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Contribution of anthropogenic and natural sources in PM10 during North African dust events in Southern Europe☆

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ABSTRACT

The influence of North African (NAF) dust events on the air quality at the regional level (12 representative monitoring stations) in Southern Europe during a long time series (2007–2014) was studied. PM10 levels and chemical composition were separated by Atlantic (ATL) and NAF air masses. An increase in the average PM10 concentrations was observed on sampling days with NAF dust influence (42 μg m^{-3}) when compared to ATL air masses (29 μg m^{-3}). Major compounds such as crustal components and secondary inorganic compounds (SIC), as well as toxic trace elements derived from industrial emissions, also showed higher concentrations of NAF events. A source contribution analysis using positive matrix factorisation (PMF) 5.0 of the PM10 chemical data, discriminating ATL and NAF air mass origins, allowed the identification of five sources: crustal, sea salt, traffic, regional, and industrial. A higher contribution (74%) of the natural sources to PM10 concentrations was confirmed under NAF episodes compared with ATL. Furthermore, there was an increase in anthropogenic sources during these events (51%), indicating the important influence of the NAF air masses on these sources. The results of this study highlight that environmental managers should take appropriate actions to reduce local emissions during NAF events to ensure good air quality.

1. Introduction

Mineral dust is one of the main components of atmospheric particulate matter (PM). Large loads of mineral particles are transported from arid areas, contributing to different effects on climate, human health, and the environment (Towhy et al., 2009; Mahowald et al., 2010; Zhang et al., 2016; Middleton, 2019). The main global dust source regions are Central Asia, the Middle East, and North Africa, with the last region accounting for 55% of global dust emissions (Ginoux et al., 2010). Some authors have reported that dust coming from the Sahara desert can be transported to the Atlantic Islands and the Caribbean Sea (Prospero, 1999; Mahowald et al., 2005), and Southern Europe (Rodríguez et al., 2011; Salvador et al., 2019). PM levels are often increased as a consequence of these dust outbreaks (Viana et al., 2002; Querol et al., 2009; Salvador et al., 2013). In the case of Europe, the current Directive (EU, 2008) establishes an annual limit PM10 value (40 μg m^{-3}) as well as a daily limit value (50 μg m^{-3}, with a maximum of 35 days of exceedances). Furthermore, a procedure was developed to calculate the North African (NAF) load of the daily PM10 value when these events occur. For this purpose, PM10 background regional levels were calculated by applying either the 30th percentile (Escudero et al., 2007) or the 40th percentile to PM10 time series at regional background stations, after extracting the data associated with NAF dust outbreaks. Subsequently, the net African dust loads were obtained by subtracting the PM10 regional background levels from the PM10 values measured at the regional background sites during the NAF episodes. The European Directive 2008/50/EC (EU, 2008) allows the discount of PM exceedances due to NAF dust events.

From a global perspective, natural sources, such as NAF events, are more frequent than anthropogenic PM emissions. However,

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anthropogenic sources are important in several urban and industrial backgrounds in Spain (Rodríguez et al., 2007; Querol et al., 2008; Pandolfi et al., 2011). These emissions, mainly derived from traffic, industrial activities, and biomass burning, can release toxic elements and compounds, resulting in health problems for the local population (Galindo et al., 2018; Tobías et al., 2018). Recent studies have emphasised the negative health effects of NAF events (Pérez et al., 2008; Tobías et al., 2011; Pandolfi et al., 2014; Querol et al., 2019). In addition to the fact that higher coarse PM concentrations pose a risk to the human respiratory system, there is also a synergic effect between natural and anthropogenic pollutants. This dust transport brings about a PM concentration change, as well as a different air chemical composition (Pérez et al., 2012). Some authors have reported the adverse effects of NAF dust on regional pollutants, for example, the planetary boundary layer (PBL) is reduced when dust outbreaks occur (Pandolfi et al., 2014), causing the accumulation of anthropogenic pollutants. Furthermore, emissions from petrochemical activities or maritime transport are frequently co-transported with desert dust (Querol et al., 2019). Epidemiological studies have demonstrated an increase in daily mortality due to cardiovascular and respiratory diseases when Saharan dust events occur (Pérez et al., 2008; Sajani et al., 2011; Jiménez et al., 2010). Considering that North African dust transport has a strong impact on the Mediterranean basin (Pey et al., 2013; Salvador et al., 2014; Cabello et al., 2016), it is of great interest to determine how NAF dust affects PM levels and their different sources in the area.

The purpose of this study was to perform a PM10 source contribution analysis of natural and anthropogenic emissions under the influence of North African dust events in a large region (Andalusia) in Southern Europe. To this end, PM10 levels and their chemical components were studied at 12 monitoring stations (rural, urban, urban-industrial, and hot-spot traffic) belonging to the air quality monitoring network of the Autonomous Government of Andalusia during the period 2007–2014. Furthermore, a PMF analysis of the PM10 chemical composition was carried out considering the air mass origin during the sampling days to compare the source contribution.

2. Methodology

2.1. Study area

Andalusia is the southernmost autonomous community of mainland Spain and is the only European region with coastlines on both the Mediterranean and Atlantic oceans, which meets with the African continent through the Strait of Gibraltar. The main topography ranges of Andalusia are shown in Fig. 1, with the two most important mountain ranges in the north and the Baetic Range in the south. The Guadalquivir basin lies between these two mountainous areas. In general, the climate is typically the Mediterranean, with dry and hot summers and mild winters. There is a climatic variety with less wet weather in the eastern area of Andalusia. Higher rainfall is found from north to south as the sea is closer. Even though annual temperatures are not lower than 15 °C, they can vary depending on the altitude and continental characteristics of the considered area. Due to its proximity to North Africa, Andalusia is also affected by the impact of desert air masses, which increases PM concentrations (Rodríguez et al., 2001; Cachorro et al., 2008; Fernández-Camacho et al., 2010).

Although Andalusia is traditionally an agricultural area, the service sector (especially tourism) has grown in recent decades. Furthermore, deficient public transport results in dense urban road traffic and, consequently, road dust emissions (Amato et al., 2014; Milford et al., 2016). Likewise, although the industrial sector represents a minor percentage of the local economy, there are two main areas highly industrialised in Andalusia, which have been extensively studied: Algeciras Bay and the Ria of Huelva (Millán-Martínez et al., 2021). Many authors have concluded that there is a high proportion of anthropogenic and natural mineral particles in PM10 (Querol et al., 2004; Querol et al., 2008; de la Rosa et al., 2010; Pandolfi et al., 2011; Sánchez de la Campa et al., 2018; Millán-Martínez et al., 2021).

PM10 concentrations and chemical composition databases were obtained during the period 2007–2014 at 12 monitoring stations distributed across Andalusia (South Spain, Fig. 1). The considered monitoring sites belong to the Air Quality Monitoring Network of the Regional Government of Andalusia and were selected considering their location (rural, urban, or industrial background), as well as the main

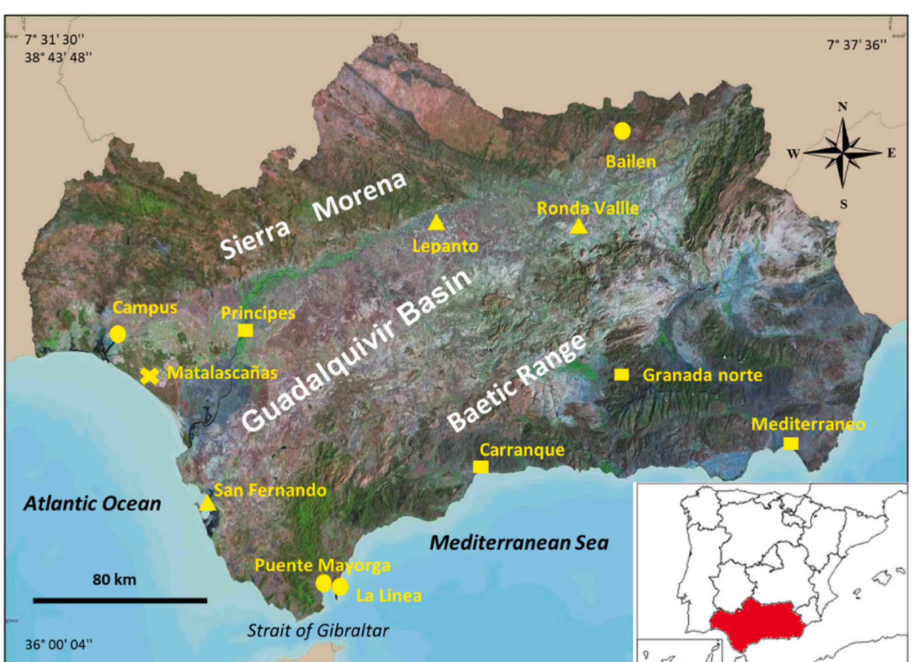

Fig. 1. Geographical location of the 12 monitoring stations considered in this study. Classification of the monitoring stations: traffic (square); urban-industrial (circle); urban (triangle); rural (cross).

nearby emission sources (Table S1):

1. Four traffic monitoring stations: Principes (Seville), Granada Norte, Carranque (Malaga), and Mediterraneo (Almeria).
2. Four urban-industrial monitoring stations: Campus (Huelva), La Linea (Cadiz), Puente Mayorga (Cadiz), and Bailen (Jaen).
3. Three urban monitoring stations, San Fernando (Cadiz), Ronda del Valle (Jaen), and Lepanto (Cordoba).
4. One rural monitoring station: Matalascañas (Huelva).

Principes and Granada Norte monitoring stations are located in the two most populated cities of Andalusia (Seville and Granada, respectively); hence, they are affected by dense urban traffic emissions (Fernández-Camacho et al., 2010; Sánchez-Rodas et al., 2017).

As previously mentioned, several monitoring stations are located in complex industrial areas. The campus is in the vicinity of the Huelva Estuary (Fig. 1), where industrial estates are established: a petrochemical complex, a phosphate industry for fertiliser production, and a Cu-smelter (Sánchez de la Campa et al., 2018). Previous studies in this area have reported sulfide-related toxic elements in PM (As, Cd, Sb, Bi, or Pb) as the main geochemical anomalies (Sánchez de la Campa et al., 2018; Millán-Martínez et al., 2021). In addition, one of the largest industrial estates of Andalusia is located close to the Strait of Gibraltar (Cadiz), which includes a petrochemical plant and oil refinery, a power plant, and a stainless-steel industry. Consequently, high levels of Ni, V, and Cr have been found at the monitoring stations in that area (La Linea and Puente Mayorga) as a result of this industrial activity, as well as the dense maritime traffic passing through the Strait of Gibraltar (Pandolfi et al., 2011; Li et al., 2018). The city of Bailen is one of the largest industrial estates producing structural ceramics in Spain, contributing to high levels of PM and SO_2 (Sánchez de la Campa et al., 2007; Sánchez de la Campa and de la Rosa, 2014).

The rural monitoring station of Matalascañas is located close to the coastal city of Huelva Matalascañas, within Doñana Natural Park and 30 km away from the industrial estates of Huelva.

2.2. PM10 sampling and chemical analysis

PM10 sampling was performed using quartz fibre filters (MUNKTELL) and high-volume captors (MCV: 30 m^3 h^{-1} and TISCH 68 m^3 h^{-1}) following the normalised method UNE-EN 12341 (UNE, 2015). One daily sample (24 h) was collected every 6 days. The mass of PM10 retained on the filters was determined by the standard gravimetric procedures (temperature, 20 °C; relative humidity, 50%), employing a Sartorius LA130 S–F balance (0.1 mg sensitivity) (UNE, 2015). A total of 4793 daily samples were collected using the above procedure.

The analytical methodology used to determine PM10 chemical composition comprises several techniques, following the modified method proposed by Querol et al. (2002). A half fraction of each filter was acid digested (2.5 mL HNO_3: 5 mL HF: 2.5 mL $HClO_4$) for the analysis of major and trace elements by ICP-OES (Jobin Yvon model ULTIMA2) and ICP-MS (Agilent model 7700), respectively. For quality control, analysis of the NIST-1633b (fly ash, Standard Reference Material) was carried out during every analytical run of both ICP techniques. The digestion procedure of the PM samples and ICP analysis was also validated using the Standard Reference Material 1648a. External calibration was performed by ICP-MS using 1, 2, and 4 SPEX CertiPrep Claritas PPT® multielement solutions (1–250 μg L^{-1} as well as HNO_3 5% blank). To minimise the possible fluctuations in the plasma, ^{103}Rh was used as an internal standard. The external calibration for ICP-OES was performed using elemental standard solutions (0.05–100 mg L^{-1} and HNO_3 5% blank). Accuracy and precision ranged from 5 to 10% for the elements studied.

Another quarter of the filter was leached with Milli-Q grade deionised water to extract water-soluble ions (SO_4^{2-}, NO_3^-, Cl^-, and NH_4^+) for subsequent analysis by ion chromatography (Methrom 883 Basic IC Plus) (Querol et al., 2002). The quality control of the results for soluble water ions was determined by solution cocktails for a low and high range of cations (1–10 mg L^{-1}) and anions (0.05–2.5 and 0.5–50 mg L^{-1}). The accuracy and detection limit for IC were 10% and 0.4 μg m^{-3}, respectively. Finally, a portion of 19.6 cm^2 of each filter was used for the analysis of the total carbon (TC) with a LECO SC-144 DR instrument.

SiO_2 and CO_3^{2-} concentrations were indirectly calculated from the stoichiometry of Al, Ca, and Mg-based on the experimental equation established by Querol et al. (2002): ($3{*}Al_2O_3 = SiO_2$; $1.5{*}Ca + 2.5{*}Mg = CO_3^{2-}$). $SO_4^{2-}{}_{non\text{-}sea\ salt}$ was obtained by subtracting the $SO_4^{2-}{}_{sea\ salt}$ (indirectly calculated by stoichiometry from the soluble Na levels) from the $SO_4^{2-}{}_{total}$. On average, 75%–86% and 67%–82% (for NAF and ATL, respectively) of PM mass were determined after analysing the collected filters.

2.3. Statistical treatment and source contribution

The chemical speciation data of the collected daily PM10 samples were used within the PMF (v5.0 EPA) for source identification and apportionment. The PMF model is a factor analytical tool used to calculate the contributions and chemical profiles of the sources developed by Paatero and Tapper (1994) and Paatero (1997). The PMF is based on the following mathematical algorithm:

$$\chi_{ij} = \sum_{k-1}^{p} g_{ik}{*}f_{kj} + e_{ij}$$

The dataset can be expressed as a matrix x of i by j dimensions, where i is the number of samples and j is the measured chemical elements, p is the number of independent factors, g_{ik} is the amount of mass contributed by each factor for each sample, f_{kj} represents the species profiles of each factor, and e_{ij} is the residue for each sample by element.

PMF is a weighted least-squares method in which individual estimates of the uncertainty in each data value need to be included in the input matrix. Several sources of error contribute to measurement uncertainty, but the associated with the analytical procedure is probably one of the most important. The uncertainties were calculated according to the methodology proposed by Amato et al. (2009).

Elements were classified using the signal-to-noise ratio defined by Paatero and Hopke (2003). Elements with $S/N < 2$ were generally defined as weak variables. The only common weak element at all the monitoring stations was As, although other sulfide-like trace elements such as Zn or Bi also appeared to be weak in some of the sites. Because the S/N ratio is very sensitive to sporadic values much higher than the level of noise, the percentage of data above the detection limit was used as a complementary criterion.

2.4. Air masses origin

The origin of air masses affecting the monitoring stations for each sampling day was determined by considering two representative locations: western Andalusia (37° N, 6° W) and Eastern Andalusia (37° N, 3° W). To this end, a five-day back-trajectory analysis starting at three different altitudes (500, 1500, and 2500 m a. s. l.) was carried out using the HYSPLIT model (Stein et al., 2015) of the NOAA Air Resources Laboratory (ARL) (https://www.ready.noaa.gov/HYSPLIT.php). Additionally, NAF events affecting the monitoring stations were also studied using aerosol and dust maps and satellite images from NRL (http://www.nrlmry.navy.mil/aerosol), SKIRON (https://forecast.uoa.gr/en/forecast-maps/dust/north-atlantic), BSC DUST (https://ess.bsc.es/bsc-dust-daily-forecast), and Earth Data NASA project (https://worldview.earthdata.nasa.gov/).

We classified the daily air masses as North African (NAF) when an African dust outbreak occurs, and the Atlantic (ATL), including the one from N, NW, SW, and W Atlantic air masses. There are also other minor air masses (regional, Mediterranean, and European origins <5%).

During the study period (2007–2014) NAF represented 26% and 31% of the total for Western and Eastern Andalusia, respectively (Fig. S1). The occurrence of NAF air masses is more frequent between March and September and is especially significant during the summer months (Fig. S2).

3. Results and discussion

3.1. Chemical composition of PM10

The interannual mean PM10 levels measured in Andalusia for the period 2007–2014 ranged from 28 μg m^{-3} (rural), 23–30 μg m^{-3} (urban), 32–36 μg m^{-3} (urban-industrial)–33-40 μg m^{-3} (traffic) (Fig. 2). PM10 concentration generally decreased in every type of monitoring station compared to previous data in the same study area. For example, de la Rosa et al. (2010) reported higher values (31–32, 35–53, 31–62 and 54–63 μg m^{-3} at rural, urban, urban-industrial, and traffic monitoring sites, respectively) in 2007. At the Bailen monitoring site, a PM10 concentration of 57.7 μg m^{-3} was obtained during the period 2003–2008 (Sánchez de la Campa et al., 2014). Furthermore, 41 and 44 μg·PM10 m^{-3} were observed at Principes and Granada Norte, respectively, from 2007 to 2010 (Amato et al., 2014). The same decreasing trend in PM10 concentration was observed at the industrial estates of La Linea and Puente Mayorga for the period 2005–2007 (37 and 38 μg m^{-3} Li et al., 2018) and at Campus site (37 μg m^{-3} for the period 2001–2008) (Sánchez de la Campa et al., 2018). All these studies conclude that the implementation of industrial emission abatement systems and the application of European directives on air quality are the main reasons to obtain lower PM10 concentrations. Fig. 2 shows that the maximum mean PM10 concentrations at the regional level were always associated with NAF episodes compared to ATL air mass origin, which has been observed in many other studies in Spain and the Mediterranean basin (Querol et al., 2019; Salvador et al., 2019; Conte et al., 2020).

3.1.1. Major components

The contribution of the major components to PM10 for each type of monitoring station for the NAF and ATL air masses is shown in Fig. 3. Higher mean concentrations of crustal components (CO_3^{2-} Al_2O_3, SiO_2, Fe, Ca, K, Fe, and P) were found in traffic sites (Granada Norte, Principes, Carranque, and Mediterraneo), reaching 34 %–42% of the PM10 mass. However, the mean concentrations observed under the influence of NAF (20.4 μg m^{-3}) were almost twice the mineral dust concentration for ATL air masses (11.4 μg m^{-3}). Lower concentrations (11.4–15.0 μg m^{-3} and 7.2–8.6 μg m^{-3} for NAF and ATL air masses, respectively) were obtained for the urban-industrial background, except for Bailen (24.7 and 12.2 μg m^{-3} for NAF and ATL, respectively), related to a relevant ceramic industrial activity (Sánchez de la Campa and de la Rosa, 2014).

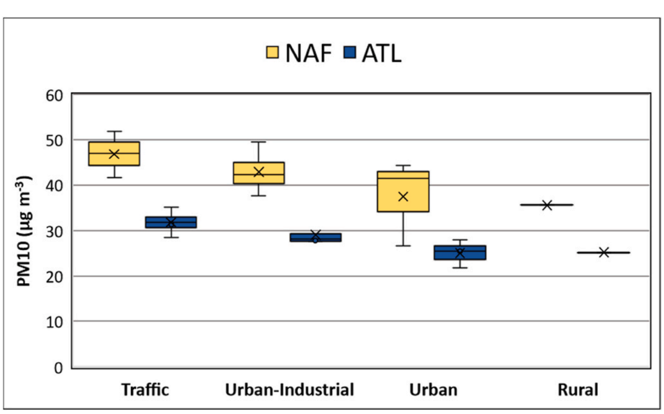

Fig. 2. Whisker and box plot of PM10 concentrations measured at the monitoring stations of Andalusia during the period (2007–2014) under NAF and ATL air masses.

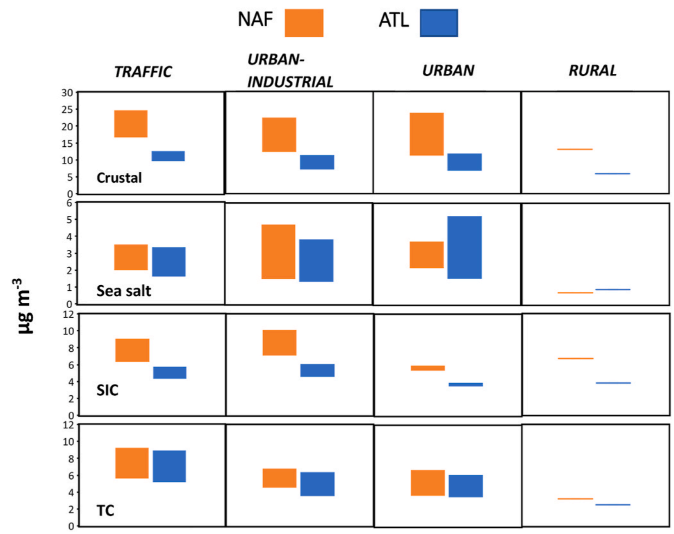

Fig. 3. Mean ranges of PM10 major components (μg·m^{-3}) measured at the monitoring stations of Andalusia under NAF and ATL air masses origin.

For urban monitoring stations, the mineral contribution ranged between 9.3 and 19.8 μg m^{-3} during NAF events, compared to the interval 5.6–9.8 μg m^{-3} registered under ATL influence. The mean concentration observed in the rural station (Matalascañas) during NAF episodes (13.0 μg m^{-3}) was more than twice that obtained during ATL air masses (5.8 μg m^{-3}). More marked concentration differences were observed at the stations (Granada Norte, Bailen, and Ronda Valle) with important local sources, mainly industrial or traffic. These monitoring sites are located in Eastern Andalusia, at higher altitudes, where the NAF air mass frequencies are higher. In conclusion, the differences between NAF and ATL samples could be due to several factors, such as site typology, local sources, and monitoring station altitude.

Regarding secondary inorganic compounds (SIC: NO_3^-, $SO_4^{2-}{}_{\text{non-sea salt}}$ and NH_4^+), high mean concentrations were found at the industrial monitoring stations as is expected due to the anthropogenic SO_4^{2-}emissions from fuel oil combustion. A remarkable decrease in SIC concentrations compared to earlier periods was observed (e.g. 10 μg·SIC m^{-3}, Amato et al., 2014). The higher mean concentrations obtained under NAF air masses of these anthropogenic compounds (8.7 μg m^{-3}) in comparison to the ATL air masses (5.4 μg m^{-3}). At the traffic sites, the concentrations found were similar to those measured at the industrial monitoring stations, with a mean value of 7.7 μg m^{-3} for NAF air masses and 5.1 μg m^{-3} for ATL influence. Lower mean concentrations were observed at urban (5.5 and 3.8 μg m^{-3} for NAF and ATL air masses, respectively) and rural (6.7 and 3.8 μg m^{-3} for NAF and ATL air masses, respectively).

The mean contribution of sea salt aerosol reached higher values at urban-industrial and rural monitoring stations (3.1–4.6 μg m^{-3}), coinciding with most of the coastal sites of the study. No significant differences were observed between the NAF and ATL air masses. The mean concentrations of TC under NAF air masses increased from 3.3 μg m^{-3} in rural background stations, to 5.4 and 5.6 μg m^{-3} in urban and urban-industrial sites, respectively. The highest mean concentration (7.2 μg m^{-3}) corresponded to traffic sites in relation to vehicle exhaust emissions. Furthermore, high levels of carbonaceous particles were also observed in Bailen, in agreement with previously published results (Sánchez de la Campa and de la Rosa, 2014). In this industrial estate, coke, olive husks, and wood are used as fuels for structural ceramic manufacturing (Sánchez de la Campa et al., 2010).

From these results concerning the crustal components, SIC and TC, it can be concluded that higher concentrations were always found under NAF events compared to ATL air masses origin, as has also been previously observed for PM10 concentrations.

3.1.2. Trace elements

The mean interannual concentrations of representative trace elements in PM10 were studied individually for each monitoring site (Fig. S3). The highest level of As was found in Campus, which was derived from nearby Cu-smelter emissions (Sánchez de la Campa et al., 2018). The difference of mean As concentrations between ATL (4.3 ng m^{-3}) and NAF (7.2 ng m^{-3}) air masses is remarkable, exceeding, in this case, the European annual target value (6 ng m^{-3}), which does not take into account synoptic scenarios and air masses origin. In the case of the Campus monitoring station, these results suggest that during NAF events, there is an increase in As concentrations favoured by their coupling with industrial plumes (Fernández-Camacho et al., 2010). In this monitoring station, it is also noteworthy that the mean levels of Cu (64.2 ng m^{-3}), Zn (63 ng m^{-3}), Pb (16.3 ng m^{-3}), Cd (0.76 ng m^{-3}), and Bi (0.96 ng m^{-3}) under NAF influence, originated from the Cu-smelter activities. However, concerning the elements with annual target values in the EU Normative, air quality thresholds were not exceeded (500 ng Pb·m^{-3}, EU, 2008; 5 ng Cd·m^{-3}; EU, 2004) in Huelva.

Lepanto is characterised by high mean levels of Cu and Zn (105 and 219 ng m^{-3}, respectively, for NAF episodes) as a result of nearby smelters of these metals. Another example of high concentrations of Cu was found in Bailen (137 ng m^{-3} under NAF) and was related to a nearby ceramic industry (Sánchez de la Campa et al., 2014).

V and Ni are other tracers of industrial activity linked to ship traffic emissions and petrochemical activities (Moreno et al., 2006). High mean Ni concentrations were observed in the Strait of Gibraltar (La Linea and Puente Mayorga), showing similar concentrations of NAF and ATL masses (14–18 ng m^{-3}) (Fig. S3), although the European limit did not exceed (EU, 2004). Levels of V also showed high mean values in these industrial monitoring sites, especially during NAF episodes (36.2 and

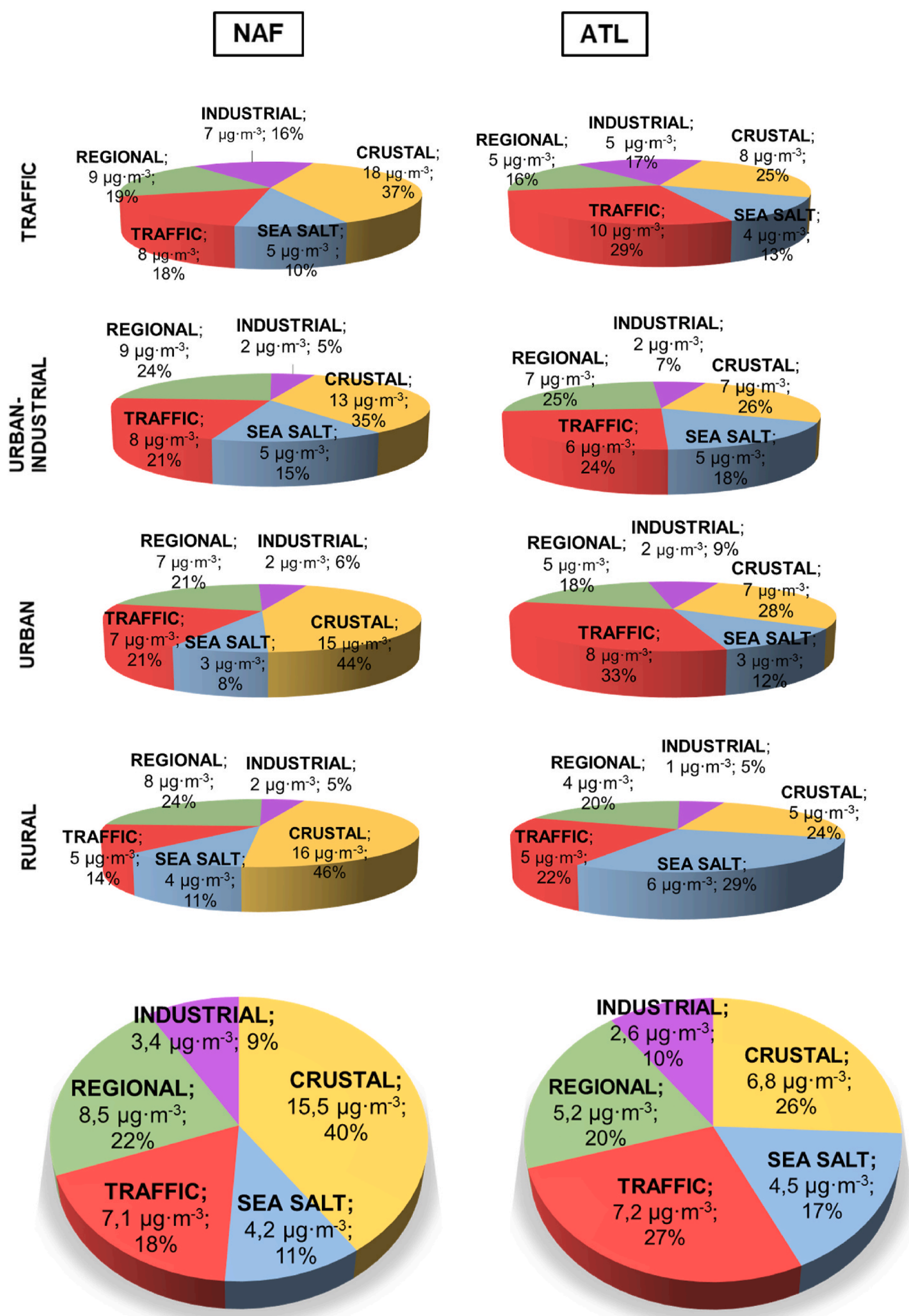

Fig. 4. Pie charts of average source contribution (µg m^{-3}, %) to PM10 for the selected monitoring stations under NAF and ATL air masses.

31.9 ng m^{-3} at Puente Mayorga and La Linea, respectively). (Fig. S3). Rodríguez et al. (2011) reported the presence of V in desert dust as a consequence of industrial emissions from North Africa. Furthermore, as has been previously observed (Sánchez de la Campa et al., 2014), the coke used as fuel in brick factories in Bailen resulted in high V concentrations (33.5 ng m^{-3} in NAF air masses).

Maximum values of mean Cr concentrations were registered at La Linea and Puente Mayorga (8.5 and 8.9 ng m^{-3}, respectively for NAF), derived from the industrial activity of a stainless-steel factory. In this case, Cr concentrations under ATL air masses (11.9 and 10.9 ng m^{-3} at La Linea and Puente Mayorga, respectively) are higher because of the dominant westerly wind in the area (Pandolfi et al., 2011). Likewise, this metal can be found in high concentrations (5.9 ng m^{-3} for NAF) in Granada Norte, and is derived from heavy traffic. The hot-spot traffic monitoring sites considered in this work showed the highest mean concentrations of Sn and Sb and trace elements related to brake and tyre wear. Average Sn and Sb levels found at Granada Norte during NAF episodes were 5.2 and 4.1 ng m^{-3}, respectively. In addition, the non-exhaust vehicle emissions caused high mean concentrations of Cu and Cr (approximately 60 and 5 ng m^{-3}, respectively) in the traffic sites.

3.2. Source contribution analysis (NAF vs ATL)

Following the PMF model described above, a source apportionment analysis using PMF 5.0 was performed to identify and quantify the natural and anthropogenic sources contributing to PM10 at every monitoring station during the period 2007–2014. Fig. 4 shows the different sources determined by considering the two main air masses originating in the study area, NAF and ATL.

The contribution of the sources is highly defined by the type and location of the monitoring stations. Nevertheless, the majority of them have the contribution of two main groups of sources in common: natural (crustal and sea salt) and anthropogenic (traffic, regional, and industrial).

The **crustal source** showed typical silicate components, such as Al_2O_3, Fe, Ca, Rb, Ti, Mn, and Sr. These soil-like elements are mainly derived from local dust resuspension and long-range transport of North African dust. As expected for an area close to the sea, a **sea salt** source was also identified with the characteristic marine elements Na, Cl, and Mg.

The **traffic source** was characterised by high concentrations of NO_3^-, NH_4^+, and total carbon (TC) due to vehicle exhaust emissions. Furthermore, high concentrations of Sn, Sb, Cu, Zn, K, Ca, and Ti were also found within this source, originating from the non-exhaust vehicle emissions (brake and tyre wear and road dust resuspension) (Amato et al., 2014).

Another source found in all monitoring sites was a **regional** one, with SO_4^{2-}, NO_3^-, and NH_4^+ as typical components. These components are normally associated with emissions from petrochemical activities or maritime transport, characterised by high concentrations of Ni, V, Co, Sn, Pb, Sb, Cr, and Mn. Moreover, an **industrial** source was identified in some of the monitoring stations with a specific chemical profile determined by nearby industrial activities.

Table 1 summarises the average source contribution of the selected monitoring stations under NAF and ATL air masses. Concerning the crustal source, a higher mean contribution under NAF (15 μg m^{-3}) influence compared to ATL (6 μg m^{-3}) air masses (Fig. 4), as a consequence of the mineral components coming from the desert dust, has been observed. Maximum mean concentrations of the crustal source were obtained at the hot-spot traffic sites (19.1 and 19.8 at Granada Norte and Carranque under NAF events, respectively) (Table 1). These high values, derived from the road dust resuspension coupled to NAF dust, are in the range observed in previous works in the Mediterranean basin (Querol et al., 2008; Pandolfi et al., 2016). In general, the concentration of the sea salt source was higher at the coastal monitoring stations with a similar contribution under NAF and ATL events (4 and 5 μg m^{-3}, respectively).

The same mean contribution of the traffic source was found for NAF and ATL (7 μg m^{-3}) in most of the monitoring sites. This fact was also observed in Principes (Fernández-Camacho et al., 2016), and can be attributed to the fine particulate fraction origin of the traffic-related compounds (Amato et al., 2014). It is also worth noting that NAF events normally occur during warmer seasons, whereas traffic sources always increase their contribution during the winter (Cesari et al., 2018; Mazzei et al., 2008). Furthermore, in some monitoring sites, this source was mixed with biomass combustion (with K as the main tracer) (Alves et al., 2011).

Regarding the regional source, derived mainly from long-range anthropogenic emissions, contributions were almost twice under NAF events in most of the monitoring stations (Table 1). A mean concentration of 8 μg m^{-3} was obtained for NAF air masses in comparison to ATL (5 μg m^{-3}), within the range described in other Southern European cities (Amato et al., 2014; Cesari et al., 2018), although no difference between NAF and ATL air masses has been found in these studies.

Different industrial sources were identified according to the industrial activity developed in the area surrounding each monitoring station.

Table 1
Mean source contribution (μg m^{-3}) to PM10 levels at the monitoring stations of Andalusia under North African (N) and Atlantic (A) air masses during the period 2007–2014.

Monitoring station	Natural Sources μg m^{-3} *(%)*				Anthropogenic sources μg m^{-3} *(%)*					
Traffic	Crustal		Sea salt		Traffic		Regional		Industrial	
	NAF	ATL	NAF	ATL	NAF	ATL	NAF	ATL	NAF	ATL
Granada Norte	19.1 *(39)*	5.1 *(16)*	2.6 *(5)*	2.0 *(16)*	14.8 *(30)*[a]	17.1 *(51)*[a]	12.6 *(26)*	8.8 *(27)*	–	–
Principes	15.4 *(35)*	6.8 *(23)*	3.9 *(9)*	3.4 *(12)*	7.3 *(17)*	8.3 *(28)*	9.4 *(22)*	5.2 *(18)*	7.5 *(17)*	5.5 *(19)*
Carranque	19.8 *(49)*	11.6 *(42)*	8.3 *(21)*	5.9 *(21)*	6.2 *(15)*	6.3 *(23)*	6.2 *(15)*	4.1 *(14)*	–	–
Mediterraneo	16.6 *(50)*	9.7 *(38)*	4.1 *(12)*	5.4 *(22)*	4.9 *(15)*[a]	6.4 *(25)*[a]	7.9 *(23)*	3.7 *(15)*	–	–
Urban-Industrial										
Bailen	16.7 *(39)*	7.1 *(24)*	4.4 *(11)*	3.1 *(11)*	6.0 *(14)*	7.0 *(24)*	11.6 *(27)*[b]	9.4 *(32)*[b]	3.9 *(9)*	2.8 *(9)*
Campus	8.7 *(28)*	4.8 *(21)*	4.4 *(14)*	4.3 *(18)*	7.9 *(25)*[a]	8 *(34)*[a]	8.3 *(27)*	4.9 *(21)*	2.1 *(6)*	1.4 *(6)*
La Linea	12.6 *(34)*	7.7 *(29)*	4.5 *(12)*	4.6 *(18)*	11.1 *(29)*	5.0 *(19)*	8.4 *(22)*	7.2 *(28)*	1.1 *(3)*	1.5 *(6)*
Pte. Mayorga	13.9 *(37)*	8.0 *(29)*	8.5 *(22)*	7.0 *(26)*	6.8 *(18)*[a]	5.8 *(21)*[a]	7.6 *(20)*	5.3 *(19)*	1.0 *(3)*	1.3 *(5)*
Urban										
Ronda Valle	17.5 *(49)*	7 *(29)*	2.9 *(8)*	2.1 *(9)*	9.3 *(26)*	9.9 *(42)*	6.3 *(17)*[b]	4.7 *(20)*[b]	–	–
Lepanto	20.1*(48)*	8.6 *(33)*	1.4 *(3)*	1.2 *(1)*	7.4 *(18)*[b]	8.3 *(32)*[b]	10.8 *(26)*	5.6 *(22)*	2.1 *(5)*	2.1 *(8)*
San Fernando	8.9 *(37)*	5.2 *(26)*	4.4 *(18)*	5.5 *(28)*	5.3 *(23)*[a]	6.1 *(30)*[a]	5.1 *(22)*	3.3 *(16)*	–	–
Rural										
Matalascañas	15.9 *(46)*	5.0 *(24)*	3.7 *(11)*	6.2 *(29)*	4.7 *(14)*[a]	4.8 *(22)*[a]	8.5 *(24)*	4.2 *(20)*	1.8 *(5)*	1.1 *(5)*

[a] Traffic + Combustion.
[b] Regional + Combustion.

At the Bailen industrial site, a source characterised by high concentrations of V, Ni, Pb, and SO_4^{2-} was found. These components, derived from brick factory emissions (Sánchez de la Campa and de la Rosa, 2010), showed a contribution of 3.9 and 2.8 μg m^{-3} for NAF and ATL influence, respectively. Two industrial sources were observed at Campus. The first one, typified by Cu, Zn, As, Cd, and Pb, corresponds to the emissions from a Cu-smelter (Fernández-Camacho et al., 2010). Another industrial source is the production of phosphate derivatives, which has also been described by other authors (Querol et al., 2002; Alatuey et al., 2006; Fernández-Camacho et al., 2012). The sum of the two industrial sources contributed to PM10 mass 2.1 and 1.4 μg m^{-3} for NAF and ATL air masses, respectively. Even though Matalascañas is considered a rural site, an industrial source derived from the two industrial estates mentioned above at the Campus site was identified. This is due to the closeness (ca. 30 km) of the rural station to the industrial activity, representing a contribution of 2.0 and 1.0 μg m^{-3} under NAF and ATL air masses.

The two monitoring stations located near the Strait of Gibraltar (La Linea and Puente Mayorga) presented an industrial source characterised by high concentrations of Cr, Ni, Zn, Mn, Cd, and Pb, related to the metallurgical activity emissions (Li et al., 2018). In this case, a similar contribution of this source was observed under ATL air masses (1.5 and 1.3 μg m^{-3} at La Linea and Puente Mayorga, respectively) compared to NAF events (1.1 and 1.0 μg m^{-3}) related to dominant western winds in the area (Sánchez de la Campa et al., 2011).

Other monitoring stations with industrial sources are Principes traffic site due to local industrial emissions from detergent production (Fernández-Camacho et al., 2016); and the urban station of Lepanto, as a result of metallurgic-related activities developed close to the monitoring station (de la Rosa et al., 2010; Sánchez-Rodas et al., 2017).

The most significant difference between the studied air mass origins was observed in the average contribution of the crustal source (15.5 and 6.8 μg m^{-3} for NAF and ATL, respectively), corresponding to an increase of 128%. This has already been postulated as the main reason for the PM10 concentration difference (Rodríguez et al., 2011; Salvador et al., 2019). However, the higher contribution of some anthropogenic pollutants to NAF events is also remarkable. Even though the traffic pollutants kept similar concentrations under both air masses, an increase in the sum of regional and industrial sources when comparing NAF (11.8 μg m^{-3}) and ATL (7.8 μg m^{-3}) events was noticed, representing a difference of 51% (Fig. 3). This may suggest an influence of the dust coming from North Africa over the anthropogenic pollutants, in addition to the well-known mineral contribution of these events.

North African dust events are associated with an increased risk of mortality (Tobías et al., 2011; Pandolfi et al., 2014; Stafoggia et al., 2016). These dust episodes cause PBL reduction due to a pushing-down effect of the warm overlying African air masses, which changes the temperature profile and lowers the inversion (Pandolfi et al., 2013). Consequently, anthropogenic emissions tended to accumulate. The fine grain size origin of anthropogenic particle pollutants and their high concentration in toxic elements have harmful effects on the health of the population. Hence, environmental managers should take appropriate actions to reduce local emissions during NAF events to ensure good air quality.

4. Conclusions

The present study highlights the importance of performing long-term series studies of source contribution using chemical data of PM10 at the regional level in Southern Europe. Mean PM10 concentrations and their chemical composition were studied during the period from 2007 to 2014 to differentiate between two scenarios: NAF events and ATL air masses origin. The results showed an increase in the mean PM10 concentrations under the NAF episodes compared to the ATL air masses. Furthermore, SIC compounds and some toxic elements (As, V, Ni, Pb, and Bi) related to industrial emissions also presented higher mean concentrations under these dust events.

Two main groups of sources have been identified by PMF, considering the origin of NAF and ATL air masses: natural (crustal and sea salt) and anthropogenic (traffic, regional, and industrial). The crustal contribution represents a gain of 128% during the NAF air masses. In addition, there was also a significant increase (51%) in anthropogenic sources, suggesting an influence of the NAF events on local anthropogenic emissions. Therefore, it has been demonstrated at the regional level that dust coming from North Africa affects not only PM10 exceedances but also their chemical composition. The population could be especially exposed to more harmful air quality during these days, and hence, additional considerations should be taken to reduce the toxic anthropogenic pollution affecting human health.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.118065.

Sample Credit author statement

María Millán Martínez: Investigation, Writing Original Draft. Daniel Sánchez-Rodas: Reviewing, Methodology. Ana M. Sánchez de la Campa: Reviewing, Methodology. Jesús D. de la Rosa: Funding Acquisition, Reviewing.

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