634. https://doi.org/10.1016/j.atmosenv.2023.119634.

Pope, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: lines that connect. J. Air Waste Manag. Assoc. 56, 709–742. https://doi.org/10.1080/ 10473289.2006.10464485.

Prats, R.M., van Drooge, B.L., Fernández, P., Grimalt, J.O., 2022. Field comparison of passive polyurethane foam and active air sampling techniques for analysis of gasphase semi-volatile organic compounds at a remote high-mountain site. Sci. Total Environ. 803, 149738. https://doi.org/10.1016/j.scitotenv.2021.149738.

Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, 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. https://doi.org/10.1029/ 2006JD008114.

Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Ruiz, C.R., Cots, N., Massagué, G., Puig, O., 2001. PM₁₀ and PM_{2.5} source apportionment in the Barcelona Metropolitan area, Catalonia, Spain. Atmos. Environ. 35, 6407–6419. https://doi.org/10.1016/ \$1352-2310(01)00361-2.

Querol, X., Alastuey, A., de la Rosa, J., Sánchez-de-la-Campa, A., Plana, F., Ruiz, R.C., 2002. Source apportionment analysis of atmospheric particulates in an industrialised urban site in southwestern Spain. Atmos. Environ. 36, 3113–3125. https://doi.org/ 10.1016/S1352-2310(02)00257-1.

Querol, X., Alastuey, A., Viana, M.M., Rodriguez, S., Artiñano, B., Salvador, P., Garcia Do Santos, S., Fernandez Patier, R., Ruiz, C.R., De La Rosa, J., Sanchez De La Campa, A., Menendez, M., Gil, J.I., 2004. Speciation and origin of PM₁₀ and PM_{2.5} in Spain. J. Aerosol Sci. 35, 1151–1172. https://doi.org/10.1016/j.jaerosci.2004.04.002.

Querol, X., Alastuey, A., Moreno, T., Viana, M.M., Castillo, S., Pey, J., Rodríguez, S., Artiñano, B., Salvador, P., Sánchez, M., Garcia Dos Santos, S., Herce Garraleta, M.D., Fernandez-Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, E., Sanz, M.J., Palomo-Marín, R., Pinilla-Gil, E., Cuevas, E., de la Rosa, J., Sánchez de la Campa, A., 2008. Spatial and temporal variations in airborne particulate matter (PM₁₀ and PM_{2.5}) across Spain 1999–2005. Atmos. Environ. 42, 3964–3979. https:// doi.org/10.1016/j.atmosenv.2006.10.071.

Querol, X., Alastuey, A., Viana, M., Moreno, T., Reche, C., Minguillón, M.C., Ripoll, A., Pandolfi, M., Amato, F., Karanasiou, A., Pérez, N., Pey, J., Cusack, M., Vázquez, R., Plana, F., Dall'Osto, M., De La Rosa, J., Sánchez De La Campa, A., Fernández-Camacho, R., Rodríguez, S., Pio, C., Alados-Arboledas, L., Titos, G., Artíñano, B., Salvador, P., García Dos Santos, S., Fernández Patier, R., 2013. Variability of carbonaceous aerosols in remote, rural, urban and industrial environments in Spain: implications for air quality policy. Atmos. Chem. Phys. 13, 6185–6206. https://doi. org/10.5194/acp-13-6185-2013.

Rampanelli, G., Zardi, D., Rotunno, R., 2004. Mechanisms of up-valley winds. J. Atmos. Sci. 61, 3097–3111. https://doi.org/10.1175/JAS-3354.1.

Rejano, F., Titos, G., Casquero-Vera, J.A., Lyamani, H., Andrews, E., Sheridan, P., Cazorla, A., Castillo, S., Alados-Arboledas, L., Olmo, F.J., 2021. Activation properties of aerosol particles as cloud condensation nuclei at urban and high-altitude remote sites in southern Europe. Sci. Total Environ. 762, 143100. https://doi.org/10.1016/ j.scitotenv.2020.143100.

Ren, Y., Wang, G., Li, J., Wu, C., Cao, C., Wang, J., Zhang, L., Meng, F., Li, H., 2018. Seasonal variation and size distribution of biogenic secondary organic aerosols at urban and continental background sites of China. J. Environ. Sci. 71, 32–44. https:// doi.org/10.1016/j.jes.2017.11.016.

Ripoll, A., Pey, J., Minguillón, M.C., Pérez, N., Pandolfi, M., Querol, X., Alastuey, A., 2014. Three years of aerosol mass, black carbon and particle number concentrations at Montsec (southern Pyrenees, 1570 m a.s.l.). Atmos. Chem. Phys. 14, 4279–4295. https://doi.org/10.5194/acp-14-4279-2014.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass', G.R., Simonelt, B.R.T., 1993. Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. Environ. Sci. Technol. 27, 2700–2711. https://doi.org/10.1021/ es00049a008.

Rolph, G., Stein, A., Stunder, B., 2017. Real-time environmental applications and display system: READY. Environ. Model. Software 95, 210–228. https://doi.org/10.1016/j. envsoft.2017.06.025.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002. Measurement of emissions from air pollution sources. 5. C1-C32 organic compounds from gasolinepowered motor vehicles. Environ. Sci. Technol. 36, 1169–1180. https://doi.org/ 10.1021/es0108077.

Schauer, J.J., Lough, G.C., Shafer, M.M., Christensen, W.F., Arndt, M.F., DeMinter, J.T., Park, J.-S., 2006. Characterization of metals emitted from motor vehicles. In: Research Report (Health Effects Institute), vol. 133, pp. 1–76.

Simoneit, Bernd R.T., Crisp, P.T., Mazurek, M.A., Standley, L.J., 1991a. Composition of extractable organic matter of aerosols from the blue mountains and southeast coast of Australia. Environ. Int. 17, 405–419. https://doi.org/10.1016/0160-4120(91) 90274-T.

Simoneit, Bernd R.T., Sheng, G., Chen, X., Fu, J., Zhang, J., Xu, Y., 1991b. Molecular marker study of extractable organic matter in aerosols from urban areas of China. Atmos. Environ. A. Gen. Top. 25, 2111–2129. https://doi.org/10.1016/0960-1686 (91)90088-O.

Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015. NOAA's HYSPLIT atmospheric transport and dispersion modeling system. Bull. Am. Meteorol. Soc. 96, 2059–2077. https://doi.org/10.1175/BAMS-D-14-00110.1.

Tauler, R., 1995. Multivariate curve resolution applied to second order data. Chemom. Intel. Lab. Syst. 30, 133–146. https://doi.org/10.1016/0169-7439(95)00047-X.

Tauler, R., Viana, M., Querol, X., Alastuey, A., Flight, R.M., Wentzell, P.D., Hopke, P.K., 2009. Comparison of the results obtained by four receptor modelling methods in aerosol source apportionment studies. Atmos. Environ. 43, 3989–3997. https://doi. org/10.1016/j.atmosenv.2009.05.018.

Theodosi, C., Panagiotopoulos, C., Nouara, A., Zarmpas, P., Nicolaou, P., Violaki, K., Kanakidou, M., Sempéré, R., Mihalopoulos, N., 2018. Sugars in atmospheric aerosols over the Eastern Mediterranean. Prog. Oceanogr. 163, 70–81. https://doi.org/ 10.1016/j.pocean.2017.09.001.

Titos, G., Foyo-Moreno, I., Lyamani, H., Querol, X., Alastuey, A., Alados-Arboledas, L., 2012. Optical properties and chemical composition of aerosol particles at an urban location: an estimation of the aerosol mass scattering and absorption efficiencies. J. Geophys. Res. Atmos. 117, 1–12. https://doi.org/10.1029/2011JD016671.

Titos, G., Lyamani, H., Pandolfi, M., Alastuey, A., Alados-Arboledas, L., 2014. Identification of fine (PM₁) and coarse (PM₁₀₋₁) sources of particulate matter in an urban environment. Atmos. Environ. 89, 593–602. https://doi.org/10.1016/j. atmosenv.2014.03.001.

Titos, G., del Águila, A., Cazorla, A., Lyamani, H., Casquero-Vera, J.A., Colombi, C., Cuccia, E., Gianelle, V., Močnik, G., Alastuey, A., Olmo, F.J., Alados-Arboledas, L., 2017. Spatial and temporal variability of carbonaceous aerosols: assessing the impact of biomass burning in the urban environment. Sci. Total Environ. 578, 613–625. https://doi.org/10.1016/j.scitotenv.2016.11.007.

Tositti, L., Riccio, A., Sandrini, S., Brattich, E., Baldacci, D., Parmeggiani, S., Cristofanelli, P., Bonasoni, P., 2013. Short-term climatology of PM₁₀ at a high altitude background station in southern Europe. Atmos. Environ. 65, 142–152. https://doi.org/10.1016/j.atmosenv.2012.10.051.

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. https://doi.org/10.5194/acp-15-7735-2015.

van Drooge, B.L., Crusack, M., Reche, C., Mohr, C., Alastuey, A., Querol, X., Prevot, A., Day, D.A., Jimenez, J.L., Grimalt, J.O., 2012. Molecular marker characterization of the organic composition of submicron aerosols from Mediterranean urban and rural environments under contrasting meteorological conditions. Atmos. Environ. 61, 482–489. https://doi.org/10.1016/j.atmosenv.2012.07.039.

van Drooge, B.L., Fontal, M., Bravo, N., Fernández, P., Fernández, M.A., Muñoz-Arnanz, J., Jiménez, B., Grimalt, J.O., 2014. Seasonal and spatial variation of organic tracers for biomass burning in PM1 aerosols from highly insolated urban areas. Environ. Sci. Pollut. Res. 21, 11661–11670. https://doi.org/10.1007/s11356-014-2545-0.

van Drooge, B.L., Fontal, M., Fernández, P., Fernández, M.A., Muñoz-Arnanz, J., Jiménez, B., Grimalt, J.O., 2018. Organic molecular tracers in atmospheric PM₁ at urban intensive traffic and background sites in two high-insolation European cities. Atmos. Environ. 188, 71–81. https://doi.org/10.1016/j.atmosenv.2018.06.024.

van Drooge, B.L., Garatachea, R., Reche, C., Titos, G., Alastuey, A., Lyamani, H., Alados-Arboledas, L., Querol, X., Grimalt, J.O., 2022. Primary and secondary organic winter aerosols in Mediterranean cities under different mixing layer conditions (Barcelona and Granada). Environ. Sci. Pollut. Res. 29, 36255–36272. https://doi.org/10.1007/ s11356-021-16366-0.

van Drooge, B.L., Prats, R.M., Jaén, C., Grimalt, J.O., 2023. Determination of subpicogram levels of airborne polycyclic aromatic hydrocarbons for personal exposure monitoring assessment. Environ. Monit. Assess. 195, 1–13. https://doi.org/ 10.1007/s10661-023-10953-z.

Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A.S.H., Hueglin, C., Bloemen, H., Wåhlin, P., Vecchi, R., Miranda, A.I., Kasper-Giebl, A., Maenhaut, W., Hitzenberger, R., 2008. Source apportionment of particulate matter in Europe: a review of methods and results. J. Aerosol Sci. 39, 827–849. https://doi.org/ 10.1016/j.jaerosci.2008.05.007.

Villasclaras, P., Jaén, C., van Drooge, B.L., Grimalt, J.O., Tauler, R., Bedia, C., 2022. Phenotypic and metabolomic characterization of 3D lung cell cultures exposed to airborne particulate matter from three air quality network stations in Catalonia. Toxics 10, 632. https://doi.org/10.3390/toxics10110632.

Wagner, J.S., Gohm, A., Rotach, M.W., 2015. The impact of valley geometry on daytime thermally driven flows and vertical transport processes. Q. J. Roy. Meteorol. Soc. 141, 1780–1794. https://doi.org/10.1002/qj.2481.

Wåhlin, P., Berkowicz, R., Palmgren, F., 2006. Characterisation of traffic-generated particulate matter in Copenhagen. Atmos. Environ. 40, 2151–2159. https://doi.org/ 10.1016/j.atmosenv.2005.11.049.

Wang, G., Kawamura, K., Umemoto, N., Xie, M., Hu, S., Wang, Z., 2009. Water-soluble organic compounds in PM_{2.5} and size-segregated aerosols over Mount Tai in North China Plain. J. Geophys. Res. 114, 2–11. https://doi.org/10.1029/2008jd011390.

C. Jaén et al.

- World Health Organization, 2021. WHO global air quality guidelines. In: Particulate Matter (PM_{2.5} and PM₁₀), Ozone, Nitrogen Dioxide, Sulfur Dioxide and Carbon Monoxide (Geneva. Licence: CC BY-NC-SA 3.0 IGO).
- Yuan, Y., Wu, Y., Ge, X., Nie, D., Wang, M., Zhou, H., Chen, M., 2019. In vitro toxicity evaluation of heavy metals in urban air particulate matter on human lung epithelial cells. Sci. Total Environ. 678, 301–308. https://doi.org/10.1016/j. scitotenv.2019.04.431.
- Zhu, Y., Yang, L., Chen, J., Kawamura, K., Sato, M., Tilgner, A., Van Pinxteren, D., Chen, Y., Xue, L., Wang, X., Simpson, I.J., Herrmann, H., Blake, D.R., Wang, W., 2018. Molecular distributions of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in PM_{2.5} collected at the top of Mt. Tai, North China, during the wheat burning season of 2014. Atmos. Chem. Phys. 18, 10741–10758. https://doi.org/ 10.5194/acp-18-10741-2018.