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Chemical composition of rainwater under two events of aerosol transport: A Saharan dust outbreak and wildfires

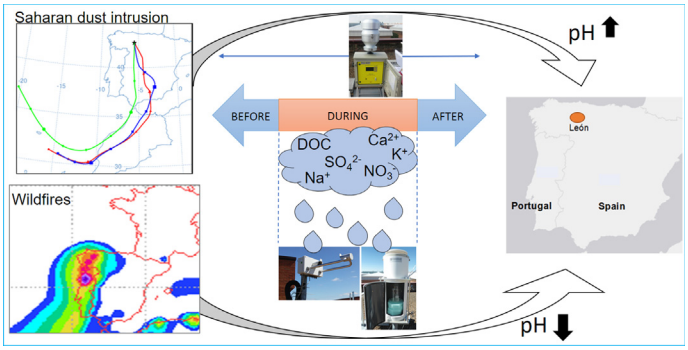
F. Oduber [a], A.I. Calvo [a], A. Castro [a], C. Blanco-Alegre [a], C. Alves [b], J. Barata [b], T. Nunes [b], F. Lucarelli [c], S. Nava [c], G. Calzolai [c], M. Cerqueira [b], J. Martín-Villacorta [a], V. Esteves [b], R. Fraile [a,*]

[a] Department of Physics, IMARENAB, University of León, León, Spain
[b] Department of Environmental and Planning, CESAM, University of Aveiro, Aveiro, Portugal
[c] Department of Physics and Astronomy, University of Florence and INFN-Florence, Florence, Italy

HIGHLIGHTS

- Rainwater composition is affected by both local and long-range transport aerosols.
- The emissions of organic species by biomass burning act by acidifying the water
- The entry of crustal elements into the atmosphere helps neutralize rainwater.
- The amount and intensity of precipitation influence the composition of rainwater.
- The rainwater composition is also linked to the physical properties of raindrops.

GRAPHICAL ABSTRACT



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ABSTRACT

A one-year campaign of joint sampling of aerosols and precipitation, carried out in León, Spain, allowed to study the impact of two special events that affected the air quality in the north of the country, on rainfall in the city: a period with wildfires and a Saharan dust intrusion. The wildfires that occurred in northern Portugal and northwestern Spain in August 2016 affected the chemistry of rainfall on 15 August 2016, causing an increase in concentrations of NH_4^+, Na^+, Cl^-, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} and NO_3^- and in the concentrations of organic acids, which was reflected in the levels of soluble and insoluble organic carbon. This led to acidification of rainwater (pH = 4.8). The second precipitation event was registered between 11 and 14 February 2017, during which the rainwater was collected in four daily fractions (P_1, P_2, P_3 and P_4). The rain sample of 12 February (P_2) coincided with a Saharan dust intrusion that reached northern Iberia that day. The chemical composition of P_2 showed an increase in the Ca^{2+} (>800%), Mg^{2+} (71%), Cl^- (62%), and SO_4^{2-} (33%) concentrations, with respect to P_1. The input of crustal elements to the atmosphere helped to neutralize the P_2 rainwater, causing pH values higher than 6.5. Once the dust intrusion left the north of the Peninsula, the composition of rainwater P_3 and P_4 revealed a mixture of marine contribution with local anthropogenic emissions, as well as a decrease in ion concentrations and conductivity, and an increase in pH values.

* Corresponding author.
E-mail address: roberto.fraile@unileon.es (R. Fraile).

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1. Introduction

Rainwater plays an important role by removing aerosols and gases from the atmosphere (scavenging), and acts through two mechanisms: in-cloud scavenging (ICS) or rainout and below-cloud scavenging (BCS) or washout (Keresztesi et al., 2017; Seinfeld and Pandis, 2016). The first one requires the presence of aerosols playing the role of cloud condensation nuclei (CCN) inside the cloud droplets, while the second one consists in the washing out of aerosols by falling raindrops (Kajino and Aikawa, 2015). The pollutants of local anthropogenic origin are removed mainly in the initial fractions of rain, dominated by the washout process. Subsequent fractions have mainly a chemical composition attributed to transport events from different regions, characterized by rainout processes (Celle-Jeanton et al., 2009). Therefore, the chemical composition of rainwater can provide information on the local sources of pollutant emissions, as well as on the impact of long-range transport emissions (such as those from Saharan dust intrusions and biomass burning events) on the air quality of a specific location (Alastuey et al., 1999; Knote et al., 2015; Kopáček et al., 2016).

The BCS process of different chemical species is affected by the intensity and volume of rainfall (Custódio et al., 2014; Luan et al., 2019; Pan and Wang, 2015). Furthermore, the physical parameters of precipitation (raindrop size distribution and volume swept by raindrops) are also important factors influencing the scavenging process and can also determine the chemical composition of the rainwater (Blanco-Alegre et al., 2018, 2019; Fredericks and Saylor, 2019). Why is the raindrop size important? In an ideal model, as a raindrop is falling, it can collide with all the particles contained in the swept volume constituted by a cylinder of radius equal to the raindrop radius and length equal to the distance travelled by the raindrop.

Biomass burning releases a large amount of gases and particles into the atmosphere. Vicente et al. (2013) reported that during wildfires, CO and CO_2 are largely emitted, while the aerosol from this source contains organic carbon (OC), Na^+, NH_4^+, Cl^- and NO_3^- in the fine fraction and K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} in the coarse fraction. Specifically, a large number of organic constituents such as phenolic compounds and their alteration products, acids, carbohydrates, levoglucosan and diterpenoids, were detected in aerosols from wildfires (Alves et al., 2011a; Vicente et al., 2011, 2012). When wildfires coincide with a rainfall event, their emissions can affect the chemistry of rainwater causing an increase in the concentration of organic acidic (e.g., $HCOO^-$, CH_3COO^-) and inorganic ions (SO_4^{2-}, Cl^-, NO_3^-, NH_4^+) (Bisht et al., 2015; Mimura et al., 2016; Sun et al., 2016). Besides, the incorporation into the drops of gaseous pollutants, such as SO_x, NO_x and organic acids, causes an acidifying effect on rainwater (Balasubramanian et al., 1999), which has detrimental effects on the aquatic and terrestrial ecosystems and an indirect negative effect on human health (Cathcart et al., 2016; Duan et al., 2016; Livingston, 2016; Rosborg and Nihlgård, 2018). Moreover, phenomena such as Saharan dust intrusions transport large amounts of mineral dust particles, characterized by high concentrations of Al, Ca, Ti, Si, Fe, SO_4^{2-}, NO_3^- and Cl^-, as well as high loads of biological material (pollen, spores and fungi), which entails an increase in the organic carbon concentration of aerosols (Oduber et al., 2019). Several authors have studied the impact of Saharan dust outbreaks on the chemical composition of rainwater, showing that dust intrusions can rise the concentration of Na^+, Ca^{2+}, K^+, Mg^{2+} and SO_4^{2-}, and cause an alkalization of rainwater due to the $CaCO_3$ content in airborne dust (Anil et al., 2017; Escudero et al., 2005; Morales-Baquero et al., 2013).

Every year, due to the high temperatures and low rainfall registered in summer, a considerable area of the north and west of the Iberian Peninsula is often affected by wildfires that can last several days (Alonso-Blanco et al., 2012; Alves et al., 2011a; Vicente et al., 2012, 2013). Fernández-Raga et al. (2017) reported that in León (NW, Spain), in summer, mainly short-duration storms occur. In these latitudes, convective phenomena in this season generally cause short and intense rainfall events, most of them lasting only 5 min. Furthermore, the Iberian Peninsula is often affected by Saharan dust intrusions, due to the proximity to the emitting sources (Alastuey et al., 2016; Escudero et al., 2007; Querol et al., 2014). However, African dust outbreaks do not usually reach the north of Spain, much less during winter, and when this happens, the episodes tend to last <4 days (Oduber et al., 2019; Querol et al., 2004). Escudero et al. (2005) reported that, in eastern Iberia, on average, during 3% of the days of the year, wet deposition occurs simultaneously with an African dust outbreak, being February one of the months with less mean number of days with this type of episodes (mean of 0.4 days) and May the month with more (mean of 2.9 days).

The combination of the study of the characteristics of the aerosol and the precipitation can constitute a key tool in the understanding of the scavenging processes. To our knowledge, there are very few studies that try to combine both aspects. Therefore, we set out to study the organic and inorganic compounds present in rainwater and atmospheric aerosol before, during and after rainfall. Thus, the main aim of this work is to study the impact on rainwater chemical composition, collected in León, Spain, during AERORAIN project, of the two most outstanding events recorded with specific characteristics linked to the sources of the pollutants: i) an episode of massive wildfires that occurred in the western Iberian Peninsula in August 2016; and ii) a Saharan dust intrusion that reached northern Spain in February 2017.

2. Methodology

2.1. Sampling site

The sampling campaign was carried out in León city, Spain, at NW of the Iberian Peninsula (42° 36′ N, 05° 35′ W and 838 m a.s.l.) (Fig. 1). In León, the climate is continental type with influence of the Mediterranean climate. Winters are cold and long, with average temperature of 5 °C and a mean accumulate precipitation of 150 mm, while summers are warm with an average temperature of 20 °C and mean accumulate precipitations of 73 mm (Castro et al., 2010). During summer, droughts are very common, although there are sporadic storms, often with hail (Fernández-Raga et al., 2017). The sampling site is located in a suburban area at NE of the city center of León, characterized by the absence of large emitting industries and a certain contribution from biomass burning and fossil fuels sources, due to the high traffic flow in the vicinity and the use of domestic heating devices in nearby towns during the colder months (Blanco-Alegre et al., 2019; Oduber et al., 2018).

2.2. Study events

This study focuses on two specific rain events, which occurred in León and that were influenced by the arrival of atmospheric pollutants from two different sources: i) wildfires that took place between 14 and 15 August 2016, in northern Portugal (about 250 km from León) and in northwest Spain (approximately 100 to 200 km far from León) and ii) a Saharan dust intrusion, coming from a distance of approximately between 1200 and 2000 km (Fig. 1), which reached León between 12 and 13 February 2017. These two rain episodes represent the extremes on pH values recorded during the one-year sampling campaign. The rainwater fractions collected and the sampling days for both events are detailed in Table 1.

2.3. PM_{10} and rainwater sampling

The samples used in this study belong to the one-year sampling campaign (between May 2016 and May 2017), part of the AERORAIN research project, in which samples of aerosols and rainwater were collected every 24 h, starting at 1200 UTC every day.

For the PM_{10} sampling, a low volume sampler (TECORA, ECHOPM), equipped with 47 mm diameter Teflon filters and a high-volume sampler (CAV-Mb), equipped with 150 mm diameter quartz filters, were

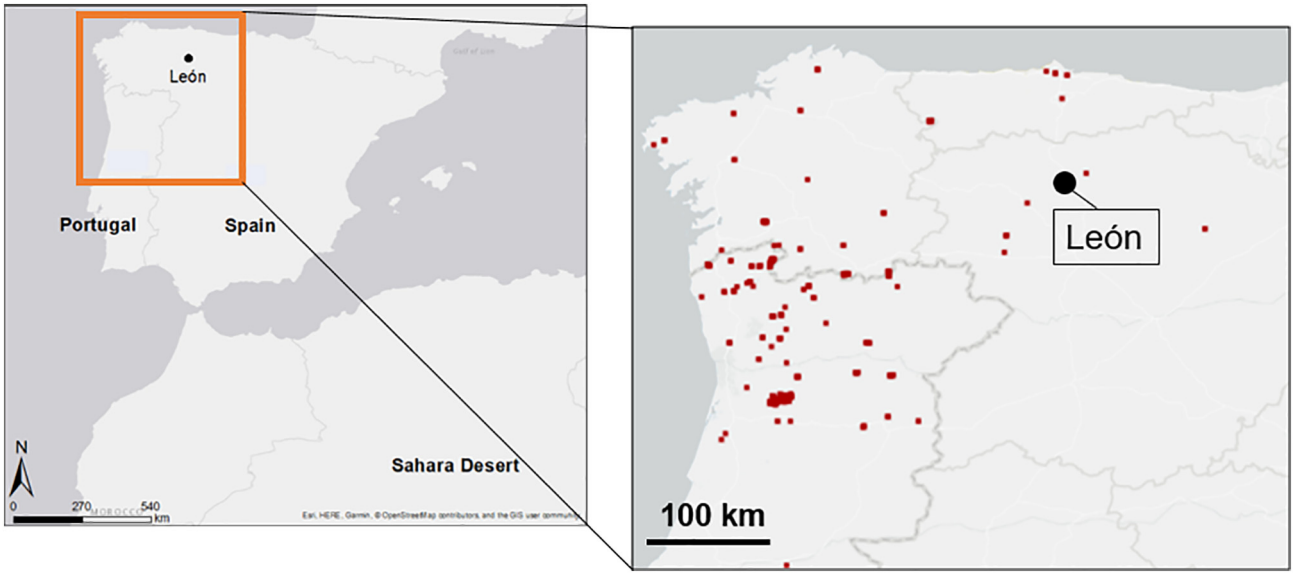

Fig. 1. Map of the Iberian Peninsula and location of León and Sahara Desert (left). Active wildfires between 14 and 15 August 2016 (right), in the NW of the peninsula, indicated by red points (map and data from NASA Fire Information for Resource Management System, FIRMS).

used. PM_{10} mass was determined by gravimetry, using an electronic semi-microbalance (Mettler Toledo, XPE105DR).

The rainwater was collected in glass bottles using a wet-only precipitation sampler (Eigenbrodt UNS 130/E). The conductivity and pH of the rain samples were determined immediately after being collected with a pH and conductivity meter (Hach, HQ 40d multi). The rain samples were filtered through a 15 mm diameter quartz filters in order to separate the insoluble and soluble matter.

All quartz fiber filters used in this work were pre-baked at 600 °C for 6 h in order to remove interfering carbonaceous material. Furthermore, some tests were carried out by filtering milli-Q water through blank filters in order to know the concentrations of ions that could be released by these filters. This background was subtracted from the concentrations registered in the filters used to filter rainwater.

2.4. PM_{10} and rain samples analysis

Quartz filters of both aerosols and water insoluble fraction of rain samples were used for the determination of organic and elemental carbon (OC and EC, respectively), by a thermal-optical system developed by the University of Aveiro (Portugal) and following the procedure described by Alves et al. (2015) and Pio et al. (2011). Besides, PM_{10} quartz filters were used for the determination of levoglucosan and other sugars, taking a portion equal to 1/10 of the total filter area and extracting the soluble compounds with 3 mL of ultra-pure Milli-Q water by ultrasonic agitation, followed by filtration with a 0.2 μm pore size PTFE syringe filter into glass vials. The analysis was carried out in a Thermo Scientific Dionex™ ICS-5000 ion Chromatograph, equipped with a CarboPac® PA-1 (2 × 250 mm) column, and a mobile phase of diluted sodium hydroxide (NaOH), using the methodology based on Caseiro et al. (2007) and Piazzalunga et al. (2010), with a multi-step gradient condition.

Teflon filters were cut into two equal portions. One of them was used for the determination of the major trace elements by PIXE (Particle-Induced X-ray Emission), following the methodology described by Lucarelli et al. (2015). The second portion was extracted with 6 mL ultra-pure Milli-Q water in ultrasonic agitation, and filtered with a 0.2 μm pore size PTFE syringe filter into glass vials for the analysis of inorganic water soluble ions: Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, F^-, SO_4^{2-} and NO_3^-. The determination of water soluble ions of both aerosols and rain samples was carried out in a Thermo Scientific Dionex™ ICS-5000 ion Chromatograph, equipped with an IonPac® CS16 (4 × 250 mm) column, with a solution of 30 mM of methanesulfonic (MSA) as eluent for cations, and an IonPac® AS11 (4 × 250 mm) column, with a solution of 30 mM of potassium hydroxide (KOH) as eluent for analysis of anions. The Dissolved Organic Carbon (DOC) content was determined by combustion and infrared detection in a Shimadzu Total Organic Carbon Analyzer (TOC-V CPH).

The following analytical checks were carried out: i) a duplicate analysis every 10 samples, ii) the extraction and analysis of blank filters, iii) the detection and quantification limits were determined from the blank filters, iv) every 10 or 15 samples a known standard was analyzed to check the quantification.

Furthermore, quality control for the entire database was verified for each rainfall sample by calculating the ion balance. The difference between the sum of cations and the sum of anions (including alkalinity) can be taken as the sum of organic acids. In the wildfires rain event, the difference between the sum of cations and the sum of anions was equal to 120 μeq L^{-1}. In the Saharan dust intrusion, this difference was 15 μeq L^{-1} for P1, 66.4 for P2, 1.6 for P3 and 4.8 for P4.

Table 1
Rainwater fractions, dates and total volume sampled of each fraction.

Rainwater fraction	Event	Rainwater sampling date	Volume sampled (mL)
F_1	Wildfires	15 August 2016	27.3
P_1		11 February 2017	31.7
P_2	Saharan dust	12 February 2017	66.0
P_3	intrusion	13 February 2017	1456.7
P_4		14 February 2017	54.6

2.5. Circulation Weather Types and meteorological parameters

A classification of Circulation Weather Types (CWTs) was carried out based on Lamb (1972). The direction and vorticity of the geostrophic flow, obtained for 16 grid points distributed over and around the Iberian Peninsula (Trigo and DaCamara, 2000), allowed to establish 26 different CWTs: eight known as "pure" weather types (N, S, E, W, NW, SW, SE and NE), two so-called "non-directional" (anticyclonic (A) and cyclonic (C)), and sixteen weather types so-called as "hybrid" types, as a result of the

combination between "non-directional" and "pure" types (AN, ANE, ANW, AS, ASE, ASW, AE, AW and CN, CNE, CNW, CS, CSE, CSW, CE, CW).

Weather data in the sampling area was obtained with a weather station, which provided information on temperature, wind and relative humidity. Precipitation was measured with a laser disdrometer (Laser Precipitation Monitor, LPM) on a 1-minute basis. Furthermore, the origin of air masses was interpreted by the determination of 48-hour back trajectories (at 500, 1500 and 3000 magl) using the HYSPLIT model (Draxler and Rolph, 2012; Rolphetal.,2017; Steinetal.,2015).

2.6. Calculations

In order to characterize the rain samples and events, volume-weighted mean precipitation concentrations (VWM), neutralization factors (NF) and source contributions were determined.

VWM (in μeq L^{-1} and mg L^{-1}) of species in rainwater was calculated as follows:

$$VWM = \sum_{i=1}^{N} C_i P_i / \sum_{i=1}^{N} P_i \quad (1)$$

where, *Ci* is the concentration of each species in μeq L^{-1} (ions) and in mg L^{-1} (for carbonaceous fraction), *Pi* the precipitation amount for each precipitation event in mm, and *N* the total number of precipitation events in each study period.

NF have been calculated following Eq. (2) (Kulshrestha et al., 1995), where C_x is the concentration of the cation of interest, $C_{SO4^{2-}}$ and C_{NO3^-} are the concentrations of sulfate and nitrate, respectively, all in μeq L^{-1}.

$$NF_x = \frac{C_x}{\left[C_{SO_4^{2-}} + C_{NO_3^-}\right]} \quad (2)$$

Source contributions were calculated taking into account the enrichment factors (EF) values, which were calculated for both the seawater and crustal material, according to Eqs. (3) and (4) (Kulshrestha et al., 1996; Zhang et al., 2007), where $\left(\frac{C_x}{C_{r\,sample}}\right)$ is the ratio between the concentration of an element *X* and that of a reference element (*r*) in the sample. $\left(\frac{C_x}{C_{r\,crustal}}\right)$ and $\left(\frac{C_x}{C_{r\,seawater}}\right)$ are the ratios between the same elements considering the reference concentrations in the crustal material or seawater, respectively (Keene et al., 1986; Zhang et al., 2007). In this study, sodium was used as seawater reference element and calcium as crustal reference. The Mg^{2+}/Na^+ ratio was evaluated in order to determine the best tracer for seawater. According to Jordan et al. (2003) a ratio >0.227 suggests a marine origin of Na^+. In this study, the Mg^{2+}/Na^+ ratio was >0.7 for both studied events and, according to this result, sodium was used as the reference element for seawater. Regarding the crustal tracer, there is no specific rule for the choice of a crustal reference element, except that it must not be affected by anthropogenic factors. Ca^{2+} is widely used as a reference for continental emissions or terrestrial crust (Calvo et al., 2012; Khan et al., 2018; Martins et al., 2019; Zhang et al., 2007), as its composition in the soil is hardly changed. The abundance of Ca^{2+} in the Earth's crust was taken from Taylor (1964) and Zhang et al. (2007).

$$EF_{crustal} = \frac{\left(\frac{C_x}{C_{r\,sample}}\right)}{\left(\frac{C_x}{C_{r\,crustal}}\right)} \quad (3)$$

$$EF_{seawater} = \frac{\left(\frac{C_x}{C_{r\,sample}}\right)}{\left(\frac{C_x}{C_{r\,seawater}}\right)} \quad (4)$$

The source contribution of seawater and crustal fractions was obtained according to Eqs. (5) and (6), respectively (Zhang et al., 2007):

$$Seawater\ fraction\% = 100\frac{\left(\frac{C_x}{C_{Na^+}}\right)_{seawater}}{\left(\frac{C_x}{C_{Na^+}}\right)_{sample}} \quad (5)$$

$$Crustal\ fraction\% = 100\frac{\left(\frac{C_x}{C_{Ca^{2+}}}\right)_{crustal}}{\left(\frac{C_x}{C_{Ca^{2+}}}\right)_{sample}} \quad (6)$$

Assuming that seawater and crustal are the main natural sources, the anthropogenic fraction is defined as:

$$Anthropogenic\ fraction\% = 100 - (crustal + seawater) \quad (7)$$

3. Results and discussions

3.1. Biomass burning event

3.1.1. Meteorological conditions

Summer of 2016 was characterized as a very hot and dry season in the Iberian Peninsula. In León, the mean daily temperature for this season was 20 ± 4 °C, reaching on 8 August a maximum of 35 °C and a minimum relative humidity of 32%. The accumulated precipitation registered during summer was 21.54 mm, with a maximum on August with 11.48 mm. The Ministry of Agriculture, Food and the Environment (MAPAMA, in Spanish acronym) reported that August was a month with average temperatures throughout the Spanish territory of 1.3 °C above the typical mean value and 75% less precipitation than the average normal value for this period. These meteorological conditions favored the occurrence of forest fires in the Iberian Peninsula, especially in northern Portugal and northwest Spain. According to the MAPAMA Annual Report (2016), 3 biomass burning episodes may have affected the particle levels in northern Spain in August 2016: i) between days 13 and 17, ii) on day 19, and iii) between days 26 and 27. In addition, the Institute of Conservation of Nature and Forest of the Government of Portugal reported that in August 2016, a total of 116,885 ha had been burned throughout the territory of Portugal.

On 14 August 2016, the NAAP images show high smoke concentrations at the north of the Peninsula caused by wildfires, while the HYSPLIT model evidenced the influx of air masses at 500, 1500 and 3000 m, from the west of the Peninsula, confirming the arrival of smoke plumes in León (Fig. 2). The weather types associated with the days 14, 15 and 16 August were NE, N and NW, respectively.

3.1.2. Aerosol chemical composition

The contribution from biomass burning emissions to the aerosol burden in León was also confirmed by the increase in the aerosol concentration. Thus, PM_{10} daily concentration increased from 19 μg m^{-3} on 13 August to 26 μg m^{-3} on 14 August, while the main biomass burning tracers, K and levoglucosan (Vicente and Alves, 2018), showed an increase of 25 and 71%, respectively, and the carbonaceous fraction (EC + OC) showed an increase of 42% (Table 2).

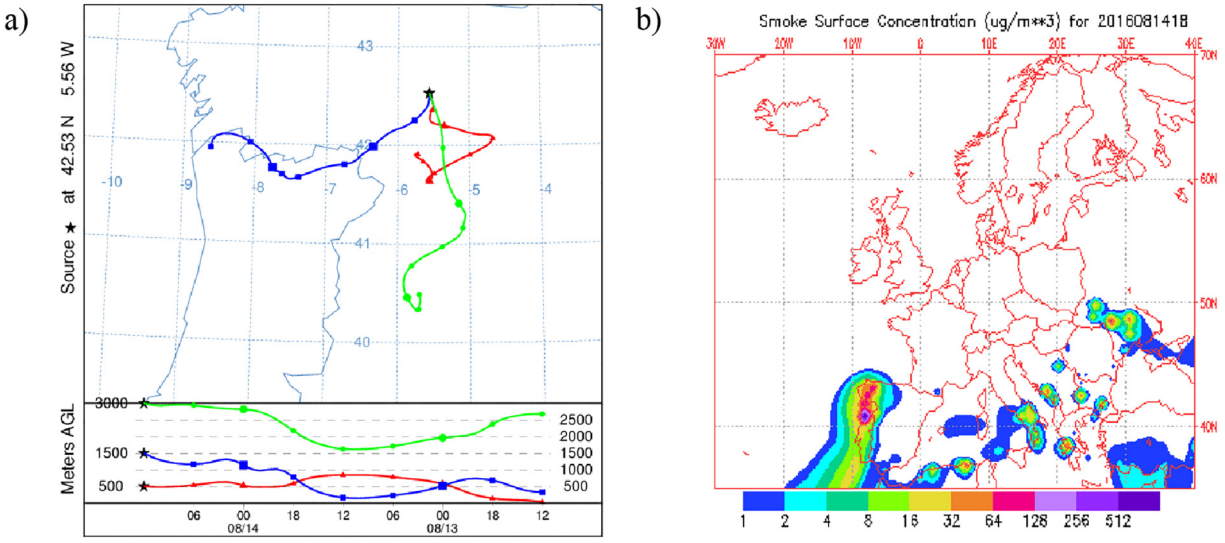

Fig. 2. a) HYSPLIT back trajectories at 500, 1500 and 3000 m agl and b) NAAPs images of smoke concentration on 14 August 2016.

3.1.3. Chemical composition of rainwater samples

Although the rainfall was scarce in the summer of 2016, between 14 and 15 August, a rain event took place coinciding with the wildfires described above. The rain event began on 14 August at approximately 2300 UTC, and ended on 15 August at approximately 0400 UTC, recording an accumulated precipitation of 3.72 mm and a mean intensity of 1.28 mm h^{-1}. On 15 August between 0400 UTC and 0500 UTC, a total of 3.09 mm of rainfall were recorded (Fig. 3), with an intensity of 4.4 mm h^{-1}. Castro et al. (2010) reported that precipitation intensities above 3.2 mm h^{-1} produce effective washout of fine and coarse particles. Besides, Kulshrestha et al. (2009) showed that short period rains of high intensity effectively remove relatively coarse mode particles possibly by below-cloud scavenging process. Moreover, Alastuey et al. (2001) reported an exponential decreasing behavior throughout the precipitation event for most ions and that between 40 and 80% of the wet-only deposition of major ions takes place during the first 2 mm.

The volume swept by raindrops during this period was mainly due to drops with sizes >2 mm, while for the lower precipitation intensity (about 0.3 mm h^{-1}) it was due to drop sizes <2 mm. Blanco-Alegre et al. (2018, 2019) showed that higher volume swept by drops caused a more effective scavenging on particles between 0.12 and 0.19 μm, and there was a significant correlation between the scavenging efficiency of black carbon particles and the number of drops with diameters between 0.375 and 2.5 nm. Therefore, this precipitation event could have been responsible for removing pollutants from the atmosphere through the washout process.

The chemical composition of rainwater showed high NH_4^+, Ca^{2+}, SO_4^{2-} and NO_3^- concentrations (153.15 μeq L^{-1}, 128.54 μeq L^{-1}, 65.19 μeq L^{-1} and 121.17 μeq L^{-1}, respectively), compared to those obtained in rain samples collected on days 8, 10, 12, 28, 29 and 30 May 2016 (Fig. 4), when, according to MAPAMA and the NAAP images (not shown here), there was no influence from forest fire emissions.

Table 2
PM_{10}, potassium, levoglucosan, elemental and organic carbon concentrations in air (in μg m^{-3}) on day 14 August and the mean values in days without biomass burning events (days between 01 and 30 May 2016).

	14 August 2016	Days without biomass burning
PM_{10}	26	20 ± 4
EC	0.7	0.4 ± 0.2
OC	3.4	1.9 ± 0.6
K	0.20	0.10 ± 0.04
Levoglucosan	0.005	0.001 ± 0.002

The high concentrations of SO_4^{2-}, NO_3^- and NH_4^+ are probably the result of nucleation of the components transported by the air masses impacted by the biomass burning. Vicente et al. (2013) reported the presence of these ions in aerosol samples collected in the smoke plumes from wildfires that occurred in Portugal. The high content of these ions in rainwater could be due to the below-cloud scavenging of aerosols and in-cloud processes (Balasubramanian et al., 1999). Cachier and Ducret (1991), who studied the impact of biomass burning emissions on rainwater collected at remote site in the Northern Congo, showed that the biomass-burning particles may act as CCN, playing an important role in cloud formation. Furthermore, Pio et al. (2008) found a correlation between diacids with K^+ and SO_4^{2-} concentrations in aerosol samples from Aveiro, Portugal, during 2003 summer intense forest fire period, showing the in-cloud secondary formation of dicarboxylic species and SO_4^{2-} from CCN derived from biomass burning.

As expected, a high conductivity value was obtained (164.9 μS cm^{-1}) due to the high concentrations of ions, while the VWM conductivity was 31.2 ± 0.1 μS cm^{-1} in the rain samples of May 2016.

The inorganic ions of the rain samples of May 2016 have source contributions similar to those obtained for F1. Thus, anthropogenic sources accounted for 92% (F1) and 96% (samples of May 2016) of sulfate, and for 100% and 99.86% of nitrate of the same rain samples. Ca^{2+}, Mg^{2+} and K^+ mainly originated form crustal sources (crustal fraction higher than 65%), while seawater represented 98–100% of the Cl^- concentrations (Table 3). High values of sulfate and nitrate in the atmosphere are usually related to secondary photochemical reactions that are more frequent in summer. Also, during the combustion of biomass, the SO_4^{2-} values can be related to the adsorption of SO_2 on black carbon particles through a catalytic effect, which promotes a very fast gas-to-particle conversion of SO_2 to sulfate (Alves et al., 2011b). K^+, Ca^{2+} and Mg^{2+} from crustal sources may arise from resuspension processes in the proximities of the sampling location.

With regard to the carbonaceous fraction of the rainwater sample F1, DOC and WIOC values were 14.7 and 1.7 mg L^{-1}, respectively, while in days without biomass burning the VWM for DOC and WIOC were 1.2 ± 2.6 and 0.274 ± 0.01 mg L^{-1}, respectively. The carbonaceous content in rainwater is related to the emission of many organic compounds during the biomass burning process and with the amount of rainfall during the event. Cerqueira et al. (2010) reported DOC values between 0.2 and 1.5 mg L^{-1} in European background sites not influenced by biomass burning events, while Godoy-Silva et al. (2017) documented values between 0.2 and 60 mg L^{-1} in a tropical agro-industrial region of São Paulo, which is frequently affected by biomass burning events. Moreover, Pan et al. (2010) described a negative correlation between DOC

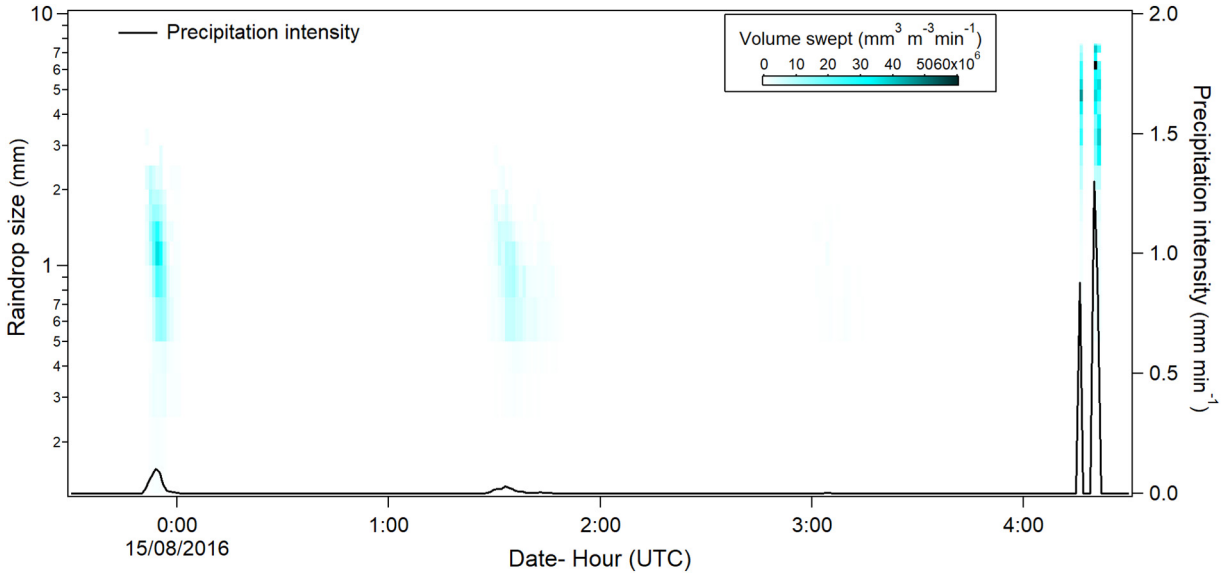

Fig. 3. Evolution of precipitation intensity (black line) and volume swept by the raindrops of each size interval (colour scale), between 14 and 15 August 2016.

concentrations and the amount of precipitation in a study carried out in northern China during the summer, when coal emissions from domestic use are insignificant, indicating that the OC tend to be effectively washed out (below-cloud scavenging) during the initial period of precipitation.

3.1.4. Acidic contribution

Previous studies have established that precipitation in a clean atmosphere has a weakly acidic pH, with a reference value ranging from 5.0 to 5.6, so that rainwater samples with pH values lower than 5.0 are considered acid rain (Charlson and Rodhe, 1982). In the present study, the rain sample F1 had an acidic pH of 4.8, whereas the rain samples of May 2016 showed a VWM pH of 6.7 ± 1, showing that wildfire emissions had an acidification effect on the precipitation of 15 August 2016. Taking into account the main inorganic soluble ions, an excess of cations was observed in relation to anions. The unbalanced ratio ($\sum$cations/$\sum$anions = 1.6) is enhanced when H^+ is added. This acidity can be explained by the contribution of organic species released during fire events. In F1, the highest neutralization factor was obtained by NH_4^+ (0.8), followed by Ca^{2+} (0.7), indicating that calcium and ammonium could prevent the acidification of the rainwater. The cation/anion unbalance suggests that the acidic pH is likely due to the contribution of acidic organic species, which is in accordance with the high DOC value. Balasubramanian et al. (1999) observed high concentrations of organic acids and HCl in rainwater collected during the dry season in Indonesia, mainly due to the incorporation of gases and particles from biomass burning emissions, causing acidic pH values. Alves et al. (2011a, 2011b) reported that dicarboxylic acids and related compounds, such as the glycolic, lactic, hydroxybutyric and levulinic acids, were the most abundant compounds in smoke particles from the plume of a wildfire that took place in Portugal. These results reflect the importance of the contribution from organic acid compounds to the pH of the rainwater.

3.2. African dust intrusion event

3.2.1. Meteorological conditions

The daily average temperature recorded in the sampling site in February 2017 was 6 ± 4 °C, and the average relative humidity was 71 ± 7%. However, during the second week of the month, there was a change in weather conditions and maximum temperatures increased to 9 °C (11 February) and 13 °C (15 February). The annual report of 2016, issued by MAPAMA, on the events that could have affected the air quality in Spain, documented that on 12 February 2017, northern Spain was affected by the arrival of a Saharan dust intrusion. The 2-day back trajectories provided by the HYSPLIT model confirmed the arrival of air masses coming from North Africa to the North of Iberian Peninsula, during this day (Fig. 5a). The NAAP model shows that the dust load from the

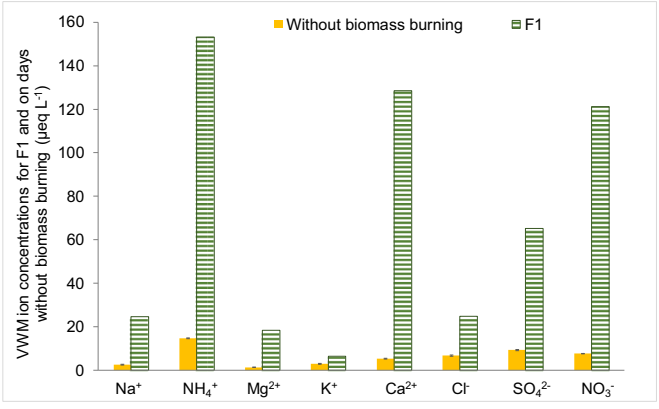

Fig. 4. Ion concentrations of rainwater fraction collected on 15 August 2016 (F_1) and on days without biomass burning influence (days 8, 10, 12, 28, 29 and 30 May 2016).

Table 3
Source contributions (seawater, crustal and anthropogenic) for inorganic ions in rainwater collected on 15 August 2016 (F_1) and on May 2016 (without biomass burning).

	Seawater fraction (%)	Crustal fraction (%)	Anthropogenic fraction (%)
F1			
K^+	9	91	–
Mg^{2+}	30	70	–
Ca^{2+}	1	99	–
Cl^-	98	2	–
SO_4^{2-}	5	4	92
NO_3^-	–	–	100
Without biomass burning			
K^+	30 ± 32	70 ± 29	–
Mg^{2+}	35 ± 34	65 ± 31	–
Ca^{2+}	4 ± 1	96 ± 1	–
Cl^-	99.7 ± 0.2	0.3 ± 0.1	–
SO_4^{2-}	3 ± 4	1.2 ± 0.6	96 ± 4
NO_3^-		0.14 ± 0.06	99.86 ± 0.06

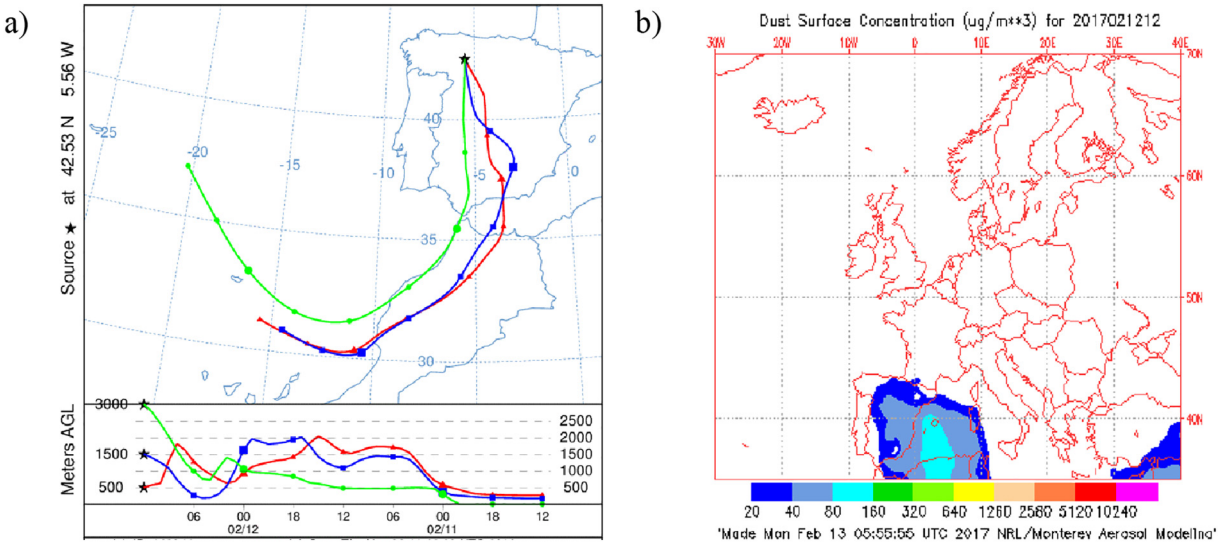

Fig. 5. a) HYSPLIT back trajectories at 500, 1500 and 3000 m agl and b) NAAP image of dust concentration, both on 12 February 2017 at 1200 UTC.

Sahara reached León on 12 February at approximately 1200 UTC (Fig. 5b), and remained until 13 February at approximately 1200 UTC. It is important to mention that Saharan dust outbreaks in winter are not common in the north of Spain.

3.2.2. Aerosol chemical composition

The increase recorded in the PM_{10} concentration, from 20 to 33 μg m^{-3}, and in the concentration of the main mineral elements (an increase >300% for Si, Al and Ca) in aerosol samples collected between 12 and 13 February 2017, evidenced the arrival of a dust cloud coming from the Sahara to León (Table 4). The high values of Si, Al and Ca are an indicator of dust of Saharan origin, due to the presence of minerals such as quartz (SiO_2), dolomite ($(CaMgCO_3)_2$), kaolinite ($Al_2Si_2O_5(OH)_4$) and calcite ($CaCO_3$) (Avila et al., 1997; Formenti et al., 2003).

3.2.3. Rainwater chemical composition

The arrival of the Saharan dust intrusion, between 12 and 13 February 2017, coincided with a precipitation event, which began on 11 February at 0300 UTC and ended on 14 February 2017 at 1700 UTC. During these 4 days, an accumulated precipitation of 20.46 mm was registered, with a mean intensity of 0.53 mm h^{-1}. Given that precipitation lasted four days, a total of four daily fractions (P_1, P_2, P_3 and P_4) were collected as Table 1 shows. The days with less accumulated precipitation were 11 and 14 February, with 0.95 and 0.98 mm, respectively (Fig. 6), while 13 February was the day with more accumulated precipitation and higher mean intensity (14.18 mm and 1.18 mm h^{-1}). In all cases, the volume swept by rain was mainly due to raindrops smaller than 2 mm. In the study carried out by Castro et al. (2010) in León, Spain, the results showed that with precipitation intensities lower than 0.6 mm h^{-1} the aerosol size distribution regains its initial values approximately 2 h after the precipitation. Moreover, Kulshrestha et al. (2009) reported that a low-intensity rain that lasts a couple of hours is responsible for the removal of fine particles.

The rain sample collected on 11 February (P_1) shows a chemical composition with high values of NH_4^+ (74 μeq L^{-1}), SO_4^{2-} (41 μeq L^{-1}) and NO_3^- (31 μeq L^{-1}) (Fig. 7). The pollutants related to local anthropogenic origin, such as SO_4^{2-} and NO_3^-, are removed mainly in the initial fractions of rain through the washout process (Celle-Jeanton et al., 2009). Thus, the chemical composition of P_1 could reflect the impact of fossil fuel combustion emissions on rainwater. Besides, between 10 and 11 February, the air masses coming from the Atlantic transported aerosols loaded with marine particles. This fact was reflected on the source contribution of P_1, where 91% of Cl^- is related to marine origin (Table 5) and in the Cl^-/Na^+ ratio of 1.3, value very close to that reported for seawater origin (1.2) (Keene et al., 1986).

On 11 and 12 February the weather types were hybrid cyclonic CE and pure cyclonic (C), respectively, and the air masses came from North Africa, keeping this scenario until 13 February. This is consistent with the observation that, between January and June, the dust transport from Africa is mainly caused by cyclonic activity over the west and south of the Peninsula (Rodríguez et al., 2001).

The chemical composition of the precipitation was very influenced by the new atmospheric conditions of this event. The concentration of crustal elements, Ca^{2+} and Mg^{2+}, reached maximum values of 96 and 13 μeq L^{-1}, respectively, on 12 February (Fig. 7).

The high content of Ca^{2+} and Mg^{2+} of mineral origin in P2 may be due to the fact that these ions are incorporated into the cloud during the transport of the air masses (rainout mechanism) (Rodrigo et al., 2003). In addition, mineral dust can act as a surface of pollutant reaction for anthropogenic contaminants (Krueger et al., 2004), which can be reflected in the increase in the concentrations of sulfate and chloride of anthropogenic origin (Fig. 7).

The crustal influence on 12 and 13 February was observed in the increase on the crustal contribution of K^+ (79 and 86%, respectively) and SO_4^{2-} (4.4 and 1.2%, respectively) (Table 5). Avila et al. (1997) reported that red rains (rain with reddish silt residues) are enriched in K about 3 times more than non-red rains. Furthermore, during this type of events, the raindrops with dust content would incorporate the anthropogenic pollutants, NO_3^-, NH_4^+ and SO_4^{2-}, as they fall (washout) (Rodrigo et al., 2003).

On 14 February, the HYSPLIT back-trajectories showed air masses coming from the Atlantic. The weather type was SW, which is characterized by humid air masses loaded with marine salts from the Atlantic Ocean. These changes were evidenced in the chemical composition of

Table 4
PM_{10}, silicon, aluminum, calcium, titanium, magnesium, iron and sucrose concentrations in air (in μg m^{-3}) on 13 February 2017 and the mean values in days without dust intrusion in León (days between 01 and 11 February 2017).

	13 February 2017	Days without dust intrusion
PM_{10}	33	25 ± 3
Si	2.9	0.16 ± 0.12
Al	1.58	0.07 ± 0.06
Ca	1.25	0.14 ± 0.06
Ti	0.081	0.005 ± 0.003
Mg	0.38	0.09 ± 0.05
Fe	0.82	0.11 ± 0.06
Sucrose	0.0024	0.0009 ± 0.0002

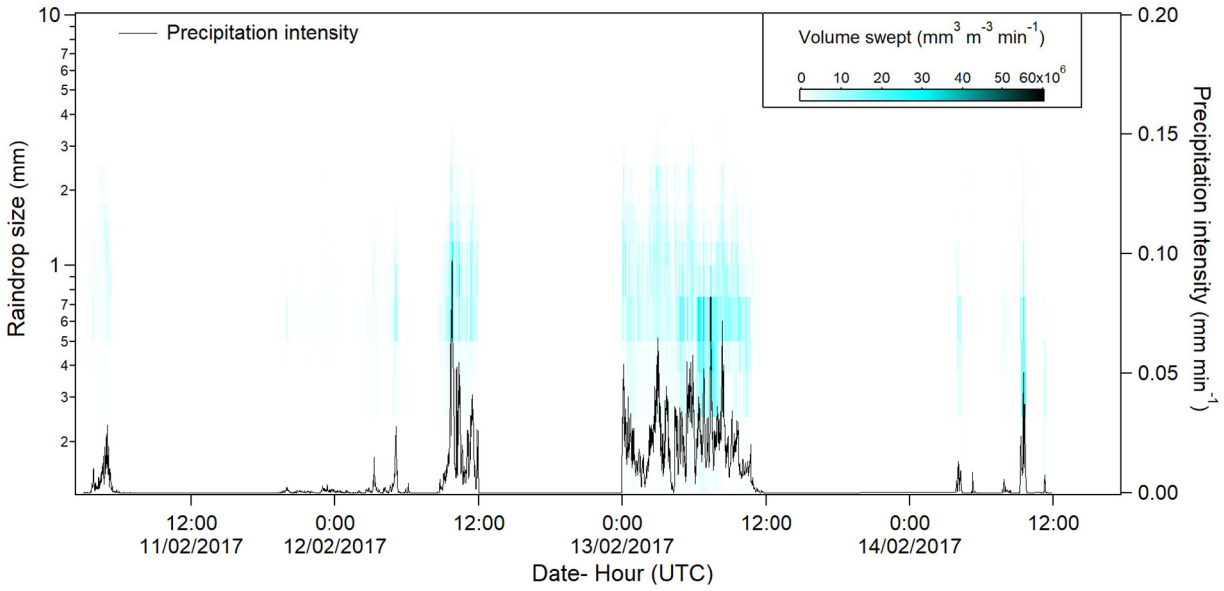

Fig. 6. Evolution of precipitation intensity (black line) and volume swept by the raindrops of each size interval (colour scale), between 11 and 14 February 2017.

the rain sample P_4. The fraction of rainwater collected between day 13 in the afternoon and day 14 in the morning (P_4) shows a decrease in the crustal element (Ca^{2+}) concentrations and an increase in the seawater elements (Na^+ and Cl^-) concentrations compared to previous days (Fig. 7). The fact that air masses changed their path (Atlantic instead of African) is the most probable explanation of a lowering of the crustal element concentrations in rain. Similar results were observed by Avila and Alarcón (1999), in the studies carried out in Montseny (Spain), about air masses coming from the Atlantic and the Mediterranean.

The analysis of the source contributions showed a seawater influence on the precipitation composition (Table 5), which was confirmed by the Cl^-/Na^+ ratio of 0.9.

During the dust intrusion, both DOC and WIOC in rain sample P_2 also showed an increase of 24% and 100%, respectively, as compared to P_1 (Table 6), reflecting an enhancement in the air concentration of organic species. Between 12 and 13 February, the airborne concentration of sucrose was 3 times higher than those observed in the days before the dust intrusion (Table 4). Sucrose is a sugar associated with pollen and plants (Bieleski, 1995; Medeiros et al., 2006); thus, the increase in the sucrose concentration may be related to the transport of bioaerosols, mixed with the local contribution from domestic heating emissions.

3.2.4. Alkaline contribution

The rainwater fraction collected on 12 February had the highest pH value of the event (7.0) (Fig. 7). Rainfall samples affected by African events usually show pH values higher than 6 and Ca^{2+} concentrations higher than 80 μeq L^{-1}, as a result of the dissolution of the calcite in the dust carried by the air masses from North Africa (Avila et al., 1997, 1998; Avila and Alarcón, 1999; Calvo et al., 2010, 2012; Camarero and Catalan, 1996; Escudero et al., 2005; Izquierdo et al., 2012; Morales-Baquero et al., 2013). On days before and after the dust intrusion (P_1 and P_4), ammonium was the main component that helped neutralize the rainwater (NF of 0.9 for P_1 and 0.6 for P_4). During the dust outbreak, calcium played an important role in neutralizing rainwater acidic components (NF of 1.3 for P_2 and 0.4 for P_3). Therefore, the high Ca^{2+} concentration during the dust outbreak was the main responsible for the alkaline pH value. Moreover, the conductivity values decreased from

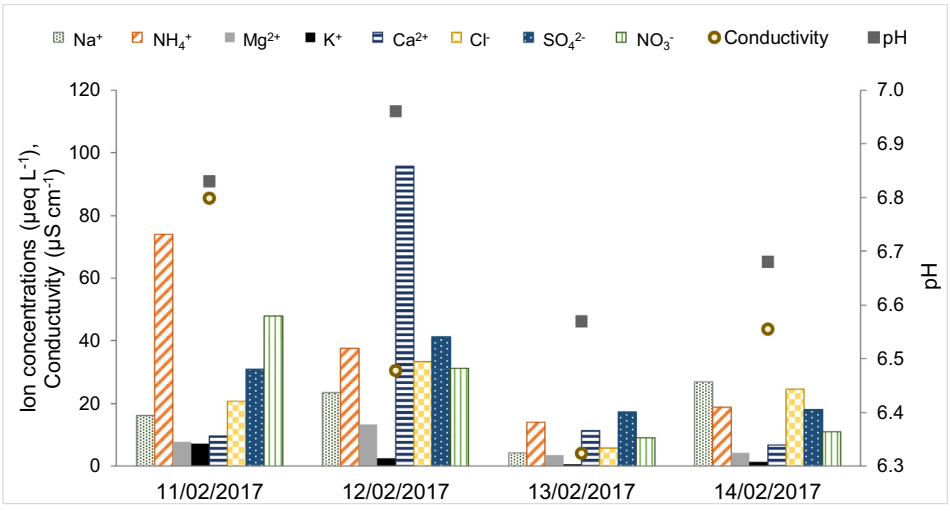

Fig. 7. Evolution of ion concentrations, pH and conductivity of each rainwater fractions collected between 11 and 14 February 2017.

Table 5
Source contributions (seawater, crustal and anthropogenic) in % for inorganic ions in rainwater collected on days 11 (P_1), 12 (P_2), 13 (P_3) and 14 (P_4) February 2017.

Rainwater sample	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	NO_3^-
Seawater fraction (%)						
P_1	5	47	7	91	6	–
P_2	21	40	1	82	7	–
P_3	14	28	2	85	3	
P_4	41	12	17	100	18	–
Crustal fraction (%)						
P_1	69	53	93	–	0.6	–
P_2	79	60	99	0.9	4.4	0.6
P_3	86	72	98	0.6	1.2	0.3
P_4	59	88	83	–	0.7	–
Anthropogenic fraction (%)						
P_1	26	–	–	9	93	100
P_2	–	–	–	16.9	89	99
P_3	–	–	–	14.6	96	99.7
P_4	–	–	–	–	81	100

86 μS cm^{-1} (P_1) to 4.0 μS cm^{-1} (P_3), as the precipitation event has evolved. Celle-Jeanton et al. (2009) observed that during a rain event, the initial fraction of the rainwater mainly had a chemical composition characteristic of local anthropogenic sources, while the subsequent fractions were influenced by transport events from different regions. Thus, the observed decrease in pH and conductivity values, the decrease in ion concentrations, and the change in the chemical composition of the P_3 and P_4 fractions, could be associated with the change in the air masses.

4. Conclusions

This study shows the impact caused by several wildfires that occurred in summer 2016 and a Saharan dust intrusion event in winter 2017, on rainwater chemistry in León.

The wildfires that took place in northern Portugal and northwest Spain in August 2016 affected the air quality of León causing an increase in the PM_{10} concentration and in the K, EC and OC values. Coinciding with these wildfires, on 14 August 2016, a precipitation event was registered in León. The rainwater chemistry was affected by the biomass burning aerosols, which was reflected in the high concentrations of SO_4^{2-} (65.19 μeq L^{-1}) and NO_3^- (121.17 μeq L^{-1}) of a main anthropogenic origin, in the high values of NH_4^+ (153.15 μeq L^{-1}), and in the high DOC (14.7 mg L^{-1}) and WIOC (1.7 mg L^{-1}) concentrations, due to the contribution of several organic compounds emitted by wildfires. The impact of biomass burning emissions on the acidity of rainwater was also observed, probably caused by a high concentration of acidic organic species, which is mirrored in the pH value of 4.8 of the rain sample.

A second precipitation event, which began on 11 February 2017 and was sampled in four sequential rain fractions, P_1, P_2, P_3 and P_4, allowed to study the effects of local and long-range transport emissions on precipitation in León, as well as to assess the scavenging effect of the rain in the atmosphere. The fraction of rainwater collected the first day (P_1) reflected the local anthropogenic contribution of the aerosol, typical of winter in León, with high concentrations of NH_4^+, SO_4^{2-} and NO_3^-. On 12 February, a Saharan dust intrusion reached the north of the Peninsula, causing an increase in the PM_{10} and in the Ca, Si, Al, Ti, Mg and Fe air concentrations, and affecting the chemical composition of the rainwater P_2, with an increase in the Ca^{2+} (>800%), Mg^{2+} (71%), Cl^- (62%), and SO_4^{2-} (33%) concentrations. A small mineral input of SO_4^{2-}, a typical anthropogenic element, into rainwater was also observed during dust outbreaks. The input of crustal elements to the atmosphere, especially Ca^{2+}, helped neutralize the rainwater, causing pH values higher than 6.5. Furthermore, during the Saharan dust outbreak, an increase in DOC values in rainwater was observed, due to a mixed contribution from dust and local anthropogenic emissions. Once the dust intrusion left the north of the Peninsula, the composition of the rainwater revealed a mixture of marine constituents together with local anthropogenic emissions, with a 100% of the Cl^- content from seawater source and a 100% of the NO_3^- from anthropogenic source.

The results showed that the rainwater composition is strongly affected by both local and long-range transport aerosol events. The amount and intensity of precipitation, as well as the volume swept by raindrops (a function of size and terminal velocity of raindrops), are also important factors to consider when studying precipitation-air pollutants interaction. Precipitation plays a crucial role in mitigating the negative impact of atmospheric pollutants on human health and the environment. The study of the influence of pollutant emissions on the chemical properties of rainwater provides useful information, which makes it possible to assess their impact on ecosystems and human health.

Table 6
Water insoluble organic and elemental carbon (WIOC and WIEC, respectively) and dissolved organic carbon (DOC) for rainwater collected on days 11 (P_1), 12 (P_2), 13 (P_3) and 14 (P_4) February 2017.

	P_1	P_2	P_3	P_4
Concentration in rainwater (mg L^{-1})				
DOC	1.41	1.75	1.69	0.40
WIOC	–	0.41	0.14	0.07
WIEC	–	0.03	0.01	0.02

CRediT authorship contribution statement

F. Oduber: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. **A.I. Calvo:** Conceptualization, Methodology, Resources, Writing - original draft, Visualization, Supervision, Project administration. **A. Castro:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration. **C. Blanco-Alegre:** Investigation, Visualization, Writing - review & editing. **C. Alves:** Investigation, Writing - original draft, Supervision, Funding acquisition. **J. Barata:** Investigation, Writing - review & editing. **T. Nunes:** Investigation, Writing - review & editing. **F. Lucarelli:** Investigation, Writing - review & editing. **S. Nava:** Investigation, Writing - review & editing. **G. Calzolai:** Investigation, Writing - review & editing. **M. Cerqueira:** Resources, Writing - review & editing, Funding acquisition. **J. Martín-Villacorta:** Resources, Writing - review & editing. **V. Esteves:** Investigation, Writing - review & editing. **R. Fraile:** Conceptualization, Methodology, Resources, Writing - original draft, Visualization, Supervision, Project administration, Funding acquisition.

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.

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