Source contribution and origin of PM10 and arsenic in a complex industrial region (Huelva, SW Spain)

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ABSTRACT

Air pollution coming from industrial activities is a matter of interest since their emissions can seriously affect to the human health of nearby populations. A more detailed study about industrial emissions is required in order to discriminate different activities contributing to pollutant sources. In this sense, gaseous pollutants (NO_2, SO_2 and O_3) and PM10 levels has been studied in a complex industrial area in the southwest of Spain (La Rabida and the nearby city of Huelva) during the period 1996-2017. Hourly, daily, monthly and annual variations of PM10 and gaseous pollutants concentrations point to the industrial activity as the main SO_2 source. Furthermore, traffic and resuspension emissions contribute to the NO_2 and PM10 levels, respectively. Results from chemical composition of PM10 at both sites during the period 2015-2017 are characterized by high concentrations of the crustal components derived from natural and local resuspension. Arsenic is found to be the main geochemical anomaly at La Rabida (annual mean of 7 $ng\cdot m^{-3}$), exceeding the European annual target of 6 $ng\cdot m^{-3}$, which supposes a risk for the nearby population. An emission source from Cu-smelter has been identified in La Rabida and Huelva. A second source corresponding to emissions from polymetallic sulfides handling in a port area has been described for the first time in La Rabida. In addition, arsenic speciation results have identified three different As impacts scenarios as a function of the dominant wind direction, the SO_2 episodes and the As extraction efficiency: impact of the Cu-smelter, impact of the bulk polymetallic sulfides and a mixed impact of both sources.

Keywords: **complex industrial area, sulfide material, PM10, pollutant gases, arsenic speciation.**

1. Introduction

Atmospheric aerosol, also referred as Particulate Matter (PM), is a main pollutant in air characterized by the wide physico-chemical variety of its components and sources (Moreno et al., 2006; Giere & Querol, 2010; Calvo et al., 2013). With the aim of identifying PM origins, different source contribution models have been applied (e.g. Principal Component Analysis or Positive Matrix Factorization; Viana et al., 2008, Belis et al., 2011, Hopke, 2016). These techniques enable the identification and quantification of natural sources (e.g. soils resuspension, desert dust or sea salt aerosols) and anthropogenic sources mainly related to exhaust and non-exhaust traffic (Amato et al., 2009), industrial (Viana et al., 2008b) and biomass burning emissions (Sánchez de la Campa et al., 2018).

Nowadays, most part of the world population is concentrated in urban areas, frequently located near industrial estates. Therefore, it is of high interest to quantify industrial sources apportionment, since their emissions can add toxic elements and compounds to atmospheric pollution, leading to a negative impact on human health (Pope et al., 2007). Sometimes, source contribution analysis are not able to discriminate different industrial activities because the corresponding studies are undertaken in urban areas. In this sense, industrial emissions can be mixed between them or with other urban sources such as traffic or local dust resuspension (Lee et al., 2003; Pandolfi et al., 2011; Fernández-Camacho et al., 2012). An exhaustive identification of sources contribution analysis is required in order to isolate the different industrial emissions and their quantification, and to compare with the results from a nearby urban area. In addition, it must be taken into account the impact of economic crisis on the atmospheric emissions in industrialized and developing countries, like the global recession starting in 2008 (Cusack et al., 2012; Monteiro et al., 2018, Li et al., 2018).

The urban area of Huelva (SW Spain) is a good example of a city influenced by complex industrial emissions (Querol et al., 2002; Alastuey et al., 2006). Trace elements such as Ni and V and pollutant gases (SO_2 and NO_X) have been studied in relation to petrochemical activities (Fernández-Camacho et al., 2012). Also, high concentrations of As and other toxic trace elements (Sb, Cu, Zn, Pb and Sn) in PM have been found in the city of Huelva (urban background) as a result of the emissions of a Cu smelter (González Castanedo et al., 2014; Chen et al., 2016). However, no source contribution studies have been undertaken within the industrial area in order to better discriminate emission sources.

The purpose of the present work is to identify the sources contribution of PM10 (coarse fraction of PM with aerodynamic diameter < 10 µm) in La Rabida (SW Spain), a monitoring stations near an industrial complex area. Furthermore, data obtained from the nearby urban station in the city of Huelva will be also considered to compare the impact of the industrial emissions at both sites. To this aim, pollutant gases and PM10 levels temporal series (1996-2017) were evaluated according to the wind direction in order to discriminate possible emission sources. Moreover, source apportionment analysis of the chemical composition and As speciation of PM10 samples (period 2015-2017), were carried out as a tool to distinguish between different industrial sources.

2. Methodology

2.1. Study area

The city of Huelva (145.000 inhabitants) is located in the SW of Spain, 5 km from the confluence of the Odiel and Tinto Rivers, which form the estuary of Huelva (Fig. 1). The province of Huelva, situated at the western end of the Guadalquivir River basin, has a Mediterranean climate with Atlantic influence. Winters are mild, with an annual mean temperature above 10 ºC, and summers are warm with a mean temperature of 25 ºC in the region, exceeding sometimes 40 ºC. Precipitation is moderate (235 $L \cdot m^{-2}$ in 2019) and occurs largely in winters since summers are dry (7 $L \cdot m^{-2}$ between June-September 2019). Data were obtained from a station of the Spanish State Meteorological Agency (AEMET, 2019) located in Huelva. The wind direction is dominated mainly by two components due to the Atlantic breeze (SW) and the topography of the area: NW (Odiel River), and to a minor extent by NE (Tinto River) (see wind rose in Fig. 1). Daily air masses origin affecting to the study area were obtained using back trajectories provided by NOAA Air Resources Laboratory's (ARL) HYSPLIT model (Stein et al., 2015).

Air quality in the city of Huelva has been deeply studied because of its high industrialization since 1960´s. The major industrial estates are settled down in two main areas at the S of the city (Fig. 1): Punta del Sebo and Nuevo Puerto. A petrochemical industry and other industrial activities such as TiO_2 production are developed at the Nuevo Puerto estate. The production of phosphate derivatives and a Cu smelter plant are the most important industrial activities in Punta del Sebo estate. The Cu production process is said to be responsible of significant emissions of SO_2, As, Sb, Pb, Zn and Sn (González-Castanedo et al., 2014).

Very close to Nuevo Puerto facilities (SW) tons of raw materials in bulk are handled by dockers, including the transport and handling of , among others, coal, ore sulfide concentrates, clinker and coke, generating PM emissions into the atmosphere. The cargo is normally unloaded from ships to a hopper with a crane and then from hoppers to trucks to be transported. This material is also moved and piled by wheel dozers. Therefore, the high probability of resuspension when they are handled can entail dust emissions affecting to nearby zones.

It is also important to note that all the industrial activities mentioned above are beside and even inside the natural site Marismas del Odiel (Fig. 1), a high value ecosystem. Thus, a sustainable development of the activities is needed in order to improve the environmental quality of this area.

Most of the prior studies on air quality in Huelva are based on the industrial impact on urban air quality in order to know the effects over its population. However, the nearby populated area to the industries has hardly been considered. La Rabida is a small town situated at the SE of Huelva, crossing the Tinto River (Fig. 1), between the industrial areas Punta del Sebo and Nuevo Puerto, and it can be considered as an urban background with industrial influence affected by two types of emissions: channelized and fugitive.

2.2. Sampling

High volume PM10 sampling for chemical analysis was carried out at two monitoring stations:

- La Rabida: urban background monitoring station with industrial influence. It is situated on the SE part of the estuary of Huelva (Fig. 1), halfway between the two industrial estates.
- Campus: urban background monitoring station located in the El Carmen University campus within the city of Huelva (Fig. 1).

At both monitoring sites sampling was performed using quartz fiber filters (MUNKTELL) and MCV high volume captors (30 m^3 h^{-1}) following the normalized method UNE-EN 12341, 2015. One daily sample (24 h) was collected every four-six days during the study period (2015-2017). The total number of samples collected was 197 at La Rabida and 183 at Campus monitoring stations. Before sampling, filters were heated 200 ºC for 4 hours and conditioned for 48 h at 20 ºC and 50% of relative humidity. Then they were weighed by standard procedures in order to calculate the gravimetric PM10 concentration.

Furthermore, a 21-year record (January 1996-December 2017) of PM10 and gaseous pollutants levels was carried out at Campus and La Rabida monitoring stations. Both stations are equipped with automatic instrumentation to monitor hourly data of NO_2 (chemiluminescence), SO_2 (UV fluorescence), O_3 (UV photometry) and PM10 (beta attenuation) following the reference methods of the European directive on air quality (EU 2008). Meteorological measurements as wind direction, wind speed, temperatures and relative humidity were obtained from the same station.

European directive (EU 2008) establishes specific techniques and methodologies to determine particulate matter levels. However, it is possible to use another kind of equipment if their measures can be corrected by comparing to the European reference method. Thus, PM10 data measured by automatic equipment were corrected with those obtained from high volume captors MCV. The inter-comparison factor obtained (Table S1 on Supplementary Data) was approximately 1, so values from automatic methods could be considered.

2.3 Sample treatment and chemical analysis

Prior to chemical analysis, sampled filters were placed in a desiccator for 24 hours at 20 ºC and 50% relative humidity, following standard procedures (UNE, 2015). They were then weighed in a Sartorius LA 130 S-F balance. Once PM10 levels were obtained by standard gravimetric methods, filters were subjected to several analytical treatments following the method proposed by Querol et al. (2001). 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 7900), respectively. For quality control, analysis of the NIST-1663b (fly ash, Reference

Standard Material) was carried out during every analytical run of both ICP techniques. External calibration was performed in ICP-MS by using cocktail solutions (1, 10, 50, 100 and 250 ppb as well as a HNO_3 5% blank). With the aim of minimizing the possible fluctuations of the plasma, ^{103}Rh was used as internal standard. The external calibration for ICP-OES was performed using elemental standards solutions (0.05-100 ppm and a HNO_3 5% blank). Accuracy and precision were in the range of 5-10% for the elements studied.

Another quarter of the filter was leached with Milli-Q grade deionized water in order to extract water soluble ions (SO_4^{2-}, NO_3^-, Cl^- and NH_4^+) for the subsequent analysis by ion chromatography (Methrom 883 Basic IC Plus) (Querol et al., 2002). The quality control of the results for soluble water ions were determined by solution cocktails for low and high range of cations (1-10 ppm) and anions (0.05-2.5 and 0.5-50 ppm). The accuracy and detection limit for IC was 10% and 0.4 $\mu g \cdot m^{-3}$. Finally, a portion of 1.5 cm^2 of each filter was used for the analysis of organic carbon and elemental carbon (OC and EC) using a Sunset Laboratory OC-EC Analyzer and following the EUSAAR-2 protocol (Cavalli et al., 2010). In this technique, an external sucrose aqueous solution was used in order to ensure the consistent operation of the instrument and the quality of the measurements.

SiO_2 and CO_3^{2-} concentrations were indirectly calculated by stoichiometry from the contents of Al, Ca and Mg, on the basis of experimental equation established by Querol et al. (2001): ($3Al_2O_3 = SiO_2$; $1.5Ca + 2.5Mg = CO_3^{2-}$). $SO_4^{2-}{}_{\text{non-sea salt}}$ was obtained by subtracting the $SO_4^{2-}{}_{\text{sea salt}}$ (indirectly calculated by stoichiometry from the soluble Na levels) from $SO_4^{2-}{}_{\text{total}}$.

For As speciation, circular fractions (1.2 cm^2) of each PM10 sample were cut using a hollow and sharp-edged steel cylinder (diameter 1.24 cm). These circular portions were extracted by using a 100 $mmol \cdot L^{-1}$ of $NH_2OH \cdot HCl$ solution as the extractant with the aid of microwave radiation (domestic microwave Samsung TDS, operated at 100 W) for 4 min. This procedure has been previously carried out for As speciation of TSP, PM10 and PM2.5 samples (Sánchez-Rodas et al., 2012). A QA/QC study of the extraction procedure of arsenic in atmospheric particulate matter has been described in Oliveira et al. (2005). The determination of individual inorganic As species (As(III) and As(V)) was achieved by coupling High Performance Liquid Chromatography, Hydride Generation and Atomic fluorescence Spectrometry (HPLC-HG-AFS). The detection limits obtained were of 0.1 ng m^{-3} for As(III) and 0.4 ng m^{-3} for As(V).

2.4. Statistical treatment and PMF

A temporal trend analysis was performed in the pollutant concentrations during the study period by using the Theil-Sen statistical estimator (Theil, 1950; Sen, 1968), available in the Openair package for R (Carslaw and Ropkins, 2012; Carslaw, 2015). The Theil-Sen function allows the calculation of the regression parameters of the data trend, including slope, uncertainty in the slope and the p value (significance of the trend). Monthly PM10 and gaseous pollutants mean values were calculated for hourly resolution data. The symbols shown next to the trend estimate relate to how statistically significant the trend estimate is: $\rho < 0.001$ = ***, $\rho < 0.01$ = **, $\rho < 0.05$ = *, $\rho < 0.1$ = +; no symbol stands for no significant trend.

The chemical speciation data of the collected daily PM10 samples were used within the Positive Matrix Factorization model (PMF v5.0 EPA) for source identification and apportionment. The PMF model is a factor analytical tool to calculate the contributions and chemical profiles of the sources affecting the receptor site using ambient species concentrations. It was developed by Paatero and Tapper (1994) and it is explained in detail by Paatero (1997). PMF is based on the following mathematic algorithm:

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

The data set can be expressed as a matrix *x* of *i* by *j* dimensions, where *i* is the number of samples and *j* is the chemical elements measured. Additionally, p is the number of independent factors, g_{ik} is the amount of mass contributed by each factor for each individual 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 so that individual estimates of the uncertainty in each data value are needed in order to be included in the input matrix. There are several sources of error contributing to the measurements uncertainty, but the associated with the analytical procedure is probably one of the most important. The uncertainties were calculated following the methodology proposed by Amato et al. (2009).

Elements were classified using the signal-to-noise S/N_j ratio defined by Paatero and Hopke (2003). Those elements with $S/N < 2$ were generally defined as weak variables. Since S/N ratio is very sensitive to sporadic values much higher than the level of noise, the percentage of data above detection limit was used as complementary criterion.

3. Results and discussion

3.1. Annual time series of gaseous pollutants and PM_{10} levels

Data availability of PM10, NO, NO_2, NO_X, SO_2 and O_3 between February 1996 and December 2017 at La Rabida and Campus monitoring stations enabled us to calculate mean annual levels of these pollutants during this period (Table S2, Fig. 2). In order to evaluate time trends, mean concentrations were plotted and analyzed for statistical significant trends. Hourly, daily, weekly and seasonal cycles were also calculated (Fig. S2).

3.1.1. NO_2

NO_2 levels at both monitoring sites diminished during the study period, with a decrease rate of -0.53 and -0.93 $\mu g \cdot m^{-3} \cdot year^{-1}$ at Campus and La Rabida stations, respectively (Fig. 2). The concentrations of NO_2 showed a noticeable reduction since 2009 with low values until the end of the period. Even in the early years when mean levels were maximum (31 $\mu g \cdot m^{-3}$ La Rabida in 1998), the European Union NO_2 annual standard (40 $\mu g \cdot m^{-3}$, EU 2008) was not exceeded. NO_2 has strong traffic and industrial origin, and hence the Spanish economic crisis (around 2008) caused a diminution of these sources. At the end of the period, NO_2 values remained constant possibly due to the economy recovery from the crisis and the development of emission reduction technology.

Mean hourly levels of NO2 at the two monitoring stations showed two maxima during the working days at rush hours early in the morning and in the evening. These peaks point to vehicle exhaust and industrial emissions as the main responsible of NO_2 concentrations. Regarding seasonal patterns (Fig. S2), NO_2 levels were higher in winter, which is typical from pollutants related to traffic. However, high concentrations during the summer were also observed. In this way, a detailed study of the pollutant was carried out over the year and it suggested an industrial source of NO_2. Two predominant wind directions were identified at La Rabida in the summer months: NW, where Punta del Sebo industrial estate is located and SE, proceeding from Nuevo Puerto industrial estate. In the same way, the high NO_2 concentrations at Campus in May come from the SW direction, pointing to industrial emissions. According to the polar plot (Fig. S3 on Supplementary Data), NO_2 concentrations in the evenings may be due to the regional traffic pollution, whereas in the morning (8:00-9:00) NO_2 levels point to both traffic and industrial sources.

3.1.2. SO_2

SO_2 concentrations showed a very similar pattern in both monitoring stations. Levels decreased considerably in 2001 at La Rabida (7 $\mu g \cdot m^{-3}$), increasing afterwards until 2007 (13 $\mu g \cdot m^{-3}$). After that, concentrations diminished until a minimum value of 5 $\mu g \cdot m^{-3}$ in 2015. At Campus monitoring station, SO_2 concentrations also showed a smooth increase until 2009 (10 $\mu g \cdot m^{-3}$) with a subsequent decrease that finished in 2015 (5 $\mu g \cdot m^{-3}$). Even though there is not an annual SO_2 limit stablished, the European normative recommends not exceeding more than 24 times per year 350 SO_2 $\mu g \cdot m^{-3} \cdot h^{-1}$. This target value is rarely exceeded, however sporadic hourly SO_2 peaks (> 20 $\mu g \cdot m^{-3}$ h^{-1}) have been measured during the study period. The number of days with SO_2 impacts has diminished throughout the years (Fig. S5), as well as the concentration corresponding to these peaks, due to the implementation of emission abatement technologies in the Cu smelter during the study period (Sánchez de la Campa et al., 2018).

Regarding the number of days per month with SO_2 impacts (Fig. S5), there is a seasonal pattern at Campus with highest number of impact days in the warmer months. At La Rabida station, a high number of SO_2 impact days can also be observed in January and February as a consequence of its closeness to the industrial estates. The combined effect of the pollution abatement strategies and the economy recession caused the reduction of this anthropogenic pollutant for the end of the period (-0.25 $\mu g \cdot m^{-3} \cdot year^{-1}$).

Considering SO_2 concentrations at La Rabida, mean hourly levels were higher between 0-5 h and 12-15 h as a consequence of the prevailing wind from the NW direction. On the other hand, high values of SO_2 concentrations are found at Campus monitoring station between 14-18 h, when the SW component dominates the wind direction. The main wind direction described in the region is according with the study of sea-land breeze regimes described by Adame (2005). Although there is not a clear seasonal pattern, SO_2 concentrations increased in March, July, August and December (Fig. S2). It has been demonstrated the industrial provenance of SO_2 in Huelva and its relationship with toxic elements (Fernández-Camacho et al. 2010; Sánchez de la Campa et al., 2018). The main SO_2 emission sources in La Rabida are derived from petrochemical activities, a Cu smelter and the production of TiO_2 pigments, being their contribution in 2016 56, 40 and 4%, respectively (Spanish Register of Emissions and Pollutant Sources; PRTR, 2016). This idea can be supported considering the SO_2 provenance coming mostly from NW direction (Cu smelter) but a secondary source can be observed in the SE (oil refinery and TiO_2 production).

3.1.3. O_3

O_3 concentrations remained constant from 2003 to 2017 at both monitoring stations (0.33 and -0.12 $\mu g \cdot m^{-3} \cdot year^{-1}$ at Campus and La Rabida, respectively).

O_3 levels reached maximum values everyday between 15-20 h (Fig. S2) at both monitoring stations, coinciding with the diurnal time when sun light intensity is higher and when sea breeze air transport prevails. In the same way, O_3 showed a seasonal pattern characterized with maximum concentrations during the warmer months.

3.1.4. PM10

In the case of PM10, a pronounced decrease can be seen at La Rabida in 2003 (Fig. 2) followed by higher concentrations until 2007, decreasing afterwards, at both monitoring stations at a rate of -1.07 and -0.80 $\mu g \cdot m^{-3} \cdot year^{-1} \cdot$ at Campus and La Rabida, respectively. The European annual target value of 40 $\mu g \cdot m^{-3}$ (EU 2008) was not exceeded during the latest years.

PM10 concentrations experiment a noticeable raise during the working days between 17 and 20 h. According to the seasonal evolution, maximum values of PM10 occur in the warmer months and March, when Sahara dust events and dry periods are more frequent (Viana et al., 2002). However, regarding the summer months at La Rabida, when the typical SW breeze occurs in the afternoon, an important PM10 source were found coming from this direction. This source is attributable to the regional anthropogenic emissions caused by handling loose materials by the dockers. Moreover, the lack of rainfalls during the summer enhances these fugitive emissions. At Campus station high PM10 concentrations are observed in the evening coming from the N direction where local roads and a highway are located and the resuspension is more likely to occur.

It is also important to emphasize the relatively low PM10 annual concentrations obtained at La Rabida during the latest years of the period (32 $\mu g \cdot m^{-3}$, 27 $\mu g \cdot m^{-3}$, and 30 $\mu g \cdot m^{-3}$ in 2015, 2016 and 2017 respectively). Therefore, the EU air quality annual standard (EU 2008) of 40 μg PM10$\cdot m^{-3}$ was not exceeded during these years. Besides that, the number of exceedances of the daily European limit value 50 μg PM10$\cdot m^{-3}$ recorded at the end of the period (2015-2017) were 53 days, 43 of which were attributable to North African dust outbreak (NAF) coming from Saharan air masses. In this way, the maximum of the 35 days of exceedances imposed by the European normative was not exceeded in any of the years 2015, 2016 and 2017 (27, 8 and 18 days of exceedances accordingly). Most of the NAF daily exceedances recorded in this latest period were observed mainly in February, March and in the summer. However, when the daily exceedances were due to anthropogenic sources, high concentrations of PM10 were showed in March, April, August, September and December, with a non-defined pattern.

3.2.Chemical composition of PM10

Mean levels of PM10, major components and trace elements and its annual statistical trend at both monitoring stations (Campus and La Rabida) during the period 2015-2017 are showed in Table S2.

The mean PM10 inter-annual concentrations, gravimetrically measured from Campus and La Rabida stations for the period 2015-2017, were 29 and 32 $\mu g \cdot m^{-3}$ respectively, in agreement with the PM10 range reported by Querol et al. (2012) for urban backgrounds with industrial influence (28-47 $\mu g \cdot m^{-3}$). Therefore, the annual 40 μg PM10$\cdot m^{-3}$ limit fixed by the European Directive (EU 2008) was not exceeded at the two considered monitoring stations.

Regarding PM10 components, high concentrations of mineral dust have been found at the two monitoring stations (8.92-9.51 $\mu g \cdot m^{-3}$), within the range described for urban-industrial backgrounds (6-13 $\mu g \cdot m^{-3}$, Querol et al, 2008). Moreover, crustal components in the two monitoring stations have increased their concentrations over time. Considering the time plots of these pollutants, sporadic peak concentrations were found during the months February-March every year, being correlated with the Saharan dust outbreak events (Pey et al., 2013).

The contribution of secondary inorganic compounds (sum of NO_3^{-}, NH_4^{+}, SO_4^{2-}) does not reach annual average concentrations higher than 6 $\mu g \cdot m^{-3}$. These values are lower than those found in earlier works performed at urban monitoring stations in Huelva (Fernández-Camacho et al, 2010). NO_3^{-} concentrations (1.95-2.09 $\mu g \cdot m^{-3}$) are consistent with the concentrations values previously observed in Huelva (Querol et al., 2012). Non-sea salt SO_4^{2-} does not reach levels higher than 4 $\mu g \cdot m^{-3}$. Time series of anthropogenic SO_4^{2-} exhibited a seasonal evolution with levels slightly higher in summer-autumn (Fig. S6), resulting from the increased oxidation of SO_2 to SO_4^{2-} that occurs in this warm period (Harrison et al., 1996; Pio et al., 1998). A converse seasonal pattern is shown by NO_3^{-} as a consequence of the low thermal stability of NH_4NO_3 in summer, resulting in the formation of the gaseous nitric acid and ammonia (Adams et al., 1999). In contrast to SO_4^{2-} and NO_3^{-} concentrations, NH_4^{+} levels presented a bimodal seasonal variation over the 3 years of the study: values normally increase during the summer time but, on the other hand, winter peak concentrations were also observed in the time variation plot (Fig. S6). NH_4^{+} measured in the cooler months is due to the formation of NH_4NO_3, whereas in the summer period $(NH_4)_2SO_4$ is the dominant specie, as it has been explained before (Cusack et al., 2012).

Annual concentrations of carbonaceous particles (OC+EC: organic and elemental carbon), ranged from 3.94 to 4.06 $\mu g \cdot m^{-3}$ as expected for this urban-industrial environment (Querol et al., 2012). OC+EC concentrations were higher at Campus station since these PM10 components come mainly from vehicle exhaust and industrial combustion.

The mean contribution (2.72 and 2.91 $\mu g \cdot m^{-3}$ at Campus and La Rabida monitoring stations, respectively) of sea salt aerosols (Na^{+}, Cl^{-} and sea salt SO_4^{2-}) was within the typical range for Atlantic coastal sites in the Iberian Peninsula (Querol et al, 2008). Maximum concentrations of Na^{+} were obtained in summer as a consequence of the stronger influence of see breezes, whereas Cl^{-} levels were lower during the summer months due to its volatilization as HCl derived from the formation of $NaNO_3$ by interaction of the gaseous HNO_3 and sea salt NaCl. It should be noted the partial anthropogenic origin of Cl^-, which can be observed in the Cl^- excess presented in some peak events.

In reference to the trace elements, As was found to be the main geochemical anomaly in PM10. Annual mean concentrations at La Rabida (7.95, 6.18 and 6.76 $\mu g\cdot m^{-3}$ in 2015, 2016 and 2017, respectively) were above the target value recommended by the EU (6 ng $As\cdot m^{-3}$, EU 2004). On the other hand, mean As concentrations measured in Campus were lower for the whole period (2.96, 3.05 and 2.46 $\mu g\cdot m^{-3}$ in 2015, 2016 and 2017, respectively). Concentrations values were consistent with those reported by Sánchez de la Campa et al. (2018) in urban stations in Huelva in recent years (2014-2015). Nevertheless, it is important to note the decrease of the As concentrations in 2017 with regard to 2015. La Rabida monitoring station is very close to the industrial area where the Cu smelter is located, and high As concentrations have been previously described as a result of its emissions (González-Castanedo et al., 2014).

Cu and Zn concentrations at Campus are similar to the values obtained by Querol et al. (2008) at urban monitoring sites of Spain. However, higher concentration are observed at La Rabida as a consequence of polymetallic sulfides handling near the station. Bi (0.93 $ng\cdot m^{-3}$) and Se (0.46 $ng\cdot m^{-3}$) at La Rabida have also characteristic values for a station close to a Cu smelter. Levels of V (6.13 $ng\cdot m^{-3}$) and Ti (71.4 $ng\cdot m^{-3}$) were especially high at La Rabida probably due to the emissions from a petrochemical plant and a TiO_2 production facility developed in Nuevo Puerto estate (Alastuey et al., 2006). Concerning other elements with limit target values in the EU air quality standards such as Pb, Ni and Cd, none of them exceeded air quality thresholds (500 ng $Pb\cdot m^{-3}$, EU 2008; 20 ng $Ni\cdot m^{-3}$ and 5 ng $Cd\cdot m^{-3}$; EU, 2004) in none of the monitoring stations. Although As, Cu and Pb did not show a clear seasonal variation, they presented random maximum peaks which probably come from the close Cu smelter or from the industrial activity.

It is important to emphasize the similar concentrations of mayor components of PM10 at both monitoring stations with the exception of Fe that may originate from the mineral fugitive emissions occurred near La Rabida station. Concerning trace elements, the high values of As, Cu, Zn and Pb at La Rabida showed a stronger industrial influence in this monitoring station.

3.3.Source apportionment analysis

A PMF analysis was performed for both monitoring stations in order to identify the natural and anthropogenic sources contributing to PM10 over the period 2015-2017. Fig. S7 shows the chemical profiles and the species percentage for each source. 5 sources were identified at Campus monitoring station: crustal 1, crustal 2, aged sea salt, Cu smelter, and traffic-biomass burning. In the case of La Rabida station, 6 sources were found: traffic, crustal, aged sea salt, regional, Cu smelter and sulfides (Fig. 3).

The crustal source is characterized by the typical silicate components as Al_2O_3, Fe, Ca, Rb, Ti, Mn and Sr. The long-range transport dust and the local resuspension are the main contributing factors of this source. Similar crustal contribution were reached at Campus monitoring site (Crustal 1: 5.3 $\mu g \cdot m^{-3}$, 19%) and La Rabida (5.0 $\mu g \cdot m^{-3}$, 16%), affected by urban and industrial resuspension, respectively. A second crustal source (Crustal 2: 3.9 $\mu g \cdot m^{-3}$, 14%) was found at Campus showing high concentrations of Y and Th. Apart from that, La Rabida is also influenced by the handling of bulk material.

The traffic source represents a higher PM10 contribution at Campus (10.6 $\mu g \cdot m^{-3}$, 39%) than at La Rabida (8.8 $\mu g \cdot m^{-3}$, 29%). It is characterized by high loads of NO_3^-, NH_4^+, EC and OC, deriving from vehicle exhausts emissions. This factor is also made up by high concentrations of Ca, K, Ti, Cr, Sn, and Sb; attributed to non-exhaust vehicle emissions (Amato et al., 2014), mostly from the brake and tyre wear as well as the road dust resuspension. Regarding traffic profile in Campus monitoring station, the presence of PO_4^{3-} points to emissions from biomass burning. Levels of these compounds were higher in the winter months, since the planetary boundary layer is reduced and pollutants are concentrated in the atmosphere.

A regional source was identified at La Rabida (5.7 $\mu g \cdot m^{-3}$, 19%) with SO_4^{2-}, NO_3^- and NH_4^+ as typical components. These components are associated to PM usually derived from emissions of petrochemical activities and the production of phosphates derivatives (Ni, V, Co, Sn, Pb, Sb, Cr, Mn and Fe). This relationship has been previously reported by other authors (Querol et al., 2002; Alastuey et al., 2006). Levels of this source were higher in summer as a consequence of the coupling of refinery emissions to the air masses proceeding from North Africa with predominant SW wind direction (Pandolfi et al., 2014).

An aged sea salt source was identified at both monitoring stations. The typical sea salt components (Na, Cl and Mg) showed similar contribution at Campus (5.8 µg·m^{-3} 21%) and La Rabida (5.5 µg·m^{-3}, 18%). This component was also characterized by the presence of Sr as a result of the dust resuspension.

In relation to the Cu smelter, a single source was isolated at the two monitoring stations considered in this work. These emissions arise from Cu smelting operations that take place in the Punta del Sebo industrial estate. They include high concentrations of As, Bi, Pb, Sb, Sn, Se, Cd, Cu and Zn; and accounted for 1.9 µg·m^{-3} (7%) and 3.5 µg·m^{-3} (11%) at Campus and La Rabida, respectively. Concerning the time evolution of this component, sporadic peaks are related to certain meteorological conditions which cause the impact of emissions from the Cu smelter. This source has been broadly described in early works in the city of Huelva (e.g. Fernández-Camacho et al., 2010). Furthermore, a sulfide-mineral source was also identified at La Rabida with a contribution of 2.1 µg·m^{-3} (7%). The high loads of Cu, Fe, Zn, Ni, Cd, Co, As, Sb and Bi suggest a geochemical profile typical from sulfide mineral concentrates. Polymetallic sulfide mineral are specifically unloaded by the dockers in the port and fugitive dust could be emitted, affecting directly to the nearby area.

3.4. Arsenic speciation in PM10

The European Air Quality normative (EU, 2004) only considers the total content of As in PM10, with a target annual value of 6 ng·m^{-3} of As in PM10. However, the degree of toxicity of As varies depending on its oxidation state or molecular structures it may be present. In this way, inorganic species such as arsenite and arsenate (As(III) and As(V)), are more harmful than methylated species. Of the two inorganic species, As(III) is more toxic than As(V) because of their interaction with sulfhydryl groups of proteins and enzymes inhibiting their function (Francesconi and Kuehnelt, 2004). The main anthropogenic emissions of As to air in the study area come from the smelting of metals and the combustion of fuels, gas and carbon. However, recent studies have also evaluated the presence and release of As from dust material handled by the dockers like coal, clinker, or ore sulfide mineral (Moreno et al., 2009). Moreover, As-bearing sulfide is the most common form of inorganic As found in coal, and it is also associate with Cu, Pb and Zn sulfides (Liu et al., 2007).

In this sense, it was possible to determine different types of As sources (channeled and fugitive) by means of As speciation analysis, combining the As extraction of the sampled filters, wind direction and SO_2 peaking days. A total of 33 PM10 samples with high As concentrations were selected during the period 2015-2016 at the two monitoring stations considered in this study. Most of the samples correspond to synchronic sampling of PM10, in order to compare results of the same days.

The ranges of As concentrations of the selected PM10 samples with high levels of this metalloid are shown in Table 1 at Campus and La Rabida monitoring stations. As(III) and As(V) concentrations determined by HPLC-AF-HG, as well as the extraction percentage obtained from PM10 samples and the dominant wind direction are also reported in Table 1. These parameters are specified for both monitoring stations depending on the major As source. There are two main As emission sources near the monitoring stations, a channelized one corresponds to a Cu smelter industry located in the Punta del Sebo industrial estate, and fugitive emissions attributable to the bulk material handled by the dockers (mostly ore sulfide concentrate). The distinction between both sources can be related to the efficiency of As extraction. In the case of the Cu smelter, As is quantitatively extracted (> 80%) from PM10 probably because it is occurring in high temperature fly ash or slag particles resulting from oxidative metallurgy. On the other hand, in the bulk material accumulated in the dock, As is an impurity of the polymetallic sulfides, from which As is poorly extracted. Regarding to these two As emission sources, three different scenarios can be considered concerning the possible impact on the monitoring sites:

(a) Impact from metallurgy emissions: The As extraction efficiency is very high, (80-100%) (Table 1) and it is usually associated with SO_2 plumes originated from the Cu smelter emissions. This situation normally occurs at La Rabida when wind direction is dominated the NW component. However, at Campus monitoring site the SW component dominates the wind direction when the Cu smelter impact occurs.

(b) Impact from bulk polymetallic sulfides: This scenario includes the impact of the resuspension of sulfide mineral concentrates handled by dockers and the resuspension of sulfide of polluted soils around the city of Huelva (Torres et al., 2017). The As extraction efficiency is low (< 20%, Table 1) and the dominating wind components at La Rabida are SW or WSW with pointing to a sulfide origin source. Furthermore, As concentrations resulting from these fugitive emissions are much higher than those resulting from the metallurgy emissions.

(c) *Mixed impact*. The third scenario is an intermediate situation which occurs with a mix of the wind directions (primarily NW and SW components) along the day and causes the association of the two As sources at La Rabida monitoring site. This situation is the most frequent and is characterized by moderate extraction yields (30-70%) of As from PM10.

It is clear from the results that the most important As source comes from the Cu smelter emissions as it has been described in prior studies (Fernández-Camacho et al., 2010; González-Castanedo et al., 2014). However, there is a fugitive As source related to the handling by dockers of polymetallic sulfides which gives rise to episodic high As concentrations in PM10. In this sense, this methodology allows us to identify two different As origin (metallurgy and bulk polymetallic sulfides), which has not been taken into account previously in the same monitoring station.

The low percentage of As extraction of sulfide mineral compared with Cu smelter emission particles indicates low biodisponibility, and in consequence a small degree of hazardous for the environment. In consequence, the importance of the As origin relies on the requirement of investigating new strategies in order to reduce the emission of As that can affect to nearby areas.

4. Conclusions

A general decreasing trends were observed for the concentrations of gaseous pollutants and PM10 in the industrialized area of Huelva (SW Spain) in the period 1996-2017. This diminution is more evident since 2008 due to the economic recession and the enforcement of air quality European Directives. From a detailed analysis of the pollutants, it was inferred a strong industrial contribution of SO_2, whereas traffic emissions contributed to NO_2 levels. The high resuspension proceeding from the bulk sulfide material handled by the dockers enhanced PM10 concentrations, especially crustal components at La Rabida monitoring station.

Arsenic was found to be the main geochemical anomaly in PM10. Factorial analysis of the chemical composition of PM10 and As speciation analysis allowed to identify two As emission sources. One of them corresponds to Cu smelter emissions already described in the study area in prior studies. However, the second one is due to emissions that take place when bulk polymetallic sulfides are handled by the dockers. The low biodisponibility of As in the sulfide mineral implies a low hazardous impact for the air quality and human health. The results obtained in this study allowed us to identify for the first time two different sources contributing to the high As concentrations in the same place of a complex industrial area.

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