



Geochemical anomalies of toxic elements and arsenic speciation in airborne particles from Cu mining and smelting activities: Influence on air quality

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HIGHLIGHTS

- Geochemical anomalies of toxic elements in PM₁₀ related to mining have been studied.
- High concentrations of Cu and As have been detected in rural and background stations.
- As speciation explains the low impact of the mining area on the rural surrounding.
- Pyrometallurgic activity produces fine particles which are transported long-distance.

ARTICLE INFO

Article history:

Received 18 November 2014

Received in revised form 13 February 2015

Accepted 19 February 2015

Available online 21 February 2015

Keywords:

PM₁₀

As speciation

Toxic elements

Iberian Pyrite Belt

ABSTRACT

A characterization of chemical composition and source contribution of PM₁₀ in three representative environments of southwest Spain related to mining activities (mineral extraction, mining waste and Cu-smelting) has been performed. A study of geochemical anomalies was conducted in the samples collected at the three stations between July 2012 and October 2013. The influence of Cu-smelting processes was compared to other mining activities, where common tracers were identified. The Cu and As concentrations in the study area are higher than in other rural and urban stations of Spain, in which geochemical anomalies of As, Se, Bi, Cd, and Pb have been reported.

The results of source contribution showed similar geochemical signatures in the industrial and mining factors. However, the contribution to PM₁₀ is different according to the type of industrial activity. These results have been confirmed performing an arsenic speciation analysis of the PM₁₀ samples, in which the mean extraction efficiency of arsenic depended on the origin of the samples. These findings indicate that the atmospheric particulate matter emitted from Cu-smelting has a high residence time in the atmosphere. This indicates that the Cu-smelter can impact areas of high ecological interest and considered as clean air.

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1. Introduction

Atmospheric particulate matter (APM) presents a complex geochemical composition with a multiple origin [1]. Anthropogenic emissions of APM are generally less relevant than the natural sources [2], but they can represent the input of high concentrations of toxic elements (e.g., Cu, Zn, Cd, Pb, As and Se) in the air. This is especially important in the case of industrial activities, such as mining and smelting [3,4].

The search for mineral raw materials containing strategic elements has increased in recent years. One of the most relevant elements is Cu, associated to massive and hydrothermal sulphides. Operations related to mining activities can affect the air quality. Exploration, extraction [5] and transport of mineral ore by trucks [6] generate elevated concentrations of coarse particles enriched in toxic elements and may impact negatively on human settlements near mining centers.

Abandonment of mining operations generates large of uncontrolled solid or liquid mining waste (several thousand million tons per year worldwide) [7]. Fine particles from tailing suffer resuspension and are dispersed around mining abandoned zones. In this case, the impact of deposition particles [8,9] is more important than respirable particles [10–12]. Particles derived from mining operations can be incorporated in household dust, affecting children [13]. Moreover, the transport of mining wastes during reclamation after accident of mining tailings dams, incorporate high concentrations of toxic elements in coarse particles (e.g., Aznalcollar Mine accident in 1998) [14].

Cu-smelters based on pyrometallurgic processes are the most important emissions sources of fine and ultrafine size APM, with high concentration of Cu, As, Zn, Cd and Pb, among others [15–18]. These pollutants can impact on soils, plants and animals, and affect the human health. Several epidemiological studies have evaluated the exposure to ambient air pollution near smelters for cancer risk [19].

In most mining centers all the operations are concentrated in the same place, being difficult to quantify the apportionment of every source of impact in the APM. In the present work we have the opportunity to quantify the contribution of three main sources mining activity, separated by around 100 km distance between them. Therefore, we present the results of a chemical characterization in PM₁₀ in three relevant localities of southwest of Spain and the Riotinto Mining District, related to Cu mineral extraction (Las Cruces Mine), Cu-smelting (Huelva city) and historic abandonment of mining waste (Nerva), from July 2012 to October 2013. The main objective is to characterize geochemical anomalies in toxic elements and As speciation in APM, and its influence areas.

2. Material and methods

2.1. The study area

The Iberian Pyrite Belt (IPB) is a mineralized Late Paleozoic mega-belt composed by volcanogenic massive sulphides, located in southwest Spain [20]. Containing around 250 Mt of polymetallic sulphides, is considered as one of the most important deposits in the World [21].

In the northern sector of IPB, the Riotinto Mining District is composed by several bodies of massive sulphide deposits, exploited since Roman times. Today is relevant the negative environmental heritage and degradation resulting of several centuries of exploitation. Several open pits have generated an important volume of mining waste with toxic elements, draining low-pH water to streams and Tinto and Odiel Rivers [22].

Las Cruces Mine is located in the eastern part of IPB, where the mineralization is covered by Neogene sediments of the Guadalquivir Valley [21]. This open pit mine is near the city of Seville (around 10 km), where the main ore extracted contains covellite with an average of 6.2% of Cu. The mineral ore is submitted to the typical mechanical operations (mining transport, crushing and grinding), that are responsible for the emission of particulate matter, mainly in the coarse fraction. Hydrometallurgy technology is used for transformation of ore into Cu-cathodes, involving some advantages compared to pyrometallurgical processes: (a) inhibits

the generation of SO₂; and (b) provides a better recuperation metal (over 90%) with respect to conventional technology of flotation, producing Cu cathodes of high quality (grade A'': 99.9935% Cu). Recently, supergene enrichment has been studied in order to characterize Au–Ag–Hg [23], originated by subsurface microbial activity [24].

Today, metallic mining is considered as a major shake-economic area due to the opening of some mines in the southwest of Spain (e.g., Aguas Teñidas and Las Cruces Mines). However, mining activities produce a deep environmental impact on the ecosystems and on the human health of the population living near the mines.

The city of Huelva has maintained a relation with mining activities for more than one hundred years. Mineral ore from the Riotinto mining district was exported through its harbor. Also, since de 1960s a Cu-smelter was placed in one of the industrial estates that surround the city. Polymetallic sulphides coming by ship from Asia and South America are transformed using pyrometallurgic smelting methods. Actually, it is the second Cu-smelter in Europe, with a total production of 247,000 t of Cu cathodes (comm. per. Atlantic Copper SLU, 2012). Another relevant industry in Huelva was based on the production of phosphoric acid by the attack of sulphuric acid with phosphorite transported by ship from Western Sahara. Both factories are localized near the city (around 2 km) in a main wind direction (Fig. 1). The sea breeze is considered representative of summertime conditions in the area of Huelva, in which can be linked to the transport of the pollution plume to Huelva and nearby areas [25].

Since 1999, the Autonomous Government of Andalusia develops an Environmental Plan for the city of Huelva, jointly with the National Research Council (CSIC). Several studies have quantified the source contribution of deposition particles [26], TSP (Total Suspended Particles [27], PM₁₀–PM_{2.5} [28–31] and ultrafine particles (<0.1 µm) [18], highlighting as several elements (As, Se, Bi, Cd, Zn, Cu) correspond to the representative geochemical anomalies near the Cu-smelter. Recently, the emission factor of Cu-smelter by size has been characterized [32], demonstrating that toxic elements are emitted in the fine and quasi-ultrafine particles (<0.33 µm). The term quasi-ultrafine has been defined by Minguillón et al. [33] (Dp < 0.25 µm; PM_{0.25}).

Several epidemiological works have related environmental factors derived of industrial plumes and mining wastes with high cancer risk [34,35], conforming the so-called “triangle of cancer” between the provinces of Huelva, Seville and Cádiz. Recently, it has been demonstrated as the cognitive behavior of children in primary schools of Huelva is related to a high concentration of Cd [36].

2.2. Experimental methods

One-year strategy sampling period was designed to assess the presence of toxic elements in atmospheric aerosol in the SW of Spain. The selected period was between July 2012 and October 2013, during which one daily sample per week was collected using Munktel® quartz fiber filters. High volume samplers (CAV-A-PM1025, 30 m³ h⁻¹) equipped with PM₁₀ inlets were used in the sampling of APM. Three monitoring stations were selected (Fig. 1):

- Urban background site under the influence of industrial emissions (University Campus monitoring station, CAM). This station belongs to the Air Quality Network of the Department of the Environment of the Autonomous Government of Andalusia. A total of 64 filters were sampled during the study period of July 2012 to July 2013.
- Rural area in the municipality of Nerva (NER) in the Riotinto Mining District. Nerva is localized around of the largest historic mining tailing of the IPB. The high volume sampler was placed on

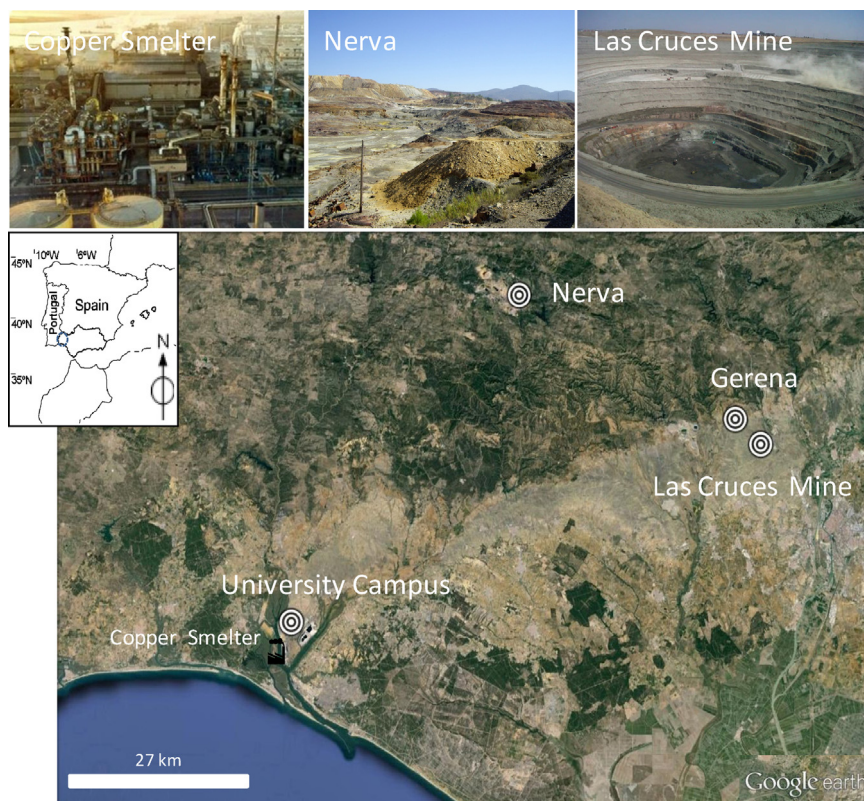


Fig. 1. Location study area of samples.

the roof of Nerva's Town Hall. A total of 45 filters were sampled in this station from July 2012 to June 2013.

- Rural area in the village of Gerena (GER), near the Las Cruces Mine (around 2 km). The high volume sampler was placed on a roof of a private house. In this case, a total of 84 filters were sampled from July 2012 to October 2013. Moreover, a sampling has been carried out in the facilities of Las Cruces Mine, in order to characterize its emission rate and geochemical profile of APM, and to compare the results with those obtained in the other monitoring stations, especially in GER.

Once the mass levels of PM_{10} were obtained by weighing the filters using standard procedures ($T=20^{\circ}C$ and relative humidity = 50%), a half fraction of each of them was submitted to an acid digestion (2.5 ml HNO_3 : 5 ml HF: 2.5 ml $HClO_4$) following a modified method proposed by [37], for the analysis of 8 major elements (Al, Ca, K, Na, Mg, Fe, Ti and Mn) by means of ICP-OES (ULTMA2 JOBIN YVON), and 43 trace elements (Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ta, W, Tl, Pb, Bi, Th, and U) by means of ICP-MS (AGILENT 7500).

The average precision and the accuracy fall for most of the elements under the normal analytical errors (in the range of 5–10%), and were controlled by repeated analysis of NBS-1633a (fly ash) reference material. The detection limit (DL) for most of elements in solution was 0.01 ppb.

The soluble fraction of a $\frac{1}{4}$ portion of each filter was extracted with MilliQ-grade deionised water at $60^{\circ}C$, and the content of major anions (SO_4^{2-} , NO_3^- , and Cl^-) and NH_4^+ in the leachates was determined by ion chromatography (DIONEX DX-120). Finally, a circular section of each filter 25 mm in diameter was used to determine the total carbon (C_{total}) content using a LECO SC-144 DR instrument, which measures the CO_2 combustion by infrared detection as a result of the oxidation of C present in the sample.

The methodology for As speciation (arsenite and arsenate) is based on high performance liquid chromatography coupled to hydride generation and atomic fluorescence spectrometry (HPLC–HG–AFS), following the method proposed for TSP, PM_{10} and $PM_{2.5}$ [38–40]. The detection limits obtained were of 0.1 ng m^{-3} for As (III) and 0.4 ng m^{-3} for As (V).

In order to identify different source contributions to ambient PM_{10} levels at the sampling site, a Principal Component Analysis (PCA) was performed using STATISTICA v.4.2 on the complete chemical data series of concentrations of PM_{10} as independent variables, according to the methodology described by [41]. PCA was performed to identify the possible sources, and a multi-linear regression analysis was applied to quantify the contribution of the main sources to PM_{10} in the monitoring stations. Factor analysis results were only accepted when the sum of the principal components accounted for >75% of the total variance of the dataset, and multi-linear regression analysis results were only accepted when the R^2 between the modeled and the gravimetric results was >0.85.

Polar plot contributions were performed using the openair package for R [42,43], (R Development, <http://www.openair-project.org/>), using meteorological data, as well as daily concentrations and chemical composition of PM_{10} .

3. Results and discussion

3.1. Chemical characterization of PM_{10} particulate matter

Table 1 summarises the daily mean concentrations of major and trace elements, and components in PM_{10} , obtained in the three monitoring stations selected for this study (GER, CAM and NER). In this table, the results obtained at Las Cruces Mine are also shown, in order to identify the geochemical anomalies related to mining extractive activity. The mean concentration of PM_{10} was $35 \mu\text{g m}^{-3}$ for GER and $27 \mu\text{g m}^{-3}$ for CAM, both values being lower than the

Table 1

Chemical composition of atmospheric particulate matter PM₁₀ in Gerena (between July 2012 and October 2013). Also, the results of comparative study of chemical composition in Huelva city, Pyrite Belt (Nerva village), and Las Cruces Mine station has been considered.

	Las Cruces Mine	Gerena	Campus UHU	Nerva
$\mu\text{g m}^{-3}$	Mean	Mean	Mean	Mean
n° filters	56	84	64	45
PM ₁₀	51.3	35	27.2	31.7
Ctotal	4.84	5.19	3.74	3.83
C org	3.81	4.71	3.36	3.50
Cnm	4.58	5.65	4.04	4.20
CO ₃ ²⁻	5.13	2.42	1.62	1.63
SiO ₂	10.3	3.84	2.43	3.66
Al ₂ O ₃	3.43	1.28	0.81	1.22
Ca	2.65	1.18	0.69	0.71
K	0.57	0.36	0.31	0.31
Na	1.08	0.96	1.32	0.85
Mg	0.46	0.26	0.23	0.23
Fe	2.03	0.51	0.43	0.48
PO ₄ ³⁻	0.12	0.09	0.14	0.08
SO ₄ ²⁻	4.41	2.42	2.78	1.77
SO ₄ ²⁻ anthropogenic	4.14	2.18	2.46	1.56
SO ₄ ²⁻ marine	0.27	0.24	0.33	0.21
NO ₃ ⁻	1.82	1.74	1.65	1.13
Cl	0.64	0.58	1.17	0.64
NH ₄ ⁺	0.58	0.52	0.51	0.33
ng m^{-3}				
Li	1.54	0.54	0.43	0.58
Be	0.05	0.03	0.02	0.02
Sc	0.34	0.16	0.11	0.15
Ti	105	43.9	35.3	44.63
V	5.83	3.75	4.16	2.87
Cr	3.99	1.40	2.34	2.12
Mn	18.3	9.46	5.47	9.30
Co	4.56	0.31	0.21	0.23
Ni	3.47	2.44	2.65	1.30
Cu	416	49.8	61.7	5.09
Zn	98.1	29.9	46.6	27.34
Ga	0.46	0.22	0.14	0.21
Ge	0.42	0.08	0.09	0.10
As	22.8	1.52	5.40	1.26
Se	0.76	0.44	0.75	0.46
Rb	2.45	1.34	0.89	1.18
Sr	9.30	3.26	2.85	2.68
Y	0.62	0.41	0.23	0.30
Zr	7.30	3.84	2.19	1.61
Nb	0.37	0.15	0.11	0.14
Mo	3.08	1.96	7.71	11.78
Cd	0.28	0.14	0.64	0.18
Sn	2.01	1.06	1.64	0.53
Sb	4.23	0.61	0.83	0.35
Cs	0.26	0.08	0.05	0.07
Ba	36.7	16.5	13.3	18.11
La	0.92	0.48	0.30	0.42
Ce	1.75	0.93	0.51	0.83
Pr	0.19	0.10	0.05	0.08
Nd	0.71	0.36	0.19	0.31
Sm	0.14	0.08	0.04	0.06
Eu	0.03	0.02	0.01	0.01
Gd	0.11	0.07	0.03	0.04
Tb	0.02	0.01	0.01	0.01
Dy	0.10	0.06	0.03	0.06
Ho	0.02	0.01	0.01	0.01
Er	0.06	0.04	0.02	0.03
Tm	0.01	0.01	0.00	0.01
Yb	0.06	0.03	0.01	0.03
Lu	0.01	0.00	0.00	0.00
Hf	0.26	0.14	0.07	0.06
Ta	0.02	0.01	0.00	0.01
W	0.35	0.03	0.02	0.03
Tl	0.24	0.02	0.03	0.02
Pb	162	7.02	12.2	3.97
Bi	4.27	0.26	0.60	0.09
Th	0.25	0.14	0.06	0.11
U	0.11	0.05	0.06	0.06

annual limit of $40 \mu\text{g m}^{-3}$ imposed by the directive EU/50/2008 [44]. The higher levels of crustal components were registered at the GER station: silica ($3.8 \mu\text{g m}^{-3}$), carbonate ($2.4 \mu\text{g m}^{-3}$), Ca ($1.2 \mu\text{g m}^{-3}$), Al₂O₃ ($1.3 \mu\text{g m}^{-3}$), K ($0.4 \mu\text{g m}^{-3}$), Fe ($0.5 \mu\text{g m}^{-3}$) and Mg ($0.3 \mu\text{g m}^{-3}$). These components mainly derive from local resuspension of the silicate phases and air masses from North Africa. The crustal components represent between 27 and 31% of PM₁₀ of the undetermined fraction by gravimetric method.

Conversely, the highest concentration of marine aerosol components were found at the CAM station, which is near the Atlantic coast (at a distance of around 4 km), with high values of Na ($1.3 \mu\text{g m}^{-3}$), marine SO₄²⁻ ($0.3 \mu\text{g m}^{-3}$), and Cl⁻ ($1.2 \mu\text{g m}^{-3}$), representing up to 12% of PM₁₀ total sampled, compared to 7% registered at the GER and NER stations.

Mean concentrations of SO₄²⁻ were higher at CAM station ($2.8 \mu\text{g m}^{-3}$), while the maximum mean concentrations of NO₃⁻ and NH₄⁺ were similar at GER ($1.74 \mu\text{g m}^{-3}$ and $0.52 \mu\text{g m}^{-3}$, respectively) and the obtained concentrations at CAM ($1.65 \mu\text{g m}^{-3}$ and $0.51 \mu\text{g m}^{-3}$, respectively). NER station has registered the lowest levels of all studied stations.

The mean concentrations of the metal and metalloids were higher for CAM station (12.2 ng m^{-3} of Pb, 2.65 ng m^{-3} of Ni, 0.65 ng m^{-3} of Cd, and 5.40 ng m^{-3} of As) than for GER and NER stations (7.02 ng m^{-3} of Pb, 2.44 ng m^{-3} of Ni, 0.14 ng m^{-3} of Cd, and 1.52 ng m^{-3} of As; and 3.97 ng m^{-3} of Pb, 1.30 ng m^{-3} of Ni, 0.18 ng m^{-3} of Cd, and 1.26 ng m^{-3} of As, respectively). Nevertheless, all these values are below the objective limit levels described by the European directive EU/50/2008 for PM₁₀ (500 ng Pb m^{-3} , 20 ng Ni m^{-3} , 5 ng Cd m^{-3} and 6 ng As m^{-3}). Other trace elements with high concentrations registered at GER and CAM stations are: Cu (49.8 and 61.7 ng m^{-3}), Ti (44.6 and 35.3 ng m^{-3}), Zn (46.9 and 27.3 ng m^{-3}), Mn (9.46 and 5.47 ng m^{-3}), Zr (3.84 and 1.61 ng m^{-3}) and V (4.16 and 2.87 ng m^{-3}), respectively.

The results corresponding to toxic elements have been compared to other rural and background monitoring stations of Spain [45] and Andalusia [46], showing high concentrations of Cu and As in this part of SW of Spain. The geochemical anomalies of As, Se, Bi, Cd, and Pb have been referred previously [46], where SO₂ emission plumes enriched in ultrafine particles of metals and metalloids (As, Cu, Zn, among others) from Cu-smelter can impact the city of Huelva. A recent study has shown that the size distribution of particulate matter derived from stack emissions of the Cu-smelter near Huelva is fine to quasi-ultrafine, and that the chemical composition is characterized by the elements mentioned above [32].

In Las Cruces Mine, the mean concentration of PM₁₀ was $51 \mu\text{g m}^{-3}$ (see Table 1). As it might be expected, crustal component concentrations (e.g., SiO₂, CO₃²⁻, Ca, Al₂O₃, K, Fe, and Mg), are higher than the registered at the other stations, which are mainly derived from the resuspension of soil and sterile wastes particles due to the movement of vehicles and milling processes during ore extraction. Regarding to SIC (Secondary Inorganic Components), these compounds are present in a range of values similar to these described in the other monitoring stations; SO₄²⁻ ($4.4 \mu\text{g m}^{-3}$), NO₃⁻ ($1.8 \mu\text{g m}^{-3}$), and NH₄⁺ ($0.6 \mu\text{g m}^{-3}$), taking account the regional character manifested by these pollutants.

The geochemical profiles described are characterized by large anomalies of Cu (416 ng m^{-3}), Pb (162 ng m^{-3}), Ti (105 ng m^{-3}), Zn (98 ng m^{-3}), Ba (37 ng m^{-3}), Mn (18 ng m^{-3}), As (23 ng m^{-3}), Zr (7.3 ng m^{-3}), Sr (9.3 ng m^{-3}), V (5.8 ng m^{-3}), Bi (4.3 ng m^{-3}) and Cr (4.0 ng m^{-3}).

Under any circumstance, the mean concentrations measured at Las Cruces Mine workplace for As, Cu Zn and Pb (22.8 ng m^{-3} ; 416 ng m^{-3} , 98.1 ng m^{-3} ; 162.0 ng m^{-3} , respectively) are higher than the values described in the Spanish existing legislation [47],

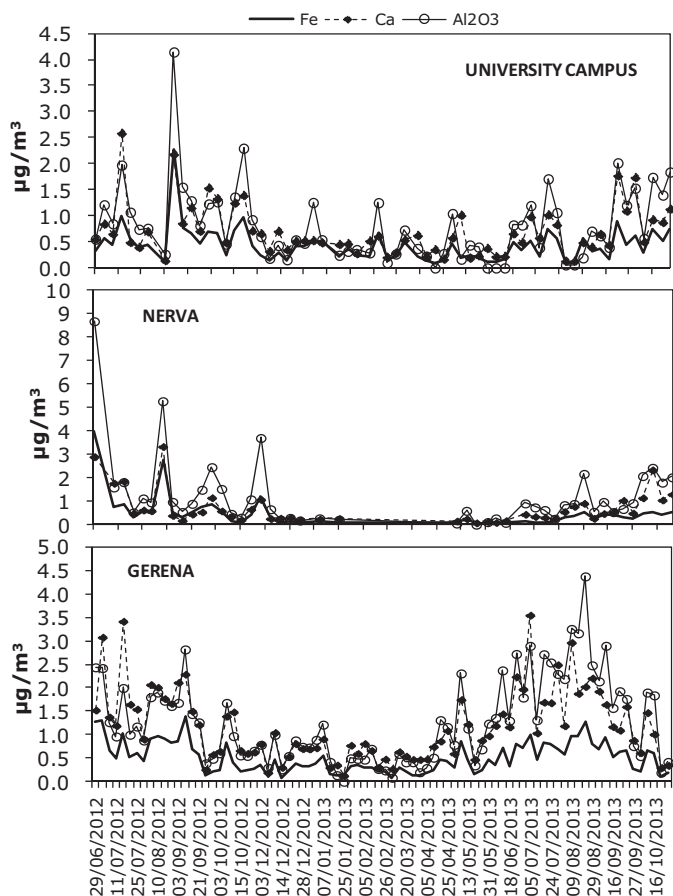


Fig. 2. Seasonal variation of Fe, Ca and Al_2O_3 in the stations CAM, NER and GER.

(As: $10,000 \text{ ng m}^{-3}$, Cu: $300,000 \text{ ng m}^{-3}$; Zn: $10,000 \text{ ng m}^{-3}$; Pb: $150,000 \text{ ng m}^{-3}$).

3.2. Seasonal evolution and contaminants vs wind direction

Seasonal evolution of major and trace elements has been presented in Figs. 2–5. Additionally, chemical composition of trace elements and components of PM_{10} vs. the direction and speed of wind has been represented in rose diagrams in Fig. 6.

In these graphics, the main sources of chemical pollutants have been identified, associated to the highest concentrations obtained, as well as the wind speed. For graphic purposes, median of hourly data of wind direction obtained in the meteorological station placed in Las Cruces Mine, have been used. Samples with daily bimodal or trimodal distribution of wind direction have not been represented.

Crustal elements present a seasonal distribution in GER station, characterized with maximum mean daily concentration in summer and minimum in winter. Such distribution was not observed in the other studied stations (e.g., CAM, daily maximum means were registered in September–October, 2012 and July 2013). In NER, the study of seasonal evolution is not representative from October 2012 to January 2013 because of the low number of representative samples, although maximum concentration peaks have been registered in the warm period.

Also, seasonal distribution has not been identified in the components of marine aerosol (e.g., Na and Cl^-). It must be pointed out that peak concentrations are sporadically distributed in all the period of study. Peak concentrations of marine aerosol are associated to SW wind direction, coming from the Atlantic Ocean.

The SIC (e.g., NO_3^- and anthropogenic SO_4^{2-}) present a seasonal distribution with a maximum in summer and a minimum in winter,

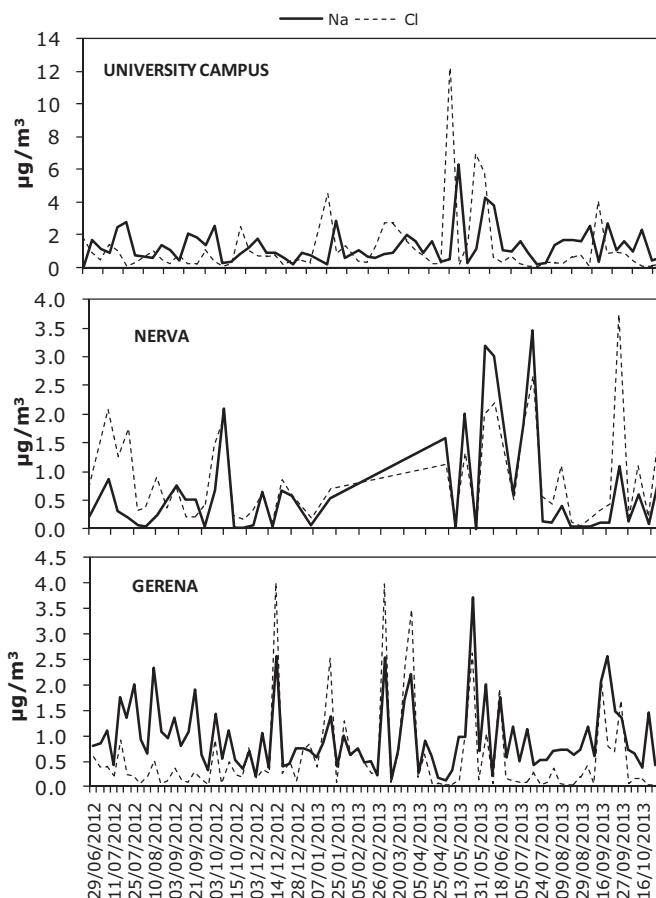


Fig. 3. Seasonal variation of Na and Cl in the stations CAM, NER and GER.

similar to the crustal component. Provenance of these compounds is variable considering the wind direction: from S-SW in GER and 2nd–3rd quadrant in CAM (see Figs. 4 and 6).

Toxic elements (e.g., As, Pb and Cu), presented a zig-zag pattern, displaying peak concentrations in 2012 at GER and CAM stations. In the case of As in GER, higher concentrations than 1 ng m^{-3} are related with wind direction from SW, opposite to the main direction of Las Cruces Mine. This same provenance is observed at CAM station, which is coincident with long-range transport of industrial plumes from the Cu-smelter in the city of Huelva, the main source of these pollutants.

In NER, toxic elements are associated to the industrial-anthropogenic origin, with a provenance variable between 3rd and 4th quadrant. These directions are coincident with the location of the main tailing wastes that surround the town of Nerva.

Overall, the distribution of toxic elements showed a zig-zag pattern, although in CAM and NER, and specifically for Cu–Pb–As, peaks concentrations are present in the summer period. In GER, a decrease in Cu concentration from December 2012 to June 2013 was observed.

One of the most important tasks is to elucidate the origin of Cu in GER. Polar plot of Fig. 6 suggests that a main contribution of this element is derived from 3rd quadrant of the wind rose, coincident with long-distance sources of Cu from Huelva. Sánchez de la Campa et al. [29] described how Cu-smelter plumes can rich the village of Paterna (ca 50 km from Gerena, in the same direction toward the city of Huelva) supporting this interpretation.

3rd quadrant in GER coincides also with tailing mining wastes of abandoned mining center of Aznalcollar [14]. However, the

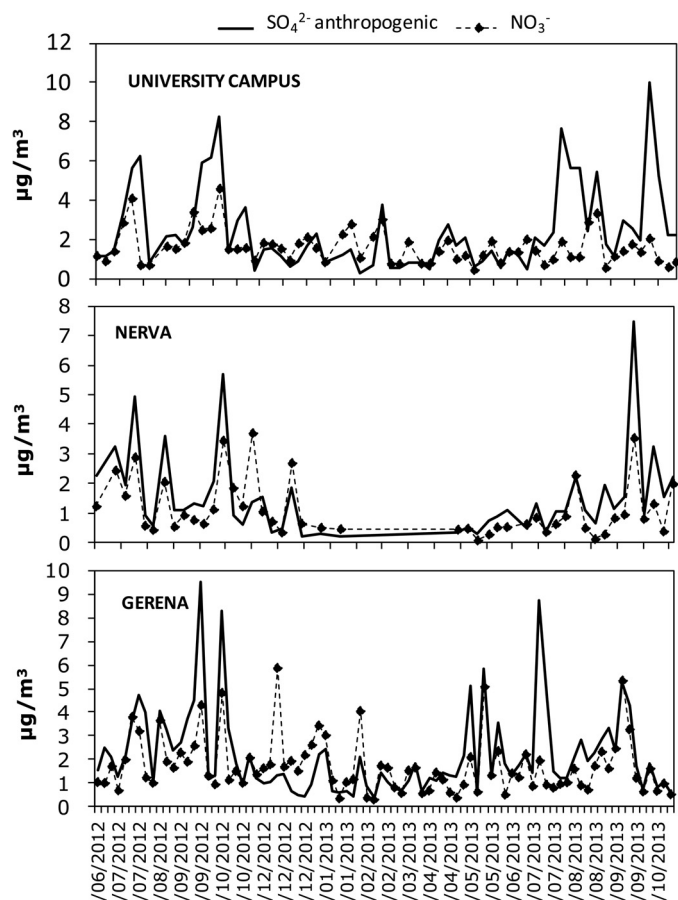


Fig. 4. Seasonal variation of anthropogenic sulphate and nitrate in the stations CAM, NER and GER.

observations in other abandoned mining area (NER), demonstrate the low availability of toxic elements to PM_{10} .

3.3. Sources contribution

A study of source contribution was performed, consisting of a principal component analysis (PCA) and multilinear regression, following [41]. This study has allowed to quantify the contribution of the sources to the total mass of PM_{10} .

PCA has been performed from 81 sampled filters in GER station (from July 2012 to October 2013). Four factors have been identified, which explain up to 76% of variation of the system (Table 2).

The first factor identified corresponds to the crustal components, representing a 46% of the variance of the system, whose major components are: Fe, Ca, K, Al_2O_3 , and SiC (SO_4^{2-} , NH_4^+). V and Ni are also associated to the chemical profile of this source, which may be related to the fuel oil combustion, and direct emissions from motor vehicles. This source, corresponding to the second factor, explains the 13% of the variance of the system.

The third factor has a similar chemical profile, when compared to Las Cruces Mine. This source explains 10% of the system variance, and is defined by As, Cd, Zn, Pb, Bi, Sn, Se and Cu. This chemical profile is coincident with the one described in industrial estate located near the city of Huelva (Pb, As, Cu, Cd, Sn, Zn and PO_4^{3-}).

The fourth factor identified is the marine aerosol (Na, Cl⁻ and Mg) mixed with elements of traffic emission affinity as C_{total} and Sb.

Fig. 7 represents the contribution of the sources to PM_{10} . The major source is the crustal component ($14.5 \mu g m^{-3}$, 42%),

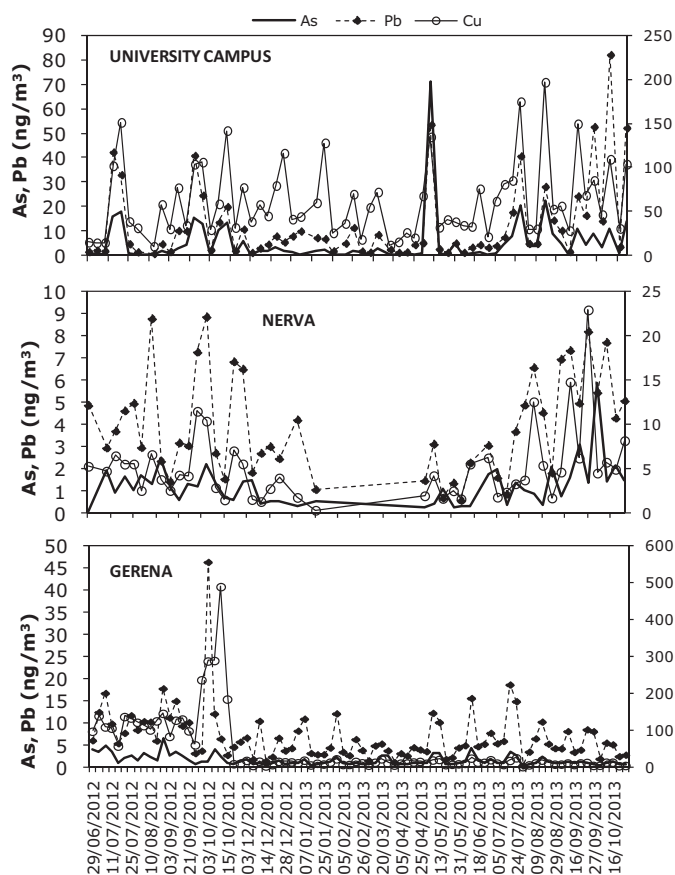


Fig. 5. Seasonal variation of As, Pb and Cu in the stations CAM, NER and GER.

followed to by the regional source ($10.6 \mu g m^{-3}$, 30%), mining activity ($5.1 \mu g m^{-3}$, 15%) and finally the marine aerosol plus traffic source ($2.8 \mu g m^{-3}$, 8%). The undetermined fraction represents up to 5% of the total mass of the PM_{10} ($1.8 \mu g m^{-3}$).

In order to know the effect of the seasonality on the composition and distribution of all sources identified on GER, a PCA has been developed for warm period. For this analysis, the samples from July to September of 2012 and from March to September of 2013, were considered. The total filters considered for the warm period amounted to 51. PCA corresponding to cold period was not performed, due to the small number of filters available, only 33, insufficient to guarantee the representativeness of the data.

PCA results of the warm period explain a 76% of the variance of the system (Table 3). It should be noted that a significant increment of the mass contribution of the crustal source relative to annual sampling has been obtained ($24.2 \mu g m^{-3}$ and $14.5 \mu g m^{-3}$, respectively) (see Fig. 8). This increment is related to the greater dryness of the soil during this period than during the cold months, favoring the resuspension of particulate matter originated from soils, as well as the more frequency of North African dust outbreak.

In CAM and NER, industrial and mining factor, were identified with similar contribution (5.4 and $4.1 \mu g m^{-3}$, 20% and 13%, respectively). Both factors present the same geochemical signatures. In NER, although the availability of toxic elements in mining waste is high [48], the rate for resuspension of coarse mining particulate matter by wind action is low, resulting in this case in a local impact.

In CAM, the high temperatures reached in the pyrometallurgical process of the near-by Cu-smelter, generate the formation of fine and quasi-ultrafine particulate loaded in toxic elements (e.g. As, Se, Bi, Cd and Pb) with high residence time, allowing long-distance transport [49]. Thus, the particulate matter emitted from this

University Campus

Nerva

Gerena

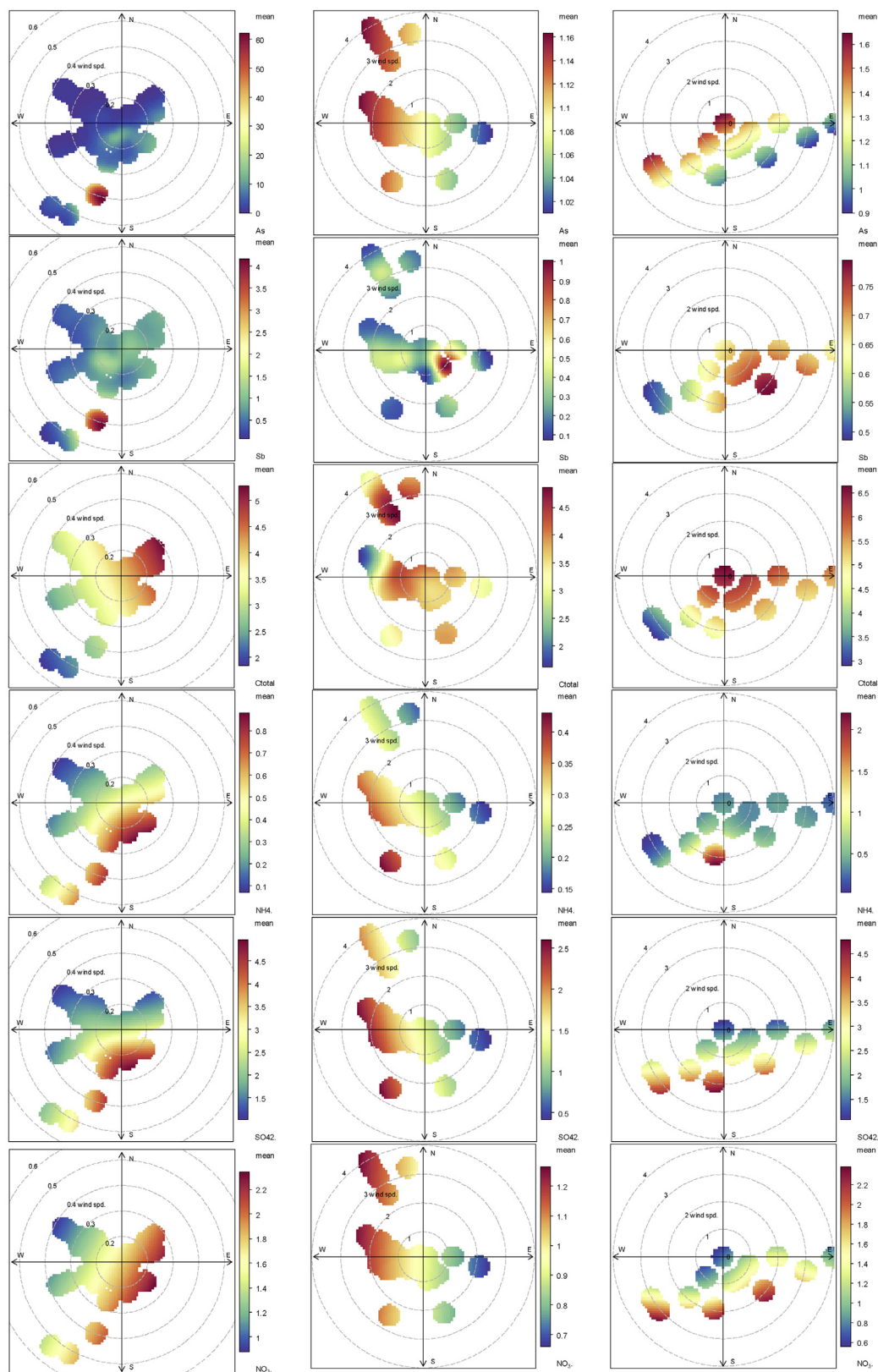


Fig. 6. Polar plots hourly mayor and trace elements at the University Campus, Nerva and Gerena stations, as a function of wind speed.

Table 2
Principal components analysis of PM10 samples in Gerena.

Factor 1		Factor 2		Factor 3		Factor 4	
Crustal		Regional		Las Cruces mining		Traffic + marine	
Fe	0.94	SO ₄ ²⁻ antrop.	0.86	As	0.85	Sb	0.69
Li	0.93	Ni	0.84	Cd	0.84	C total	0.67
Mn	0.92	V	0.84	Zn	0.69	Sn	0.38
La	0.92	NO ₃ ⁻	0.83	Pb	0.64	Bi	0.32
Sc	0.91	NH ₄ ⁺	0.83	Bi	0.60	Cr	0.27
Rb	0.91	Mo	0.54	Sn	0.58	Rb	0.24
Ti	0.91	Se	0.51	Se	0.56	Pb	0.23
Ca	0.89	Na	0.49	Cu	0.55	Fe	0.21
Al ₂ O ₃	0.89	Pb	0.44	Co	0.35	Al ₂ O ₃	0.21
Be	0.87	Cr	0.43	Sb	0.33	Sc	0.20
Sr	0.87	Mg	0.37	Ti	0.23	Be	0.20
Co	0.82	Sr	0.27	Mn	0.22	K	0.19
Mg	0.79	Sb	0.26	Sc	0.20	Zn	0.18
K	0.78	Cu	0.22	SO ₄ ²⁻ anthrop.	0.20	Co	0.15
PO ₄ ³⁻	0.74	K	0.21	La	0.20	La	0.15
Cr	0.59	La	0.21	NH ₄ ⁺	0.19	Li	0.14
Sn	0.41	Co	0.18	Fe	0.18	NH ₄ ⁺	0.11
As	0.38	Li	0.17	Rb	0.16	Mn	0.11
C total	0.36	Sc	0.17	Li	0.15	Ti	0.08
Bi	0.32	Sn	0.17	V	0.14	Ca	0.08
V	0.32	Rb	0.16	PO ₄ ³⁻	0.14	Mo	0.07
Se	0.30	Mn	0.11	Cr	0.13	As	0.04
Sb	0.28	Be	0.11	Ni	0.10	NO ₃ ⁻	0.04
Ni	0.26	Ti	0.10	Mg	0.10	Cu	-0.01
Mo	0.21	C total	0.10	Be	0.08	Cd	-0.02
SO ₄ ²⁻ anthrop.	0.19	Fe	0.08	C total	0.06	Ni	-0.03
Cd	0.17	Ca	0.05	Sr	0.06	Sr	-0.05
Pb	0.13	Al ₂ O ₃	0.04	Al ₂ O ₃	0.04	SO ₄ ²⁻ anthrop.	-0.08
Na	0.08	Cl	0.03	Ca	0.04	PO ₄ ³⁻	-0.11
Cu	0.06	Cd	0.00	K	0.01	V	-0.15
NH ₄ ⁺	-0.02	As	-0.01	NO ₃ ⁻	0.01	Se	-0.16
NO ₃ ⁻	-0.03	Zn	-0.06	Na	-0.08	Mg	-0.37
Zn	-0.07	Bi	-0.07	Cl	-0.12	Cl	-0.73
Cl	-0.21	PO ₄ ³⁻	-0.09	Mo	-0.24	Na	-0.76
Eigen value	15.8		4.4		3.5		2.0
Variance	46.4		13.0		10.2		5.9
Eigen value	15.8		20.2		23.7		25.7
%	46.4		59.4		69.6		76

Table 3
Principal components analysis of PM10 samples corresponding to the warm period in Gerena.

Factor 1		Factor 2		Factor 3		Factor 4	
Crustal		Regional		Las Cruces mining		Marine + traffic	
Fe	0.92	SO ₄ ²⁻ anthrop.	0.93	As	0.93	Cl	0.81
Ca	0.91	V	0.92	Cd	0.88	Na	0.79
K	0.86	Ni	0.92	Pb	0.83	Mg	0.49
Al ₂ O ₃	0.85	NH ₄ ⁺	0.83	Zn	0.74	NO ₃ ⁻	0.41
Co	0.72	NO ₃ ⁻	0.82	Bi	0.65	Cd	0.12
PO ₄ ³⁻	0.72	Na	0.53	Cu	0.57	V	0.11
Mg	0.70	Mg	0.41	Co	0.49	K	0.07
C total	0.70	Cr	0.37	Sb	0.49	Ni	0.03
Cr	0.55	Co	0.20	Fe	0.24	PO ₄ ³⁻	0.02
Sb	0.38	K	0.20	PO ₄ ³⁻	0.20	Cu	0.01
Bi	0.32	Sb	0.20	C total	0.20	As	0.01
Pb	0.29	Cu	0.20	Cr	0.17	Ca	-0.04
As	0.20	Pb	0.15	K	0.13	SO ₄ ²⁻ anthrop.	-0.04
Ni	0.17	Fe	0.06	Mg	0.12	Cr	-0.08
V	0.15	Ctotal	0.03	Ni	0.09	NH ₄ ⁺	-0.11
Cd	0.07	Bi	0.02	V	0.07	Co	-0.15
Cu	0.06	Cd	-0.01	SO ₄ ²⁻ anthrop.	0.06	Zn	-0.17
NO ₃ ⁻	0.05	As	-0.02	NH ₄ ⁺	0.04	Fe	-0.18
Zn	0.00	Ca	-0.03	Ca	0.00	Pb	-0.22
SO ₄ ²⁻ anthrop.	-0.01	Al ₂ O ₃	-0.03	Al ₂ O ₃	-0.01	Bi	-0.26
NH ₄ ⁺	-0.04	Cl	-0.05	NO ₃ ⁻	-0.04	Al ₂ O ₃	-0.29
Na	-0.06	Zn	-0.11	Na	-0.09	C total	-0.32
Cl	-0.29	PO ₄ ³⁻	-0.17	Cl	-0.16	Sb	-0.49
Eigen value	8.1		4.8		2.9		1.7
Variance	35.4		20.7		12.6		7.3
Eigen value	8.1		12.9		15.8		17.5
%	35.4		56.1		68.7		76

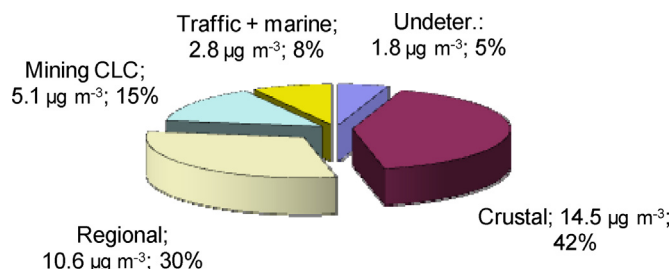


Fig. 7. Sources contribution of PM₁₀ in the period July 2012 to October 2013 in the Gerena station.

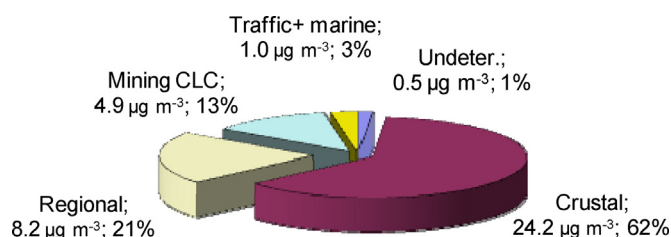


Fig. 8. Sources contribution of PM₁₀ in the warm period in Gerena.

metallurgical complex can reach areas of high ecological interest and considered as “clean air” (e.g. Doñana National Park [29]).

3.4. Speciation of Arsenic in Las Cruces Mine and Gerena station

In order to clarify the origin industrial and mining sources derived from this work, a specific study of speciation of inorganic arsenic has been performed using select samples of PM₁₀ of GER and with high concentration of this element (above to 4 ng m⁻³). A total of 25 samples were selected (Table 4).

GER samples showed a similar As(III)/As(V) ratio than other PM₁₀ samples in described in the city of Huelva [39,40] and Las Cruces Mine, As(V) being always the main one for the three locations. This ratio indicated the following proportion of the extracted arsenic species: 92% As(V) and 8% As(III) for GER, and 97% As(V) and 3% As(III) for Las Cruces Mine and Huelva. The similar values obtained for this parameter made it unsuitable to distinguish a different origin of the arsenic in PM₁₀ at the three locations.

As an alternative, the mean extraction efficiency (comparing the sum of the extracted arsenic species vs. de total As content of the sample) was considered. In this case, the mean extraction efficiency of the arsenic species from the PM₁₀ samples of GER was close over 90%, similar to the extraction efficiency values reported for samples from Huelva [38]. However, when the extraction procedure was applied to the samples of Las Cruces Mine, the mean extraction efficiency was low, about a 30%.

The different extraction efficiency for GER and Las Cruces Mine indicates a different mineralogical composition of the particulate

Table 4

Total arsenic concentration, arsenic species and percentage of arsenic extraction in PM₁₀ samples of Las Cruces Mine and Gerena, collected between 2012 and 2013. Data of Huelva corresponds to 2008, for comparison. Results expressed as ng m⁻³ (mean ± standard deviation). N indicates the number of samples.

Sampling site	N	As _{total} ^a	As(III) ^b	As(V) ^b	% Extraction
Las Cruces Mine	23	36.2 ± 25.6	0.3 ± 0.2	8.5 ± 4.3	30 ± 15
Gerena	2	5.6 ± 1.1	0.4 ± 0.3	4.9 ± 0.9	95 ± 9
Huelva ^c	22	16.4 ± 11.7	0.4 ± 0.3	14.9 ± 13.1	94 ± 19

^a As_{total} calculated after acid digestion and determination by ICP-MS.

^b As(III) and As(V) calculated after liquid extraction and determination by HPLC-HG-AFS.

^c Adapted from Sanchez-Rodas et al. [39].

matter at both sites. The explanation for the low recovery of Las Cruces Mine samples lies on their high sulphide content. This mine is located in the Iberian Pyrite Belt, a major mining area hosting volcanogenic massive sulphide deposits [50]. Arsenic is usually related to the presence of sulphur as sulphide that is present in the metal-bearing phases (pyrite, chalcopyrite, sphalerite and arsenopyrite), as it has been already described in more detail [48].

On the contrary, the 90% extraction efficiency at GER indicates that the sulphur should be present mainly as sulphate. The extraction procedure, based on aqueous extraction with a hydroxylammonium chloride solution, can dissolve easily the soluble sulphates present in GER, and therefore also the As. However, the As associated to the insoluble sulphides at Las Cruces Mine is difficult to extract, resulting in a extraction efficiency of 30%. This corroborates that the As in GER has a different origin from the As found at Las Cruces Mine, as it has been previously indicated by the source contribution study.

4. Conclusions

The characterization of geochemical anomalies in toxic elements in APM from mining and smelting influence areas was investigated in three sampling locations of the SW Spain during the period of June 2012 to October 2013. High concentrations of toxic elements (e.g., Cu and As) have been detected in comparison to other rural and background monitoring stations of Spain.

In urban background station (University Campus) As, Se, Bi, Cd, and Pb have been associated to SO₂ emission plumes enriched from a Cu-smelter which impact in the city of Huelva. A zig-zag pattern is identified for toxic elements (As, Pb and Cu) on all the stations. However, in Gerena the higher concentration of As is associated to wind direction from SW, opposite to the main direction of Las Cruces Mine, and coincident with long-range transport of industrial plumes from the Cu-smelter in the city of Huelva, the main source of these pollutants. In Nerva rural station, the higher concentration of toxic elements are coincident with the location of the main tailing wastes that surround the town of Nerva.

The results of speciation of inorganic arsenic in the rural station (Gerena) samples showed that the As(III)/As(V) ratio and the mean extraction efficiency of arsenic species were similar to other APM samples described in the city of Huelva (close to a 90%). However, in Las Cruces Mine samples the mean extraction efficiency was low (a 30%), which is related to high sulphide and sulphate content, respectively.

We conclude that the ore extraction and the abandoned mine wastes next to human settlements and near to mining centers, has a lower influence than the pyrometallurgical activities. In this latter case, ultrafine particles enriched in toxic elements are formed and transported long-distance, thus affecting negatively the air quality.

Acknowledgments

This study was supported by the Department of the Environment (project 10/2013/PC/00) and the Department of Innovation, Science and Enterprise (project 2009-RNM 5163M and 2011 RNM 7800) of the Autonomous Government of Andalusia and Projects CGL2008-06270-C02-02/CLI and CGL2011-28025 of Spanish Educational Ministry. Also, we want to thank Las Cruces Mine for technical support during this study.

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